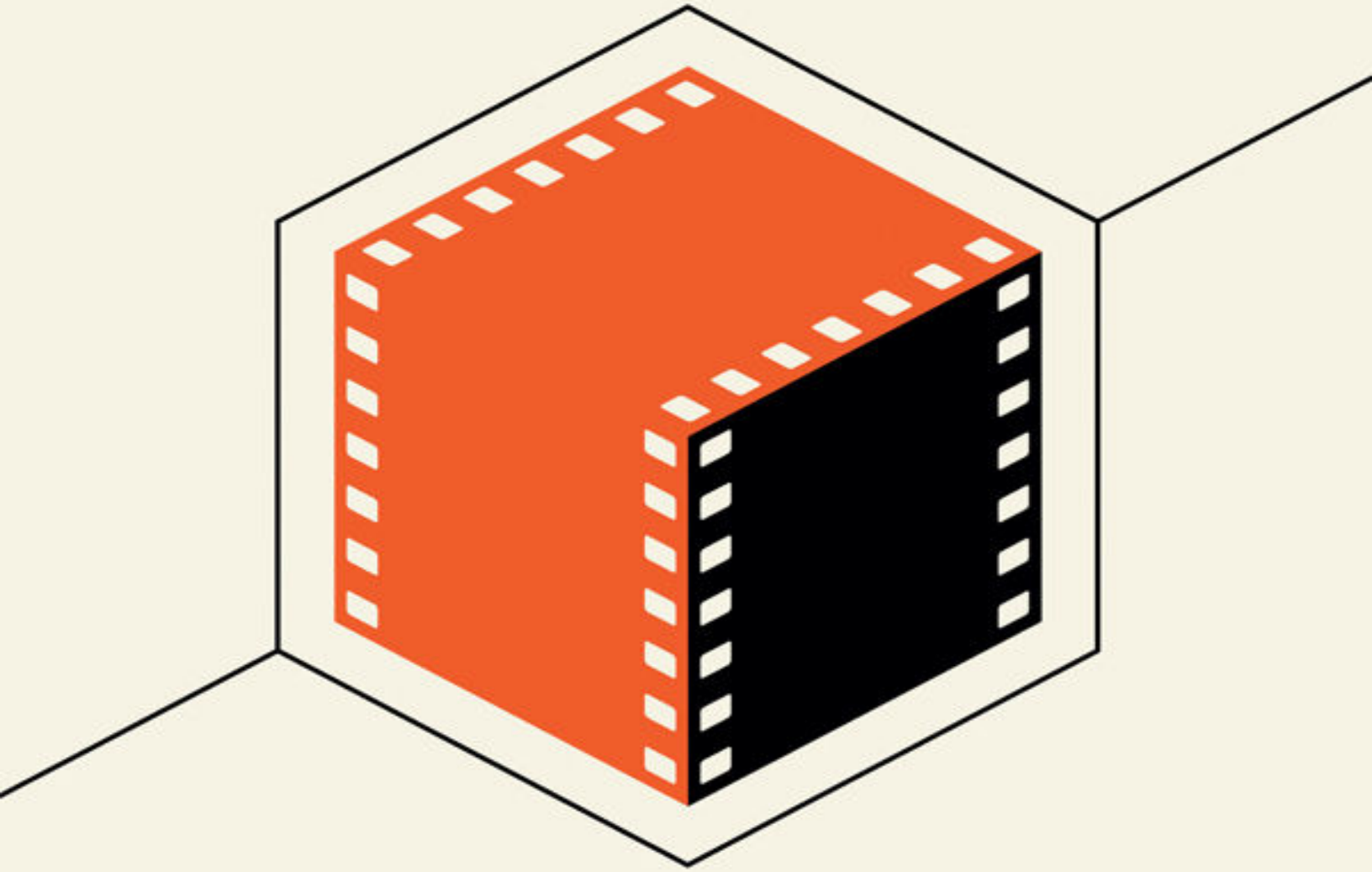


THE FILM DEVELOPING COOKBOOK

BILL TROOP WITH STEVE ANCHELL

A Focal Press Book

SECOND EDITION

ROUTLEDGE

THE FILM DEVELOPING COOKBOOK

SECOND EDITION

The Film Developing Cookbook, 2nd edition is an up-to-date manual for photographic film development techniques. This book concentrates on films, their characteristics, and the developers each requires for maximum control of the resulting image.

For two decades *The Film Developing Cookbook* has helped photographers acquire a working knowledge of photographic chemistry—what photo chemicals do and why—for black and white film developing. Now reissued in a revised and fully updated edition, this must-have manual for photographic film development techniques covers films, their characteristics, and the developers each require for maximum control of the resulting image. Readers will learn how to mix and use photographic solutions from scratch, and even how to create new ones. Includes invaluable information about films, developer ingredients, formulas, speed increasing, mixing and storing stock solutions, stop baths, fixers, washing, and chemical safety.

A must-have for analog photography enthusiasts and any photography students using the darkroom. For in-depth discussion and questions on all things film or darkroom join the Darkroom Cookbook Forum, www.darkroomcookbook.com.

BILL TROOP *is the principal author of The Film Developing Cookbook, widely considered to be the standard contemporary work on black and white film*

processing and chemistry. As a photo chemist, he has designed many products including TF-4, the first commercially available alkaline fixer for black and white film and papers. In technology he was the first writer to champion RAID systems for personal computers, and he has designed several typefaces.

STEVE ANCHELL *has taught digital and darkroom classes at Oregon State University, and has conducted workshops since 1979 at institutions such as the International Center for Photography, Santa Fe Photographic Workshops, and UCLA. He is the author of The Darkroom Cookbook, The Variable Contrast Printing Manual, and Mirrorless Interchangeable Lens Camera.*

We dedicate this book to the memory of Grant Haist and Geoffrey Crawley.

The Film Developing Cookbook

Second Edition

Bill Troop
with Steve Anchell

Routledge
Taylor & Francis Group
NEW YORK AND LONDON

Second edition published 2020
by Routledge
52 Vanderbilt Avenue, New York, NY 10017

and by Routledge
2 Park Square, Milton Park, Abingdon, Oxon, OX14 4RN

Routledge is an imprint of the Taylor & Francis Group, an informa business

2nd printing

First edition published by Focal Press 1998

Library of Congress Cataloging-in-Publication data

A catalog record has been requested for this book

ISBN: 978-1-138-20486-7 (hbk)
ISBN: 978-1-138-20487-4 (pbk)
ISBN: 978-131-5468-45-7 (ebk)

Publisher's Note

This book has been prepared from camera-ready copy provided by the author

INTRODUCTION TO THE SECOND EDITION

You could have knocked me over with a feather when Focal Press asked me to do a second edition of FDC. I was truly happy to have a second chance to write the book. I knew Steve and I could make it better.

> *"Nobody is going to love your pictures like yourself."*
>
> —DIANE ARBUS DURING THE FIRST CLASS SHE TAUGHT, 1970

We took a more minimalist approach with the first edition: always asking ourselves, do people really need to know this? Will they ever use it?

I've taken a more generous approach this time. A major change is to include a lot more references to standard works like Haist and Mason, and I've quoted from them more freely, mainly because they are now much harder and more expensive to obtain, and few will actually want to wade through them. So I've distilled a lot of information that I thought would be most useful and interesting.

I have been much more proactive careful about sourcing the statements I make in this edition. With Steve's help, I think I've done it so that it won't get in the way for people who aren't interested and will be easy to use for people who are.

Silver photography has always been a manufacturing miracle, in that to this day, a lot of what happens in the manufacture and subsequent exposure

and processing of film is still unknown. I can't think of another manufacturing or engineering or scientific field where there are as many unknowns as there are in photography. So every now and then, I have pointed out areas where I hope future research will be done.

My reasoning is that someday a millionaire hobbyist will read this book and sponsor the research. Or maybe some Ph.D student will need a novel subject for a thesis, and will give it a whirl. Who knows? We're writing the future here—and we may not even be alive to see it bear fruit. But we must cast the stones in the water. When we published the first edition of The Film Developing Cookbook in 1997, how could we know that Sandy King would be inspired to take up pyrocatechin and do such great work with it? Who thought Kodak would try to bring Super 8 back? Maybe there will be cooperative or government support at some point? What will happen when microfilm, with all its problems, outlasts digital storage? Where there are questions, we must pose them.

Films from the three major manufacturers, Kodak, Ilford and Fuji, are still made to an extremely high standard. Of the smaller companies, Foma is producing more film than ever before and with a higher level of quality than before. We are impressed by Adox's ambitious production and future plans. Of all these companies, Adox is the one that combines high engineering skills with profound aesthetic understanding. And then there are all the even smaller companies, each with something special to o≠er. Though we have seen some painful contraction in the Kodak and Fuji lines, it seems as if there are now more film choices than there were 20 years ago.

Both Steve and I wish you happy hours in the darkroom and hope to take some small part in the creation of your work.

INTRODUCTION TO THE FIRST EDITION

It's all because of the little yellow box. This book owes its existence to T-Max film. As author of *The Darkroom Cookbook* I have heard from many associates and students about the difficulty they have obtaining quality images with T-Max film. Many solutions have been put forth; all are compromises.

Finally, I called my friend and photo-chemist, Bill Troop, and asked if he had any suggestions. Bill has designed many fine formulas for developing both films and papers; many are referenced in this book. Bill's reply was, "No, but I have some ideas." Not only ideas. Bill had a manuscript he had begun on film processing as early as 1980 which was floating around his home somewhere. He dug it out, sent it to me, and we began the collaboration which led to this book. —*Steve Anchell*

When this book was conceived, photographic engineering was still an important field. But photographic manufacturers were moving from traditional silver halide science to digital as fast as they could. They laid o≠ thousands of photographic scientists and replaced them with electrical engineers and computer scientists. I had counted on seeing a lot of fundamental research completed before I finished my book: research into new developers, new films, and new fixing techniques. This was never to be. It was a depressing time for photography!

I put the book aside until I met Steve Anchell, four years ago. He proved to me that there are still countless dedicated photographers who are interested in exerting the greatest possible control over film processing. So

Steve and I set about completely rewriting and re-researching my material. We have tried to include all the essential information yet make it interesting enough for photographers to enjoy reading. *—Bill Troop*

This book has three special emphases: how to use di≠erent developers to achieve a wide range of pictorial e≠ects, how to mix and use solutions from scratch (and how to create new ones), and how to process film for maximum archival permanence. Although photographic processing is a chemical process, it is not necessary to know anything about chemistry. It is necessary to understand what photographic chemicals do, and why, just as it is necessary for a cook to understand what salt does and what pepper does. And, just as a cook has to learn how to use heat and sharp knives without getting burned or cut, so do photographers have to learn how to use processing chemicals safely.

This book's purpose is to help readers acquire a relevant knowledge of black and white photographic chemistry as painlessly as possible. We also hope it will serve as a reference and refresher for photographers at all stages of their skill.

Much of the technical information in this book has never been published before. This we owe to the generosity of the many scientists who shared research with us, determined that it should not perish. The silver halide is still with us, and doesn't look as if it's going to budge soon. Long may silver photography live.

ACKNOWLEDGEMENTS

For this edition, I thank first of all Carolyn Crawley, wife of the late Geo≠rey Crawley. She made it possible for me to view Crawley's archives, and when there were lacunae, went to heroic lengths to obtain missing information. This book is incomparably richer because of her help.

Richard Perry of Paterson Photographic went to enormous trouble to dig through Patersons' old files to complete missing information. We are so grateful to him and everyone at Patersons who helped.

This edition shows on every page the expertise of Kodak's Ron Mowrey, who for more than ten years has been a support. To have been able to take advantage of his knowledge for all these years—from a man who was one of the editors of Grant Haist's book—has been a privilege.

I deeply appreciate Lynne Haist's re-iteration of Grant Haist's permission to quote from her father's *Modern Photographic Processing*. It is the one book no researcher in this field can be without. More than that, Dr. Haist answered thousands of my questions over decades with unfailing diligence, authority, patience, and humor.

I was fortunate to have much personal help from several legendary Kodak scientists whose work stretched back to the 1920s: C.N. Nelson, R.W. Henn, T.H. James, and H.D. Russell; and from L.F.A. Mason of Ilford and Edmund Lowe of Edwal.

The youngest of Kodak's black and white greats, Dick Dickerson and Silvia Zawadzki, have been markedly generous in sharing information.

Geoffrey Crawley, for many decades the editor of the British Journal of Photography, was the 20th century's most distinguished independent

researcher in black and white photochemistry. For almost three decades he unreservedly gave me the benefit of his expertise.

The US Navy's Marilyn Levy, whose POTA formula caused waves in photochemistry, was generous with her expertise and her wit.

Douglas Nishimura of the Image Permanence Institute kindly checked our chapter on image permanence.

Mirko Böddecker of Adox and Eric Joseph of Freestyle Photographic have been enormously patient and helpful. Bud and Lynn Wilson of Photographers' Formulary have been supportive for many years.

Prof. Nicholas Green from the Department of Chemistry, University of Oxford, has been helpful in resolving some questions.

I am most grateful to Ryuji Suzuki for special insights on ascorbates.

For this edition I owe a special debt to Rudolf Leitgeb who read and re-read the manuscript with relentless focus. He deployed his broad knowledge to challenge us. Where there was a weak point or inconsistency, he pounced. His contribution to this edition could not be overstated.

Finally, I would like to thank Steve Anchell. This edition was supposed to be my baby only. But I realized that we were a team and the book wouldn't be the same without him. His editing, advice, judgement, and practical experience have been an enormous help to me. And he has been an inspiration, as he is to all his students.

We both acknowledge the friendship and wisdom of four photographers who helped us become better photographers, better chemists, better people: Berenice Abbott, Ansel Adams, Lisette Model and Brett Weston.

INDEX OF FORMULAS

Xtol, 61; Mytol, 119

"Above all, "don't be one of those who learns everything so quickly that you never really learn anything well."

—J. GHISLAIN LOOTENS

CONTENTS

Index

SPECIAL THANKS

Thanks first to Focal Press for colossal feats of patience and faith during the first edition, and the same during this second edition.

To the memory of Kathleen Tinkel, who set up a publishing system and design template that have proved enduring.

Dov Issacs, Principal Scientist at Adobe, kindly gave me help without which it would have been impossible to keep on using Kathleen's system to print this book in 2019.

Mike Adams, with his encyclopedic knowledge of photographic equipment and the late Ken Hansen, the one and only prince of camera dealers, have been pillars of support.

Finally, to the memory of Ana Luisa Morales who provided the anchor without which the ship would have foundered on many reefs.

—Bill Troop

A special thanks to Donna Conrad who spent many hours editing this book. To the extent we have achieved readability, we owe it all to her.

—Bill Troop and Steve Anchell

ABOUT THIS BOOK

There are a few things you need to know to get the most out of this book. Formulas which appear in the text are almost always given in working solutions. If, for some reason, the formula is a stock solution, it will be noted as such.

This does not mean we are opposed to stock solutions. It is simply that formulas can only be accurately compared with each other when they are broken down to working solutions. Trying to compare stock solutions is difficult, at best. We print what we think are the most useful stock solutions in Appendix I.

We have found certain developers and techniques that we feel are significantly superior to others in their class. We have placed these in what we call Quck Guides. If you want to know how we came to our conclusions, and the alternatives, read the rest of the section or chapter.

Not every chapter contains a Quick Guide. This means we have not identified any formula or technique which we like more than the others, or, as in the case with Chapter 1, there is nothing to recommend.

Different developers will produce different EIs on different films. With very few exceptions we do not attempt to give corrected EIs with the developer/film combinations.

> **All quantities are in grams and liters.**
> **The abbreviation g/L means grams per liter.**
> **We use g for grams, L for liter, ml for milliliter.**

Square brackets indicate where we have inserted our own opinion or correction into a quote.

I use ‘we’ when I am fairly confident that the statement speaks for both of us, and ‘I’ when I feel the statement comes from me. At other times, I use Anchell, Troop, or SA and BT.

Organizations and groups:

APUG: the popular photography forum on the Internet, is now called **Photrio**, www.photrio.com; older links do not always work.

IPI: Image Permanence Institute, www.imagepermanenceinstitute.org

KRL: Kodak Research Laboratories, Rochester

Kodak Harrow or Harrow: Kodak's recently-closed division in Harrow, England; this was a different research team from the Rochester scientists who are better known in the US.

GLOSSARY

Chemicals

Capitalization: following contemporary usage, we do not capitalize chemical names unless they are trademarked and not in common usage. Phenidone with a capital P refers to the trademarked chemical; phenidone or phenidones without a capital p refers to a group of related chemicals whose tradenames are Phenidone, Phenidone A, Dimezone, and Dimezone-S. Strictly speaking trademarked chemical names should always be capitalized. In photographic chemistry, as a practical matter, all the phenidones are interchangeable. Like Phenidone, metol is a trademarked name. However, it has evolved into common usage as lowercase.

3G hardeners: refers to hardeners used in some modern black and white films since the 1990s from some major manufacturers. A typical example is known as BVSM or (bis(vinylsulfonylmethyl)ether. Some others in this class are known by the abbrevations BVSAE, BVSME, BVSEE, BVSP, BVSHP, and TVSE.

borate: a chemical related to borax, e.g. borax, metaborate, or boric acid.

BZT: the antifoggant benzotriazole is abbrevatived in many ways: BTA, Btri, BAT, and more. Photographers have traditionally used BZT.

Calgon: this trademarked product, introduced in 1933, originally consisted solely of sodium hexametaphosphate (SHMP or sodium polymetaphosphate

or amorphous sodium polyphosate), and was widely used as a water-softening agent and sequestrant. When the word Calgon appears in photographic literature, it means sodium hexametaphosphate. However, the product now sold as Calgon is based on zeolite and polycarboxylate and should not be used in photography. The terms “Calgon S” and “Calgon (old)” refer to the original SHMP product. The term comes from “calcium gone” and refers to the compound’s ability to complex with calcium ion and so prevent calcium scumming.

Common abbreviations for developing agents

CQ: chlorohydroquinone, sometimes called chlorquinol in the past; **HQ**: hydroquinone; **HQMS**: hydroquinone monosulfonate; **MQ**: the combination of metol and hydroquinone; **PQ**: the combination of Phenidone and hydroquinone and broadly the combination of any form of phenidone with hydroquinone; **PMQ** the combination of phenidone, metol, and hydroquinone

DEA: diethanolamine—alkali and silver solvent

DTOD: 1,2-di(hydroxyethylthioethane) in Kodak's preferred nomenclature, **or** 3,6-Dithia-1,8-octanediol; CAS no. 5244-34-8—a silver solvent for developers and also fixing agent

DTPA: pentetic acid or diethylenetriaminepentaacetic acid—the most widely used sequestrant in photography today

EDTA: ethylenediaminetetraacetic acid—sequestrant

Hypo: sodium thiosulfate, formerly sodium hyposulfite or hyposulphite; occasionally ammonium thiosulfate is called "ammonium hypo".

HTTT: tetrahydro-5-(2-hydroxyethyl)-1,3,5-triazine-2(1H)-thione; CAS no. 26957-73-3; EC number 248-140-3; a fixing agent

Kodalk: Kodak's tradename for sodium metaborate

MOP: Kodak Research Lab shorthand for Dimezone-S

Ppd in small caps is para-phenylene-diamine or, loosely, its derivatives

PMT: the antifoggant 1-phenyl-5-mercaptotetrazole

PVP: polyvinyl pyrrolidone, used as an antistain agent in HC-110.

TEA: triethanolamine—alkali and silver solvent

Other terms

When G. Crawley first published the FX developers in 1961, he used the convention **FX XX**. In later years, he amended this to **FX-XX**. My policy is now to standardize on FX XX.

Xtol is spelled in all caps by Kodak, but its inventors, Dickerson and Zawadzki always spell it Xtol in their publications, and we have followed this usage.

Reserve acidity (or **reserve alkalinity**), **total acidity**, and **buffer capacity** are terms to describe related concepts. Buffer capacity refers to a solution where the pH does not change much when small amounts of acid or alkali are added. For example, consider a 1% acetic acid acid stop bath. It is not buffered. It has a pH around 2.9 when fresh. When you add alkaline film developer to it, the pH rises quickly. When fresh the stop bath may take a few seconds to stop development. But after a few uses, it may take 30 or more seconds to stop development. Now consider a buffered stop bath that contains 5% acetic acid buffered with sodium acetate (chapter 12). The pH is 4.6. The pH is higher but will remain *much* more stable when small amounts of alkali are added. The buffered bath will stop development within a very few seconds over a long working life. The buffered stop bath has a *higher pH*, but it has *higher total acidity*, so it will stop development faster than the unbuffered solution with lower pH. See chapter 12 for more detail; also the chapters on developers and fixers. During film development, development byproducts can change the pH of the developer. Thus buffering can be an important part of film developer design. It is not always desirable that a film developer should be well-buffered. Generally speaking, fine grain developers need to be well-buffered (which helps promote the appearance of low graininess), while high definition developers are often unbuffered, because

that promotes the production of sharpness-enhancing adjacency effects. Stop baths and fixers should, as a rule, be well-buffered.

> *Other points on dichroic fog raised by Haist: He notes that it is easily produced on some high-speed modern films when processed in developers containing silver solvents such as thiocyanates. "Apparently, certain speed-increasing emulsion addenda provide or are instrumental in forming nucleation centers for the formation of a scum of metallic silver on the emulsion surface. Manufacturers … often warn against the use of solvent developers for processing such films." To remove the fog with minimum damage to the image, a slow acting reducer is required, such as the working solution of an acid ammonium thiosulfate fixer with 15–30 g/L of citric acid added. Film should be washed well after this treatment.*

Clearing time is defined in chapter 13.

Dichroic fog is discussed by Haist (258–260, 543, 563) at length. "Dichroic fog is one form of developer fog that may be encountered by almost every processor of photographic film. It is also one of the easiest forms of fog to identify. This two-color fog is is composed of metallic silver, usually on the surface of the emulsion. The color depends on how a negative is viewed: by transmitted light, the color is red to orange-red; by reflected light, the color is yellowish green, often having a silvery, metallic hue. The exact color depends upon the size of the silver particles, so that the range of colors may be considerable. By reflected light a film negative may appear opaque, giving the appearance of incomplete fixation." Dichroic fog is most often produced by a solvent developer which is too solvent for the film being used. It can also be produced when film is placed directly from the developer into the fixer, especially when the fixer is near its exhaustion point, so that development continues in the highly solvent fixer.

Induction period: the waiting period before development observably begins; for example the induction period of the phenidones is shorter than for most other developing agents.

MP: motion picture

Push processing means underexposing and overdeveloping in order to record a usable image with a handheld camera in low light situations. See chapter 10.

Pull processing means decreased development where the film has been down-rated in speed. This is a valuable technique for potentially increasing the pictorial quality of all films but particularly tabular grain films. It can decrease micro-contrast by making more development centers available. See chapter 2.When we refer to **Ilford** films such as HP5 and FP4, we imply the + designation.

When we refer to **Ilford** films such as HP5 and FP4, we imply the + designation.

USP refers to U.S. Patent. **BP** is sometimes used for British Patent.

BIBLIOGRAPHICAL NOTE

The following are frequently cited by name:

Haist: Grant Haist, *Modern Photographic Processing*, John Wiley & Sons, New York, 1979, Volumes 1 and 2. All references are to volume 1 unless noted, usually as Haist V2 or Haist II. The following numbers are the page numbers. (e.g. Haist 532; Haist II 247; Haist V2 349).

Mason: Mason, L.F.A. *Photographic Processing Chemistry*. 2nd ed. London: Focal Press, 1975.

Crawley 60/61 or BJP 60/61: "Notes on Present Day Monochrome Emulsions and Their Development", *British Journal of Photography*, v. 107, p. 651 (8 parts from 1960 to 1961).

BJP: The British Journal of Photography. Citations should be in volume, page, year order; **BJP Annual**, the annuals of the BJP by year.

PCS: Crabtree, J. I. and G. E. Matthews. *Photographic Chemicals and Solutions*. Boston: American Photographic Publishing Co., 1939. This enormously useful if dated book is particularly valuable for those who have to deal with issues such as poor water supplies and equipment.

Henry: Richard Henry, *Controls in Black and White Photography*, Focal Press, Boston & London, 1986, 2nd edition. The 2nd edition is

significantly better than the 1st.

Adams, The Negative: Ansel Adams, *The Negative*, New York Graphic Society, New York, 1981.

Focal or Focal Encyclopedia: *The Focal Encyclopedia of Photography*, 3rd edition, ed. Richard Zakia and Leslie Stroebel, Focal Press, Boston & London, 1993. References to later editions are noted as such.

Hutchings: Gordon Hutchings, *The Book of Pyro*, 3rd (revised) printing. Granite Bay, CA: Bitter Dog Press, 1998.

JSMPE: Journal of the Society of Motion Picture Engineers. Citations are usually in the standard order of volume number, page number, and year. So JSMPE 43, 248, 1943 means volume 43, page 248, from the year 1943. There will sometimes be an additional v. or p. for clarity.

FDC 1: first edition of this book, 1998; **DCB** plus number: the several editions of Steve Anchell's *The Darkroom Cookbook*.

Private communications give the initials of the author to whom the communication was made, for example: "Grant Haist to BT, 1993". Other photographic scientists mentioned are **P. Glafkides** and **T.H. James**, see the bibliography for their principal works. Authors we refer to frequently but who are known for their journal articles rather than a book, are **G.I.P. Levenson** of Kodak Harrow who made countless contributions to 20th century photographic research, **R.W. Henn**, who was responsible for many Kodak developers from DK-20 all the way up to HC-110, and **Loyd A. Jones**, whose cornerstone papers from the late 1930s and 1940s provide us with still-definitive answers on speed, exposure and tone reproduction and who also published important early material on acutance. We also mention

C.N. Nelson, Jones's collaborator, who later devised a fixed-point system for determining film speed that is essentially still in use, if misunderstood, to this day. (The original fractional gradient system of Jones was cumbersome to calculate before the age of microcomputers and programmable calculators. It could advantageously be restored, and should be studied by anyone who wants to get to grips with what speed determination really means. Very briefly, the speed point is the minimum exposure that will result in printable shadow detail. It is the point on the characteristic curve where the gradient is one-third of the average gradient of the curve measured over 1.5 log units. It is often below 0.1 over base+fog.)

ONLINE HELP

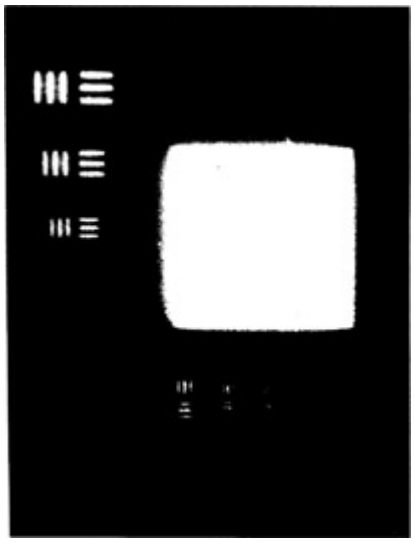
Issues specific to the *The Darkroom Cookbook* and *The Film Developing Cookbook* can be discussed at www.darkroomcookbook.com.

An errata page for *The Film Developing Cookbook* is published at www.graphos.org.

The Analogue Photography Users Group, formerly **APUG**, is now **Photrio**, at www.photrio.com

Many links to analogue photography sites, blogs, and discussion groups are located at www.digitaltruth.com/links.php. This site also hosts the *Massive Dev Chart*, the world's largest source of processing times for developing black and white film.

Chapter 1
DEVELOPER CATEGORIES

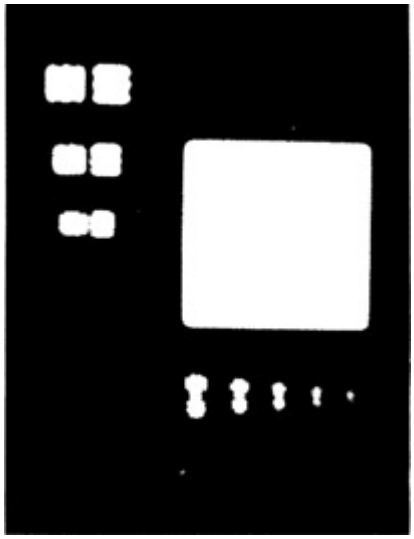


Each combination of a particular developer and film yields a unique negative. Differences may be great or small, but there will be differences. And those differences are an important ingredient in the recipe that, as photographers, we use to create our unique signatures.

This chapter outlines the main developer types, and suggests how to match them to particular films, formats, and pictorial situations. There are four key qualities to consider: sharpness, graininess, contrast, and speed.

Definition in photography

Definition in photography is the *subjective* impression of how clear the detail in a photograph appears. Definition includes many interrelated factors: graininess, contrast, resolving power, and sharpness.



Sharpness is the most important of the four. Sharpness has an overwhelming effect on viewers. On a gut level, we can forgive a photograph nearly any technical fault, as long as it appears to be sharp. But what does sharpness actually mean? Subjectively, we all seem to know. But sharpness is as hard to define as it is to measure: distinctness of outline or contour, abruptly or strongly marked—these are some of the ways people have attempted to pin down the concept of photographic sharpness.

Acutance is an objective measure of sharpness. Developers which enhance sharpness are often called *acutance, high acutance*, or *high definition* developers. Different developers, as well as agitation techniques, can have an enormous effect on acutance levels and, consequently, how sharp negatives will appear.

Resolution or *resolving power* is measured by examining a target comprised of parallel black bars on a white background, set up in a lines per millimeter arrangement. The smallest set of bars that is discernible equals the resolving power of the film or lens at hand. Decades of experience have shown that resolution is a poor guide to perceived sharpness—see the illustration at the right.

Other ways to measure photographic quality include DQE (Detective Quantum Efficiency) and MTF (Modulation Transfer Function).

The top photo shows good resolution but poor sharpness. The bottom photo shows poor resolution but good sharpness. For Geoffrey Crawley's definitions of sharpness and definition, see *Chapter 5*.

Graininess

Basic *grain size* is predetermined by the manufacturer. Slow films have finer (smaller) grains, fast films have coarser (larger) grains. *Graininess* is the *subjective perception* of grain. *Granularity* is a theoretically objective measurement which correlates with our subjective perception of *graininess*.

Graininess can be significantly altered by the developer and by the time film spends in the developer. Moreover, each developer creates its own unique grain pattern: tight; fuzzy; soft; hard-edged; or somewhere in between. The grain pattern can make or break an image. For a portrait or a commercial photo you will probably want a virtually invisible fine grain pattern. However, a photographic essay on junkies in a shooting gallery might have greater impact if the photos are sharp with an obvious grain pattern.

> *"We search for truth; sometimes we find beauty."*
>
> —LISETTE MODEL

As a general rule, solvent developers emphasize fine grain at the expense of sharpness; non-solvent developers emphasize sharpness at the expense of fine grain.

Contrast and gradation

There are three kinds of contrast: macro, local and micro. The curve we measure with a densitometer and usually see in film tests and manufacturers' literature is the *macro* characteristic curve—the contrast of large areas of the negative. These curves are generally measured by a device which covers a 2mm diameter area, a substantial portion of a small negative.

The *micro* characteristic curve is measured over a much smaller area. The micro characteristic curve of a film is always greater in contrast than the macro characteristic curve. A range of tones in a small area is reproduced with higher contrast than a similar range of tones in a large area. However, an area that was micro characteristic on a 35mm negative may be almost macro characteristic on an 8x10 negative of the same scene. Therefore, the larger the film, the truer will be the reproduction of micro-contrast.

Macro-contrast refers to the big effects that will tell us what grade of paper we will need to print a negative, or whether we can print a negative at all. A high contrast negative will need a low paper grade or filter; a low contrast negative will need a high paper grade or filter. In most cases, macro contrast depends not so much on the developer but how long the film is developed. The greater the development time, the greater the contrast.

When Zone System photographers expand or contract their negatives (N+1, N-1, etc.) they are manipulating macro contrast.

Local contrast is a synonym for gradation—a term we often use to discuss tonality and tonal differences.[1] It refers to macro contrast, but only over small parts of the characteristic curve. For example, when we refer to midtone gradation, we mean the separation between Zones III and VI.

A developer with "rich midtone gradation" increases separation in the midtone part of the curve (Zones III to VI). A developer with high toe contrast has a short toe (Zones I and II). The straight line starts almost at

once, and midtones might be compressed. A “brilliant developer” has a steep shoulder: highlights (Zones VII and higher) are widely separated but could be hard to print. A *compensating developer* has a smooth, long shoulder. Highlights can be dull, but easy to print.

Macro gradation characteristics are built into the film, and can be determined by testing with a densitometer. However, different developer formulations, dilution techniques, and agitation methods, have a significant effect on local contrast/gradation.

> *Micro-contrast explains why we can experience difficulty printing fine highlight detail with tabular grain films. Even though they have fine grain and high sharpness, tabular grain films have too much micro-contrast in highlight areas. The reason is that the lateral dimensions of flat tabular grains (which face the light) are so much larger than conventional grains. Because they do not scatter light as well as conventional grains, when there is an abrupt change in exposure level, there is also a tendency to high contrast in micro areas. The visual result is high sharpness but poor gradation.*

Micro-contrast effects are not as well known, but they are just as important as macro and local contrast when evaluating image quality. These areas, though not apparent to most viewers, play a great role in the emotional response to the image. They can be emphasized through the choice of developer *and degree* (overall time and frequency) of *agitation.*

The micro-contrast characteristic curve is steeper than the macro-contrast curve. How much and where depends on the film, the developer, and the *size* of the film. In practical terms, when you are using a film/developer combination with high micro-contrast, you will notice that small areas, like specular highlights, may be hard to print. Since micro-contrast relates to *size* it is automatically lower with larger film sizes. That is the main reason

photographers interested in capturing the finest highlight detail use the largest sheet film they can.

While it is possible to make a good, sharp landscape photo with 35mm, the same scene with a 4x5-inch view camera will reproduce micro areas with infinitely smoother gradation. On the other hand, as long as there is no camera shake or excessive movement by the subject the high micro-contrast of smaller negatives can give the impression of biting clarity to a negative. But this impression is achieved at the expense of smooth gradation in small areas. With high micro-contrast, small light-grey areas may become almost white in the print, and small dark-grey areas may become almost black. That is what we mean when we talk about 'losing smooth gradation in small areas'. But there is a benefit: we gain sharpness. (One way digital sharpness filters work is by increasing micro-contrast while attempting to leave macro-contrast unchanged.)

Speed

Developers can be divided into three speed categories:

those which decrease the film's rated speed
those which maintain the film's rated speed
those which increase the film's rated speed

In general, developers that decrease speed produce lower graininess, while those that increase speed produce higher graininess. In addition, developers that increase speed usually have less latitude for incorrect exposure than developers that maintain or decrease speed, while developers that decrease speed sometimes provide more latitude.

Negative quality

If there is any secret to obtaining high sharpness and fine grain, it is to ensure that the negative has a low density range. Maximum density should not exceed 0.9 above base+fog for small negatives, or about 1.2 for larger negatives. This means that 35mm negatives of normal scenic contrast should ideally be developed to print well on grade 3 paper.

> *Crawley 60/61 discusses developer interlocks in more detail than is usual in the literature. The reason may be that Crawley was one of the few chemists who had the opportunity to design such a wide range of developers over a long period of time.*

Medium and large format negatives should be developed to a slightly higher contrast, to print on grade 2 paper. That said, our suggestions for specific grades are offered in a general spirit, since manufacturers of graded papers don't use these numbers consistently.

Developer interlocks

In photography, you never get something for nothing. Every time you increase quality in one area, you lose it in another. Nothing better illustrates these interlocks than a discussion of fine grain developers.

Generally speaking, a fine grain, solvent developer causes a loss in film speed. A developer that offers both fine grain and good speed, such as undiluted D-76, has poorer sharpness than a non-solvent developer such as FX 1. By the same token, when a super-fine grain developer is used to develop a negative to high contrast the fine grain effect is usually lost, without necessarily regaining sharpness, though some of the speed loss may be reversed.

> *Low alkalinity means low activity, and practical experience for the past 100 years has shown this is a prerequisite for fine grain. But why that should be so is controversial. At a low pH, grains tend to develop only partially. In Geoffrey Crawley's view, there is less swelling of the gelatin, which preserves the power of the gelatin to protect against grain "clumping." (See chapter 5 for more detail on this contentious term.) It is actually groups of grains, not individual grains, that are visible to the eye as graininess. Others theorize that the development process affects grain clumping less than hitherto supposed, except in the rare case of infectious development used in some lithographic processes. Whatever the reasons behind it may be, if you want fine grain you must have low alkalinity.*

Choosing a developer

So how do you choose a developer? Maybe the easiest question to ask is whether you prefer fine, smooth grain, or high sharpness. Once you answer that, you can choose from one of the two main developer groups: solvent (fine grain) or non-solvent (high sharpness).

Solvent developers (fine grain)

A solvent developer etches the silver halide crystals in the emulsion, giving finer silver halide grains to work on and providing a source of silver ions to compete with the chemically reduced silver particles, which are coarser. But solvency alone is not enough to obtain fine grain. It is just as important to maintain low alkalinity—which for developers means between pH 7.5 and 8.5 (most often 8.2 to 8.5). D-23, D-76, Microphen, and Xtol, are solvent developers.

Another name for solvent developers is *solution physical developers*, a term which indicates that some of the silver dissolved by the solvent is replated back onto developing sites on the film. There is generally, but not always, some loss of perceived sharpness as a result of this, but also a further smoothing of the appearance of the grains. There are at least four mechanisms at work in a solution physical developer to produce fine grain:

the etching of the grains
the replating of dissolved silver back onto the grains
low activity resulting in less developed and therefore smaller grains
low activity resulting in less aggregation of large groups of grains

Non-solvent developers (acutance)

Non-solvent developers are also called *chemical* or *surface* (as opposed to physical) developers. *High definition* or *high acutance* developers belong to this class.

In a solution physical developer like D-76, silver density builds up both by the chemical action of the developer and by the physical action of dissolved silver replating itself onto the silver image. Though all developers have some solvent effect, a true non-solvent developer has minimal solvent action.

SOLVENT SPEED DECREASING	SOLVENT SPEED MAINTAINING	SOLVENT SPEED INCREASING
D-25	Adox MQ-Borax	Acufine
DK-20	Rudinal + 6% sodium sulfite	FX 3,4,7,8,9,10,11,15,18
FX 5	Ansco 14, 15,47	ID-68
Microdol-X, Perceptol undiluted	D-23, D-76/ID-11	Microphen
Most phenylenediamine developers	FX 1b	Xtol
	Microdol-X, Perceptol (both 1:3)	

NON-SOLVENT SPEED DECREASING	NON-SOLVENT SPEED MAINTAINING	NON-SOLVENT SPEED INCREASING
Beutler Low Contrast	D-61a, DK-50	Beutler, Neofin Blue/Red

NON-SOLVENT SPEED DECREASING	NON-SOLVENT SPEED MAINTAINING	NON-SOLVENT SPEED INCREASING
Most pyro-only developers	D-76/ID-11, D-23 (all 1:3)	FX 1, FX 2
Most glycin-only developers	HC-110	PMK, Pyrocat-HD
Universal/D-72	Rudinal	Xtol l:3to 1:5, Edwal FG7
	Unitol	Acutol, Aciispecial, FX 37, FX 39
	pyro-metol & metol-glycin	Windisch, TD Pyrocatechin

The problem with proprietary formulas was summarized by Richard Henry. He states that it is scientfically abhorrent to use secret chemical formulas. He noted that Rodinal, HC-110, and Kodak's packaged D-76 had all changed formulation several times, making it impossible for anybody to check anybody else's results or know where you stood at any given time. "We could solve this problem by refusing to use secret formulations and make up our own solutions from chemicals of known purity." In cinema film development, where a mistake could cost countless thousands, "secret" formulas are seldom used.

Although the grain structure produced by a non-solvent developer is *coarser*, it usually appears to be *sharper*. This sharpness can effectively mask the appearance of the increased graininess.

Some developers can belong to both the non-solvent and the solvent categories, depending upon how they are used. For instance, undiluted D-76

is a solvent fine grain developer. But diluted 1:3, it becomes a non-solvent high definition developer.

The table above categorizes several developers. “D” or “DK” indicates Kodak, “ID” Ilford, “FX” or “Acu-” Geoffrey Crawley formulas.

Commercial developers versus published formulas

All developers start deteriorating from the moment they are mixed with water. For this reason, developers packaged as a liquid are the least reliable. No matter how carefully they are preserved and packaged, their shelf life is limited. Some manufacturers compensate by making them about 10% stronger. D-76 is the one significant exception. Up to a certain point, it becomes more active after mixing (chapter 5).

For the same reason, powder developers, which have good shelf life, should not, whenever practical, be mixed as stock solutions to be kept for many months. Ideally, a developer should be mixed as a working solution and used as soon as possible.

Even unmixed powder developers are not indefinitely stable. Dry chemicals, placed in contact with one another, react and change their characteristics. It is a manufacturing feat to package a stable, single-powder developer. Two-packet developers, with the alkali in one packet, and the acid or neutral chemicals and developing agents in the other, will invariably have a better shelf life. Best of all is to keep all chemicals separate until just before mixing, and to use fresh chemicals.

Proprietary versus published formulas

A problem with proprietary formulas is that the manufacturer can make "improvements" without notifying the public. There is no law that requires photo manufacturers to notify users when there is a change in a developer, paper, or film. Photographers who have spent years getting used to a developer may suddenly find it has been significantly changed without notice. Even worse, a proprietary formula may be taken off the market completely, leaving the photographer high and literally dry.

The simple cure for this problem is to find a published formula (or several) that meets your needs, and mix it yourself as necessary. Its properties will never change, it will never become obsolete, and you do not have to worry about it losing potency.

Manufacturers often counter that their proprietary formulas are periodically "optimized" to conform with improvements in films. We do not subscribe to this reasoning. The "optimizations" manufacturers are most interested in are new cost-cutting techniques. In addition, no manufacturer can afford to make a black and white film that will not perform reasonably well in D-76, the world's most popular developer. For this reason, many published developers that worked well with films 50 years ago work just as well with current films. Indeed, both Kodak and Ilford have stated that T-Max and Delta films are still optimized for D-76.

Finally, each film developer has a unique personality. Most commercial developers are formulated to balance a number of qualities to suit the taste of the "average" photographer. In any case, always suspect any developer that claims to be "optimized" for a wide range of films. *It is possible to optimize for one film; it isn't possible to optimize for all films.*

The appearance of prints

Just how different will prints look, depending on whether a solvent or a non-solvent developer is used? As a first point, the difference is tied to the degree of enlargement. Differences between the developer types become more apparent as the degree of enlargement increases. If you contact print an 8x10-inch negative, it should look sharp and fine grained with smooth gradation, no matter what kind of developer you use. With enlargements from 120 and 35mm film different developers have a much greater effect on the final print.

In general, solvent developers give smoother midtone gradation, and finer grain. Non-solvent developers produce a clarity that is visually effective, but at the expense of increased grain and less smooth gradation. The increased graininess of non-solvent developers becomes especially apparent in out-of-focus areas, or areas with large expanses of untextured tone. For this reason, they are better suited for highly detailed subjects with great depth-of-field.

Film size

With small and medium formats, the principal goal is to obtain a negative that will print with good sharpness first, fine grain second, and good gradation third. In the larger formats we do not have to worry about sharpness and fine grain. We can concentrate on using the developer to coax the best possible gradation from the film.

With 4x5 and larger film, image quality will be good even if the developer does not enhance the film's inherent grain and sharpness. Even if we were to enlarge a 4x5 negative 10x (to 40x50), it should appear sharp and grainless *if* the viewer stands at a normal viewing distance of about ten feet, much further away than for an 8x10 print. If the viewer stands only two or three inches away from *any* print, it may appear fuzzy. However, only teachers, and students who are trying to learn spotting techniques, should look that closely. Anyone else is not appreciating the photograph.

35mm and roll film

With small formats, it is necessary to give the least possible exposure that will still record adequate shadow detail. This means the negative needs to be as thin as possible. The thicker the negative, the more grain and the less sharpness when you enlarge. However, the penalty for minimum exposure is reduced shadow gradation in the negative. Special printing techniques like dodging and burning are often the only way to get a thin negative to show shadow gradation as rich as a thick negative.

Developers for small format films

Most small format films today have fine grain, high sharpness, and fairly long-scale gradation. The fine grain and high sharpness are essential since the film will often be enlarged at least 8x. The ability of the developer to produce long-scale gradation is important because development of individual frames on a roll of film is not possible. The developer must provide a large margin for a wide range of exposures, including incorrect ones, at a single developing time.

Three types of developers work best with small formats:

1. Fine-grain developers
2. Dilute fine grain developers
3. High definition developers

Fine grain developers will produce the finest grain and lower, smoother, micro-contrast, with some loss in sharpness. High definition developers will produce excellent sharpness with increased grain and less smooth micro-contrast. The world's most popular developer, D-76 1:1, does not excel in either department. But it is an unbeatable and reliable compromise developer for a wide range of situations. That is a valuable feature when you cannot develop negatives one by one.

Large format

The primary concern of large format photographers is gradation, which is controlled by developing sheet film individually for different times or with different developers.

With large format films, we have the ability to overexpose by one or more stops with minimal gain in graininess or loss of sharpness. We therefore gain easily printable shadow detail. The Zone System, as it is largely practiced, has a built-in overexposure safety net.

Developers for large format

The development control which large format photographers seek can best be achieved when the developer is reasonably slow. This is especially true when tray developing several films since you can not hope to achieve uniformity with short development times. Glycin developers are particularly valuable for developing sheet film in a tray or in a rotary processor, because glycin is highly resistant to the two major problems associated with each of these processes, aerial oxidation (trays and rotary processors) and bromide streaking (rotary processors).

> *"Technique is important. But the eye is the only certainty we have. The eye, and the way it connects to the heart."*
>
> —LISETTE MODEL

Large format users often choose a developer exclusively from the point of view of contrast control. Many use HC-110, because it can create a wide range of micro- and macro-contrast effects through dilution. Others prefer Rodinal, and some will use only PMK or another pyro developer, because of pyro's unrivaled highlight separation. Then there have been photographers like Arnold Newman, who never used anything but D-76 1:1, and knew how to get the most out of it.

Applications

The suggestions below are our subjective opinions, but they may help you decide what developer to use to obtain a specific effect in portraiture, landscape, photojournalism and street photography.

Portraiture

Studio portraits allow close control over the photographic process. Lighting can be adjusted so all tones reproduce as desired, and a perfect exposure can be made.

With large format sharpness will be assured no matter what developer is used. When desired, some softening might be possible using a super-fine grain developer (chapter 7).

With smaller formats you must decide whether you want the revealing clarity of a high acutance developer, or the more flattering smoothness of a solvent developer like D-76. Rodinal would be an excellent choice between the two extremes, although it is not easy to get good results with Rodinal and fast 35mm films. In medium and large formats Rodinal works fine with fast films.

In a portrait the most significant specular highlights are the catch lights in the subject's eyes, which usually reflect the shape of the primary light source. Many portraits have hard, bright white, unpleasant catch lights. A compensating developer can help to print these more naturally. A very high acutance developer, like FX 1 or FX 2, might actually increase the density of these areas, especially if they are very small. Once again, a compensating developer with less of an acutance effect, such as Rodinal, would be a good

choice. Alternatively, a tanning developer may turn out to be the process which fulfills your personal vision.

We recommend conventional films for portraiture. They seem to capture highlight detail more naturally. If a tabular film is used, downrate the speed and pull process.

Landscape photography

The most frequent problem encountered in landscape photography is how to record a greater than normal subject range on film. Our recommended developers for landscapes are PMK, FX 2, Rodinal 1:75 or 1:100, or most two-bath developers. Other possibilities are solvent developers diluted 1:3, such as D-76, D-23, or Xtol. Of these, Xtol will have the highest speed. All produce printable highlights in high contrast natural light situations. For extreme subject ranges, 12 stops or more, we suggest experimenting with one of the ultra-low contrast developers in chapter 11.

> *"Fortunately, the practice of photography does not depend upon a complete understanding of how the photographic process works."*
>
> —GRANT HAIST

For low contrast scenes (fog, mist, rain), a stronger developer like undiluted D-76, Xtol or FX 15, Rodinal 1:25, or Diluted DK-50 would all be good choices. Interestingly, although PMK is often recommended for high contrast subjects, it has been found to work well for the reproduction of delicate low contrast subjects in fog and mist, because of its outstanding midtone separation. Since it is a two-solution developer, it can, like all two-solution developers, be adjusted for low contrast subjects by increasing the amount of Solution A by 25 to 100%.

For landscapes on tabular grain film, we suggest reducing the speed by 1–2 stops and then pull-processing in Xtol. For low contrast scenes, use Xtol as you would for conventional grain films: undiluted for low contrast scenes; diluted between 1:1 and 1:4 or even greater for high contrast scenes. Alternatively, D-23 and D-76, both diluted 1:3, have proven value, but developing times may be long.

Developers for 35mm and roll film with mixed contrasts

35mm or roll film will often have a wide mix of contrasts on one roll. Our best suggestion are compensating developers such as FX 1, FX 2, D-76 1:1, Xtol 1:2 or 1:3, PMK, WD2D, Rodinal 1:50–1:75 or a two-bath formula. The wide range of today's graded and variable contrast papers will do the rest.

Developers for press and street photography

Developers for press and street photography must be fault-tolerant. You need as much latitude as possible, since you often do not have time to measure exposure carefully. The ideal developer should not emphasize acutance too much because high acutance developers actually magnify motion and camera shake effects.[2]

D-76, undiluted or 1:1, has long been the press photographer's developer of choice.

A speed increasing developer can give a small gain in underexposure latitude in exchange for a loss in overexposure latitude. Two developers which give a 60% speed increase without losing much latitude are FX 15 diluted 1:1 and Xtol diluted 1:1 or more.

Press photographers also need fast development times and some insurance against accidental overdevelopment when processing is rushed. Two-bath

developers can be useful in this respect.

Our best advice to street photographers is to use a film with as much latitude as possible. By latitude we mean tolerance to underexposure, overexposure, underdevelopment and overdevelopment. Throughout

> *The film that was intentionally designed, more than any other, to have the maximum latitude possible, and to provide good sharpness and fine grain under the broadest possible circumstances, was Verichrome-Pan in its incarnations from the late 1950s until it was discontiued in the 1990s. With an EI of 125, easily ratable to 250, this was the most forgiving film Kodak ever made. Now that Kodak is beginning to revive some of its old films, we hope Veri-chrome may one day join that list.*

the past four decades, Kodak's conventional grain films have had greater latitude than any others, with Tri-X being the hands-down favorite of press and street photographers. 21st century Tri-X is finer in grain than ever before. It's almost like having Plus-X at higher speed. But it is no longer as flexible, and the grain has lost something of its appealing gritty edge. We now prefer Ilford HP5+ for street photography.

None of the tabular films have the flexibility preferred for street work. You can gain latitude by downrating the speed by a stop or two. But street photography needs speed.

NOTES

1. Focal Encyclopedia.

2. Crawley 60/61 was the first to explain why this happens. A high acutance developer works by increasing the contrast of minute portions of the negative. But this only works if the negative is sharp to start with. If there are blurred or outof-focus areas, the increased contrast actually magnifies the blurriness. In other words, a high acutance developer gives you more of what you've already got: it will make a sharp negative sharper; it can make an unsharp negative fluffier.

Chapter 2
FILMS

This chapter covers the continuous tone, pictorial films available today. Although we are continuing our personal recommendations, we want to state upfront that films do have a tendency to change without notice, as do photographers' opinions. In addition, there is a whole new world of film rebranding which didn't exist at the time of FDC1. We will do our best to chart it.

Speed classification

Black and white film can be divided into two basic groups: speed and type. For this discussion, speed is based on the manufacturer's ISO rating, not personal exposure indexes.

Slow—ISO 64 and below

Slow films have the finest grain and highest sharpness. They inherently have a shorter tonal scale than faster films. One technique long known to extend the scale of slower films is double coating with two emulsions.

Medium—ISO 80 to 250

Still the best for all-round photography, these films have long-scale gradation, fine grain, and reasonable speed.

Fast—ISO 320 to 800

Fast films are best for street photography, action, wildlife, sports, news or anything that requires hand held cameras. Tonal scale is long, exposure latitude is very good. Traditionally, they weren't recommended for landscapes and scenics unless you used sheet film 4x5 inches or larger. However, fast tabular grain films such as Delta and T-Max 400 have grain comparable to medium speed conventional films such as FP4. And post-2007 Tri-X is finer in grain than ever before, almost comparable to discontinued

Plus-X. All other current conventional grain EI 400 films are grainier than current Tri-X.

> *Those who want old-fashioned Tri-X grain could try developing Tri-X in high definition developers; or use a different film.*

Ultra fast—ISO above 800

Ultra fast films are ideal for extreme low-light, law enforcement, fine art (where you want to exploit graininess for aesthetic effect), sports, street photography, and photojournalism. There were four 35mm films in this category in FDC1; today there are only Delta 3200 and the newly re-released Kodak P3200. At the time of writing, we find that, in 35mm, HP5+ is the most effective film for pushing to 1600 and 3200 today (chapter 10).

Film types

Speed aside, pictorial films can be characterized into six broad types: conventional, tabular, chromogenic, document, infrared, orthochromatic, and transparency. Where the film's name does not include its speed, we have noted speed in parentheses next to the film's name. Sometimes these types overlap: for example, a transparency film can have conventional, tabular, or mixed grains. Many of today's films include the EI rating in their name.

> *"Why should I use a meter? What if the darn thing broke on me when I was out making a photograph? Then what would I do?"*
>
> —BRETT WESTON, 1992

Conventional grain films

Adox Scala 160/Silvermax, Scala 50, HR-50, CHS 100 II
Agfaphoto APX 100 and 400
Arista Edu Ultra films (ISO 100, 200 and 400)
Bergger Pancro 400
Ferrania ISO 80
Film Washi (various specialty films)
Foma 100, 200, 400 and Retropan (ISO 320)
Fujifilm Neopan Acros 100, Neopan Acros 100II

Ilford Pan F+ (ISO 50) FP4+ (ISO 125), and HP5+ (ISO 400)
Note: we usually drop the + when discussing these films.
Ilford/Harman generic ISO 100 and 400
Japan Camera Hunter Streetpan 400

Kodak Tri-X (ISO 400), Double-X cinema film (ISO 250) (marketed as Cinestill BWxx)
Luckyfilm ISO 100
Rollei 100 and 400
Orwo UN54 (ISO 100)

Tabular grain films

Kodak T-Max 100, T-Max 400, P3200
Ilford Delta 100, 400, 3200
Foma 200 (mixed grain)
Orwo N74+ (mixed grain)

Chromogenic films

Ilford XP2 Super

Document films

Kodak Technical Pan (Tech Pan) (ISO 25) (occasionally available from frozen stock
Agfa Copex-Rapid (under various brand names; probably frozen)
Adox CMS 20 (currently manufactured in 35mm, 120, 4x5)
From time to time other films in this category become available. See chapter 11 for more detail on these films.

Infrared films (ISO ratings without filtration)

Ilford SFX 200
Rollei Infrared (400) (real manufacturer probably Agfa)
Film Washi ISO 400 near-infrared (NIR)

The simplest way to improve sharpness, fine grain, and gradation of small areas is to use a larger film size. This may not be convenient or economically feasible. But it works.

Orthochromatic films

Ilford Ortho Plus (ISO 80; sheet film sizes only)
Rollei Ortho 25 (manufacturer unknown)
Film Washi W-25, hand coated on Kozo paper

Transparency

Adox Scala 160; Adox Scala 50
Fomapan R100
Harman Direct Positive Paper

A note on branding

As will be seen, many of the films available today are branded products that all originate from the same source. We're not marketers, and we wish anyone who can run a photographic business well, but we don't find this trend helpful, except in one way: the branded films are often cheaper yet appear to be comparable to the premium standard-setters. Are they

identical? We know they are close, but only the manufacturers know for sure if they are the same, and the manufacturers will never tell.

Conventional grain films and their evolution from the 1950s

This category includes all black and white films before the introduction of tabular grain films in 1988. Most films manufactured today are still conventional as they remain more popular than tabular films.

Conventional films run the gamut from shorter scale, slow speed, very fine grain emulsions such as Pan F to long scale, fast emulsions with medium grain such as Kodak Tri-X and HP5.[1]

Are they thin or thick?

There is a saga running through fine art photography communities.

Films before roughly 1950 had thick emulsions, straight line curves, and enormous flexibility for varying macro contrast (expansion and contraction in Zone System terms).

Films after 1950 rapidly switched over to thin emulsions and ushered in the modern era of conventional film. Their low gelatin-to-silver ratio allows these modern films to be sharper and finer grained than older thick emulsions. But they lost their flexibility for varying contrast.

One legend has it that thin emulsion films were discovered in the early 1950s when the German film manufacturer Adox accidentally coated a large run of film with too much gelatin. In an attempt to rectify their costly mistake they scraped off a micro layer, going too far in the other direction. Hoping to be able to sell the film, they tested it and discovered that it produced sharper images, with finer grain, than had previously been possible.

Whatever the truth of the matter is, the 1950s soon saw "thin" emulsions from every manufacturer. But could emphasizing the difference between thick and thin emulsions have been marketing hype rather than fact? Independent researcher Gordon Hutchings measured the relative thicknesses of so-called thick and thin emulsions and has not found any substantial differences.

> *"We are only as good as our materials."*
>
> —ROGER DAVIDSON

Thus, when we speak of thick and thin emulsions today, we may be referring more to emulsion *style* rather than physical fact. (To make things yet more confusing, 'thin' is sometimes used to distinguish single from double or multi-coated emulsions.)

Or are they chaotic or precise?

We think it's more helpful to consider how the style of emulsions has evolved since the 1930s. This has accelerated in recent decades as manufacturers have gained new skills. As Mirko Böddecker of Adox has explained it, "Old emulsions were mainly pour-in-the-bucket-style uncontrolled emulsions. They had a chaotic grain distribution not only in grain size but also in shape. Because of the resulting non-perfect covering capabilities, more silver needed to be coated. A result was natural high latitude, since in a negative, unlike a positive, not all silver is developed out. The downside was poor control in manufacturing (less easy to reproduce and stabilize), and larger grain size for the same speed, and of course a higher price for the extra silver. Today we have controlled emulsions (double jet 'makes' in physically separated reaction chambers in the kettles). We can

now intentionally design emulsions in respect of crystal size, shape and distribution. While injecting we check the parameters and steer against offsets. We tend to manufacture smaller bands (one type of shape in not too polydisperse a distribution). The narrower the band, the more stable the 'make'. Then we mix these together (or coat in several layers if there is reason to do this) or use other ways of shaping the grain size in the following production steps in order to design the curve, encompassing such desiderata as latitude, transformation of light and colors to shades of grey, etc. Today we can make films much more to the point where we want them, reproduce them with consistent quality, and stabilize them better. These techniques let us combine tabular grains with classic grains, for example as Fuji does in some of the excellent Acros films. We can gain the same Dmax with less silver and with finer grain."

As a marketing ploy, the emphasis on thin emulsions backfired with the fine art community. Zone System users came to believe that the older thick emulsion films had allowed them more ability to change contrast (expansion and contraction in Zone terms) than the newer films did. The Zone System people were right, but maybe for the wrong reasons. From 1950 onwards, grain distribution has steadily become less "chaotic" to use Mirko's useful term, and films have, in turn, steadily lost flexibility.

Yet there has been an almost reciprocal gain along the way. As flexibility to under and over-exposure was lost through better emulsion control, new flexibility was gained through double-coating techniques that were perfected in the 1950s.

For example take Kodak Tri-X. It is a modern, well-controlled emulsion. But it is double coated (with a fast emulson and a slow emulsion) to provide immense latitude in exposure. Many good modern films work this way.

So: we do still have large exposure latitude. Why then is not possible to do Zone-style expansion and contraction during development as easily as we could with the old style films? I surmise that "chaotic" emulsions offer more flexibility during development than the newer emulsions. It is also worth considering that more creative development techniques can provide

expansion and contraction techniques that Zone System users may not yet be familiar with.

> *"The first thing a young photographer needs is a rich spouse."*
>
> —LISETTE MODEL

Finally, it is possible—and we may now never know the truth—that some of the flexibility Zone System users thought they were achieving with the older films was due to measuring artefacts that were common in the 1930s and 1940s due to the imprecision of the light meters, sensitometers, and densitometers of the day. Even Kodak found, in the 1950s, that some of the most critical sensitometric measurements it performed in the 1940s were incorrect. An example is the famous "hump" in paper curves noted in the L.A. Jones papers.[2] Though surprising to the researchers, and measured and re-measured time and time again with the best equipment available, the readings were finally accepted at the time. They were later found to be wrong. There was no hump. This error was never corrected in the photographic literature. That's a pity, because photographers outside of research labs need to know how possible it is, even easy, to mis-measure and mis-interpret their own technical data.

> *Not only were sensito-metric results prior to the 1950s subject to considerable error, but there was another foundational problem in the early Zone System work: exposure meters are not calibrated to 18% grey but to 12–13% grey. This fact (part of the ANSI standards for exposure meters) was first mentioned by George Wakefield, and subsequently by us in FDC1, and discussed by Dickerson and Zawadzki in 'Is 18% Gray a Myth?', Photo Techniques, May/June 2008. Ansel Adams was*

astonished when we discussed this with him, but pertinently pointed out that it doesn't really affect the Zone System since the system is calibrated to a user's particular equipment.

Can nostalgia and reality meet?

Two films with extremely long scale and flexibility were Kodak's Verichrome Pan roll film (and 35mm in South America) and Ektapan sheet film. These irreplaceable (double-coated) films are now discontinued and no direct substitute for either is available. But a remarkable film, Eastman Double-X (EI 250), *is* still available in 35mm, and is beginning to be used by still photographers. Double-X is very much its own film: it is in no sense a replacement either for Verichrome or for Plus-X. RMS granularity for Double-X is 14, compared to 9 for Verichrome and 10 for Plus-X. However, MTF curves for Double-X show peaks in the lower frequencies rather than the higher frequencies, a behavior that is indeed typical of Verichrome Pan. This "style" of sharpness was considered desirable in the 1950s, but most manufacturers today prefer to work for higher levels in the high frequencies. Roughly speaking, with the Verichrome and Double-X style, larger, coarser areas will appear more visually snappy; with the newer style of films, smaller areas will appear sharper at the expense of larger outlines.

Or consider, historically, one of the best "thick" emulsion films, Kodak Super XX. This film was widely used for Zone System work, and many alternative or darkroom processes such as gum printing, platinum/palladium, cyanotypes, dye transfer, enlarged negatives, and separation negatives. It responded beautifully to pyro developers such as ABC, SD-1, and PMK. Yet we have seen that the sheet films available today also work well with these processes. We cannot use the same developers and techniques that were used in the 1940s, but with new techniques, we can obtain the responses and results we need.

Contemporary conventional grain films in detail

Adox is the name of Germany's first photography company. Today, headed by Mirko Böddecker, it holds the technology of many extinct European film and paper manufacturers, including Agfa, Efke, and Forte. Production is gradually increasing so it is not possible to know exactly what this company will be producing when you pick up this book. At press time, Adox is offering films at ISO 50 and 100. CHS 100 II is an Efke 100 successor with modernized emulsion and superior coating technique.

Agfa films according to the formulas in use by Agfa before it closed doors in 2006 are not available today with one notable exception: **Adox Scala** (see the section on Transparency films) and the identical film sold for negatives as **Adox Silvermax**. They are the true Agfa APX 100 emulsion, but thicker (and on a clear base), to provide additional Dmax for transparencies. Under its two names this film comes closest to the great 1930s-style silver-rich, mixed-grain-size emulsions. Adox plans to revive Agfapan 25 in the foreseeable future.

Agfaphoto APX 100 and 400 were formerly frozen stock from Agfa, but at present they are Harman 100/400.

Bergger does not make film but unlike many rebranders, it tries to offer specialty film that is not available elsewhere. We think this is an admirable attitude. Its success is variable. Reports on its current offering, Pancro 400, a new film introduced in 2017, and available in a wide range of sizes, are encouraging. It is a double layer film made with modern technology.

Ferrania has revived an ISO 80 emulsion that was used in motion picture films in the 1960s. Presently available only in 35mm, 120 is planned.

Film Washi, established in 2013, bills itself as the world's smallest photographic material manufacturer. It makes a number of original and

interesting films, some coated on paper which require special care in hand processing.

Foma 100, 200, 400 and Retropan (ISO 320) are often budget-priced. Most are made according to older technology and are thus extremely welcome in today's depleted marketplace. (The exception is 200, which is a mixed conventional plus tabular emulsion.) They are responsive to different developing techniques. In the past there were occasional quality control concerns with Foma films but these issues seem to have been solved in production at the time of writing.

Freestyle's widely used **Arista Edu Ultra** films (100, 200 and 400) are stated to be made in the Czech Republic. It seems unlikely that there is a film manufacturer in the Czech Republic other than Foma.

At the time of writing **Fujifilm**'s Neopan Acros 100 was the only available black and white film from that company. Manufacturing was scheduled to be discontinued in October 2018 with sales to continue throughout 2019. Stocks would remain for some time, however. This film is extremely fine in grain and sharp for its speed, with outstanding reciprocity characteristics. Neopan 100 Acros uses a technology called 'Precision Iodide Distribution Control Technology' which is a way of controlling many image characteristics, such as microcontrast and sharpness. It is claimed to provide considerable resistance to processing variations. Similar techniques were pioneered by Kodak decades ago but how and in which films they are used, and to what effect, is still a closely held secret. We applaud Fuji for having made the rare decision to give photographers some useful information about the technology behind the film. In June 2019, Fujifilm announced Neopan Acros 100II, a new version utilizing new technology to deal with substitutes for certain raw materials that had, apparently, become unobtainable.

In the late 1930s, radical changes were made in Kodak and Agfa films due to the near simultaneous discovery of gold sensitization which allowed a 2–4x speed increase. Super-X, the EI 125 material of choice for

cinematographers, was replaced by Plus-X, and many detested the film. Kodak also introduced Super-XX, an EI 200 material. Many cinematographers found that by overexposing and underdeveloping Super-XX, they could obtain the characteristics they loved in discontinued Super-X. ("Movies and Methods, Volume II", Bill Nichols, 1985, p. 66). That scenario is not unlike what we are doing today with tabular films: by creative choice of available materials and skillful processing, you can often get the particular look you are after. Note: Koslowsky discovered gold sensitization for Agfa in 1936 and fast films followed. Kodak claimed it did not have gold sensitization until after the war. Yet by 1951, it was confirmed that Kodak had gold sensitization soon after Agfa. (W.F. Berg, Photographic Sensitivity and Chemical Sensitisation of Emulsions. Zeitschrift Für Naturforschung Section A-a, Journal of Physical Sciences, 1951.)

Ilford Pan F+ is the only slow general purpose pictorial film now made. It is not as fine grained as APX 25 was, but due to its lower contrast and longer scale, is easier to handle in a broad range of developers and situations. Its tonal scale is longer than the old Pan F. Though we count Pan F+ as a long scale film, it is not as flexible as Panatomic-X was. However, it is still available. Ilford FP4+ is another favorite of ours. FP4+ responds well to a wide range of developers and techniques. It produces a full tonal scale, fine grain, and high sharpness and works beautifully with Xtol 1:3, classic high definition developers like FX 1 and 2, and tanning developers like PMK. It is an excellent film to use as a basepoint standard for measuring the qualities of other films. HP5+ is Ilford's ISO 400 film, and is now our favorite for that speed.

Ilford/Harman also makes a two budget films, 100 and 400, that are thought to be very close to FP4+ and HP5+. They are said to be of lesser quality in some way that has never been precisely defined. Perhaps such a definition would be impossible. These films are branded under various names. Some we know of are **Kentmere** 100/400, **Agfaphoto** APX 100/400

and **Rollei** RPX 100/400. We welcome these additions to the palette of traditional-look films. We designate these films **Harman** 100 and 400. It is possible that these films have been customized in some way, and the branders would certainly like customers to think they were. Regardless, these are excellent, good value films.

Japan Camera Hunter is an interesting outfit that, somewhat like Bergger, looks for films nobody has. Its current offering, Street Pan 400, is an old surveillance film that is apparently being remanufactured. It has extended red sensitivity, reportedly into the near-infrared range. Contrast is notably high.

Kodak Tri-X has been the most popular fast film since it was introduced for 35mm in 1954 (it had been available as sheet film before that). Tri-X is reported to account for over 80% of all black and white film sales. For its fast speed it has fine grain, high sharpness, and good tolerance to under- and overexposure. At the time of FDC1, we found Tri-X more pushable than Ilford's HP5+. Since then, Tri-X has become a finer grained film but no longer seems pushable the way that HP5+ now is. Tri-X is now more like Plus-X, but with two stops more speed.

Little known but of great interest is **Kodak Double-X** cinema film (ISO 250). This emulsion was first released in 1959 and reportedly has not been changed much since. It is still used for major Hollywood pictures shot in black and white. 35mm canisters are available from Cinestill (among others), who brand it as BWxx. More on page 15.

As of 2017, **Luckyfilm**, an offshoot of Lucky Group (which partnered with Kodak in the early 2000s) is making a new ISO 100 film called

At press time we became aware that Svema film is available again. Svema was a Ukrainian company which ceased production in 2000. Its equipment and expertise appear to have been taken over by Astrum, also located in Shostka, and the film is being marketed under the Svema brand. **Svema** *(Astrum) and* **Tasma** *are two former-USSR companies*

reportedly still manufacturing film (there may be others). They are available from the **Film Photography Store**. *Several other films that we have not covered are either available or are in the pipeline.*

New SHD 100. This inexpensive film is currently widely available and has been more enthusiastically received than earlier versions. We don't yet know what grain type the emulsion is.

Orwo, historically the East German sister company to Agfa at Wolfen, still makes several traditional and special purpose films. Due to a licensing agreement in effect at the time of writing, Orwo films are marketed for cinematography, but those who wish can load their own canisters, and individual 35mm rolls are available from time to time. Orwo UN54 is a single emulsion layer conventional grain films at ISO 100. N74+ is a double layer film with some proportion of more modern crystal technology, at ISO 400. Orwo also makes several unique specialty films, including one for film preservation that is used by the US Library of Congress and the Smithsonian.

Rollei does not manufacture films. It is a marketing company only.

Conventional films from no longer extant manufacturers

Forte's assets have been absorbed into Adox and there are active plans to restart manufacture.

Efke's products appeared to be irreclaimably lost as much of the equipment has been destroyed. But the formulas still exist, and are held by Adox, which has made considerable progress towards getting these films back into production.

Tabular films

Tabular films take advantage of new technology for growing thinner silver crystals so they have more surface area and less depth than conventional silver crystals. It is like comparing flagstones (tabular grain) to boulders (conventional grain). Tabular grain films use approximately 30% less silver than conventional films (perhaps making them more popular with manufacturers than photographers). As noted in chapter 1, the larger size of the crystals causes higher contrast in minute areas, resulting in higher sharpness but poorer gradation of fine detail.

Kodak's name for tabular films is T-Max; Ilford's is Delta; Fuji's is Sigma. Delta films are slightly grainier than their T-Max siblings; some of Fuji's, now discontinued, were less grainy. The aspect ratio (height versus width of each T-grain) of the T-Max films is about 1:8: a thin, long, flat grain. The aspect ratio of Delta films is about 1:5, shorter and thicker. However, the thicker grain of Delta films still has far more light gathering surface than any conventional film. Because the grains in Delta films are smaller, they are potentially able to hold fine highlight detail better than T-Max films.

Tabular films are harder to process because they can be sensitive to very slight changes in development time and temperature. For example, most conventional films require at least a 30% increase in development time to produce a noticeable change in contrast and density. Some tabular films will exhibit a significant change with only a 10% increase in development time.

All tabular grain films provide finer grain and higher sharpness than conventional films of the same speed. But if you value smooth gradation of fine highlight detail, a conventional film will provide more satisfactory results.

Tabular films are not a replacement for conventional films; they are an addition to the palette. Like everything in photography, improvements in

one area lead to compromises in another.

> *We are less hostile to tabular grain films than we were in FDC1. Tabular grain films have higher micro-contrast than conventional (cubic) grain films, so they appear to be sharper and more 'digital' and seem to have less subtlety in fine details. That can be an advantage, depending on the subject. Tabular grain films can be made to behave more like conventional grain films if you over-expose them by up to two stops, and develop for 20–30% less time. Following this recommendation should improve results by making more development centers available, thus reducing micro-contrast. Most people at Kodak involved in the T-grain program believed that when T-Max 100 was overexposed and under-developed, it matched or exceeded the quality and subtlety of Panatomic-X. Similarly, T-Max 400, exposed at 100 and suitably developed, is a viable alternative to Plus-X and even Verichrome Pan, though nothing can replace the precise and much-loved characteristics of those discontinued films. Many manufacturers now combine tabular and conventional grains either in multiple layers or within a single emulsion.*

Chromogenic films

Chromogenic films are black and white films based on color technology and should be developed in C-41 chemistry. The resulting dye images have fine grain, excellent gradation, high sharpness, and wide exposure latitude, especially to gross overexposure.

Some believe that chromogenic films are the only modern films to offer the exceptional wide-scale, "straight-line" gradation of pre–World War II films. That's a hard claim to prove, and might just mean that, like all chromogenic films, they have exceptional tolerance to overexpo-sure. What we know is that they are a valuable technical and aesthetic choice.

Ilford XP-2 Super is the only chromogenic black and white film available now. It is reportedly made by Fuji. We recommend it with enthusiasm. However, because, like all C-41 films, it is not archival, and because development control is so limited, it is not discussed further in this book. For those who wish to process their own chromogenic films many photographers have successfully used Tetenal C-41 chemistry. However, *good* C-41 *laboratory* processing, with separate bleach and fix steps, is likely to result in a more stable image with longer life. Valuable negatives can also be copied to silver via several possible strategies, or scanned for digital storage. There are also many experimental techniques for developing this film conventionally, a process Ilford sanctions. More information is available on the internet.

Document films

Document films have ultra fine grain and extremely high-contrast. They are designed to copy line drawings and text and other applications where extreme contrast is desired. This umbrella term encompasses “high contrast copy film” and microfilm. In the 1960s it was discovered that these monodisperse films could be used for continuous tone pictorial photography when developed in special low contrast developers.

Document films produce the finest grain and highest sharpness the photographic process is capable of. These are the films to use for 40x enlargements. But even with the most advanced development techniques, their tonal range is limited compared to other films. When using document films, image quality is more dependent upon developer choice than with any other film type. Full details on the document films available and the developers to use with them are in chapter 11.

Infrared films

Edward Weston said, "The camera sees more than the eye." But with infrared, the film sees more than the camera. These films offer photographers an entirely new way of seeing. While these films certainly have applications in aerial, scientific, law enforcement, and advertising photography, they also have special applications for fine art photographers.

Four black and white infrared films were available from Kodak, Ilford, Efke and Konica at the time of the first edition. Of those, only Ilford's is still available, but there are two new entrants from Rollei and Washi, both of which appear to be Agfa Aviphot Pan 200, with a spectral sensitivity cutoff at 750 nm. Ilford's film, said to be based on HP5 but with special sensitizing dyes added, has about the same cutoff.

Kodak High Speed Infrared had much greater infrared sensitivity, up to about 900 nm, while the Efke ran to about 820 nm. The Kodak and Efke films had to be loaded and unloaded in total darkness—the price you had to pay for true infrared sensitivity. In the field, you had to use a light-tight changing bag.

The much-prized halo or glow effect of Kodak High Speed Infrared is said not to have been due to infrared per se but to the lack of an anti-halation layer, leading to greater light scatter.

To get the most out of infrared, expose through a red filter. Infrared images made without a filter appear to be black and white photos missing key tonal values—an effect that can be either interesting or dull.

Yellow, orange and red filters can be used for a mix of pictorial and infrared effects. The stronger the filter, the more infrared will be recorded. The lighter the filter, the less. We recommend B+W filters for their high optical quality. The two filters most commonly used with infrared film are Wratten 25 and 29 red. The B+W equivalents are 090 and 091. To achieve full

infrared effect requires B+W 092, a true infrared cut-off filter. However, the filter factor is high, 5–10X.

The speed of infrared films depends on the filter and the amount of infrared light in the scene. For example, the lower the sun is on the horizon, the more infrared light in the scene. Ilford SFX 200 film, without a filter, is rated at ISO 200. At midday with a No. 29 filter the effective EI will be 50, but at sunrise or sunset the EI will be greater.

For all types of photography, portraiture, landscape, and architecture we like SFX 200. It can be loaded or unloaded in open shade (avoid bright sunlight with all films as a matter of course).

Orthochromatic films

Continuous tone ortho films were once the most popular for celebrity portraits, especially of men. Look at any vintage poster of Elvis, James Dean, or Bogie and notice the rich, grey skin tones, dark lips and brooding eyes. They were taken with ortho film in the heyday of Hollywood's black and white glamour photography. Karsh of Ottawa used ortho for his famous images of Winston Churchill, Ernest Hemingway, and many others. In recent years, Tri-X Ortho was the preferred ortho film, but like so many fine Kodak films, it has been discontinued.

Check with manufacturers for ortho films which continue to be available occasionally. With the right choice of developer these films should still be capable of pictorial contrast, producing a full tonal scale, minus red.

Doing it today: As a practical matter, it is easy to give panchromatic films an ortho look by moderately filtering out red. An 80A or 80B blue filter will accomplish this with minimal speed loss. (You can also use this technique to tame films with too much red sensitivity, such as Tech Pan or other films with extended red or near-infrared sensitivity.)

The great ortho portraits we've been talking about are not just the product of ortho sensitivity, but also, all the other characteristics of the films of the 1930s and 1940s. To achieve the effect today, we would suggest using an old-fashioned pan film such as Eastman Double-X, Foma 100 or Retro, or Adox Silvermax, and an 80A filter. With more modern films (particularly tabular), pull-process: down-rate by a stop or two and under-develop to compensate. Good lighting technique is another essential ingredient in this kind of portraiture.

Transparency films

The best way to achieve a full scale black and white image is to produce a high quality transparency and display it on a light box or view by projection. No other black and white process, negative to print, can compare with the tonal scale and luminance of a transparency.

All films can be made to produce a black and white transparency when processed with reversal formulas, kits, or by a specialist lab. Kodak particularly recommends Tmax 100. However, there are two films especially designed for transparencies: Adox Scala (35mm only), and Fomapan R100 (8mm, Super 8 and 16mm for movie cameras). They have transparent film bases, and extra silver to allow a Dmax of 3, rather than the 0.9 or 1.2 that is common for negatives.

Adox Scala is identical to the old Agfa Scala, which itself is a silver-enhanced version of Agfa APX 100. Recommended processing is in Adox Scala Reversal Kit or a professional lab.

By dramatic contrast, Kodak has demonstrated (and patented) a true ISO 24,000 *direct* positive black and white film with image characteristics similar to Tmax 400, based on technology developed by Paul Gilman. A small production run in 2006 was promised and then cancelled by Kodak. As this film is relatively easy to produce and process, we can hope it may appear in the future, perhaps after the patent has expired.

> *The technology behind Gilman's ISO 24,000 to 40,000 reversal film is discussed, opaquely, in US patents 7,198,889 and 7,214,464, both from 2007.*

Uncommon roll and sheet film sizes

New film specially cut for old roll film sizes such as 101, 103, 116, 112, 124, 127, 616, 620 and 828, is still available, as are custom sheet film sizes. Use the internet to find them. For custom sheet film, it may be useful to contact manufacturers directly. Search engines will also lead you to some guides as to how to convert some of the older roll film format cameras to work with 120 size roll film.

Frozen and out-of-date film

Buying frozen film (and paper) and freezing your own are becoming popular concerns now that some irreplaceable films (such as Tech Pan) are only available long out of date, and nearly unusable if not frozen. Films can suffer freezer burn, just as food can. The most important precautions with film are to double bag it in sealable plastic bags, expelling as much air as possible (a vaccum process would be helpful) and storing in a good freezer that is kept at a consistent temperature as far below zero degrees Fahrenheit as possible. As speed goes up, the keeping qualities of frozen film go down: ambient radiation and the naturally poor keeping qualities of faster films are responsible for this. Slower films can sometimes be frozen for decades with little falloff in quality.

Paper-backed films, such as 120 are at particular risk as the paper can stick to the film and cause permanent damage. If freezing roll film, by all means get 220 if you can.

If you have to process out-of-date film and paper that has not been stored well and which may be highly fogged, you can experiment with organic antifoggants, and will probably have to accept considerable speed loss. Strip-testing the material you have to deal with is the only way to fine tune the process. For obvious reasons, it is best to use the minimum amount of organic antifoggant possible for the conditions of a particular job. Fog, as Marilyn Levy famously observed, is something you can just print through. Alternatively consider the potassium iodide prebath technique developed by Dickerson and Zawadzki at Kodak in the mid-1980s.[3] These techniques were devised for films that had been exposed for several decades but not yet developed. However, they may prove effective in dealing with film that is just out of date.

Where does mystery film come from?

To the best of our knowledge, the only companies that actually manufacture emulsions today are: Kodak, Ferrania, Fuji, Ilford, Foma, Lucky, Orwo, Adox and the company we think of as Agfa-Gevaert, but which is now known simply as Agfa, with the website agfa.com. (Agfa still manufactures various technical films including the Aviphot and Avitone lines.) There are some small companies in the former USSR and China still producing film which we don't know much about. Any of these may be the source for some of the mystery films coming on the market today. And it is probable that some of these companies are supplying emulsion for other companies to coat, possibly to the other companies' specifications. The industry is immensely secretive about this information. We think this is a mistake: we believe customers would be glad to know the ultimate source of their products. But we have not been able to acquire any information beyond what we have provided here.

What might the future bring for film?

Even with the most modern equipment and computer control, film is incredibly difficult to make. And that's before you add the difficulties of working with techniques such as 2-electron (pioneered by Agfa-Gevaert but commercialized by Kodak) that so far are only used in a handful of Kodak color films. The fundamental patents have expired, but that doesn't mean we will be seeing 2-electron from anyone else soon. We will continue to see innovation, but at a slow pace, and there may be teething problems with new emulsions. We look forward.

NOTES

1. Although slow films typically have short tonal scales and fast films typically have long tonal scales, it doesn't have to be this way. Kodak's discontinued Panatomic-X was a slow, fine grain film with a remarkably long scale. The secret, as with Verichrome-Pan and some other notable fllms, was double-coating with both a slow and a fast layer.

2. Private communication from C.N. Nelson, a member of the Jones team who was still active in the 1990s. The most relevant paper is Loyd A Jones and C.N. Nelson, "The Control of Photographic Printing by Measured Characteristics of the Negative", J Opt Soc America, v 32, Issue 10, pp 558–619.

3. An article by Dickerson and Zawadzki in *Photo Techniques*, Nov/Dec 2009, discusses the challenges the authors experienced when tasked with processing film that had been exposed many decades previously. They developed two protocols for working with such films. The first was to presoak the film for two minutes in a 0.1% solution of potassium iodide, followed by seven minutes in D-76. This was particularly effective for some films that had been exposed 30 years before, producing excellent prints. They developed a second and more aggressive protocol for even older films: the same potassium iodide bath followed by short development, often for only two or three minutes, in Kodak Rapid X-Ray Developer (KRX). They reported that a roll of film thought to have been exposed 70 years before produced prints, on grade 5 paper, with recognizable faces.

Chapter 3
DEVELOPER INGREDIENTS

"The abundance of developing agents only increases the number of ways in which identical effects can be obtained."

—C.E.K. MEES

If photochemistry is a science, it is the least scientific of all the sciences. It often seems harder to establish a scientific truth in photochemistry than in psychology or sociology. Reviewing the photographic literature we note near certainty on a number of fundamental issues from the turn of the 20th century through World War II. After that, the tide turns to progressive uncertainty on nearly every aspect of photographic science.

In the old days chemists habitually made broad assertions concerning photo chemicals which may have owed more to witchcraft than to reasoned science. Today, careful scientists shroud even conceptually simple procedures such as pH measurement in disclaimers. This makes it difficult to discuss developing chemicals authoritatively.

"...the composition of the solution [rather than the developing agent] plays the dominant part in determining the ... properties of the developer."

—C.I. JACOBSON

In our discussion of chemicals used for film development we have attempted to find a viable middle ground between the freewheeling half-myths of the early photo chemists and the cool ambivalence of today's best scientists. In doing so, we have culled the most valuable insights from more than a hundred years of accumulated observation by scientists and artists, which has an aggregate value of its own. We have tried to emphasize information that is consistent between the present and earlier eras. But we have found it necessary to discard many familiar characterizations, such as reduction potential, which modern chemists have rightfully rejected.[1] Above all, we have kept in mind the best wisdom of contemporary scientists who say that what matters is not so much the developing agent, as the formula in which the developing agent is placed, and the way that formula is *used*.

Ansel Adams remarked, "Variations in developers are, in truth, so small that with certain adaptations of exposure and use, almost any developing formula can be used with almost any negative material." In truth, tests can be arranged to show that differences between formulas are trivial. But experienced chemists and photographers know that individual formulas have unique characteristics and each developing agent has its own visual personality.

Developers of excessively low reduction potential such as glycin and HQ will give still greater sensitivity depression and materially alter the curve shape in comparison with results obtained with surface-acting high reduction potential developers. By a careful choice of developer it is possible not only to vary the threshold sensitivity of an emulsion but to alter its characteristics.

—R.B. WILLCOCK

Developing agents

Many natural substances are capable of developing film including, as reported by Grant Haist, "polluted lake and river water, old red wine, citrus fruit juice, and even human urine."[2] Of the thousands of chemical compounds that have been studied, only a few are commonly used in black and white photography today. The chart overleaf does not include

Properties of the Major Developing Agents

Common Name	Hydroqumone	Chnrhydroquinone	Catechol	Pyrogallol	p-Aminophenol	Amidol	Met
Scientific Name	1,4 dihydroxyben-zene; para-di-hydroxybenzene	2 Chloro- 1,4-di-hydroxybenzene; 2-chloro-1,4,-benzenediol	1,2-Dihydroxy-benzene; ortho dihydroxy-benzene	Pyrogallic acid; 1,2,3 trihydroxy-benzene; 1,2,3-benzenetriol	4-Amino-l-hydroxy-benzene hydrochlor-jde; para-hydroxy aniline	2,4-Diami no-phenol dihydrochloride	Mor para ami sulf met ami phe sulf
Commercial Names	Quinol, Tecquinol, Hydroquinol	Adurol Chlorquinol	Pyrocatechin	Piral, Pyro	Activol, Azol Kodelon, Para, Rhodinal	Acrol, Dianol	Elor Gen Gra Pict Pho Rho
Form	Needle-shaped crystals	Needles or leaflets	Needles from water	White crystals	Free base: plates from water; HCI salt: crystalline	Crystals	Cry
Solubility in water (g in 100 ml at 20C)	8	92	30	40	Free base: 1.2; HCI: salt 145.5	25	4

the phenylenediamine derivatives used in color developing and occasionally in black and white (see chapter 7), aminophenol derivatives, Phenidone derivatives used in commercial products, or ascorbic acid derivatives.

DEVELOPER THRESHOLDS

The table below shows the pH thresholds at which several developing agents become active. This is for single agents only. Combined agents may produce different results.

Amidol	4.0
Phenidone (2g/L)	6.0
p-Phenylenediamine	6.25
Metol (4g/L)	7.25
Pyrogallol	8.0
Chlorohydroquinone	8.5

The table below shows the pH thresholds at which several developing agents become active. This is for single agents only. Combined agents may produce different results.

Bromohydroquinone	8.5
Glycin	9.0
p-Aminophenol	9.35
Pyrocatechin	9.5
Hydroquinone	10.0

Notes: Developing agent concentration was 0.1 of the molecular weight of the compound in 1L unless solubility limited the amount to that shown in the table. Development time did not exceed 60 seconds at 90F.

Source: Malon H. Dickerson, “Notes on the Design of Developers for Rapid Photo Processing,” *Phot Enl*, 5:109 (1954).

Author’s note: These numbers are useful guides, not absolutes. There isn’t a sharp cutoff point between activity and lack of activity. For example HQ can show small activity at pH 9; metol is still usable at pH 7 (D-25); superadditive developer combinations don’t follow these rules.

Ascorbic acid and its isomers

Ascorbic acid is vitamin C. It is the least toxic developing agent on the photochemist's shelf. Researchers have long known of its value in photography, yet it has only found commercial use since the 1980s. It is superadditive with the phenidones and metol. Researchers have not agreed on its practical properties. Some claim that ascorbates can only be used at high alkalinity; others that moderate alkalinity is tenable and desirable. Ascorbic acid itself is not specified in most formulas. The usual form is sodium isoascorbate. R. Suzuki states that using the acid form or the salt makes no difference if the final pH is the same. More information will be found in chapters 5 and 9. Due to Zawadzki and Dickerson's work at Kodak in the 1990s, phenidone-ascorbate developers are now considered to provide higher emulsion speed *and higher image quality* than PQ developers.[3] This finding came as a surprise both to chemists and to photographers.

Amidol

Around the 1930s Amidol, a *p*-aminophenol derivative, had some vogue as a low contrast developer used in a water bath process. Ansel Adams used an amidol water bath for his most famous picture, *Moon-rise Over Hernandez*. But that was in 1941. When Adams tested Amidol water bath development with modern films in the 1980s, he found the process tended to produce streaking. (Adams, *The Negative*)

Amidol is the only common developing agent that functions well at a neutral or acid pH. It is extremely active at moderate pH (Haist 180). These are attractive and unique characteristics.

What has held Amidol back are its extremely instability in solution and its tendency to stain. Numerous suggestions were made in the interwar period to improve stability (Haist 180). Amidol has sometimes been used in both low temperature and high temperature developers, and has more recently been suggested by Gordon Hutchings as a speed enhancer for PMK (see *The Book of Pyro*). Although amidol has largely fallen out of favor as a film developer, it still has adherents as a print developer. Polaroid patented derivatives in 1963 that avoided colored reaction products and were substantially more stable (USP 3,091,530).

Why did Ansel Adams find streaking with Amidol in the 1980s? The water bath process encourages streaking. We suspect Adams's problem probably had as much to do with the inherent uncertainty of the water bath process, as with Amidol itself. To avoid streaking, we suggest glycin-based developers (chapter 7).

Chlorhydroquine (CQ)

CQ has a number of characteristics which make it desirable as a negative developer. Used alone it is said to be five times more active than hydroquinone; used with other agents, it is reported to be somewhat less superadditive than hydroquinone with metol and Phenidone—a potentially valuable characteristic. It is about ten times more soluble than hydroquinone and was used in the past to formulate concentrated developers. It is active at pH 8.5, unlike HQ, which requires pH 10.

Until the 1960s CQ was used mostly in print developers where it can produce brown to red tones by direct development. No commercial developers based on CQ exist today. The manufacturing process is both dangerous and expensive. The only grades available are technical grades (avoid brown mush) or reagent grades costing upwards of $50 per gram. Crawley was one of the last chemists to publish a film developer with CQ: FX 9 (chapter 7); he also used the Phenidone-CQ combination in his FX 12 print developer.

Update: CQ has not been discussed as a significant developing agent for many decades. So it was a surprise when we discovered that CQ was a significant factor behind the success of several commercial developers made by smaller manufactuers in the late 20th/early 21st centuries. Among these were one-shot high definition developers such as Edwal FG-7 and several of the Paterson FX film developers, including the version of FX-39 manufactured up to about 1995. What made CQ so attractive to the modern chemist? Crawley and Lowe found that when used with Phenidone, the results are sharper and more pictorial. CQ avoids the excessive regeneration syndrome that occurs with the pure PQ combination because it is, in practice, less superadditive. The fact that CQ *is* less superadditive on a practical basis may have as much to do with impurities (typically 15%) in the manufactured product. Reagent grade CQ would provide a different result.

It is now known that CQ was removed from FX-39 around 1995 when it was no longer possible to buy the chemical at adequate purity and a reasonable price. At that point, Crawley reformulated with Glycin and thought, in this instance, that the results were superior.

With FG-7, supplies were not a problem because during manufacture, CQ was synthesized from benzoquinone by reacting it with hydro-chloric acid. FG-7 was discontinued by the last small manufacturer to make it because of safety concerns during manufacturing. One of the curiosities of this developer is that we can't be sure, as Ron Mowrey has observed, exactly how much CQ this process actually produced. The process may produce some hydroquinone monosulfonate (HQMS)—but that may have been what made it so good.

Finally, CQ is the only developing agent known to help prevent dichroic fog, see chapter 7.

CQ in the future: As an agent other than HQ to combine with metol, the phenidones, or PPD derivatives (but not PPD itself, chapter 7), CQ would be a more attractive chemical to use in film development if a consistent, affordable grade were easy to source. There are several alternatives, for example glycin, ascorbate and HQMS. Crawley found that in proper balance, the PMQ combination (Phenidone-metolhydroquinone) helped balance out what he termed 'the tendency of Phenidone to run away with the highlights.' Though uncommon, the PMQ combination has been used by Kodak, notably in Polymax T developer. Although sold as a print developer, Polymax T, at high dilutions, could function as a high definition film developer.

> *Crawley often used the term 'run away with the highlights' as shorthand to encompass a complex range of regeneration, micro and macro gradation, and adjacency effect issues that particularly occur with the PQ combination.*

Finally a semantic note: the term "chlorquinol" (or "chloroquinol") has been used in older photographic and general chemistry literature to denote CQ. Today chlorquinol is used as a synonym for the chemical chloroxine, a

different chemical with no known photographic activity.

For this reason we discourage the term “chlorquinol” in photography.

Glycin

Glycin is one of the most undervalued developing agents. It is additive or superadditive with Phenidone and metol. It can successfully be combined with either or with both. I used the pyrocatechin-glycin combination in the commercial developer for document films, TD-3. Since glycin is slow acting, it is rarely used alone.

> *"The camera never lies, but it is possible to be selective amongst the many statements it makes."*
>
> —MICHAEL GILBERT

Although once quite popular, especially in combination with *p*-phenylenediamine (PPD) for fine grain developers and with metol or Phenidone for high sharpness, it is now almost entirely ignored in favor of MQ and PQ combinations. This is partly due to its greater cost. But it is also due to the fact that in powder form, glycin does not keep as well as other agents. Fresh glycin should be a delicate tan color; the lighter the better. It needs to be added to a developer solution after all the sulfite has been dissolved. Once in solution, it has good keeping qualities.[4]

In solution glycin is stable and resistant to aerial oxidation even in low sulfite solutions, and is nonstaining and fog-free (Haist 180). Furthermore, it seems to confer resistance to aerial oxidation on other agents that it may be used with, such as PPD, the phenidones, and metol. Resistance to aerial oxidation and fog makes it especially desirable for developing sheet films in trays, and potentially valuable in mechanized processing.

In practice, glycin is often used in formulations with a low amount of sulfite since, as Crawley observed, it can become excessively solvent when placed in a high sulfite solution. This tendency can be mitigated when glycin is combined with other superadditive agents, such as the PQ combination. Crawley used this triple combination in his high speed negative developer FX 11 (chapter 5) and in some of his commercial developers as well (FX 20/Acuspeed, chapter 10; FX-39, chapter 6).

In modern formulas glycin is almost always combined with metol or a phenidone. These mixtures are less active than the PQ or MQ combination. Such developers can be very sharp, with excellent speed and grain characteristics, as well as lower contrast than MQ or PQ combinations (see FX 2, chapter 7).[4]

A substitute formula for Unitol could be constructed by altering the FX 2 stock solutions given in Appendix 2. Replace the metol with 1/10 its weight in Phenidone or Dimezone-S, and replace the carbonate with 10% sodium metaborate. Experiment by using 1.5x solution A to make the working solution.

Johnson's Unitol used the Phenidone/glycin/Kodalk combination. It was widely used in the UK from the 1950s to the 1990s. It was noted for beautiful midtone gradation. The FX 2 metol-glycin combination features strong midtone gradation, translucent highlight discrimination, and high acutance.

Developers containing glycin have a reputation for preventing bromide streaking when using continuous agitation.

Not widely manufactured today, an excellent grade of glycin is available from Photographers Formulary, which makes fresh batches every two weeks.

Hydroquinone

Hydroquinone is a high contrast developing agent. Its reaction products accelerate development. It is rarely used alone, except in special formulas for technical applications. Its main value is in MQ and PQ formulas (see superadditivity, later in this chapter).

Hydroquinone is sensitive to cold and should not be used at temperatures below 60F/15C. It requires a pH of 10 to be fully active, or pH 9 to be slightly active, but can efficiently regenerate metol or Phenidone below that pH. A reaction product of hydroquinone, hydroquinone monosulfonate (see below), is used in some commercial developers.

> *"One developing agent is best, two is okay, three is very suspect, and four the guy is definitely a jerk."*
>
> —Bob Schwalberg

Hydroquinone monosulfonate (HQMS)

HQMS is an important oxidation product of HQ that is formed as a natural part of development. However, employed as a separate chemical, it is in itself a developer, though typically requiring at least ten times more HQMS than HQ. Its primary use in photography has been as a constituent of the first developer in some of the last versions of the E6 process where HQ itself was found to be too active at the high desired processing temperatures (100F/38C), because HQ activity rises greatly with temperature increase.

It has been speculated that a phenidone/HQMS developer can produce more desirable images than a PQ developer, because the lower activity and different regeneration kinetics produce better-controlled microcontrast and adjacency effects. We know of only one black and white developer which has ever been formulated with it. In Acurol-Ng, HQ, HQMS, Phenidone, Dimezone, and metol are employed for a grandiloquent total of *five* separate developing agents. At first glance, such a promiscuous, or rather polygamous, feat has not been recorded in photographic literature since the heady 1930s when Harry Champlin's developers were popular. However, in fairness to the formulator, using lesser quantities of more ingredients means fewer regulatory headaches in EU countries. In such a formulation, it is difficult to see how HQMS could be having much overall effect on the developer kinetics. Using HQ along with HQMS defeats the main chemical purpose of using HQMS.

> *Mason 136, states, "... the P/HQMS mixture is softer working than the PQ mixture ...." This important quality makes HQMS valuable in developers where low cost and high concetrat-ability are not paramount concerns. A simple process for synthesizing HQMS from HQ, sodium sulfite, and hydrogen peroxide, is given in USP 4,366,234. We cannot find an independent source for HQMS solubility, but have been provided with data to show it is in excess of 45% in water at room temperature.*

In a PQ developer, the HQ oxidizes and forms HQMS, itself an active developer though less active than HQ. This is good news for continuous replenishment systems, and for print developers, but not good for high definition one-shot development, because it means that sharpness-enhancing effects may not be formed to the desired degree. But this mechanism doesn't occur when using HQMS *instead* of HQ: when the HQMS oxidizes, the further reaction products are not renewed. This allows sharpness-enhancing adjacency effects to proliferate.

Unlike phenidone, metol is only weakly superadditive with HQMS (Mason 136–137). This helps explain both why MQ developers tend to be sharper than PQ developers and also why PQ developers have more capacity than MQ upon oxidation during use. The main problems with HQMS are that it is expensive and weak. Practically speaking, 10 times as much HQMS may be required, compared to HQ.

Metol

Metol is the most versatile developing agent. Developers as disparate as fine grain D-23 and high acutance FX 1 can be made using metol alone. No other developing agent can achieve these effects so reliably, and with full utilization of emulsion speed.

> *One agent not otherwise listed here is hydroxylamine sulfate, though it has been known to have developing activity since 1884. This substance was in the past considered to be not stable enough to be used in practical developers. However, more recently it has been discovered to be stable and possibly superadditive when combined with substituted PPDs, such as CD4. This combination is used in the color developer in the C41 process. In light of more recent research, the action of hydroxylamine can be interpreted differently, according to Ron Mowrey. He believes it only has a stabilizing effect on the PPDs and that the various authors of the research showing super-additivity (cited in Haist) were misinterpreting their observations. His position is supported by Mason, who classifies this chemical primarily as an antioxidant. However, Mason also cites its uses as a developer, for example in so-called flash processing, where development is heat-activated and takes less than a second. In this case, hydroxylamine is, advantageously, destroyed by the heat.*

Part of metol's value is that its reaction products slow down development. This results in lower contrast, and easier to print negatives. The reaction products of most other developing agents accelerate development.

Metol is considered to be a *sharp* developing agent because of the ease with which it creates adjacency effects. Metol can produce either high sharpness or fine grain images—though not both in the same developer.

Metol has been known to cause an acute skin irritation known as metol poisoning. Metol poisoning often manifests itself only after years of exposure. Once the skin has become sensitized it usually remains so. Avoid direct contact. As with all photographic chemicals, always wear surgical or neoprene gloves (Appendix III). Haist notes (p. 352) that as early as 1923, metol's allergenicity was reported to be due not to metol itself, but to PPD impurities that metol as then manufactured contained. These may no longer be present in the chemical as manufactured today. Metol is not the chemical it was 100 or even 50 years ago.

para-Aminophenol

p-Aminophenol was considered by Bob Schwalberg to be the finest developing agent. He had two reasons for this opinion: the first was the century-long success of Agfa Rodinal, the most famous developer to use this chemical. Rodinal is the oldest continuously manufactured proprietary product in photographic history.

The second was *p*-Aminophenol's reputation for low fog. Schwalberg reasoned that anything which caused less fog had to have a beneficial effect on the photographic process. (Popular Photography, Dec. 1979)

p-Aminophenol produces sharpness-enhancing edge effects at high dilutions. On the other hand, Schwalberg did not believe that this entirely explained its sharpness: he believed (probably erroneously) that the low fog level was just as important. Notably, Crawley believed that metol is sharper. Outside of Rodinal, there is now little commercial exploitation of *p*-Aminophenol.

More moderate pH *p*-Aminophenol developers have not been adequately investigated with modern films. However, there was much 20th century research on *p*-Aminophenol derivatives (Haist, p. 174 ff).

para-Phenylenediamine (PPD)

PPD and its derivatives are unique developers because they are also silver solvents. Because of its low activity (Haist 181), PPD has a special ability to maintain delicate highlight detail (Crawley 60/61; chapter 7). However, it is difficult to make PPD or PPD-derivative black and white developers that create sharp images, due to the solvent action of these chemicals (chapter 7).

All PPD-related developers are considered to be highly allergenic and toxic. Many of the derivatives (e.g. CD3) are *claimed* to be less toxic, and may not be more toxic than most other developing agents. PPD and some aminophenols are still used widely in hair dyes; but what the possible long-term health consequences may be remains controversial. We suggest handling them with extreme caution. (In 2014, Wella/P&G introduced PPD derivatives engineered not to be allergenic.)

> *Phenidone is required in very small amounts yet is difficult to dissolve. Home photochemists have tried many techniques to make Phenidone stock (see APUG/Photrio), but we are not persuaded any of them are stable or lack side effects, especially in the case of the ethanolamines. Some approaches to stabilizing phenidone in liquid are discussed in Haist, 525–529. In one invention a concentrate contained 5g Phenidone, 15 ml of lactic acid, and butyrolactone to make 50 ml. Another called for 95 ml glacial acetic acid, 5 ml water, and 20 g Phenidone. This time-tested technique is used by Kodak in the X-omat ICM D-1 Developer. For the separate problem of improving the life of single solution Phenidone developers, John & Field claimed lactic or boric acid buffers to increase stability (Brit. pat. 931,007, 1963).* **Note**: *Grant Haist cautions that impurities in some grades of Phenidone and Dimezone may cause mild fogging. This highlights how important it is both for manufacturers and for homebrewers to obtain the best grade of a chemical. Phenidone dissolvability may depend on age or grade.*

Phenidone and Dimezone

Phenidone is an economical, efficient substitute for metol in developers with hydroquinone, since approximately one fifth to one twentieth as much Phenidone is needed to obtain similar activity. Phenidone is rarely used alone, since it has exceedingly low contrast, and is poorly preserved by sulfite unless another developing agent is present.

The term 'phenidone' is often used to refer to a class of very similar developers called 1-phenyl-3-pyrazolidones or phenidones. These include the original Phenidone—Phenidone-A (1-phenyl-3 pyrazolidone), and also Phenidone-B (1-phenyl-4 methyl-3-pyrazolidone), Dimezone (1-phenyl-4–4'-dimethyl-3-pyrazolidone) and Dimezone-S (1-phenyl-4-methyl-4'-hydroxymethyl-3-pyrazolidone). When we write phenidone with a small p, we mean any of the phenidones discussed in this paragraph. But Phenidone with a capital P should always mean the original trademarked chemical.

In general, PQ developers yield 1/3 to 2/3 of a stop speed increase over similar MQ developers, as long as development is kept to a low or moderate contrast (chapter 10; Mason 147). It is now well known that the speed advantage disappears when development is "pushed" to a higher contrast.

The phenidones have low bromide sensitivity in highly alkaline solutions. However, they are sensitive to bromide in moderately alkaline solutions (borax or buffered carbonate).

After the initial enthusiasm for Phenidone/hydroquinone (PQ) developers in the 1950s and 1960s, it was realized that most PQ developers are not sharp when compared to their MQ equivalents. It is thought that the reason for this is high regeneration activity as the developer oxidizes. HQMS is formed and gives development a second lease on life. The result is unpredictable highlight microcontrast and impaired sharpness because not enough adjacency effects are formed.

The fine grain developers in the FX series were, as Bob Schwalberg noted at the time, the first PQ developers that were as sharp or sharper than their MQ equivalents. He also noted that Paterson Acutol was the first high definition developer to use Phenidone or, later, Dimezone-S. (One trick with Acutol was using metol in addition to PQ, which Crawley abbreviated PMQ; another was hyper-buffering, Chapter 6.)

Although successful fine grain Phenidone developers have been published (Chapter 5), very few successful formulas for non-solvent PQ developers have been published—for some of the few, see FX 37 and Acuspecial in chapter 6.

The phenidones have been used in proprietary developers such as Kodak HC-110, T-Max and Xtol; Edwal FG-7; Paterson Acutol and Unitol; and countless Ilford developers. The PQ developer concentrates published by Wiederman (Jacobson and Mason) have little practical value today.

It is essential to know that Phenidone does *not* keep well in alkaline stock solutions though it can be used as such in concentrates of moderate alkalinity. But hundreds of derivatives have been synthesized, many of which keep better in more alkaline liquid solutions. Most successful commercial PQ developers use these later generation derivatives. Apparently the best is Dimezone-S, nicknamed MOP at at the Kodak Research Labs.

> *Weighing out tiny amounts of the phenidones has been simplified by inexpensive microgram scales which weren't available at the time of FDC 1. A google search will even reveal a method to make your own microgram scale cheaply. But dissolving phenidones is a perennial problem. Phenidone and Dimezone should usually be dissolved after the sulfite and alkali have beeen completely dissolved. Mason (85) states that Phenidone derivatives have lower solubility than the parent, but our experience is that dissolvability depends on the grade of the chemical. It may take a few minutes for any phenidone to dissolve completely, but it will. Patience is the missing ingredient.*

Phenidone has been experimentally combined with pyrogallol—a strongly superadditive combination. It has also been used alone or with small amounts of other agents in super-low contrast developers that are mostly used to obtain pictorial gradation on high contrast document films (chapter 11).[4] It is also superadditive with ascorbates (chapter 5) and with pyrocatechin. Derivatives of Phenidone seem to have super-additive properties that are identical to the parent chemical, and conventional wisdom holds that Phenidone can be replaced by Dimezone or Dimezone-S gram for gram, though this is *not* an invariable rule.

The phenidones have long had a reputation for low toxicity and allergenicity compared to most other developing agents. The amount of Phenidone or its derivatives used in a developer is typically so small that the possibility of toxic exposure is minimized. Until further studies are made, it will not be possible to give a clearer picture.

Pyrocatechin (Catechol)

This high contrast agent has sometimes been used in place of hydro-quinone. In very small amounts, it can function as a low contrast developing agent. It is superadditive with Phenidone but less so than hydro-quinone, a characteristic that can be highly desirable. The combination of pyrocatechin and glycin was suggested by Crawley as a useful mildly superadditive combination. An important feature of pyrocatechin is its ability to tan and stain images proportionally *when sulfite is low* (chapter 8). Haist notes, 'This stain image is effective in intensifying the lower image densities, making weak densities more effective.' Low sulfite usually means less than 5g/L of working solution developer. Mason (p. 171) reports Russian research from 1968 which showed that Phenidone, not in itself a tanning agent, can accelerate tanning both in pyrocate-chin and in hydroquinone developers. The combination of Dimezone-S, HQ and pyrocatechin is used in HC-110 as confirmed by the Kodak MSDS dated July 29, 2016, though not in most earlier MSDSs.

> *Grant Haist told me that he thought image-wise tanning and staining were probably more stable than the silver image, but we are not aware of any studies to demonstrate this. However, the scientific literature has no known report of a problem—that is passive confirmation of Haist's belief.*

Pyrogallol (Pyro)

Pyro is photography's oldest developing agent still in use. In recent years it has regained popularity due to the re-pioneering efforts and formulas of Gordon Hutchings and John Wimberley. It is often combined with metol in modern formulas (chapter 8). This is considered a mildly superadditive combination. Pyro is superadditive with the phenidones and ascorbic acid. As with pyrocatechin, it is often prized for its tanning and staining properties (chapter 8).

Developing agent combinations

Additivity is where two combined agents produce precisely the same amount of silver together that they produced separately.

> *How much, or whether, a developer combination is superadditive, depends on the pH. At pH 9 or above, the MQ combination is highly superadditive. But at pH 8.5 or below, MQ is at best barely additive, due to hydroquinone's low activity at this pH. However, the PQ combination is strongly superadditive even at lower pH, because hydroquinone regenerates Phenidone so efficiently.*

Superadditivity is defined by Grant Haist as "the cooperative action in which two developing agents produce more silver from exposed silver halide materials than the sum of the silver developed by the agents used individually. The primary developing agent of the pair is thought to be strongly adsorbed to the silver halide grain and to be regenerated by the second agent."[2] More simply, superadditivity is where two combined agents produce more silver together than they would produce separately.

Subadditivity is where the two combined agents produce *less* silver than they produced separately.

In practice, the degree of super-, sub-, or additivity a developer combination shows depends heavily on the experimental conditions.

Superadditivity

This discovery of superadditivity had a transfiguring impact on manufacturers. It meant savings in chemicals on an enormous scale. But did it really benefit photography?

On the face of it, stronger developer combinations should be good for everybody. Using less chemistry means less exposure to hazardous chemicals, and less toxic wastes.

Yet there are some real problems with superadditivity. From a theoretical standpoint, the phenomenon is still imperfectly understood by scientists. From a practical standpoint, the developer byproducts of superadditive developers can regenerate in unpredictable ways. Overdevelopment of small highlight detail may result. This is particularly noticeable with PQ developers, and helps explain why single-agent developers have remained popular.

Although PQ is a less controllable combination than MQ, PQ solvent developers have always been popular because of their 60% speed increase over D-76. One method for dealing with PQ was proposed in FX 15 and also utilized in Acutol. In these formulas metol is added to the PQ combination. According to Crawley, this improves discrimination of fine highlight detail and sharpness. Though Crawley didn't state it, the chemical implication is that the over-efficient superadditivity kinetics of PQ are disrupted when PMQ is used.

Research at Kodak shows that the superadditive combination of a phenidone with an ascorbate is more desirable than the traditional PQ combination,[3] as we have noted earlier.

We believe that rewarding future film developers may be based on single agents or weakly superadditive combinations. In this respect, we note the reputation that pyro-metol and metol-glycin developers have for being able to hold fine separation in the extreme highlights.

There have not been adequate studies to show whether combinations such as Pheni-done/pyrocatechin or Phenidone/ascorbate are strongly or weakly superadditive. But we do know, from the results photographers have achieved with these combinations in recent years, that they are valuable.

Accelerators, preservatives, restrainers & other additives

In addition to the developing agent virtually all film developers have three additional constituents:

an alkali accelerator
a preservative for the developer (usually sodium sulfite)
a restrainer against fog

Sometimes a single chemical may play many parts. For example, in Kodak D-23 sodium sulfite acts as the accelerator, preservative, and silver solvent.

Alkali (Accelerator)

pH levels indicate the relative acidity and alkalinity of a developer. pH 7 is neutral; under 7 is acid; over 7 is alkali. The higher the pH the higher the activity of the developing agent. Only a few developing agents, such as amidol, can function in neutral or acid solutions.

An alkali is necessary to increase the pH of the formula, accelerating the activity of the developing agent. The most common alkalis are, in order of *increasing* strength:

sodium bicarbonate
borax
sodium metaborate
sodium and potassium carbonate
sodium and potassium phosphate
sodium and potassium hydroxide

> *"Some alkalis, such as sodium hydroxide, appear to have a disintegrating action on the gelatin of the emulsion layer. This action gives the silver particles a greater chance to come together to form clumps, thereby increasing graininess. Developing agents requiring the stronger alkalis may become associated with the production of grain, even though some of this may be due to the action of the alkali." Haist, 395.*

Some developers have buffered alkali systems, to maintain the pH near the same level over the course of the development process. Both metaborate and borax are sometimes called "self-buffered" alkalis; both can be, buffered further, e.g. with boric acid or sodium bisulfite.

Borax is the mildest common alkali. It is used in low contrast and fine grain developers. The decahydrate is the preferred form.

Sodium metaborate (Kodalk or Kodak Balanced Alkali), the reaction product of borax and sodium hydroxide, has a pH between borax and carbonate. The octahydrate is the preferred form. The old maxim promulgated by Kodak in the 1930s, that varying the amount of metaborate would allow you to adjust the development time without affecting other variables, belongs to a more innocent period in sensito-metric science. It has since been discarded.

Sodium carbonate comes in three forms, crystalline, monohydrate, and anhydrous (also known as desiccated). The crystalline grade contains ten molecules of water; the monohydrated, one molecule. During storage the

crystalline form loses water and the anhydrous absorbs it. Thus both tend to approach the strength of the monohydrate, which remains comparatively constant. For this reason the monohydrate is preferred.

Haist 250 describes his work with the uncommon alkali sodium dicyanamide. When added to D-76, it produced "very long, loosely packed silver filaments"; increasing the amount of this chemical "caused progressive increases in both emulsion speed and contrast of the silver image." (see p. 52)

Potassium carbonate is available in both anhydrous and crystalline forms. The crystalline contains 1.5 molecules of water and a small amount of bicarbonate buffer, depending on the grade. The potassium salt readily absorbs water from the air and should be stored in airtight containers.

Potassium carbonate is more soluble than sodium carbonate, hence its use in highly concentrated solutions. The two should not be interchanged without some compensation.

Correction: Some authorities state that sodium and potassium alkali can be advantageously combined. (Mason, p. 34, citing P. Glafkides *Phot. Chem.* v. 1 p. 63, 1958, "… there still appears to be some evidence that the potassium ion has a small enhancing effect on development compared with the sodium ion [due] to a small increase in the development of the internal latent image." See chapter 10.)

Phosphates come in many forms, all of which approach the pH of the hydroxides without being as dangerous to handle. Phosphates can be considered as replacements for hydroxides when high alkalinity is desired though they are considered to be more polluting.

"Sodium sulfite proves the existence of God."

—BOB SCHWALBERG

As powder, the phosphates are, apparently, less stable than the other alkalis.

One reason phosphates have been little used is that they can cause a scum if the film is plunged directly into a fixer that contains alum hardeners. Since the use of alum hardeners is waning, this need no longer be a major concern.

Sodium hydroxide and potassium hydroxide (caustic alkalis, potash) are the strongest common alkalis. They absorb both moisture and carbon dioxide and so must be protected from air. **Read the cautions in Appendix III before handling the caustic alkalis**.

The **ethanolamines** are an important class of practical alkali; they are also solvents, and are discussed overleaf in the section 'Potassium thiocyanate and other solvents'.

The Preservative

Schwalberg's maxim in the column quote is a tribute to the fact that sodium sulfite can act as a preservative, an alkali, a silver solvent in fine grain developers, and, in a pinch, even as a fixer. (British patent 960, 872 (1964) describes a monobath that contains only metol and a large amount of sodium sulfite.) What it does, and when it does it, depends on the amount of sulfite used, the time the film spends in the solution, and the other ingredients present. Its complex role in MQ and PQ developers has been extensively researched, but the full story on this multi-faceted chemical is not yet known. According to Haist (p. 255 ff.) "Developers containing high concentrations of sodium sulfite may produce fine grain images by another result of solvent action. The silver halide grain is pitted and etched by the removal of the silver ions by the sulfite. The physical size of the grain is diminished. The distance

between nearby grains may be increased. Grains that touch may be separated from contact. When the distance between the silver halide grains is increased, the distance between the masses of silver filaments produced by development will also be increased, resulting in a more even distribution in the developed image. This image will appear to the eye to be less grainy, because the solvent action of the sulfite has reduced the clumping of the grains before complete development has occurred."

Potassium bisulfite or metabisulfite was occasionally used in stop baths formulated in Germany before the Second World War. This occasionally resulted in the conversion of sodium to potassium thiosulfate in the fixing bath, which led to prints which were not fixed completely. As Bob Schwalberg told the story, customer complaints were diligently investigated by Agfa's Dr. Edith Weyde in the 1930s, and led to her basic patents for diffusion transfer photography. After the war all German patents were nullified, leaving Dr. Edwin Land of Polaroid free to make history with instant photography.

Modern formulas use anhydrous sodium sulfite. For older formulas which specify crystals, use half the amount of the anhydrous grade. For most developers, sulfite is dissolved first, then the developing agents, then the alkali. The one exception is developers containing metol. In this case, first add a pinch of sulfite to the water, then the metol, then the rest of the sulfite, and finally the rest of the chemicals.

Potassium sulfite is occasionally used in concentrated formulas such as Rodinal and DD-X. We do not generally recommend using it due to the possibility of carryover of potassium ion into the fixer. When a developer contains a large amount of potassium salts (only likely in highly concentrated developers), it is prudent to be vigilant about double-rinsing the material before it reaches the fixer. Otherwise carryover of the potassium ion may cause potassium thiosulfate to be formed, which could impede fixing—though there is not universal agreement on this point (chapter 14). However, potassium salts may increase film speed (chapter 10).

"Sulfite is the almost universal preservative in developers because of its known and unknown actions."

—GRANT HAIST

Sodium and potassium bisulfite

Bisulfites are weakly acidic. They are often used in A/B stock solutions to preserve the developing agent. When carbonate is added to the working solution, the bisulfite (preferably sodium) is immediately broken down into sulfite and bicarbonate, producing a useful buffering effect.

Potassium thiocyanate and other solvents

Besides sulfite, there are numerous other solvents which are employed, mostly in commercial developers, to enhance fine grain. The simplest is sodium (or potassium) chloride (common salt), used in Microdol-X since the late 1940s (chapter 7). Even earlier, thiosulfate was used. Potassium thiocyanate was estimated by T.H. James to be about 30 times more powerful than potassium chloride (Haist, 227). Moreover, James has observed a superadditive effect when sulfite is combined with thiocyanate. Kodak developer DK-20 (1938) employed 100 grams of sulfite plus 1 gram of thiocyanate. Already by the 1960s, this developer was observed by Crawley and others to produce dichroic fog on modern films. However, the sulfite/thiocyanate combination, in lower concentration, has been shown to

work beneficially with both black and white films as well as in the E6 First Developer process and many other reversal formulas. As Haist remarks, "The best concentration is the largest amount of thiocyanate that can be added without causing the undesirable fog." It has been noticed by Henn that in some highly solvent developers, the use of CQ can prevent dichroic fog. No other developing agent was discovered which had this property. (Chapter 7)

The metaboratebisulfite buffer system used in Xtol is well worth considering for new or modified moderate pH developers, except, usually, those containing either pyrocatechin or pyrogallol (see last page of chapter 8).

More recently, an important alternative to thiocyanate has been found: a thio ether called DTOD, or 1,2-di(hydroxyethylthioethane). It is a fluffy white powder, moderately soluble in water at room temperature. The use of this chemical was first championed at Kodak by Ron Mowrey as long ago as 1966 when he incorporated it into the fixing stage of an experimental rapid bleach-fix process. Mowrey has stated that although DTOD is a weak fixer on its own, it shows good super-additivity with thiosulfates. His process trimmed 30 seconds from the fastest blix that had been achieved up until that time. DTOD is thought to be potentially less harmful to the environment in that it does not degrade but does not (yet) appear to be toxic. It has been specified in some versions of the Kodak E6 Developer used in the 1990s and, we presume, afterwards. The only published black and white developer we know of that employs DTOD is Kodak D94a, which specifies 0.42g/L. This developer is suggested for use with some black and white cinema reversal film processes. It has been noticed that when DTOD replaces thiocyanate, better edge effects are produced, resulting in higher sharpness. Mowrey notes that thiocyanate is known to increase swell. DTOD does not. This might be one of the contributing factors to increased edge effects because with lower swell, the iodide concentration will be higher. DTOD is also used in some other areas of photographic manufacture, and will likely be manufactured for the foreseeable future.

"If you've got too much fog, you've got too much alkali."

—GRANT HAIST

Another important family of solvent used in modern developers is the ethanolamines such as di-ethethanolamine (DEA) and tri-ethanola-mine (TEA). These function as both alkali and solvent (both in the sense of dissolving silver and in the sense of dissolving other ingredients) in commercial developers such as HC-110 and Ilfotec HC. TEA is used in a popular formula, PC-TEA. Ethanolamines have been used in a few alkaline fixer products. Although we prefer not to use ethanola-mines, mainly because of their solvency, Grant Haist (250) emphatically noted that he found diethylamino-ethanol (DEAE) to be "especially useful" for its ability to minimize swelling in the gelatin layers.

N.B. When any strong solvent is used with modern films, an anti-silvering agent or, in Henn's vocabulary, an "anti-stain agent" may be required to prevent dichroic fog and other problems. Such agents include chlororesorcinol, benzophenones, polyvinyl pyrrolidone (PVP), and various mercaptans (chapters 5, 6 and 7). If the developer contains CQ, antistain agents may not be necessary.

Bromide and iodide are called inorganic restrainers or antifoggants. Benzotriazole and the other organics are called organic antifoggants or restrainers. There has been a tendency to use the word restrainer for bromide and iodide and to use the word antifoggant for the organic antifoggants. Grant Haist stated that the terms organic antifoggant and inorganic antifoggant should be used instead.

The Restrainer

A developing formula may not differentiate adequately between exposed and unexposed silver halide in the emulsion. In addition to developing the image grain, it may also develop non-image grains to produce an overall fog (non-image density).

Restrainers were once thought to be necessary in virtually all developers to reduce fog. It is now realized that restrainers usually impair image quality, and are often only necessary to correct too strong an alkali. Hence Haist's advice to reduce alkalinity instead of reaching for a restrainer. While it is generally best not to use restrainers, very few developer formulas don't contain them, especially those containing any one of the phenidones, all of which have a tendency to fog. The most famous formulas that don't contain restrainer are Rodinal, D-76, Xtol, and POTA. It's significant that these formulas are so enduring.

Potassium bromide is the most popular restrainer. It works well with all developing agents, including Phenidone at the moderate pH of borax or a carbonate/bicarbonate buffer. However, without careful formulation, bromide can reduce film speed. Nevertheless, in carefully balanced formulas, potassium bromide does have a desirable effect (see the FX solvent developers in chapter 5). It is typically used at 0.1 to 1 g/L of working solution. Above 10 g/L it can be noticeably solvent and physical development may give the silver a warm or yellowish hue.

Potassium iodide as a practical restrainer has not been as thoroughly investigated as bromide. It may prove to be superior to bromide in some developers with some films. Generally 1/100 to 1/1000 the weight of bromide is used. It is sometimes used in combination with bromide.

> *Two desensitizers pinacryptol green and phenosafranine were recommended in PCS particularly to control "streaked aerial fog". How well these old or more modern desensitizers will work, either as antifoggants or as desensitizers, depends on the developer and the film.*

Benzotriazole (BZT; Kodak Antifoggant No. 1) is often used to reduce fog found in high pH developers which contain Phenidone. It is often used in print developers to achieve a colder tone. Methyl-benzotriazole is similar.

> *G.I.P. Levenson has confirmed that adding any amount of bromide to D-76 will result in a loss of speed. This can occur when full-strength D-76 is re-used ('Saving Sulphite', Funct. Phot., 2 (8): 9 1951)). Bromide is released by the film and builds up in solution, lowering speed. For this reason, most photographers now use D-76 as a one-shot, diluted 1:1. As Mason has observed, phenidone-based developers are much less sensitive to bromide. This is one of many factors which works in Xtol's favor when it is used full-strength.*

Other important organic antifoggants include 6-nitrobenzamidazole (Kodak Antifoggant No. 2) and 1-phenyl-5-mercaptotetrazole (PMT), which is the strongest of these three and also acts in numerous other complex ways, including as an anti-silvering agent.

There are other antifoggants in use, some listed in Haist and Mason. Kodak introduced and patented one of the newest, 3-nitrobenzene sulfonic acid sodium salt, in 2002. Its particular benefits are: lower cost, greater safety, and stability to decomposition when color negative (and presumably other) developers are used only intermittently. It is only available from Kodak as AF-2000. The concentration is 7%. The recommended working dilution is 5ml/L.[5] It is said to be safer and more stable than the product it replaces, Kodak Antifoggant No. 9 (3,5-dinitrobenzoic acid, which has been around since the 1930s).

Crawley stated that organic antifoggants work by insolubilizing the halide grains, while the inorganic restrainers work by rehalogenizing (thus selectively slowing development of) the grains that have been most weakly struck by

light. Mason states that both organic and inorganic antifoggants may be necessary in phenidone developers, while Haist observes that both have the same practical effect.

Pinacryptol Yellow is a desensitizing dye with some restraining action on some films. See FX 2, chapter 6.

Both Haist and Mason suggest using BZT at 0.2% per liter of working developer, and PMT at 0.02%. We suggest trialling ten to one hundred times *less* of each.

Wetting agents

Wetting agents are highly purified, low-foam detergents which are normally used as the final step in the development process, just before the film is hung to dry. They allow water to run off more evenly, preventing water spots.

> *In older research, it was observed that for a short developing time, bromide is a better antifoggant, while for longer developing times, iodide is. (A.P.H. Trivelli and E.C. Jensen, 'Antifogging Agents in Developers. I.,' J. Frank. Inst. 210:287 (1930)) More recently, it was claimed that in Rapid Access Developers, very little or no antifoggant may be necessary. (Discussed in US Patent 6,669.331, 2003)*

Wetting agents such as Kodak Photo-Flo, Edwal LFN or Tetenal Mirasol are sometimes added to a developer or used in a presoak. The theory is that they will smooth the flow of developer over the emulsion surface, producing more uniform development. Because even nonionic detergents can create unexpected results, we do not recommend using wetting agents except *after* washing. Most wetting agents today are probably non-ionic polyethylene glycol derivatives. They are usually selected to be as neutral as possible but Tetenal Mirasol claims to have anti-static and anti-fungal properties. It is not known how long the anti-fungal property lasts. Kodak Photo-Flo contains a polyethylene glycol known under the tradename Triton X-100. Mirasol is a more complex product and has a pleasant scent. But Photo-Flo has the better safety and usage record. It also includes a glycol. (MSDSs c. 2017)

Water; sequestering agents

Water is a crucial, often overlooked, constituent part of all photographic formulas. Many water-less photographic processes have been invented, but they are beyond this book's scope.

In general, the wide variety of impurities found in water, among them calcium and magnesium salts, are present in such small quantities that they have little effect on photographic solutions. However, bearing in mind that the mineral content of tap water can change from one day to the next it is always safer to use distilled water for mixing developers. Minute impurities in water are especially problematic with pyro, catechol, and ascorbates. Distilled water is the best way to ensure quality negatives.

> *"If God had not invented water, I would have had to do it myself!"*
>
> —Dr. Erno Laszlo, Greta Garbo's cosmetologist

Tap water can vary from pH 5 to pH 9 but this is usually insignificant as water's ionic strength is so low. Water may be treated with chlorine, bromine, or ozone. Haist observes that it is best not to assume that tap water is photographically sound, particularly if you are in a part of the world where clean water is hard to find.

In most commercial products, a sequestering agent is used to immobilize harmful mineral impurities. One example, which may be the most preferred, is DTPA, or diethylenetriamine pentaacetic acid penta sodium salt (40%), often used at 0.2% or less. Crawley was not alone in suspecting that sequestrants may have an adverse effect on definition. One reason, according to Haist (272, citing Mason), is that "As do most organic amines, the EDTA-type compounds act as silver solvents, promoting physical development and the possibility of dichroic fog." Yet manufacturers have little choice but to include them. Sodium hexametaphosphate (formerly Calgon, Haist 268, but the commercial product is now different, p. xii) and its relatives don't have this particular problem but aren't as effective and are less stable, hence are usually only seen in older formulas.[6] Mason (61) warns that the EDTA/DTPA type of sequestrant is thermally unstable above 80F.

Unfortunately, as Mason (142) states, "The sequestering agent content in a liquid concentrate must be based on the maximum dilution recommended, and on the assumption that hard water will be used for this." **Note:** An advantage of using distilled water and mixing your own solutions is that sequestrants are usually not necessary. They may be necessary with ascorbate developers even when distilled water is used, to sequester contaminants introduced by other ingredients.

With tap water, a viable alternative *may* be to boil it for three minutes, and stand overnight. Boiling removes gases. Standing overnight allows particulate matter to precipitate out. Decant carefully.

Generally, stop baths and fixers are not as sensitive to water variations as developers. If a problem does appear, use distilled water.

Filters can help protect films from water impurities. If a filter is not available use several layers of an additive-free paper towel, or a coffee filter. Water with any visible color should not be used in photographic processing unless it can be effectively filtered to sufficient purity. How to test suspect water? Run a test film through an entire processing sequence and look for unexpected problems.

Softened water should not be used in developers. If it cannot be avoided, use distilled water instead.

Sea water cannot be used for mixing most photographic solutions. Sea water *can* be used as a hypo clearing wash after fixing with acid hypo solutions, but a thorough final rinse in fresh water is obligatory.[7]

NOTES

1. ‘In general, no successful correlation has yet been made between developer activity and the redox potentials of the developers.’ T.H. James & G.C. Higgins, Fundamentals of Photographic Theory, Wiley, NY, 1948, p. 88.

2. Focal Encyclopedia 3rd edition (articles by Haist).

3. U.S. Patent 5,853,964; Dickerson & Zawadzki, ‘The Genesis of Xtol’, Photo Techniques, Sept/Oct 1999.

4. US Patent 3,772,019 (1972) is for an ultra-low contrast glycin-Phenidone developer by the H&W Company. It was intended for obtaining normal contrast on document films (chapter 11). US Patent 3,938,997 (1976) is for “Rapid access, air stable, regenerable iron chelate developer solutions” by Fisch and Newman of 3M. Many superadditive combinations are listed. One possibility includes EDTA, ascorbic acid, and glycin. This could be an interesting jumping-off point for further research.

5. US Patent Publication Application 2001/0046648 A1 by Françoise M. Thomas for Kodak Chalon. If this patent were actually granted, it could be close to expiry.

6. Mason, pp. 56–57.

7. Eaton & Crabtree, “Washing Photographic Films and Prints in Sea Water” JSMPE 40:380 (1943).

Chapter 4
DEVELOPMENT PROCEDURES

Film size equivalents

The following film sizes are approximately equal to 8x10 inches, or 80 square inches (80 inches^2, 80 in^2, 80”^{2}). Throughout the text, whenever 8x10 inches of film or 80 inches^2 is referred to, it will be considered equivalent to:

> *I was taught to agitate film as vigorously as possible, to prevent uneven development and bromide drag. For reasons I did not then understand, my photographs never seemed to have the tonality I saw in the work of more experienced photographers.*
>
> *Several years later photographer Jim Goff asked me why I was agitating my film like a washing machine. He told me to use slow, gentle inversions, say one every two seconds, for five to ten seconds each minute, to improve the tonality of my images. I tried his method, and after adjusting the development time, was able to achieve the tonality which had previously eluded me.*
>
> —ANCHELL

1 —35mm roll, 36 exposures; a roll of film
1 —120 roll
4 —4x5-inch sheets
2 —5x7-inch sheets
1 —8x10-inch sheet

Developer volume recommendations for 8x10 inches of film

Optimum development requires a large amount of developer per film.

To maintain quality and consistency use the following volumes for each 8x10 inches of film, regardless of the processing method—even rotary processing.

Undilute developers—a minimum of 250 ml (D-76, Xtol, DD-X 1:4). We strongly recommend 300 to 350 ml to ensure the film is *entirely covered* with solution, as it should be. Coverage is not the same as capacity. Capacity is how much film can be developed before the developer weakens or exhausts.

Dilute developers—at least 500 ml (D-76 1:1, Rodinal 1:25 to 1:50, FX 1, FX 2, HC-110 1:31 from concentrate, PMK).

Very dilute developers—1 liter (D-76 1:3, Rodinal 1:100, FX 2 1:1, HC-110 1:90 from concentrate).

These amounts may sound extreme. But saving on developer is penny wise and pound foolish. If there are ways of making photography cost-effective, skimping on film developer is not one of them.

Many users of color processors such as the Jobo CPE-2 or CPE-3 have successfully developed black and white film with a minimal amount of developer. While it is possible to obtain a printable image, it is not possible to obtain an optimal negative, and that is our goal.

Where it is not possible to maintain our recommended volume of developer, for example when using a stainless steel tank, leave one or more rolls of film out. Fill the space at the top with empty reels.

Undilute developers can be used to develop up to ten and, in the case of Xtol, even 15 8x10s per liter, and many developers can be replenished. We do not recommend either technique. Two reasons, from PCS, 80 years ago, are sufficient: "… the solution accumulates a silver sludge and particles of gelatin which are apt to be picked up on the surface of the film" and "The [replenished or used] developer may also acquire fogging or staining properties." Another reason is loss of speed (p. 37, sidebar). Re-usable developers are a great achievement of photographic engineering. But they are never optimal.

"EFFECT OF AGITATION: AS the constituents of the developer absorbed in the swollen gelatin become used up, more must diffuse in from the bulk solution to

maintain the rate of reaction. The reaction products must also diffuse out into the bulk solution for the same reason. If the bulk solution does not receive adequate agitation the layer adjacent to the surface of the gelatin will become partially exhausted with the result that the two-way diffusion in and out of the gelatin layer is slowed down, resulting in a reduction in the rate of development. The importance of agitation was illustrated by Ives and Jensen (JSMPE, 40, 107 (1943)). At low development times, both density and gamma were increased by 30 and 100% by high agitation. Because of the large effect of this variable and the difficulty of precise control, it is preferable to use a sufficiently high degree of agitation that moderate changes in agitation have no detectable effect. There are, however, some cases where a minimum of agitation must be given—e.g. in high acutance developers. In these cases the agitation must be carefully controlled if successive results are to be as reproducible as possible."

—MASON, 123–4

Agitation

Agitation may be the least understood step in the development process. Agitation not only affects contrast, but also sharpness, film speed, and the total time of development. For example, continuous agitation reduces development time by 15 to 20% or more. It also increases the rate of development in the highlights, suppresses the adjacency effects which enhance film sharpness, and can cause bromide streaking. We do not usually recommend continuous agitation for black and white films. For exceptions see the section below, on Jobo Rotary Processors.

Most defects due to uneven development appear within the first 30 to 60 seconds, and are magnified as the development process continues.[1] Clearly, agitation should be continuous for the first 30 to 60 seconds. But it must be intelligent. The goal is to break up standing waves and prevent laminar effects which prevent the developer from randomly moving over the film. The only way to achieve this is to change direction on each inversion of the tank, or when lifting the tray when developing sheet film. As Mason writes,

“In any method of agitation it is imperative not to get streamlined flow over the emulsion surface. The flow of the developer over the emulsion surface must be as random as possible, otherwise one of the various forms of ‘streaming’ may result.”

Finally, and perhaps most important, once you have established a satisfactory agitation method for a particular film and developer, always stick with that method to ensure consistent results.

Agitation recommendations for roll film

There is much conflicting advice on how often to agitate and for how long. We know we should agitate for 30 to 60 seconds for the first minute. But what about the rest? Should the next cycles be every 30 seconds or every 60 seconds? Should the cycle last for 5 seconds or 10 seconds. We will try to impose some order on this confusing situation.

Question: For the first minute, do you agitate for 30 or 60 seconds?

Answer: If you can fully immerse the film into the developer in less than 5 seconds, then 30 seconds for the first minute is enough. If it takes longer than 5 seconds to completely wet the entire film surface, agitate for the entire first minute. The bigger the tank, the more important this becomes. 60 seconds is safest in all circumstances.

Question: For the next minutes, do you agitate once every 30 seconds or once every 60 seconds?

Answer: It depends on the total development time. If your development time is less than 5 minutes, agitate every 30 seconds. If your total development time is longer, agitate every 60 seconds.

Question: Do you agitate 5 seconds or 10 seconds on each cycle?

> *When I began my career in photography plastic reels had a reputation for absorbing chemicals, and they could not be loaded wet. Then I was introduced to Paterson Super System 4 tanks and reels. I think there is no better tank or reel for*

> *manual film processing. Although the reels do not absorb chemistry and they can be loaded wet, that is not the only reason I recommend this system. The main reason is the wide mouth, for rapidly pouring solutions in and out. The only way to come close to the fill and dump speed of the Paterson tank with a metal tank is to turn off the lights, remove the lid, and fill (or dump) the tank in the dark.*
>
> —ANCHELL

Answer: Agitate for 10 seconds. Five seconds is not enough to create movement or flow disruption.

To invert the tank, lift it with both hands, your right hand covering the lid to prevent it from popping off, and your left hand under the base. Twist the tank away from your body, clockwise, as you turn it upside down. Twist it counterclockwise back to the starting point as you turn it right side up. One complete inversion should take about 2 seconds. For the next inversion, reverse the twisting direction: twist the tank towards your body, counterclockwise, as you turn it upside down and clockwise on the return. Before placing the tank down, gently tap the base on a hard surface to dislodge air bubbles.

In sum, our recommendation for tank development with times over 5 minutes is to agitate for the first 30 to 60 seconds, then for 10 seconds every minute. For times less than five minutes, agitate for the first 30–60 seconds, then once every 30 seconds for 10 seconds. This applies to all developers unless specifically noted otherwise, or unless experience warrants agitating more frequently.

Minimal agitation

This technique was rediscovered by Geoffrey Crawley in the 1960s[2] and enthusiastically adopted by Ansel Adams in the 1980s.[3] Its purpose is to provide maximum sharpness through the formation of extreme adjacency

effects, and to slow down highlight development to allow easier printing of extreme highlight details.

To use minimal agitation, agitate continuously for the first 60 seconds, then for 10 seconds every *third* minute. Increase development time by about 50% over normal.

This method should only be used with non-solvent, high definition developers that take 8 minutes or more to develop film, or with solvent developers that have been sufficiently diluted so that times are at least 8 minutes. Crawley recommended it for FX 1 and FX 2 with a 50% increase in development time (usually to 15 to 18 minutes) and with Acutol and Acuspecial. Adams recommended HC-110 1:90 from concentrate with developing times around 18 minutes.

Given longstanding questions around the reformulations of HC-110, other dilute solvent developers may be considered. Xtol 1:3, D-76 1:3 or D-23 1:3 (all at 75F/24C if necessary to keep development times to about 18 minutes) would be good candidates. This method can also be used with tanning developers at normal dilutions (particularly Pyrocat-HD) and of course with Rodinal and all high definition developers.

If you want to tray develop sheet film with minimal agitation or stand development (see p. 47), develop one sheet per tray.

With this technique, Crawley emphasizes the "interesting internal contrast and acutance effects" that can be achieved. Adams emphasizes the reduced highlight contrast with HC-110 at 1:90 from concentrate. **Note**: This is the *only* technique Adams recommended for contracted development with modern films. This extreme contraction is a feature both of minimal agitation and the fact that a high definition developer at "normal" dilution is already highly dilute. Even in a full strength developer like D-76 or Xtol, when agitation is minimal, there will be moderate contraction due to suppressed highlight development.[1]

If you need to do tank development with high precision for a developing time less than six minutes, a two tank system can be used. The first tank contains the developer, the second contains the stop bath or water rinse. Shortly before development is complete, turn the lights off and remove the lid from the tank. At the moment development is complete, pull the films out of the tank, drain for ten seconds, then immediately immerse in the second tank. If a water rinse is used instead of an acid stop bath it should be a running water rinse for at least one minute or five complete changes. For very short times, an effective acid stop bath may be preferred. In either case, agitate continuously in the rinse for one minute. Use the buffered stop bath TS-7 in chapter 12. An ordinary stop bath that has been used a few times is not much more efficient than a water rinse, no matter what the indicator dye reports (chapter 12).

Draining

The ideal draining time after development is 10 seconds (chapter 12, footnote 1). Within 10 seconds most of the developer will have drained off the film, leaving about 14 ml of developer either on the surface of the film or absorbed in the emulsion (for 80 inches^2 of film). Increasing the draining time beyond this point does not appreciably increase the amount of developer that drains off the film, but it does permit development to continue, and increases the probability of streaking as the remaining developer rapidly exhausts. Adding a wetting agent to the developer does not materially alter this figure.

Tanks and trays for sheet films

For hand inversion tank processing of 4x5-inch sheet films we recommend the combination of a Paterson System 4 Multi-Reel 3 tank and MOD54 4x5" sheet film holder. This allows processing of up to 6 4x5 sheets in 1 liter of solution.

In the past we recommended the Jobo 2521 tank and 2509N reel but these are no longer made. Do not use the Jobo 2550 4x5-inch film developing tank as it is made for rotary processing using minimal developer and will not allow full coverage of sheet film when used manually.

Three box developing systems for 4x5-inch film are currently available. We prefer the HP Combi tank to the Yankee tank because it can be inverted and can be used with glass plates. It is easily broken. Handle it with care. Filling and emptying is slow unless you remove the leakproof lid in the dark. A re-engineered, modernized take on the Combi principle with faster fill/empty is made by Stearman Press.

B&W KING makes 4x5 and 5x7 stainless steel developing tanks and reels, based on the old Nikor design. Reports are that these tanks work well but, like most stainless steel tanks, may leak slightly when inverted. A solution is to wrap the lids with electrical tape. The manufacturer recommends stirring. We do not, unless it is combined with inversion.

For tray processing of sheet film, use a tray at least one size larger than the film (e.g., 8x10 tray for 5x7 film, 11x14 tray for 8x10 film). The minimum tray size we recommend, even for 4x5 sheet film, is 8x10 inches. This ensures adequate developer volume.

Tray inserts or "sloshers" or "baskets" for sheet film keep sheets separated in the tray and prevent emulsion scratching and uneven development. They have been manufactured in the past and can be made by DIY-ers. Using them eliminates potential agitation, aerial oxidation, and handling problems when tray developing sheet films.

Deep tank development

Deep tank development of film was primarily used by commercial film labs where it was both time and cost-effective to mix large quantities of developer and use replenishment. Today the film racks for 35mm and 120 film, and film hangers for large format film are no longer being made and must be found on the used market. Deep film tanks in 4x5, 5x7, and 8x10 sizes are currently available from Kodak as there are still some commercial labs that use them.

There are several advantages of deep tank processing. It is not as easy to damage film as with tray developing, and when properly replenished the sheer volume of developer insures complete development of every film. In addition, it is very easy to add individual sheets of film for Zone System plus and minus development.

Development is done in total darkness. Sheets of film are slid into hangers in the dark and retained by a hook or trap. The film notches are placed in the upper left corner of the hanger. The loaded hangers are placed in an empty tank until all are ready. The loaded hangers are then lifted together and placed into the tank containing developer. Agitation is accomplished by lifting the entire set of hangers completely out of the tank, tilting to one side for five seconds, lowering them back into the developer, then lifting and tilting to the other side for five seconds; this should be repeated twice on each side. When developing time ends, the hangers are lifted and drained by tilting to either side for ten seconds, then moved to the second tank. Unless the second tank is fitted with a hose at the bottom for running water, a stop bath is used with continuous agitation by lifting and tilting. When the running water or stop bath is complete the film is again moved en masse to the tank containing fixer, and so on. The lights may be turned on when fixing is one-third complete with a minimum of one minute. The films can be left in the hangers for washing in order to avoid scratches.

With rotary processing, we recommend 30% more water to compensate for excessive agitation. Contrarily, in chapter 8, we recommend

increasing the strength of developer when using pyro or other staining developers. This conflicting advice exposes the compromises inherent in rotary processing. Rotary processors are designed for color developers, which are specifically designed to work when the film is exposed to air during processing. The only black and white developers we can wholeheartedly recommend for rotary processing are undiluted, high-sulfite types, like D-76, Microphen, and Xtol. It is a cornerstone of black and white film developing technique that we avoid exposing film to air. With a rotary processor, we invite air in. Each user must decide if the price is worth it.

Jobo rotary processors

Many photographers like the convenience of developing film with continuous agitation in a Jobo rotary processor. Unfortunately, continuous agitation interferes with the formation of sharpness-enhancing edge effects. The loss of sharpness enhancing will rarely be seen on 4x5-inch or larger negatives with less than 10x enlargement (40 x 50 inches). The effect will be noticeable on 35mm negatives enlarged to 11 x 14 and certainly by 16x20 inches. If you do not intend to enlarge small format negatives beyond 8x10 this may not be an issue. Continuous agitation also exaggerates highlight development at the expense of shadow development. It thus results in lower speed and a shorter tonal scale. One way to adjust for this is to use a more dilute developer. Whatever developer you use, dilute it with at least 30% more water and increase your development time. Another major problem with Jobo processors is that the film spends a large amount of time exposed to air. This encourages aerial oxidation, which is a particular concern when using pyro or other tanning developers. In this case, it may be necessary to increase the strength of the developer (chapter 8).

Loading film onto reels

Care is required when loading film onto reels. If the film is forced onto the reel it can buckle, leaving indelible marks on the negatives. (It's easy to recognize this effect from the characteristic crescent moon or eyelash shapes left on the film.) The best way to become expert in loading reels is to practice over and over again. Practice at first with lights on, with film dedicated to this purpose, then with your eyes closed or in the dark.

> *Cut the film leader between sprocket holes to avoid sharp hooks which could dig into the reels.*

Loading plastic reels

Hold the reel in one hand with the film in the other. The opening of the reel should be towards the film hand. Make sure that the openings, on either side of the reel, are lined up with each other. Gently push the end of the film (35mm should have the leader cut off) into the opening until slight resistance is felt. At this point it is safe to hold the end of the film and pull it past the initial resistance point. Be careful to follow the curve of the reel so the film does not jump the track.

Once the film is started hold the sides of the reel with either hand and slowly begin to rotate the sides forward and back. This will "walk" the film onto the reel. Continue until the entire film is on the reel and safely past the opening.

When film is very damp and hard to load onto a plastic spindle, try loading under running water—in total darkness of course. While damp film tends to stick to plastic, wet film has more slide.

A wet or damp reel can be almost impossible to load. Never force the film. Dry the reel to the extent possible (a hair dryer is useful on low heat), then clip the corners of the film end to be inserted at a 45 degree angle. Do not clip too far back on the corner or the film may jump the track. One trick is to use a curved toenail clipper.

Loading metal reels

Although loading metal reels is not as convenient as loading *dry* plastic reels, with practice it is almost foolproof, and it is unlikely that film will be damaged, even if the film or reel is damp.

Hold the reel in one hand, feeling for the spiral opening. The opening should point towards the opposite hand, the one holding the film. Very gently pinch the film between your index finger and thumb. This will create a slight bow towards the emulsion side of the film (the emulsion side is the inside curve of the film, facing the spool when it is rolled up). Insert the film into the center of the reel. It should engage a clip or "teeth" placed there to keep the film from slipping. (If there are no teeth, if the clip has fallen off, or if you cannot get the film to go under the clip, simply insert the film between two of the center bars that separate the sides of the reel; the clip or teeth are only an aid to keep the film from slipping—they are not required otherwise.)

While maintaining the gentle bow in the sides of the film, slowly rotate the reel, allowing the film to load from the center out. Stop occasionally and feel the back of the film (it is coated with an anti-halation and anti-scratch coat so do not worry about fingerprints, if your hands are clean and dry).

The film should feel round and symmetrical within the reel. If anything feels odd, off, or cock-eyed, remove the film and begin again.

When the film is completely loaded, run your thumb and forefinger between the two outside spirals of the reel. Feel all four quadrants of the reel separately. If you feel film pushing through the sides of the spiral unspool the film past the point where the film pushes through, all the way if necessary, and reload. If you fail to do this you will have irretrievable underdevelopment where the film is touching the back of the film in front of it.

As with plastic reels, practice, practice, practice.

Developing sheet film in a tray

Agitation affects the rate of development, especially in the highlight regions of the negative. Consistent quality is only possible when agitation is uniform for each film or batch of films.

"The difference between a good photograph and a great photograph is subtleties."

—Jim Goff

The potential to damage negatives when they are wet is high in tray processing. Take care, follow the procedures below. Go slow and pretend you're handling delicate porcelain.

Don't develop more than six 4x5-inch negatives at a time. It can be done, but more than six films at a time is a prescription for disaster.

For up to four 4x5 negatives, use a minimum of one liter of developer in an 8x10" tray. If you add a fifth or sixth negative, increase the minimum volume of developer to 1200 ml. For very dilute developers (p. 39) increase the volume to 2 liters for up to 6 sheets. You may need to use a larger tray.

For 5x7 film use an 8x10 tray; for 8x10 use an 11x14 tray. Follow the basic guideline of 1 liter of developer for each 8x10 inches of film surface: four 4x5, two 5x7 or one 8x10-inch films. These recommendations insure full immersion, full development, and ease in handling multiple sheets.

You will need four trays and a method for washing the films after development. A good way to wash sheet film is in a Paterson High Speed Print Washer. The Paterson washer is a wash tray with inserts that will allow either four 4x5", two 5x7", or one 8x10" films to be washed at a time. Alternatively, use sheet film hangers and a deep tank.

Tray arrangement

To develop a single sheet of film, arrange the trays as follows:

Tray 1, Developer
Tray 2, Stop bath (acid or water)
Tray 3, Fixer
Wash

Procedure for one sheet of film.

1. With clean, dry, chemical-safe gloves on, and in total darkness, remove the single sheet of film from the film holder or its light tight storage container. Slide the film smoothly into the developer making certain it is completely immersed. Immediately begin rocking the tray for one full minute. The method is to gently raise either corner of the tray nearest you approximately 3/4 of an inch (2 cm); lower it gently; then immediately raise and lower the tray from the middle of the side nearest to you; finally raise and lower the final corner nearest to you. Repeat this for at least 3 agitation

cycles, allow the tray to rest for one full minute, then repeat for 3 agitation cycles. Continue this procedure until 10 seconds prior to the end of the developing time.

Note: To prevent aerial oxidation with some developers do not remove the film from the solution during development.

2. 10 seconds before the end of the developing time carefully remove the film by holding one corner and allowing it to drain before moving it to tray 2, the stop or water bath. Continuously agitate the film in tray 2. Drain for 10 seconds before moving to the fixer in tray 3.
3. Agitate continuously for a minimum of one minute before turning on the room lights.
4. Drain the film and move to the wash.
5. When washing is complete immerse in a wash aid for one minute, then hang by one corner only. You may carefully wipe excess water off with a single clean finger. Wipe one side at a time and only wipe each side once. Film is most susceptible to damage when it is wet and most damage occurs when it is being hung to dry. Don't handle wet film more than necessary.

Procedure for multiple films

When developing multiple films you will need to add **one more tray** at the beginning. This is a holding tray of clean water. The films will be collected in this tray, one at a time to prevent them from sticking to one another. We recommend you practice this procedure in the light until you are comfortable with it. Then practice in the dark. Once you get the routine down it will become second nature.

This procedure for multiple films is not the one recommended in most texts. It is Anchell's personal method. It is intended to minimize exposure to air to prevent aerial oxidation, especially with pyro developers, and reduce the risk of damage when handling negatives.

1. Remove the film(s) to be developed and store in a light tight box. Do not attempt to remove the film directly from the film holder into the first tray of water as your gloves will be wet and contaminate the other films, which will then stick together or to the film holder—you don't want to be present when this happens.
2. Move the films, one at a time, from the box to the holding tray of water, emulsion side up. Traditionally the notch code is placed in the upper right of the tray. Gently press one film at a time under the water and let it remain there for about 15 seconds before placing the next film on top and pressing it down.
3. When all sheets are in the water, pull on a pair of clean, dry, chemical safe gloves. Learn to do this in the dark. **N.B**. Latex gloves for cleaning are not chemical safe unless specified on the package.
4. With the film still in the water bath, carefully peel back the collected corners of the top sheets from the bottom sheet and hold the corner just outside the solution. With your other hand, carefully slide the bottom sheet towards the back of the tray until its edge clears the stack you are holding. Let go of the stack, then carefully place the single sheet on top and repeat with the next bottom sheet —do not drain the film, just leaf through as quickly as you can without being careless. **N.B**. Developing film in a tray is not life or death. Take your time. Your film will be safely developed and any variations from moving faster or slower will be unnoticeable. Keep count of the sheets and do this for two complete cycles. Prewetting will prevent the films from sticking together in the developer.

   Note: Add one negative to each shu±e count so that the bottom negative ends on top. For example, if you are developing 4

negatives, shu±e as if you have 5, etc.

5. After the second full cycle in tray 1 (plain water), reach one hand under the full stack, like holding the back of a child's head—and with the same degree of delicacy—and pull the far end out of the plain water presoak while holding your other hand under the bottom edge of the stack to keep individual films from sliding out. With both hands in place, tilt and drain the entire stack for 10 seconds (don't try to drain individual sheets), then move to the developer in tray 2, and gently press the entire stack under, emulsion side up. Immediately begin to leaf through the stack from bottom to top for one full minute At the end of the first minute, rock the tray for 15 seconds, as described under the procedure for a single sheet, then shu±e through the negatives again, making certain that the negative that began on the bottom ends on the top. Repeat the shu±e/15-second rock cycle until the end of the development time.

"Agitation? You should see me in the darkroom. That's agitation."

—LISETTE MODEL

Note: It is not possible to perform intermittent agitation with a batch of films as can be done with one sheet (see the procedure for one sheet of film, above).

6. Ten seconds before development is complete, lift the entire batch as described in step 5 and allow to drain before placing in tray 3, the stop or water rinse. Immediately begin leafing through the stack continuously for at least two cycles (acid stop bath) or four cycles (standing water).
7. Move the film to the fixer in tray 4.

8. Agitate continuously for 1/3 the total fixing time with a minimum of one minute before turning on the room lights.
9. When fixing is complete, drain the film and move to the wash. If you do not have running water to wash with, then leaf through the film, for two complete cycles, then change the water. Repeat this a minimum of five times.
10. When washing is complete move the films one at a time and immerse in a wash aid. When all the films are in the wash aid, leaf through them for one minute, then hang to dry.

STAND DEVELOPMENT

Stand development is a technique which relies upon highly dilute developers and extremely long development times of thirty minutes to several hours with no agitation after the initial minute. This technique was popular in the early 20th century with glycin developers which are less likely to produce streaking than other developers.[2]

> *The French photographer Atget used development by inspection with stand development. Berenice Abbott has described a visit to his studio: he would leave her every twenty or so minutes to dash into the darkroom and inspect his negative to see if it was ready or not.*[4]

A speed increase would be expected with stand development because development of the highlights is suppressed by lack of agitation while the shadows continue to develop. One would therefore also expect a high degree of highlight compensation. But in practice, an almost normal macro gradation and normal speed are obtained with modern films. This is because, even though there is no external agitation, agitation through interlayer effects in the film (over such a long period of time) provides the necessary interchange between fresh and exhausted solution. However, although macro gradation may remain close to normal, micro gradation does not, and the combination of this plus exaggerated adjacency effects provides a refreshingly different kind of print. Extreme edge effects, and some haloing, are occasionally the result of such development. These edge effects are often desirable, but, especially with very long times (more than an hour),

undesirable edge and other effects, including streaking and haloing, may result.

FX 2 or TFX-2 diluted 1:1 (i.e., half-strength working solution, see chapter 6) are ideal stand developers. The small amount of metol prevents the speed loss typical of straight glycin. Glycin as primary developing agent inhibits streaking though it may not eliminate it.

Pre-baths (or pre-soaks) in water are not usually recommended with modern films. We recommend a 2-minute pre-bath with stand development, because even, bubble-free wetting of the film is critical.

Historically, glycin has been the developing agent of choice for stand development. It can be done with many other developers, such as Rodinal and HC-110, though we do not recommend those two for stand. For combining stand and tanning development, we recommend one of the simple pyrocatechin-carbonate developers found in chapter 8, or Pyrocat-HD, at half normal strength. When testing a new developer for stand development use only negatives exposed for that purpose that you can afford to lose. In such an approximate process, testing can answer two broad questions: 1) are development time and dilution sufficient to obtain normal density with the film/developer/time combination you have chosen? and 2) will this combination result in dichroic fog?

The shorter end of the suggested times for stand development, i.e. 45 minutes, works best. Longer times tend to provoke dichroic fog with modern films. This suggests that physical development takes place with longer times. To explore multi-hour development, we suggest trying the antistain agents discovered by Henn, chapter 7; also 5 and 6.

To avoid air bubbles give the film a two minute plain water pre-bath.

Traditionally, stand development is done with large format negatives in a tray. When developing in a tank, immerse the film in the developer, which must be sufficient to cover the film completely. Then rap the tank sharply on the table twice, then gently agitate for 60 seconds. Be sure to alter the direction of agitation throughout the 60 seconds. The film and developer must then be left alone. Using FX 2 or TFX-2 at 1:1 (1/2 normal working strength), 35 to 60 minutes is a good target for slow to medium speed films. After the developing time is over, rinse for two minutes in running water, then fix and wash.

Stand development is an inherently non-standard process. The developer will respond differently to different negatives and different degrees of exposure. But temperature should be standardized between 70F/21C and 75F/24C to bring some consistency to the process. Precise developing times are irrelevant with stand development, as a large difference in contrast only occurs with changes of at least ten minutes, but temperature should be consistent. If the room temperature is not within 5 degrees of your standard temperature, place the developing tank in a large water bath to maintain the temperature during development. It is nearly impossible to overdevelop conventional film with stand development and FX 2, but tabular films are more sensitive.

A variation of stand development is semi-stand development, e.g. 10 seconds agitation every 20 minutes. The intention is to minimize streaking and haloing. Semi-stand reflects early 20th century practice: the film was often taken out of the developer every 20 minutes to be inspected under a safelight.

Stand development is one of the safer alternative techniques you can use with modern films. In the past it was possible to experience dichroic fog with fast films and times over 90 minutes. For this reason among others,

stand development has not been recommended for fast films. However, some contemporary fast films are proving satisfactory, depending on the developer.

Minimal agitation and stand techniques in perspective

Stand development is an adventure. It can produce unusual, arresting results. But there may occasionally be a weird negative and, rarely, a spoiled negative.

By contrast, minimal agitation (p. 41) is a reliable professional technique. To achieve some of the benefits of minimal agitation while reducing extreme edge effects and highlight compression, agitate each second minute, rather than each third minute. Increase normal time by 30% rather than 50%.

NOTES

1. Silvia Zawadzki to BT, 1998.

2. Crawley 60/61.

3. Adams, The Negative.

4. Berenice Abbott to BT, 1989.

Chapter 5

SOLVENT DEVELOPERS (FINE GRAIN)

The fine grain myth

At any given time in photographic history photographers have endeavored to achieve better image quality than they could get with the films then available. By the early 1900s, astronomers and other scientists were clamoring for better image quality. By the 1920s image quality had become an enormous concern for the emerging movie industry. By the 1930s, with the new popularity of 35mm cameras, still photographers became more vocal than ever on this score.

Enhanced image quality came slowly to still photography, because early researchers saw it in terms of finer grain, not higher sharpness. The method most widely used by still photographers to reduce graininess was a highly solvent developing agent, such as *p*-phenylenediamine (PPD) which dissolved part of the silver grains, thereby making them appear smaller—a type of development we now call super-fine grain.

It is significant that this method was never adopted by the movie industry, as very early on Hollywood discovered that PPD destroyed image definition. Cinema production has always been so expensive and quality demands so high that no unsharp process could be tolerated. When a tiny piece of 35mm film is projected onto a gigantic cinema screen, it must have definition!

In still photography, sheet film users could use PPD developers without harm—there is not much that can ruin the sharpness of an 8x10 negative—and there were even some interesting effects that could be achieved with PPD on older, thick emulsion films. But few 35mm users could afford the loss of sharpness and speed.

QUICK GUIDE RECOMMENDATIONS

- D-76 undiluted or 1:1 is still the standard by which all other developers are judged. FX 15 and Xtol are sharper and offer a 2/3 stop speed increase. We particularly recommend Xtol for all fast films, especially in 35mm.
- For all tabular films, Xtol is the solvent developer of choice.

The introduction of D-76 in 1927 was the breakthrough the movie industry was looking for. D-76 was the *first fine grain developer that did not destroy sharpness.* It was also the first fine grain developer to provide full emulsion speed. D-76 is what we would now call a *moderate fine grain* developer. It has a fine grain effect, but not a strong one. Though it was quickly superseded by more reliable developers for motion picture processing, it became and remains the standard by which all future black and white developers would be judged, both for still and cinema photography.

It was not until the 1940s that traditionalist still photographers finally got the message Hollywood had accepted at once. Super-fine grain developers lost their mystique. Moderate fine grain developers, exemplified by D-76, became overwhelmingly popular and retain their dominance to this day. The coup de grace for super-fine grain developers was that fast films of the 1950s could produce dichroic fog with highly solvent developers.

"Fine grain is essentially a property of the emulsion: the greater the emulsion speed, the worse the graininess. This is due to the relationship between grain size and sensitivity, and the greater tendency for the larger grains to clump on development. (By 'clumping' here is meant the optical effect of the statistical distribution of the developed grains, by which the grains appear to have come together in groups.) By suitable choice of development conditions, however, the graininess of any emulsion may be reduced to the minimum possible for that

emulsion. Even in the fastest emulsions the sizes of the individual grains are too small to be of any significance in normal degrees of enlargement. The result of the clumping of grains on development is the 'graininess' of the image, and this shows up on fairly low magnifications. Fine grain results if this clumping is reduced to a minimum, the smaller the emulsion grain, the less the tendency to clump. This clumping can be reduced to a minimum by suitable development conditions—this is 'fine grain development'."—Mason, p. 145.

Solvent developers

Solvent developers are often called “fine grain” developers because chemicals are used to reduce the appearance of grain. As mentioned in chapter 1, solvent developers dissolve some part of the silver grains in the film, making them appear smaller and “less grainy.”

It is generally recognized that solvent developers do not produce as sharp an image as non-solvent developers. This is due to a number of factors, even now not fully understood, of which dissolution of the grains by the sulfite in the developer is only one.

Though the ‘solution physical development’, typical of solvent developers can lead to loss of sharpness, not all primarily physical development is unsharp. In the 1950s and 1960s, during the heyday of monobath research, several sharpness-enhancing adjacency effects were observed as being exclusive to primarily physical development.

Perhaps as important as solvency *per se* is to keep the developer at a moderate *buffered* pH between about 7.5 and 8.5.

Moderate fine grain developers

When discussing fine grain solvent developers we refer to a developer of the D-76, D-23 or Xtol type, used undiluted. Unlike older fine grain formulas which used solvent developing agents such as PPD, or a strong solvent such as thiocyanate or even thiosulfate, modern fine grain developers rely on a high concentration of sodium sulfite for solvency.

One hundred g/L of sodium sulfite is the typical amount used for a visible fine grain effect. More sulfite can be used, but 125 g/L is the practical limit. This assumes a developer that contains no other silver solvent. Almost without exception, such developers use MQ, PQ, or metol alone. Xtol uses the Dimezone-S-ascorbate combination, and contains 85 g/L of sulfite. (There is an important exception to this generality. *Concentrated* fine grain developers such as Aculux (FX 24), which are similar to reversal First Developers, are moderate high definition developers which are made solvent by adding a small amount of, usually, potassium thiocyanate—see p. 60 and chapter 7).

As mentioned, developers of this class are called "moderate fine grain" developers to differentiate them from the older super-fine grain developers. What they offer for today's conventional films is appreciably finer grain than a non-solvent developer, full emulsion speed, and excellent gradation, with only a moderate penalty in sharpness.

Diluted fine grain developers

Diluting fine grain solvent developers offers many advantages. At a moderate dilution of 1:1, sharpness is increased while effective film speed is maintained. Graininess is slightly increased on dilution, since the solvent effect is not as great, but the increase is small, because the film spends a longer time in contact with the sulfite while in the developer. Moreover, using developers as diluted one-shots is the best way to ensure consistency and quality.

> *Readers will notice the cautious way in which the term "clumping" is used and defined in the quotation from Mason in the callout on the opposite page. This would probably be approved by Kodak's Dickerson and Zawadzki, who wrote an excellent article in the January/February 2008 issue of "Photo Techniques" skewering the myth of 'grain clumping.' That term, in their view, is carelessly used by many authors. Their major point is that "clumping" is a perceived visual phenomenon, not a measurable physical phenomenon.*

Dilution also affects gradation in important ways. D-23 and D-76 cannot handle high contrast subjects unless diluted. Ansel Adams believed that highlight blocking in undiluted D-76 was due to the *solvent* effect of sodium sulfite. This is a misperception. Sulfite is the culprit, but for different reasons: in undiluted D-76 and D-23, the amount of sulfite is too high to permit the developing agent to exhaust in the highlights. Thus, the gentle shouldering-off of highlights typical of compensating developers does not occur. Dilution cures the problem.

When these developers are diluted between 1:1 and 1:3, they show comparable highlight latitude to compensating developers of the high definition type. Furthermore, at 1:3 dilutions they also offer enhanced acutance characteristics approaching those of high acutance developers. While acutance is not as high as specially formulated high definition developers such as FX 1 and 2 (chapter 6), graininess is not as high, either. In addition, some phenidone-based solvent developers are capable of a 30% to 60% speed increase. Finally, tabular grain films seem to work best with solvent developers diluted at least 1:1, or with non-solvent developers.

D-76

D-76 was the most important developer of the 20th century, and it still is. It is the overwhelming favorite developer of 35mm photographers.

How can a developer maintain popularity and offer optimum quality when films have changed so much in the intervening years? One reason is that no manufacturer will risk marketing a film that does not perform well in D-76. In fact, most films made today are optimized for D-76.

Not everyone is unanimous in agreeing that D-76 is the optimum developer for today's films, or even that it is the optimum developer of its type—a low pH, moderately solvent, fine grain developer. Geoffrey Crawley states that D-76 does not fully exploit either the inherent sharpness or speed of modern films, and does not offer high enough definition to take advantage of the enhanced image quality available with today's lenses. Kodak's Xtol can be seen as a radical update of the D-76 developer type.

KODAK D-76	
Water at 125F/52C	750 ml
Metol	2g
Sodium sulfite anhydrous	100 g
Hydroquinone	5g
Borax decahydrate	2g
Cold water to make 1 liter	

Additives to Kodak's single package product have, at times, included boric anhydride to stabilize the combined dry chemicals and Calgon or, later, DTPA, as sequestrant. Several patents from the 1940s onwards discuss boric anhydride and phthalates as stabilizers in single-package developers (e.g. USP 2,606,118). Perversely, this patent goes out of its way to avoid claiming for developers with

borates, though it does include metaborates. Yet we know that to this day D-76 contains boric anhydride because it's listed in contemporary MSDSs. One thing we can affirm: many sequest-rants are photographically active. Those who have reported a difference between D-76 as manufactured and as mixed fresh have support from both Mason and Haist.

Even so, D-76 will probably be manufactured for as long as black and white silver halide photography is viable. As a result, commercial modifications of MQ-solvent developers have been few because the safest course has always been to use D-76, and call it something else, as with Ilford's ID-11.

As sold today in the single-powder package it took Kodak 30 years to perfect, D-76 contains ingredients not specified in the original formula. These include DTPA and boric anhydride. It is believed that special manufacturing techniques are employed to make the metol dissolve before the sulfite.

The sequestrant helps ensure that the developer can be used in almost any geographical area, even though such precautions are not necessary in most parts of the US and Europe. Some D-76 experts believe these additions degrade image quality.

It has been wondered why Kodak has never done anything to alleviate the 90-year-old problem of pH rise in D-76. Kodak has, actually, published many buffered variations, for example D-76d. But the D-76 product has never substantially changed because experience has shown that variations to the basic formula usually have a negative impact on speed, sharpness, or grain. The same is true of Ilford's ID-11. As pointed out in the callout overleaf, Henn's solution to the problem was D-23, which he believed to be a superior developer, though it does require slightly longer developing times to match D-76's speed. But D-76 remains the most popular developer.

They recommend mixing the developer from scratch.

Note: Although Kodak D-76 and Ilford ID-11 are ostensibly the same formula there are a few differences as manufactured. Ilford sells ID-11 in two separate packages. The first contains metol, the second sulfite. ID-11 is thus probably closer to the original formula.

D-76 and film speed

In theory, a developer like D-76 which dissolves part of the silver should reduce effective film speed. Yet D-76 is often cited as offering the best exploitation of a given film's speed/grain capability. One reason is that, in the first stages of development, the sulfite in D-76 dissolves a small amount of silver and uncovers latent image sites which would not otherwise be available for development. This amounts to an effective gain in speed, a serendipitous effect not planned by Capstaff when he formulated D-76. It was well into the 1960s before researchers began to understand this mechanism. (Mason 112)

D-76 modifications

A major problem with D-76 was discovered in 1929, just two years after its introduction. At the pH of fresh D-76, which should be about 8.3, the hydroquinone is essentially inactive. However, upon storage over a few months, the pH of both D-76 and the replenisher formula, D-76R, can rise as high as 9, enough to activate the hydroquinone. At that point D-76 creates higher contrast. Thus D-76 can be variable in use, a poor characteristic for a developer that is supposed to be a standard by which to measure all other developers (Haist 362).

To correct this situation variations such as D-76d have been introduced. D-76d includes a buffer of 8 grams of boric acid, with the borax also

increased to 8 grams to match the original pH.

D-76c is a "low and normal contrast" variation intended for "photo-micrography, metallography, and spectroscopy." It has the addition of 0.04 grams of potassium iodide and 1 gram of potassium bromide. The rationale is that base+fog with D-76 is somewhat higher than with many other developers, and it has been argued by some that it is desirable to have minimum fog with technical films.

A radical variation on D-76 was proposed by Haist and J. King in US Patent 3,563,740. By adding sodium dicyan-amide to D-76 greater speed and contrast could be gained through greater silver coverage.

Grant Haist studied the problem and devised a remarkably simple solution. Omit the hydroquinone! If either the metol or the borax is increased by half a gram per liter, a solution indistinguishable in working properties from D-76 will result, but without the inconsistency.[1] The pH will still rise upon storage, but without the hydro-quinone, the effect will be negligible. (Haist 367 and JSMPE 42 p. 315, 1944) This variation, which we designate D-76H, is strongly recommended to all users of D-76 who mix their own. We have adopted it as the standard against which we measure other developers. D-76H is easy to mix and is also available in kit form from the Formulary as TD-16.

D-76H (HAIST)	
Water at 125F/52C	750 ml
Metol	2 g
Sodium sulfite anh.	100 g
Borax decahyd rate	2.5 g
Cold water to make 1 liter	

Comopare this also to the US Navy Developer N-2, chapter 7, p. 87, which eliminates both the HQ and the borax of D-76.

Various versions of the ASA standard developer (the developer recommended by the American Standards Association, now known as ANSI, in which films were measured until 1993) resembled D-76 except that the alkali was replaced with a carbonate/bicarbonate buffer, and potassium bromide was added. None of these modifications precisely matched the image quality of the original D-76, but they were more consistent for testing purposes.

D-76 VARIANTS	**D-76c**	**D-76d**	**D-76H**	**D-76R**
Metol	2	2	2.5	3g
Hydroquinone	5	5	-	7.5 g
Sodium sulfite anhydrous	100	100	100	100 g
Borax decahydrate	2	8	2	20 g
Boric acid	-	8g	-	-
Potassium bromide	1g	-	-	-
Potassium iodide	0.04 g	-	-	-
Water to make 1 liter				

Among the most interesting variations of D-76 are those in the original disclosure by Capstaff[2] which have not been mentioned in the photographic literature since. To raise contrast, the amounts of metol, hydroquinone, and borax should be increased slightly. To lower contrast, these chemicals should be decreased slightly. He advised keeping the sulfite level at 100 g/L of solution to maintain the fine grain effect. One assumption underlying this suggestion is that the extent of the desired fine grain effect is tied to the amount of time the film

spends in the sulfite-rich solution. This may be worth trying, with careful attention to the effect on speed. It's important to note that D-76 produces fine grain images not just because of sulfite, but because, compared to most developers, its pH is low and it is, by comparison to its predecessors, well-buffered. Another suggestion to modify contrast (Vesey, in Haist 364) is to agitate more for higher contrast and less for lower contrast. Vesey claimed a paper grade either way, or N+1 to N-1 development with this technique.

When D-76 is diluted it becomes more sensitive to the pH of the water. If your water is not pH neutral, use distilled water to obtain consistent results. Using distilled water is good practice for all developers.

Storing D-76 formulas

After mixing, the stock solutions will last up to six months if kept in a bottle filled to the top and sealed with a tight cap. However, for best results, all photographic solutions should be used as soon after mixing as possible. If the developer is to be diluted for use, be sure to dilute just before using, and discard the working solution after one use.

Penny wise, pound foolish

Although undiluted D-76 may be reused without replenishment we do not recommend this practice for small volume processing. Consistent quality can best be assured when *any* developer is used only once and discarded (one shot). However, if you choose to reuse D-76 without replenishment, develop a maximum of 7 rolls per liter. Increase development time approximately 5% for each additional roll developed in the used solution.

For those who wish to replenish the undiluted developer, especially commercial film labs, use D-76R replenisher. This is an acceptable procedure, but it must be re-emphasized that optimum results can never be obtained when a developer is reused. We make no apologies for this statement to those who try to save money by replenishing. There is *always* some compromise in image quality, including potential speed loss due to the build-up of bromide from previously developed film (a problem lessened but not eliminated with moderate pH phenidone-based developers). Where replenishment is essential, Xtol is claimed to give more consistent quality than D-76, and is designed to be self-replenishing. One of the reasons this works is that the phenidone/ascorbate system is less sensistive to bromide released by the film than MQ; another is that Xtol's buffering system is more effective.

D-23

D-23, published in 1944, was intended by Henn to be a simple to formulate replacement for D-76. Indeed, one of the stated functions of D-23 is to provide a more reliable alternative to D-76, especially when replenishment is obligatory (as in the commercial labs of fifty years ago).[3]

KODAK D-23

Water at 125F/52C	750 ml
Metol	7.5 g
Sodium sulfite anhydrous	100 g
Water to make 1 liter	

Ancestors to D-23 include Rudolph von Ehrhardt's 1934 formula of 15 g Metol and 100 g sodium sulfite to 1L water and Hans Windisch's better-known 1938 formula of 2.5 g Metol and 25 g sodium sulfite to 1L water, close to D-23 1:2.

D-23 has acquired a reputation for being a low contrast developer. This reputation may not be deserved. True, the formula does not contain hydroquinone, considered to be a high contrast developing agent, but the hydroquinone is not active in fresh D-76, and would not be active at the pH of D-23 even were it included.

Photographers who consistently find that D-23 offers finer grain, less speed, and lower contrast than D-76 are probably under-developing their film. With increased development times, D-23 will be found to work almost identically to D-76. Thus, D-23 is not a low contrast developer (that is, lower in contrast than D-76) unless it is either diluted or used as the basis for a two-bath developer (chapter 9). The confusion arises because D-23 is about 10% less active than D-76, yet Kodak was, historically, hell-bent on maintaining identical developing times for the two developers.

Seldom remarked is that D-23 eliminates the problem of pH rise in D-76. D-23 is sometimes diluted as much as 1:3, but developing times become long. A technique to shorten them is to develop at 75°F, just as recommended when Microdol-X is used 1:3.

A white scum of calcium sulfite may occur on films processed in high sulfite, low alkalinity developers such as D-23 and D-25, unless a sequestrant is added. This scum is soluble in acid stop baths and in fresh acid fixing baths, especially if the film is well agitated. It is slowly soluble in wash water, and may also be wiped or sponged off wet film, although light deposits may not be noticed until the film is dry. The non-swelling acid stop bath, SB-5 is recommended for its removal (1% acetic acid plus 45 g/L of sodium sulfate). For more on D-23 and particularly D-25, see chapter 7 and Appendix IV.

Research on solvent developers

Not much useful research on solvent developers has been published since the introductions of D-76 and D-23. One of the main contributors to work on solvent developers with modern films was Geoffrey Crawley, for decades editor of the *British Journal of Photography (BJP)*, who writes as follows on modifying D-76:[4]

> It is possible to adapt Standard MQ Borax [the *BJP*'s cumbersome name for D-76; it is also occasionally referred to as the "Eastman Borax Developer"] to give better sharpness and definition, and this has been done in the ASA standard fine grain developer and in the Adox Standard MQ Borax formula, which is as follows: metol 1 gram [2 grams according to Haist], sodium sulfite anhydrous 80 grams, hydroquinone 4 grams, borax 4 grams, potassium bromide 0.5 grams, water to 1 liter. The concentration of sulfite is 20 grams lower than in D-76, which reduces the amount of physical development and improves sharpness. The sheen[5] referred to earlier in D-76 appears to be caused by the nature of borax [or Kodalk] alkalinity (in a sensitive carbonate developer the introduction of 0.1 grams per liter of borax will produce a slight sheen). The addition of potassium bromide to a borax developer suitably rebalanced will remove this sheen virtually entirely, and improve definition, for it appears to prevent discontinuities usually caused by borax. The buffering of borax with boric acid does not seem to improve definition, although the borax sheen is reduced and sharpness improved. Adox MQ Borax has slightly longer times than D-76, as the contrast rises more slowly. A further step away from the parent D-76 can be made by replacing the metol in the Adox formula with Phenidone; this necessitates a reduction in the borax content, and a doubling of the bromide, both due to the greater activity of the Phenidone. A resultant formula worked out by the author is FX 3.

Geoffrey Crawley and the FX series of developers

In 1960 and 1961 Geoffrey Crawley published an extensive series of articles on developers in the *BJP*, including many new formulas, which he designated FX. The formulas included D-23 and D-76–type developers that were optimized for modern films *and* lenses. Over many decades, Crawley sporadically updated this information and published new FX formulas. As this is the most original (and continuous) research in recent photographic history into the nature of the development process it will be extensively discussed in this and the next two chapters.

> *Although little used today, D-23 was the basis for Henn's super-fine grain developers D-25, Microdol, and Microdol-X, also little used today. A question arises: why the high level of metol, when a quarter of the amount would do? The answer is, to increase reliability in the case of overlong storage or over-use. Keep in mind this developer was designed in the 1940s when black and white film developing was probably at its peak and Kodak had a great economic interest in accident- and idiot-proofing its processing. Furthermore, for those making up D-23, the greatest likelihood was that the chemicals were made by Kodak, so Kodak profited when unnecessary amounts were used and then thrown down the drain. At that time, of course, enviromental protection concepts were in their infancy. A final note: exact weighing is not critical with this developer, which has sometimes been made up by the teaspoon method. BT is opposed to teaspoon methods but SA thinks it is important to be informed about it in cases where it is absolutely*

necessary (see DCB4). Truly, with D-23, it doesn't make a substantive difference.

To begin, Crawley found that classical super-fine grain developers based on PPD (Sease) or thiocyanate (Kodak DK-20) tended to produce dichroic fog with modern films. Even so, he believed these developers might have uniquely useful characteristics (see chapter 7). He notes that the older solvent developers had been optimized to exploit the speed/grain characteristics of films, but the question of sharpness had not been considered. It was the purpose of his FX series to offer the optimum balance of speed, grain, and sharpness for modern films.

Crawley stated that the "natural" speed of a film is about a third–stop higher than obtained with D-76, and that it is possible to gain this speed advantage, or slightly more, while maintaining high image quality. This can be achieved in several ways:

1. The use of the Phenidone/hydroquinone (PQ) mixture, often supplemented with a third agent to prevent problems that sometimes arise with the PQ combination.
2. Careful balancing with bromide to prevent loss of sharpness Crawley believed is inevitable with developers containing borates.
3. Careful adjustment of the alkali systems to provide optimum quality. This usually amounts to a slight decrease in the solvent effect, compared with D-76.

Originally, the FX developers were optimized for three distinct film groups which were defined according to their typical microscopic grain structure. By the 1970s, this classification was no longer thought by Crawley to be necessary as, prior to the introduction of tabular grains, all films had become more or less uniform.

Some FX developers were dropped from the BJP formulary, such as FX 7 when the film classification system was abandoned. Others were replaced by

improved versions. We have chosen to list them all, including excerpts from Crawley's notes, for photographers who may wish to experiment further.

FX solvent developers are designed to offer enhanced sharpness at full strength. Dilution will improve highlight compensation.

The table on the next page shows the FX *solvent* developers, except for FX 5, FX 9, and FX 10 which are included in chapter 7. Non-solvent FX developers are discussed in chapter 6.

The FX developers are worth looking at by all photographers who would like improved versions of the D-76–type developer. If you don't want to wade through the series, FX 15 is the one to try. FX 15 is useful today as a speed increasing developer, and offers better image quality than D-76 and most commercial PQ developers, but Xtol is superior.

Note: A problem with the FX formulas is that they have often been printed with errors, even in the *BJP Annuals*, throughout the 1970s and 1980s. Photographers who have used some of these developers with poor results probably were using incorrectly published formulas. Effort has been made to ensure that the formulas published here are correct. Each one was checked by Mr. Crawley for FDC1.

FX SOLVENT SERIES	FX 3	FX 4	FX 7	FX 8	FX 11	FX 15	FX 18	FX 19	
Metol	-	1.5	1.5	1.5	-	3.5	-	-	g
Sodium sulfite anhydrous	75	100	115	100	125	100	100	100	g
PhenJdone	0.25	0.25	0.25	0.25	0.25	0.1	0.1	0.75	g
Hydroquinone	6	5	5	5	5	2.25	6	7	g
Glycin	-	-	-	-	1.5	-	-	-	g
Sodium bisulfite	-	-	-	-	-	0.5	0.35	-	g
Borax	2.5	2.5	-	-	2.5	2.5	2.5	-	g
Sodium metaborate	-	-	4	-	-	-	-	-	g
Sodium carbonate anhydrous	-	-	-	-	-	1	-	-	g

FX SOLVENT SERIES	FX 3	FX 4	FX 7	FX 8	FX 11	FX 15	FX 18	FX 19	
Disodium phosphate	-	-	2	-	-	-	-	-	g
Boric acid	-	-	-	-	-	-	-	-	g
Potassium bromide	1	0.5	2	-	0.5	1.5	1.6	-	g
WATER TO MAKE 1 LITER									

Notes on the FX Developers (Remarks in quotation marks by Crawley)

FX 3

"Development times about 10% shorter than D-76, speed increase of 30%, or a half stop in practice. An excellent general purpose negative developer, giving the full natural speed, gradation, sharpness, and definition characteristics of the film."

FX 3 was dropped from the BJP Formulary, having been replaced by FX 15, which offers a 60% speed increase and better overall quality.

> *Sharpness and Definition: Crawley has a particular and useful way of using the terms sharpness and definition. He defines sharpness to mean the acutance of major subject outlines. Definition he uses to mean the acutance of very fine detail. More technically, sharpness refers to low frequency information on a modulation transfer function (MTF) curve, while definition refers to high frequency information. More simply, sharpness means sharpness in large areas, while definition means sharpness in very small areas.*

FX 4

"In FX 4 the metol-Phenidone-hydroquinone combination is used. This reduces overall contrast and allows the shadows to increase in contrast more than in FX 3 by the time normal gammas are reached. Speed increase over D-76 is now 50–60%, roughly equivalent to Microphen. The presence of metol also assists discrimination in the highlights, which in some PQ developers are liable to 'run away'…."

Crawley's uniquely expressed insight into some of the problems inherent in the classic PQ combination has continued to interest photographic chemists who are sensitive to the subtleties of black and white image quality. The 1998 patent for Xtol (discussed below) also alludes to these problems.

FX 7

Said to be similar to FX 4, but intended for use with Ilford films, as manufactured then. According to Crawley, the older Ilford films gave better results in developers based on a metaborate system. FX 7 is no longer listed in the BJP.

FX 8

"The other surviving member of the group of scientifically balanced fine grain developers we are examining is D-23. It gives excellent sharpness, but definition is not outstanding. It is very suitable for lenses of lower resolving power, as is the PMQ combination, FX 8. FX 8 develops the full natural speed of the emulsion, to give about a 30% increase over D-76. Times are similar; sharpness is good, but definition, as with D-23, is not exceptional. The low alkalinity favors the characteristics of Pheni-done; granularity, perhaps due to lack of buffering (as with D-23) does not quite reach the best

of the speed-grain interlock. Nevertheless, like D-23, it is a useful formula in practice, and keeps well in tanks."

"They say my print quality is bad. Darling, they should see my negatives!"

—LISETTE MODEL

FX 8 is no longer listed, having been replaced by a new formula, FX 19, which attempts to bring the qualities of D-23 to a Phenidone developer. In 1960, Crawley was attempting to provide developers to match different lens qualities. Today, nearly all lenses are so good that this is no longer necessary. But it is a point worth keeping in mind by photographers who deliberately use unsharp lenses, or for situations where subject motion and camera shake cannot be avoided.

Note: Crawley argued that with a poor lens, edge effects in the negative may obscure rather than enhance sharpness. Later researchers have come to similar conclusions.

FX 11

FX 11, using the combination of Phenidone, hydroquinone, and glycin, was intended to offer the maximum possible true speed gain, which Crawley felt was 100% over the film's ISO rating.

"FX 11 gives higher film speed than either Promicrol or Microphen. It probably gives the highest speed available at present in a solvent developer, with balanced toe contrast to ensure good gradation with thin enlarging contrast negatives. It has built in 'sheen' to mask granularity by slight diffusion; definition is not outstanding owing to the high rate of physical development, but sharpness is fairly good. Its sensitometry and sheen is such that with correct exposure and development, no marked rise in granularity should be noted over commercial formulae despite its higher speed exploitation."

Note: By Crawley's measurements Microphen and Promicrol offer only a 60% speed increase.

> *In its day, D-76 was considered to be a low contrast developer, and it was, compared to most of what was then being used. But even by the 1940s, when D-76 usage had become so overwhelmingly popular, it was considered to be a normal contrast developer. The FX solvent developers are all comparable to D–76 in this respect.*

"In FX 11 a preference for thin negatives with a density scale of about 0.8 or 0.9 over fog and base, and normal contrast was assumed; the sensitometry of the developer is such that best quality is reached at that point, and it is not therefore very suitable for formats over 6x9 cm where a higher density scale is often required: By the time this higher contrast is reached, negative quality—granularity, sharpness and definition—will have fallen off. To obtain best quality at a higher contrast, with no effect on the increased film speed, increase Glycin by 0.5 gram/liter; development times will increase slightly."

This speed increase may still be obtained on conventional contemporary films, and to an extent with tabular films. However, with tabular films, which seem to respond less well to high-sulfite formulas, we recommend diluting FX 11 1:3 or more.

FX 15 (Acutol S)

FX 15 was available for years as Paterson Acutol S. When Paterson discontinued it, Crawley published the formula, as many wished to continue to use it. It offers a 60% speed increase, with sharpness comparable to non-solvent high definition developers. It is a further development of FX 3,

offering an improved characteristic curve. It is the only published FX developer with a buffer system.

Crawley notes that FX 15 is more flexible than the other FX developers when it comes to extended development of low contrast negatives ("expansion" in Zone System terminology). Crawley recommends it full strength for portraits, and diluted 1:1 for landscapes. Zone System photographers may find it useful for moderate expansion and contraction. With tabular films it should be diluted 1:3 or more. If developing times become too long with high dilutions, develop at 24C/75F, or increase the alkali by adding 0.5 g to 1 g of carbonate plus 1 g of borax, per liter of diluted working solution (1:3 to 1:5) plus a gram or two of bisulfite to maintain buffering. At this point FX-15 becomes a modern buffered non-solvent well-suited to tabular and mixed grain type films.

Promicrol, and Atomal-F and Orwo A-49 as manufactured from about the early 1950s up until c. 1990, are closely related cousins. Agfa's original 1935 Atomal was based on HEAP, patented in 1929 by I.G. Farben. It contained HQ and pyrocatechin as additive agents. After WW2 Agfa disclosures, John and Field at May and Baker discovered that HEAP was highly superadditive with glycin. They introduced Promicrol, and Agfa, in turn, introduced Atomal-F, which was reportedly almost identical to Promicrol. See chapter 7.

FX 18

In 1961 Crawley felt that it was impossible, no matter what "alchemy" was tried, to improve the speed/grain exploitation offered by D-76, though it was possible to improve the speed/grain/acutance exploitation. However, in 1966

he published a new formula, FX 18, that was also available commercially from Paterson (simply as FX 18).

FX 18 is said to offer slightly finer grain than D-76, and also a speed increase of 30% while maintaining or somewhat increasing the level of sharpness. As with D-76, use of FX 18 diluted 1:1 is encouraged.

FX 19

FX 19 was an improvement on FX 8. Both were designed as replacements for D-23, offering the advantage of slightly higher speed.

D-23 is said by Crawley to yield slightly finer grain than D-76, with about a 10% loss of speed, and somewhat poorer sharpness. D-23's poorer sharpness is due to the relatively high concentration of metol which, in conjunction with the high sulfite content, allows little oxidation of the developing agent when the solution is fresh.

Promicrol & Atomal-F

Almost the only solvent developers without either metol or phenidone that ever achieved commercial success were May and Baker's Promicrol and Agfa's Atomal. The only thing they have in common with D-76 is the sulfite level. They use a different alkali, and a combination of different developing agents.

PROMICROL	
Hydroxyethy-o-aminophenol (HEAP)	6g
Sodium sulfite anhydrous	100 g
Glycin	1.13g
Sodium carbonate anhydrous	11.6 g
Water to make one liter	

Although the Promicrol patent specified that the developer was a super-fine grain type, it has almost always been used as a speed increasing developer, producing slightly higher graininess than D-76. It has been widely assumed that the formula for Promicrol was identical to the one published in the patent. Crawley informed us that this assumption was correct. Agfa's Atomal is closely related and treated in detail in chapter 7.

Regarding techniques for increasing the speed of modern films, Haist extensively cites (471–472) a study by Paul Farber in U.S. Camera 31 (3): 44 (1968), using Tri-X as it then existed. Farber found that three popular developers of the day, Acufine, Diafine and Ethol UFG, not only did not increase speed, but in some cases actually decreased it. He also found

that undiluted D-76 at 50% and 100% overdevelopment did not increase speed over undiluted D-76, only contrast. "Farber concluded, 'Latensification seems to be the only process which actually increases film speed.' He achieved an exposure index of 800 for Tri-X film, thus doubling the rated film speed. After exposure at an exposure index of 800, the exposed film was unwound in the dark and taped to a wall, with the film emulsion facing away from the wall, at a distance of 10 ft from a safelight with a dark green No. 3 safelight filter and a 10-watt [standard incandescent] bulb. The film was given this low intensity exposure for 15 to 30 min., then developed normally in a developer recommended for it."

Glycin has a slightly solvent effect, but when used in a high sulfite solution the rate of physical development can become high. According to Crawley, "Glycin, by itself, with modern films, provokes dichroic fog as soon as the concentration of sulfite rises above about eight times its own. Results with PPD suggest that when a solvent developing agent is suitably energized, it is able to cope with a much more powerful solvent effect and will not then provoke dichroic fog in a formula in which it would undoubtedly do so on its own. Consequently, the energized Glycin does not provoke dichroic fog in the excess sulfite"….

The possible solvent effect of glycin is little mentioned in the literature but when I asked T.H. James about a greenish coloration with my low-sulfite pyrocatechin-glycin developer, TD-3, he said that in his opinion, it was due to partial physical development.

Promicrol as manufactured at the time of writing is a reformulaton with no relation to the original formula. HEAP is no longer available.

Other solvent developers using phenidones

Although little has been done to improve MQ-Borax developers, there has been considerable activity in the introduction of developers based on D-76 that use a phenidone instead of metol as the primary developing agent. Phenidone developers offer increased speed, but, unless very carefully formulated, also increased fog, and poorer definition.

Two major commercial PQ-solvent developers have been Acufine and Microphen. Microphen seems to have been optimized for Ilford films. There are those who feel that it does not perform well on other films. This may no longer be true as many of the differences in the way conventional films behaved in the 1960s have since become negligible.

Despite claims to the contrary, neither of these developers ever offered a true speed increase of, at best, more than 60%, or two-thirds of a stop. Graininess with Microphen is higher than with D-76; sharpness reportedly higher with Acufine. Neither developer made great inroads on the popularity of D-76, perhaps because gradation is not as good, though both are still manufactured. Certainly, highlight latitude is reduced with push processing, a technique recommended as a matter of course with both Acufine and Microphen.

Although Ilford and others have published formulas for PQ fine grain developers, those we are aware of have been considered adequate but not outstanding performers. It must be noted again that the speed increasing effect of PQ developers only occurs when developing to low or normal contrast. The moment the film is “pushed” the speed advantage of a PQ solvent developer over D-76 disappears. For this reason D-76 has been considered, until recently, to be the best all-around developer for push processing.

Acufine is a PQ D-76 modification with a carbonate/bicarbonate buffer instead of borax (a technique favored in Crawley's early work), and the old-fashioned use of Calgon as sequestering agent, which is particularly undesirable in this type of developer (Mason, 56–57).

ACULUX FX 24

Metol	3.25 g
Hydroquinone	10g
Phenidone	0.650 g
Sodium sulfite anhydrous	65 g
Sodium carbonate	10g
Borax	5g
Potassium bromide	2g
Potassium thiocyanate	2.5 g
Methylated spirits (or isopropyl or ethyl alcohol)	6-25 ml

Dilute 1:9. This formula is given only for illustrative purposes, to show one technique for achieving moderate fine grain development in a concentrate. Crawley modified this developer many times over the years, using different amounts of the basic chemicals and also making more radical changes, such as adding glycin and other borates.

Liquid concentrate solvent developers

We have been primarily discussing developers that are descendants of D-76. By their very nature, such developers cannot be prepared as liquid concentrates, since the required amount of the solvent, sodium sulfite, is too high, and this would be true even if potassium sulfite were used. (An exception is Ilfotec DDX, discussed in chapters 6 and 10; but here the recommended dilution is 1:4 which most manufacturers consider too low for a concentrated liquid developer.) Therefore another approach is required. One solution is to employ another solvent. Speaking strictly from this point of view, it is possible to classify HC-110 as a concentrated solvent developer, even though we have chosen to classify it as a non-solvent developer based on typical use. It is discussed more fully in the next chapter along with Ilfotec DD-X and Ilfotec HC, all of which are somewhat indeterminate in classification. The alkali used in HC-110 is diethanolamine, a powerful solvent. To counteract the solvent effect, a special so-called 'antistain' agent, PVP, is used to prevent dichroic fog.

To our minds, a more successful approach was taken by Crawley in the Aculux series of developers he formulated for Paterson. These are moderate high definition developers with the addition of a carefully determined amount of the silver solvent potassium thiocyanate. A problem is that each film has a different tolerance to thiocyanate. Therefore, the minimum amount must be added which, as films evolve, needs to be modified. There were three major versions of Aculux, and minor adjustments over the years.

KODAK E-6 FIRST DEVELOPER	
Kodak Developing Agent DA-1 (potassium hydroquinone monosulfonate	23.5 g/L
Dimezone-S	1.5 g/L

KODAK E-6 FIRST DEVELOPER	
Potassium sulfite (45% solution)	45.5 ml/L
Sodium thiocyanate (51% solution)	1 g/l
Sodium bromide	2.54 g/L
Potassium iodide	45 mg/L
Potassium hydroxide (45% solution)	6.5 ml/L
Aminotris [ATMP]	1.0 ml/L
Pentetic acid pentasodium salt [DM]	4.8 ml/L
Potass, carbonate (47% solution)	14 g/L
Sodium bicarbonate	12 g/L
pH @ 25C:9.65	

This version is from US Patent 5,212,098,1993. It shows the use of HQMS but not, then, of DTOD. While the earliest versions of the E-6 developer probably contained HQ rather than HQMS, a constant up until fairly recent years was the thiocyanate. We have been unable to document the use of DTOD to replace thiocyanate, but we believe this has been done. These quantities represent the working solution. Note some liquids are weighed. ATMP is a chelating agent and sequestrant, considered superior to Calgon.

It was shown by James that potassium thiocyanate and sulfite have a superadditive solvent effect (Haist 227), and it was at one time thought that thiocyanate in small amounts might increase film speed. Certainly, in a developer such as DK-20, the overall result is to decrease speed by at least a stop. On the other hand, Crawley showed how thiocyanate could be used in a speed-maintaining or speed-increasing developer, as did Kodak in the Ektachrome developers discussed next.

It is interesting to note that an approach similar to Crawley's has been taken by Eastman Kodak in the important First Developer of the E6 process. In this developer, it is critical to achieve both high sharpness through edge effects *and* finest possible grain consistent with that. Kodak combined Dimezone-S with hydroquinone or, in later versions, HQMS, and a solvent. The solvent was potassium thiocyanate during most of the lifetime of the E6 process and in earlier Ektachrome processes. (We can speculate that this may have been how Crawley got the idea.) However, in the very last formulations, an improvement was made. DTOD (discussed more fully in chapters 3 and 14) replaced the thiocyanate. A new take on the Aculux type of developer might advantageously use that technique.

Xtol: the latest evolution of the solvent developer

The most recent advance in solvent developers is Kodak Xtol. Recognizing the problems inherent in PQ developers with regard both to environmental and image quality, Silvia Zawadzki and her co-workers replaced the hydroquinone with sodium isoascorbate—successfully challenging some long-held assumptions about ascorbic acid and its isomers (i.e., ascor-bates) in moderate pH developers. A close representation of the formula for Xtol is published in US Patent 5,756,271 (1998), which Zawadzki regards as a teaching patent.

XTOL: US PATENT 5,756,271	
Part A:	
Sodium sulfite anhydrous	10
Diethylene-triamine-pentaacetic acid, pentasodium salt [DTPA]	1
Sodium metaborate (8 mole)	4
4-Hydroxymethyl-4-methyl-1-phenyl-3-pyrazolidone	0.2
PartB:	
Sodium sulfite anhydrous	75
Sodium metabisulfite	3.5
Sodium isoascorbate	12
Add Part A to 750 ml of water at room temperature; follow with Part B and water to make 1 liter.	

Xtol is the current state of the art in solvent developers. Several things distinguish Xtol from earlier developers:

1. The use of Dimezone-S instead of plain Phenidone. There is general consensus among researchers that this is the preferred form of phenidone to use in liquid concentrates.

> *Is ascorbate really the primary developer in Xtol? An informal observation that might confirm Zawdzki's assertion is that fog levels in Xtol are so low that an antifoggant is not required. Xtol is thus one of the few phenidone developers we know of not to specify an anti-foggant, other than Marilyn Levy's, which are known for their fog levels (chapter 8), and FX 8 & 19 (this chapter)*

2. The use of sodium isoascorbate instead of hydroquinone. This seems to eliminate some of the sensitometric unpredictabilities observed in PQ developers for years. It is not as strong a combination as PQ, but seems more desirable from the standpoint of image quality. One reason is the unpredictable complex kinetics of PQ development, when phenidone reacts (or you might say, over-reacts) to the non-linear reaction products of hydroquinone. Related is the troublesome phenomenon of local pH increase, an effect which is magnified where least desired, in the highlights. Replacing hydroquinone with sodium isoascorbate results in a more predictable exhaustion pattern, more edge effects, greater sharpness and, surprisingly, greater speed.

   Earlier literature suggested that ascorbic acid, like hydroquinone, is almost inactive under pH 9. Its primary use in Xtol would therefore seem to be to activate and regenerate the phenidone. But Zawadzki believes that ascorbate is the primary developing agent in Xtol.
3. Xtol is the first viable ascorbate developer formulated to work at a pH as low as 8.2. Ascorbate has been characterized as a very

"sharp", surface-acting developing agent. That, in combination with the low pH, results in negatives that achieve a better speed/grain/sharpness relationship than is possible with traditional developing agents.

4. A significant feature of this developer is that it is intended to be mixed at room temperature.
5. The developer serves as its own replenisher. This is possible for four reasons:

> *We emphasize that the only chemical which has been established to be useful in keeping phenidone-ascorbate solutions stable is DTPA. You can minimize potential problems with phenidone-ascorbate provided you have enough DTPA to meet your conditions. If you use distilled water, the DTPA's strength is exclusively available for mineral impurities in your other chemicals.*

- the developer has no restrainer
- the developer is highly buffered
- the developer is not highly sensitive to bromide
- modern films release bromide but also release accelerators, which tend to neutralize the restraining effects

The patent for Xtol notes: "It has been observed that the properly replenished developer composition of this invention has less degradation by-products over time and can be used for a longer running time. It has also been unexpectedly found that the developing compositions provide up to one-third to one-half stop in real speed improvement over hydroquinone developing compositions. Granularity is also reduced, and most films show about 10% more enlargeability." Most people who have worked with phenidone-ascorbate have noticed the "10% greater enlargeability" of the

Xtol patent claims. This is a considerable achievement and is what keeps photographers interested in this developer type.

The paper test described to the right is the ideal solution for safely working with Xtol. This is especially true if you will be storing stock solutions for weeks or months. Fresher is better, but Xtol stock solutions do normally last well. Test, and there will never be doubt; you will be able to enjoy the benefits of this developer without worry.

Countless internet threads can be found that will guide you to alternatives. These fall into two categories: Using ethanolamines or glycols to prepare more stable stock solutions, or additional chemicals that are claimed to stabilize working solutions. Salicylates have been explored; others were never made public and their efficacy was never established. We are not persuaded by the alternates.

With Xtol exhaustion colored reaction products do not appear as a warning sign.

The overwhelming problem remains that not a single scientist anywhere has been able to replicate 'sudden Xtol death'. In science a problem is seldom solved unless it can be reliably repeated. We note the work by R. Suzuki in this area, which has yet to be published.

Xtol is thus the first productized developer formula from Rochester KRL to claim a speed increase. Fine grain and sharpness are also improved when compared to D-76 and T-Max developers. Xtol is now the developer most highly recommended by Kodak for T-Max films. It has been observed that dilution increases speed and sharpness with Xtol. Dilutions of 1:3 or more were formerly recommended. At these dilutions Xtol is effectively a nonsolvent developer, but grain is still fine.

Xtol problems and their solution: the paper test

In the early days of Xtol, reports emerged of inconsistencies and sudden death, particularly when it was prepared from 1-liter packets. The 5-liter and larger packets didn't seem to have a problem. A peculiarity is that the problem could not be reproduced by anyone, anywhere. That made it difficult to investigate. (These reports showed an early use of the internet as a potent product complaint forum.)

Kodak took two steps in 2002 to resolve the problem: the 1-liter packages were abandoned; and Kodak no longer suggested dilutions higher than 1:1 because, we believe, at higher dilutions, DTPA levels were not high enough to counteract impurities in some water supplies.

The 1-liter packages have been re-introduced without controversy.

For those who are nervous about using this or a similar developer, there is a simple test to use before developing. Quoting from Michael Covington at the unofficial Xtol resource webpage, "You'll need a small scrap of photographic paper that doesn't have a developer agent incorporated; I use Ilford Multigrade IV RC, but many others work just as well. Try the test with a known good sample of developer before relying on it. To perform the test, expose the paper to full room light (white light, not safelight) and put a drop of Xtol on it. Then, 30 seconds later, put a another drop of Xtol on it in a different place. After 30 more seconds, rinse the paper under running water and put it into the fixer, then wash and dry as usual. The first spot should be dark gray, and the second one, medium gray. After fixing they will be quite warm-toned."

It has been said that the Xtol formula has changed since the days of the patent example. We have no reliable information on this point. Perhaps

manufacturing and packaging have improved to the point that mishaps are not more common with Xtol than with any other developer.

Xtol at higher dilutions

The original recommendations for higher dilutions (greater than 1:1) are still available online at digitaltruth.com. We recommend using Xtol as a one-shot at these greater dilutions because it increases the range of effects you can achieve. Although highly-diluted Xtol results in slightly higher grain, the benefits are increased sharpness and more of an S-shaped curve, with better midtone gradation. Use distilled water at higher dilutions; alternatively add more DTPA.

Experiment: Xtol can be used at high dilutions (1:2 to 1:10). Speed and sharpness are increased. However, developing times can become inconveniently long. This could be compensated for by raising the temperature, but we would prefer devising an accelerator stock solution and adjusting it through experimentation. We would suggest trialling a solution of 40 grams Kodalk and 20 grams sodium bisulfite. When Xtol is used between 1:5 and 1:10, try adding this accelerator at the rate of 100 ml per 900 ml of diluted Xtol solution. If you find you prefer to use Xtol at higher dilutions, then we would suggest, for trial, making it up according to the patent, but increasing the Kodalk by 100% and the bisulfite by 50%.

In the early days, Steve Anchell lost an important job to Xtol, and has never used this kind of developer since. Caveat emptor: just do the paper test before developing. Use distilled water for stock and working solutions of ascorbate developers. Potential problems come down to impurities in water and source chemicals. Mixing vessels and tanks should be spotless.

Xtol at 1:5 to 1:10 is no longer a solvent developer.

N.B. PQ and MQ developers behave differently on dilution. MQ has "normal" fall-off in activity, "but those based on the Phenidone/hydroquinone mixture only show a small fall-off for a large degree of dilution." (Mason 122–123) Is the same true of phenidone/ascorbate?

N.B. When you make up Xtol using distilled water for stock and working solutions, it may be possible to lower the level of DTPA. How far will depend on mineral impurities in your other chemicals. But at higher dilutions, it is likely you will have to increase the level of DTPA.

The future: economics versus innovation

Although Xtol points the way to several promising paths future formulators of black and white developers could follow, it may also be noted as the swansong for black and white chemistry at Kodak. Kodak is no longer supporting research and development of black and white developers. Xtol is for the foreseeable future the last film developer which will be researched with the monumental thoroughness that only Kodak has had the financial and intellectual resources to achieve. The future now belongs to individual innovators. They will need to have patience and luck on their side.

Other successful ascorbate developers now on the market appear to be Xtol clones. This is legal, as the patent has expired. Many ingenious variations have been proposed and published in internet forums. A goal has been to make a stable liquid concentrate. We see no evidence that this can be done without undesirable side-effects. For example, the developers of Patrick 'Gadget' Gainer (PC-TEA) employ ethanolamines, causing silver solvency problems which Gainer did not address. See DCB4 for formulas and helpful suggestions from Gainer. Among them is adding sulfite to the working solution, which we recommend.

Two-solution liquid ascorbate concentrates?

We don't know of any successful way to produce a concentrated liquid ascorbate developer either as one solution or two solutions. Two-solution concentrates are inherently more stable than single solution concentrates, but we don't think there is technology available to make these for commercial purposes, where shelf life over 12 months would be expected, and user life after opening of at least six months. The researcher Ryuji Suzuki was particularly active in searching for solutions to this conundrum.

NOTES

1. Grant Haist to BT. An article in *Darkroom & Creative Camera Techniques*, Sep/Oct 1985 by Paul Schranz shows a small density loss when HQ is removed from D-76, which Schranz suggests is due to loss of the superadditive effect. The loss could be due to artifacts, including failure to monitor pH of the solutions. With borax, pH can rise when the developer is being mixed, sufficient to activate the hydroquinone. Nor did Schranz, as Haist did, test to see whether the differences could be eliminated by slightly increasing either the remaining metol or the borax. Finally, Schranz did not, as Haist did, conduct image evaluation tests on the resulting negatives.

2. *Eastman Duplicating Film, Its Properties & Uses*, Eastman Kodak, Rochester, NY, 1927.

3. R.W. Henn & J.I. Crabtree, *An Elon-Sulfite Developer and an Elon-Sulfite-Bisulfite Fine-Grain Developer*, J.PSA 10:727 (1944).

4. Crawley 60/61.

5. I asked several Kodak heavyweights about the borate sheen phenomenon. Henn, Haist, Harold Russell, and T.H. James all said they had never noticed it. But Mason (34) throws Crawley a lifeline of admittedly indirect support: "Developers based on borates often give results which differ greatly in some respects from developers of the same pH based on other buffer systems."

FX 55	
Part A:	
Sodium sulfite anhydrous	25 g
Sodium metabisulfite	12g
Potassium carbonate anhydrous	20 g
Sodium bicarbonate	1.5g
Water to 1 liter. Keeps over one year.	
PartB:	
Sodium L-ascorbate	1.3g

Phenidone	0.1 g
For 1 liter working solution, dilute Part A1+9. To this working dilution, add Part B with stirring. The Phenidone may be slow to dissolve.	

Source: Amateur Photographer, 13 Sept 2008

However, we think concentrates with a useful life of six months could be prepared for home and professional use. One starting point is Crawley's formulas. Here we publish the hitherto public FX 55 and the hitherto proprietary FX 50.

N.B. Always use the paper test devised for Xtol before using any phenidone-ascorbate developer.

FX 50 and 55

FX 55 is fairly straightforward. The disadvantage is that the small amount of Phenidone needs to be weighed precisely. The advantage of this developer is that the ascorbate and Pheni-done are always fresh. No DTPA is present, so water and chemicals free of impurities, particularly copper and iron, are essential to make this formula viable.

FX 50X, 7 JANUARY 2002	
Part A:	
Sodium sulfite anhydrous	85–100 g
DTPA (40%)	78 ml [?]
Sodium ascorbate	18–20 g
Dimezone-S	1.5g
Sodium metabisulfite	50 g
Potassium bromide	3.75–4.0 g
Water to 1 liter. Do not keep more than six months and if possible cover used solutions with nitrogen.	
PartB:	

Potassium carbonate anhydrous	90 g
Sodium bicarbonate	5g
For 1 liter working solution, dilute 1 Part A +1 Part B + 8 parts water.	

We cannot tell if Crawley was using the highly buffered carbonate to avoid infringing on the Xtol patent, or if he would have preferred to use the Kodalk-bisulfite buffer. We are inclined to think that in this case, he preferred to avoid borates.

For FX 50 we have not been able to locate a directive to the manufacturer. Instead, we have to rely on Crawley's terse notebooks, which contain a range of some chemicals. To the left, we reproduce FX 50x as it appears in a notebook entry dated January 7, 2002. In particular, the level of DTPA is unclear and may have still been evolving. It is already much higher than in the patent example for Xtol but, in turn, recent SDSs suggest that Xtol as now manufactured contains more DTPA.

N.B. If this developer is made up with distilled water for stock and working solutions, there *may* be no need for the DTPA. But iron and copper could be introduced as impurities from other ingredients. By and large, with phenidone-ascorbate developers, it is better to err on the side of larger amounts of DTPA, in spite of its undesired solvent effect.

Regarding liquid concentrate ascorbate developers, Ryuji Suzuki cautions that oxidizing ascorbate may destroy other reducing agents during storage. He adds, "Ascorbic acid engages in different oxidative reactions depending on the pH, so the details vary, but acidification of the stock solutions does not prevent their oxidation." He emphasizes that ascorbate concentrates don't behave like MQ or PQ concentrates.

For either of these developers, we don't think it is critical what type of phenidone is used. Use Phenidone, Phenidone A, Dimezone, or Dimezone-S,

as convenient. Crawley specified Dimezone-S because it would potentially have the longest life. Although Dimezone-S is specified both for Xtol and for FX 50, both had teething problems. Xtol has survived as a commercial product while FX 50 has not.

N.B. Crawley discovered that exposure to light could adversely affect the storage qualities of phenidone-ascorbate solutions.

N.B. These concentrated ascorbate developers belong to the non-solvent category. We discuss them here because they evolve from Xtol. Xtol itself is a non-solvent developer at dilutions of 1:3 or greater.

Crawley's notes indicate that the target pH of FX 50 is even lower than Xtol's 8.2.

Chapter 6
NON-SOLVENT DEVELOPERS (HIGH DEFINITION)

QUICK GUIDE RECOMMENDATIONS

- FX 1 and FX 2 give a one-stop speed increase with slow and medium conventional films. Use FX 1 for maximum sharpness. Choose FX 2 for smoother gradation. Both work well with FP4+, at EI 200, for street photography or ultra-sharp landscapes, and all other conventional grain films. These developers can be used with tabular films but their special qualities are less apparent.
- FX 37 and FX 39 can be used with all modern films, particularly tabular grain films.
- Acutol and Acuspecial are excellent with conventional films and usable with tabular.
- PMK, WD2Dand Pyrocat-HD are distinctive high definition tanning developers (chapter 8) for all films.
- Rodinal has its own unique gradation. It is a good choice when you want something between the fine grain of D-76 and the biting clarity of FX 1. We recommend dilutions between 1:50 and 1:100. Tabular films minimize Rodinal's uniqueness; conventional films maximize it.

This chapter concentrates on *high definition* developers—the most important category of non-solvent developers. These are the developers which coax the utmost clarity out of the photographic process. Most of the tanning developers discussed in chapter 8 are also high definition developers.

All high definition developers are non-solvent, though all non-solvent developers are not high definition. While it is virtually impossible to formulate a developer without some degree of solvent action, non-solvent developers keep this effect to the practical minimum. However, what distinguishes a high definition developer from a plain non-solvent is the formation of adjacency effects which enhance sharpness.

Acutance and adjacency effects

The science of image evaluation grew out of research initiated by Kodak in the 1940s. Originally, two criteria were measured: resolution and graininess. Researchers soon realized that resolution was not an adequate index to perceived sharpness.

In the early 1950s Kodak scientists developed what they hoped was an objective test for sharpness, known as the *acutance* measurement. Revolutionary in its time, this test has since been widely criticized. It has to some degree been replaced by various modulation transfer function (MTF) measurements. Though tremendously valuable for testing negatives, MTF values are often inconclusive and inconsistent.

Richard Henry noted that the acutance test does not measure adjacency effects.[1] Yet adjacency effects have the greater importance in determining the subjective impression of visual sharpness. A further problem with scientific measurements of acutance and MTF is that researchers often use continuous agitation, in a vain attempt to impose some measure of consistency on an inherently inconsistent process, yet *continuous agitation suppresses adjacency effects.*

Border and fringe effects

The two most common adjacency effects are known as *border* and *fringe* effects. These effects are most obvious at the border between two areas of strongly different density, for example, a tree silhouetted against a bright sky. The area of low exposure—the tree—has relatively little silver to develop. As development approaches completion and slows down in the tree area, the relatively fresh developer remaining passes across the border into

the sky area. There it produces a small region of increased density at the edge, on the highlight side. This is called a border effect.

> *"Edge effects give a print a delicate 'etched' look that has a tactile three-dimensional feel."*
>
> —GORDON HUTCHINGS

At the same time *by-products* of development from the heavily exposed area—the sky—diffuse into the lightly exposed areas of the tree, and retard its development near the border. This creates a region of lower-than-normal density at the edge on the tree side. This is the fringe effect.

Occasionally two lines are produced as a result of border and fringe effects. These are called Mackie lines.

In sum, border/fringe effects work to make the edge of a *bright* object *brighter*, and the edge of a *dark* object *darker*. The result is enhanced sharpness.

Eberhard and Kostinsky effects

A special form of the border effect is the Eberhard effect, which describes the fact that the smaller an area, the greater its density. If there are two neighboring areas of equal exposure, each less than 4 mm in size, the smaller of the two areas will have higher density and greater edge contrast.

The Eberhard effect has often been confused with the Kostinksy effect. The Kostinksy effect describes the spatial distortion of two adjacent images of high exposure, for instance stars which are close together in astronomical photography. It is important to recognize that there do not have to be two adjacent high density images for the Eberhard effect to take place.

The Eberhard effect was defined before the relationship between micro- and macro-contrast was recognized. The Eberhard effect is primarily the recognition that micro-contrast is always higher than macro-contrast. It is the starting point for the study of micro-contrast.

Adjacency effects in perspective

If sharpness through adjacency effects were always desirable, all developers would be high acutance. It is not. As sharpness increases other image quality criteria—grain and micro-gradation—suffer. So before choosing a high definition developer, or any developer for that matter, you need to know what kind of image it will produce with the specific film you are using and whether the developer's effect is appropriate for the photographic statement you wish to make. The distinctions are not always clear. There is crossover where fine grain developers end and high definition developers begin.

See "Modern-era PPD Developers" in chapter 7 for some points raised by Crawley and Mason that are pertiment to better understanding high acvutance developers.

In scientific photography it is often necessary to avoid adjacency effects because they can interfere with precise measurements. But their serendipitous appearance in general photography often enhances the aesthetics of the image. Indeed, today's digital techniques for increasing image sharpness derive from the early studies of adjacency effects. A digital sharpness filter works to enhance edge sharpness by making the edge of a light object lighter, while making the edge of a dark object darker—just like a chemical adjacency effect. The practical application of this effect can be seen on the unflattering color covers of supermarket tabloids.

Achieving acutance effects depends on many things: film, developer, technique during development, and subject. Some modern films are sharp because of precision iodide placement techniques. High acutance developers have less effect on such films. If the subject does not have significant contrast between light and dark objects, adjacency effects will be minimal. During development, less agitation means more adjacency effects. Finally, there is the issue of lens resolution. Crawley has pointed out that high definition development requires high definition lenses. An image taken with a Diana, or with a soft-focus lens, is unlikely to benefit from high definiton development because adjacency effects may magnify lens arte-facts unpleasantly. (In the 1950s, when low resolution lenses were common, Verichrome Pan was specifically designed to give sharpest results with subpar equipment by providing maximum contrast at larger frequencies rather than smaller frequencies, in MTF terms. Ironically, V-P also gave better results with the best lenses, when compared to its professional sibling, Plus-X.)

An important point to remember is that adjacency effects are caused by dilute, partially exhausted developer, and minimal agitation. They can be achieved with both *dilute* solvent and *dilute* non-solvent developers, or even full-strength but *partly exhausted* solvent developers (e.g ripened PPD, see chapter 7).

Granularity with high definition developers

Non-solvent developers, particularly high definition developers, make grainier-looking prints. There are three main reasons.

1. There is little solvent effect to dissolve the grain edges.
2. Higher alkalinity encourages grain aggregation, sometimes called clumping (pp. 50–51 sidebars), which the eye perceives as graininess.
3. Increased local density in small details (i.e., micro-contrast), a hallmark of high definition developers, can enhance the subjective appearance of graininess.

This increased sharpness can *mask* the increased appearance of grain in busy scenes. However, where large areas of undetailed density appear—such as smooth faces, large sky or snow areas, or out-of-focus areas—the grain can be obtrusive. High definition developers may not be suitable for such scenes, particularly with 35mm film.

Adjacency effects, which produce sharpness, can also magnify the visual appearance of camera shake in the final print. When using a maximum sharpness developer like FX 1, FX 2 or Acutol or Acuspecial, it may be necessary to use a tripod or avoid slow shutter speeds.

Compensation and gradation

Virtually all high definition developers are *compensating* developers which produce a longer tonal scale due to reduced highlight (and midtone) contrast. In sensitometric terms, the shoulder is reached sooner, and its slope is more gentle than with normal development. Compensating developers are especially useful for high contrast scenes.

Speed increase with high definition developers

Many high definition developers, particularly FX 1, FX 2, and some other Crawley developers, can produce a true speed increase of 50 to 100 percent with conventional slow to medium speed films—ISO 250 or lower. Other developers with this effect are the Beutler Developer, the Neofins, and the Windisch Pyrocatechin (under ideal circumstances). We have not seen this increase with conventional high speed films. The effect is usually less with tabular grain films.

This is a true speed increase—it should not be thought of as pushing. It is mainly a function of the dilution/compensation mechanism and works as follows: as the developer is very dilute, it exhausts quickly in the midtone areas, and more quickly in the highlight areas, where there is a lot of exposed silver to be developed. The film has to be developed longer than usual to obtain adequate density in these areas. At the same time, the developer does not exhaust quickly in the shadow areas, so these areas are free to develop much more than would be possible with

Classifying a developer as solvent or non-solvent is not always straightforward. Some developers can be both, depending on usage. For example, Xtol full strength is a solvent developer but Xtol 1:3 or greater is a non-solvent developer, and Xtol 1:1 falls in between. Similarly, D-76 1:3 is a non-solvent developer, though it is seldom used at that dilution. HC-110 is technically a solvent developer but it is used at such high dilutions that the solvent effect is minimal. So we classify it as a non-solvent developer because of the way it is used, but note its solvent

effects. Crawley's two Phenidoneascorbate developers are non-solvent but we place them in chapter 5 because they are descended from Xtol and follow on logically from the discussion of Xtol there. Several non-solvent developers have been converted to solvent by the addition of 5–10% sulfite solution, such as FX 1, Rodinal, and FG-7.

an ordinary developer. The result is an increase in shadow density, which amounts to a true increase in speed. (By contrast, push processing increases midtone and highlight density while only slightly increasing shadow density.)

Buffering

Another contributing factor to the speed increase is poor buffering. High acutance developers are usually based on small amounts of carbonate or hydroxide as the alkali, which means they are poorly buffered. This tends to increase the local exhaustion of highlights, and thus enhance speed. A well-buffered developer often gives a more proportional density growth, both in macro and micro areas.

Advantages of the speed increase

This speed increase can be useful in an unforeseen way: A slow film such as Pan F+, with an ISO of 50, can be exposed at EI 100 if it is to be processed in a high definition developer. Compare this to a medium speed film like FP4+, processed in D-76 at EI 125. The effective speed difference between the two films is now only one third of a stop, due to the speed increase of the acutance developer. But despite the slight increase in graininess of Pan F+ processed this way, overall image quality will be better than FP4+ processed in a fine grain developer. This is because a slow film almost always produces

better image quality than a fast film, even when the slow film's speed is increased in a speed enhancing high definition developer.

Likewise, FP4+ or Foma 100 developed in FX 1 or FX 2 rated at EI 200 will give superior results to Tri-X rated at EI 200 and processed in a speed-losing fine grain developer like Microdol-X or Perceptol, even though both films now have the same EI rating.

Ignoring the speed increase

There is another way of dealing with the increased speed of high definition developers: ignore it. Take advantage of the improved toe contrast to achieve enhanced shadow separation. This is the preferred technique of many Zone System photographers who strive for a thick negative (density range of 1.2 to 1.5). Technically, this is overexposure and overdevelopment.

While the Zone System technique works well with large and medium format films it can ruin 35mm negatives unless modified. With tabular grain films, overexposure and overdevelopment are more of a problem. Controversially, Crawley believed that with the current generation of tabular films, somewhat denser negatives give the best results. This is related to different diffusion effects during enlargement. But for conventional films, thin negatives (density range of 0.9) will be sharper and less grainy, both objectively via measurement and subjectively.

Speed maintenance with high definition developers

Not all high definition developers increase speed. Rodinal, HC-110, BJP Dilute DK-50, and D-76 1:3, do not.

In the case of BJP Dilute DK-50 and D-76 1:3, the alkali may be too weak. In the case of Rodinal and HC-110 the sulfite content may be too low (some sulfite is thought to be necessary to uncover latent image centers that a pure surface developer would leave undeveloped; HC-110 may be *too* solvent even when highly diluted).

Highest acutance, highest grain increase, engraving-like gradation, 1 stop speed increase
FX 1
FX 21 (Acuspecial)
Kodak High Definition Developer (HDD) (historical)
Beutler, Neofin Blue
Some pyrocatechin developers (Chapter 8)

Classifying high definition developers

The tables to the right summarize the different types of high definition developers. The list is not exhaustive and includes some developers for historical reasons only.

Formulating high definition developers

Generally, a true non-solvent developer contains less than 30 grams of sulfite per liter of working solution and no other agents that would promote solvency, like sodium chloride or an ammonia derivative. Though 30 g/L of sulfite will still produce some solvency, depending on the amount of time the film spends in the developer, it is not until about 50 g/L that the solvent action which marks the moderate fine grain developer begins to take effect.

High acutance, less grain increase, more pictorial gradation, 2/3 stop speed increase
FX 37, FX 39 & FX 14 (Acutol)
PMK (Chapter 8)
FX 2, Formulary TFX-2

The sharpness-enhancing effects of high definition developers are primarily due to the adjacency effects that occur when the developer is partially exhausted. Sodium sulfite preserves the developing agent in solution; reducing it lets the developing agent exhaust in a controlled manner. Controlled exhaustion is the underlying principle of all high definition developers.

Good acutance (visibly higher than D-76 but not as high as categories 1 or 2), normal speed, less grain increase, good midtone gradation
BJP Dilute DK-50
Kodak HC-110
Agfa Rodinal
Unitol (historical)
Edwal FG7 (historical)

The German photochemist Willi Beutler believed, in the 1930s, that the main purpose of lowering sulfite was to reduce the solvency of the developer, thus increasing sharpness. We now know this is only a small part of why non-solvent developers increase sharpness. When a non-solvent developer has too much sulfite it does not create adjacency effects, and there is little apparent increase in sharpness. The overall image quality in such a developer will not be as good as D-76.

At its simplest, a high definition developer is a highly dilute metol-carbonate developer carefully formulated to keep a number of factors in balance. Key chemical considerations include:

Solvent developers well-diluted to become non-solvent: good acutance but less than category 3, normal speed, flat highlight gradation, least grain increase
D-76, FX 15, D-23, Microdol-X, Perceptol, all diluted 1:3 or 1:4. Kodak Xtol 1:3 is a special case, offering a speed increase at that dilution and unusually high sharpness and speed for a diluted solvent developer.

1. Sulfite: approximately 5 g/L of working solution.
2. Alkali: sodium carbonate is the alkali of choice, usually at 2 g/L or more. Some experts on high definition developers, particularly Crawley, believe that borax and metaborate impair definition, giving a "fuzzy" appearance to the grain. For a variety of reasons, it is sometimes necessary to use sodium hydroxide, sometimes in combination with weaker alkalis such as carbonate. In FDC 2 we have paid particular attention to Crawley's use of alkali buffer systems in the newly published formulas here.
3. Metol is the most preferred developing agent, followed by glycin, para-aminophenol, pyrocatechin, and pyrogallol, usually in total amounts between 0.25 and 1 g/L of working solution. A single developing agent is often preferred, except in the case of glycin and pyro, which are almost always combined with metol to increase

speed. A phenidone can be carefully combined with HQ, HQMS, CQ, MQ, pyrocatechin, glycin, or an ascorbate.

> *Crawley apparently discovered the acutance-lowering effects of bromide through his own research. Confirmation was later published by Mason: "High acutance developers also contain little or no bromide, so that the effects of local developer exhaustion at the edges between high and low exposure areas are enhanced. These lateral diffusion effects have been discussed in Chapter 4 (p. 114), the conditions obtaining in high acutance developers giving a pronounced edge effect—i.e., a higher density change across the edge than the macro sensitometric contrast suggests." (Mason, 149)*

4. Restrainer: minimal or none. Potassium bromide and the organic antifoggants *may* decrease sharpness. Exceptions are Pinacryptol Yellow used in FX 2, and potassium iodide used in FX 1 and HDD.[2] Phenidone high acutance developers almost always require either potassium bromide, an organic antifoggant, or both, and careful balancing to prevent loss of sharpness. Xtol is a rare *phenidone*-based formula balanced to require *no* restrainer.

Although this list provides practical guidelines, it should not be taken as gospel by those experimenting with their own developers. For instance, a distinction is often drawn between "chemical," surface, non-solvent, high definition developers on the one hand, and "physical," solvent, fine grain developers on the other. Chemical developers are supposed to produce good acutance, while physical developers are supposed to produce fine grain but poor acutance.

This is not always the case. Physical development can produce many acutance-enhancing adjacency effects, while grain is not always fine with

physical developers. Many monobath developers, where physical development is high, show coarse grain as compared to D-76, but higher sharpness. When chemicals to suppress physical development are added to these monobaths, sharpness is decreased (Haist II 162–3).

A high definition developer does not have to have a minute concentration of developing agent if the sulfite is very low. In both Kodak HDD and Windisch Pyrocatechin, the developing agent is 2 g/L while the sulfite is less than 2 g/L, ensuring controlled decomposition of the developing agent. However, this approach is both more expensive and less environmentally sound than the more elegant technique used in FX 1, where the smallest possible amount of developing agent (0.5 g/L) is used in combination with a higher amount of sulfite (5 g/L) to maintain the desired protective effect.

N.B. With all dilute developers, develop no more than two rolls (total 160 square inches) per liter of working solution. With the most extreme dilutions (e.g. Rodinal 1:100), develop only one roll.

Decades of experience now confirm that the best starting point for formulating a high definition developer is the type of formula codified by Crawley in 1960: one-half gram of developing agent to five grams of sulfite, and the appropriate amount of carbonate, per liter of working solution. In tanning developers such as PMK, sulfite is lower to ensure adequate imagewise staining.

Commercial high definition developers

The first high acutance developer marketed as such was Kodak's High Definition Developer (HDD), introduced in the late 1950s. It attracted a great following, but was discontinued in the early 1960s. T.H. James, Kodak's principal research scientist, told me that his understanding of the situation, related to him by others, was that due to changes in Kodak films, HDD no longer gave optimum performance.[3] He could not confirm that he agreed. Others suggested that poor shelf life was the culprit. Others thought there was nothing wrong with HDD at all, except the political misfortune to come from Harrow, not Rochester.

> *Crawley suggests that Kodak HDD contained 2 grams of metol, 1 gram of sulfite, 0.5 gram of sodium hydroxide, plus a trace amount of potassium iodide (as in FX 1), to a liter of water.*

Photographers in the UK and Europe have traditionally used high definition developers more than their American counterparts. HDD was never marketed in the US; and the high definition developers Crawley formulated for Paterson, among them Acutol (FX 14), FX 39, and others, have only occasionally been available in the US. The Crawley developers are noted for minimizing the midtone compression typical of most high acutance developers.

> *We had previously understood that Tetenal's Neofin Blue was a simple pyrocatechin-carbonate developer with enough sulfite not to promote*

tanning, probably 5 g/L. This may have been true at one time. However, an MSDS dated May 2010 states that Neofin Blue is now (like Acutol/FX 14) a PMQ developer, with potassium carbonate as alkali. Specified pH is 10.4, suggesting it is not, like Acutol, buff-ered. Might Tetenal and Crawley have collaborated? It should now be clear that the original Beutler Developer has, in spite of countless claims to the contrary, nothing to do with the more sophisticated Neofin developers, except that they are all based on the concept of using the smallest possible amounts of developing agent, sulfite, and carbonate. A developer similar in proportion (though not dilution) to Beutler's was published in L. David's 'Ratgeber in Photographieren', 1910 & 1913 editions, as noted to us by Ed Zimmerman, who has also provided earlier citations in the German technical literature going back nearly to the invention of metol in 1892. (Also see sidebar p. 78.)

An important high acutance developer available in the mid-1950s in the US was Mallinkrodt's FR X-22, which was reportedly a modern variant of the Beutler formula. Beutler formulated two well-known high acutance developers in the mid-1950s for Tetenal: Neofin Blue, optimized for slow films, and Neofin Red, for fast films. However, at introduction, Red was promoted for Adox KB17, a slow film, while Blue was promoted for Adox KB14, a very slow film. Both formulas appear to have been much modified over the years. Only Neofin Blue is still available: in small plastic ampoules, an effective though expensive way of dealing with the problem of decomposition in liquid concentrates. A formula published by Dignan and others as "Neofin Blue" is Beutler's metol formula from the 1930s.

Phenidone and high acutance

It is difficult to formulate Phenidone versions of solvent developers like D-76 that display good sharpness—Crawley's FX formulas were the first, and remain the best, with the almost sole exception of Xtol. It is even more difficult to obtain good sharpness with non-solvent Phenidone developers. One reason is the too-efficient regeneration of the PQ combination, which inhibits the developer exhaustion products which enhance sharpness. Another reason is Phenidone's low sensitivity to bromide, at the medium to high pH levels typical of acutance developers. For a published formula, FX 37, discussed later in this chapter, is an outstanding choice in a PQ nonsolvent (especially with tabular films), but stock solutions should not be stored more than three months. The best commercial developers do not use the PQ combination alone. They either add a third agent, or they replace the HQ.

The first commercially successful Phenidone non-solvent developer was Unitol, which has been popular for decades in the UK, and until recently was made by Paterson. This interesting developer used glycin instead of hydroquinone, which helps both stability and sharpness. It appears that the developer more recently sold under this name is a reformulation without glycin.

The first successful phenidone-based high definition developer was Paterson's Acutol, also called FX 14. Utilizing the PMQ combination, it was an amazing achievement for 1961, and remained popular in the UK and Europe until manufacture ceased in the early 2000s though it is now available again. In the US, Edwal's FG7, combining phenidone and CQ, had great popularity in the 1960s and 1970s. Although it is not the sharpest developer in its class, it has a pleasing balance of sharpness, grain, gradation and speed. A reformulation in the early 1980s did not affect its desirable

image properties, but did cause shelf life problems, which led many photographers to abandon it (Dimezone-S was replaced by less-expensive Phenidone). It was an excellent choice when you could be sure the developer was manufactured less than six months before use. At the time of writing, FG7 was not being manufactured (due to the difficulty of synthesizing or partially synthesizing CQ from benzoquinone and hydrochloric acid during the mixing process) but we have hopes it will be restarted at some point in the future.

Superb shelf life (comparable to Rodinal) *was* a hallmark of Kodak's HC-110 when it was introduced around 1971 (see the HC-110 section overleaf for more on this developer), though subsequent tinkering with the formula by Kodak has caused frustration. **N.B**. In discussions of this kind keep in mind that sharpness enhancement through development is less effective with tabular and other high-iodide emulsions.

Geoffrey Crawley's developers for Paterson

The range of high definition developers Crawley formulated for Paterson includes Acutol (FX 14) for high definition, Acuspecial (FX 21) for engraving-like high definition, Acutec (FX 35) for document films and FX 39 for tabular and other modern films. All were designed as one-shots. At this time, FX 39, in its third major version, is still manufactured by Adox and is deservedly popular. Some of the other formulas are becoming available again from Photographers' Formulary.

Acutol is the oldest, dating back to 1961. As might be expected, it was recommended for conventional films, more particularly, medium and slow films at or below ISO 200, providing a speed increase of 2/3 to 1 full stop. Like FX 2, this developer is formulated to obtain maximum sharpness consistent with good midtone gradation. A related developer, Acuspecial, is, like FX 1, formulated for maximum, 'engraving-like' sharpness, and there is in consequence some midtone compression, though not as much as with most extreme high sharpness developers. For slow and medium speed conventional films, Acutol and Acuspecial are probably the sharpest commercial developers available. Both are designed to be used half strength for further compensation. FX 39 is a 1990s introduction, especially designed to provide the highest possible sharpness with tabular grain films.

FX 14 (Acutol)

Acutol was revolutionary in 1961. As Bob Schwalberg noted, it was the first Phenidone-based developer that was as sharp or sharper than D-76 1:1, Rodinal 1:50 or the Beutler developers. Acutol remains one of the

outstanding choices for conventional grain films. It should also be considered a candidate for hand-coated emulsions. Thanks to Patersons and Carolyn Crawley, we are disclosing the working solution of Acuspecial (FX 21), which clearly shows the principles at work in Acutol, even though the amounts of the chemicals are very different. Both these formulas were designed to be mixed in 1,000 liter quantities and even at that quantity, weighing out and mixing are not easy.

Without disclosing the actual formula, the basic principles of Acutol are revealed by this breakdown:

- about 1 g total of developing agent (Phenidone, metol and hydroquinone in this case),
- about 2.5 grams of carbonate as in FX 1
- precise buffering through the use of sodium bicarbonate and sodium citrate
- a very small amount of potassium bromide
- a miniscule amount of potassium iodide (though more than is present in FX 1)

Little-known but of great significance is the negative developer used by 20th Century Fox in 1945. It is a precursor to the high definition developers of the 1960s. It is described as a "comparatively weak developer" by Leshing and Ingman, JSPME 44, no. 2, Feb. 1945. The formula is Metol 0.4 g, HQ 0.3 g, Sodium sulfite 75 g, Potassium bromide 0.33 g, to 1 Liter, pH 8.90. Only sulfite provides the alkali. With less sulfite and the addition of carbonate, this might look like a Beutler or Crawley type developer. It may be that higher sulfite was required because of turbulence and aeration issues in the processing machinery. At this pH the HQ will have little activity so, with only 0.4 g/L of metol (5% of what D-23 uses), this does approach what we now think of as a high definition developer. The formula is related to Crawley's FX 1b,

which came 15 years later. Because the sole alkali is sulfite, grain should be fine for this kind of developer. As far as I can tell, Crawley never experimented with precisely this kind of developer. Its principles may be worth attention today.

Because of the buffering, and consequent lower pH, it can be seen that without the Phenidone, developing times would be too long.

It is instructive to compare this developer to FX 1 and FX 2, later in this chapter. Both those developers came earlier. FX 1 contains half as much developing agent and is not buffered. FX 2 contains the same total weight of developing agent and is slightly buffered.

Acutol is a sophisticated evolution, combining everything Crawley learned from his work on those developers. The precise buffer and restrainer systems are of great interest. FX 14 and 21 were the first and remain the only high definition developers we know of to use such finicky buffer/restraint systems. (Kodak D-16, an important early buffered developer for motion picture film, is a remote ancestor, p. 83.) The result is a high degree of sharpness but avoidance of the 'soot and chalk' syndrome which less sophisticated high definition developers can display.

Acutol remains the outstanding phenidone-based high definition developer for conventional films. The only phenidone-based developer that rivals it for overall image quality is Xtol and Xtol is an entirely different category of developer, belonging to the moderate solvent class, though when diluted it becomes a high definition non-solvent. Is Acutol the *maximum*-acutance formula for conventional films? No, for that, you will need FX 1 or FX 21 (Acuspecial).

Other high definition developers do not utilize a high degree of buffering. The alkali system is either carbonate or hydroxide alone. The reasoning is that this will produce the maximum level of adjacency effects, and the greatest increase in speed. The penalty is excessive micro contrast and flattening of midtone macrocontrast. Acutol illustrates how buffering can be used to smooth density growth while carefully controlling adjacency effects

through developer exhaustion. In Acutol, Crawley compensates for the possible loss of speed buffering brings by employing Phenidone.

Of all photographic chemists, Crawley perhaps best understood how to get the most out of buffer systems. His approach to restrainers, also, was subtle: he saw restrainers less as simple antifoggants and more as systems which, in proper balance, could enhance definition. But if there is anything at all we can learn from studying Acutol, it is that there are no quick and easy routes to success. Crawley spent years testing and evolving the formula for Acutol. His first notes on the formula date from the mid-1950s. He was still adjusting it half a century later, producing a masterclass in chemical perfectionism.

The practical speed increase of Acutol is 2/3 to 1 full stop with slow and medium conventional grain films. The film of choice to use with this developer has long been considered to be Ilford's FP4+. While it was available, Verichrome Pan was my favorite film to use with Acutol. Another candidate is Adox Silvermax. I also recommend Acutol for the latest Foma and Arista-Edu films, especially now that Foma production has consistently improved; and Eastman Double-X.

Hand-coated emulsions are an excellent way to showcase Acutol's acutance-enhancing technology. However, depending on how important it is to control grain, a moderately solvent developer such as D-76 might be preferred.

Crawley believed that FX 37 and F 39 were the preferred developers for most tabular and mixed-grain emulsions, but Acutol will perform well with them. Acutol's edge enhancement technology won't do as much good for most tabular films, but it won't do any harm either.

At the time of writing, Photographers' Formulary is working to make the most recent version of Acutol available again.

Experiment: In the future we hope to see more independent formulas that take advantage of the kind of precise buffering we find in the FX developers and in Xtol. Careful testing is the key. We note that of all those involved in modern developer formulation, the ones who worked most closely with microdensitometer testing were Crawley in Britain and

Zawadzki and Dickerson in Rochester. (High quality scanners are emerging as a workable alternative to traditional microdensitometers.)

FX 21 WORKING SOLUTION	
Metol	0.1433 g
Sodium sulfite anhydrous	2.0 g
Hydroquinone	0.0733 g
Potassium carbonate anhydrous	1.3 g
Phenidone	0.0083 g
Sodium metabisulfite	0.41 g
Sodium bicarbonate	0.26 g
Sodium citrate	0.26 g
Potassium iodide	0.0055 g [?]
Potassium bromide	0.022 g [?]
Water to make 1 liter. Dissolve in the order given, adding a pinch of sulfite before the metol. Acuspecial as sold was 30x this strength. These amounts cannot simply be multiplied by 30 as various solvents are needed to get to that concentration and mixing becomes difficult. However, we would suggest multiplying these amounts by 15 to make a stock solution.	
It is impossible to tell from the available notes exactly what amounts of bromide and iodide were intended. Use these amounts as guides.	
Instead of agitating once every minute, this developer can be agitated for 10 seconds once every three minutes, for additional compensation and adjacency effects, with an approximately 50% increase in developing time. Develop an absolute maximum of three films (80 square inches each) per liter-**preferably only two films per liter**.	
For more compensation and more adjacency effects, this working solution dilution could be halved (the given amounts to two liters of water). But no more than one film (80 square inches) per liter of half-strength solution should be developed. Development times will be longer. At this dilution, FX 21 should work well with document films (Chapter 11).	

FX 21 (Acuspecial)

Acuspecial was manufactured between circa 1969 and 1980. It was discontinued because it is a specialist developer for which demand was not great. At the time of writing (2019) it is being prepared for limited manufacture by Photographers' Formulary. With FX 21, Crawley revisited the goal of maximum, 'engraving-like' sharpness that he had previously addressed with FX 1, the public formula discussed later in this chapter. Like Acutol, it is designed to perform best on slow to medium speed conventional grain films. Crawley's goals were to keep midtone gradation as generous as possible consistent with the overriding goal of maximum sharpness. Most important in this extremely dilute type of developer, he wanted it to be reliable and resist streaking and inconsistency. He noted that control of contrast is unusually great with this developer, which makes it of interest to Zone System photographers. The adverse effects of such a developer on gradation will be less with large format than with miniature films. Chemically, Acuspecial could be roughly seen as a highly diluted version of Acutol. It contains less than a quarter of the same developing agents, less sulfite, and a more complex and more alkaline buffer system to compensate.

Kodak HC-110

An important liquid concentrated developer that offers excellent stability (second only to Rodinal) great flexibility and good definition coupled with only a moderate increase in grain is HC-110, formulated by Henn, King, and Surash at Kodak in the 1960s. It became one of Ansel Adams's favorite developers—for a time—and remains popular with many of his followers. It is an extremely unusual developer for two reasons: it is based on the phenidone/hydroquinone/pyrocatechin combination and, though liquid, it contains no water. Although the formula has been modified over the years, a rough idea of its composition can be gleaned from the example in US Patent 3,522,969, 1971.

US PATENT 3,552,969, FOR HC-11O	
2,2′-lminodiethanol-sulfur dioxide addition product	31 g
2,2′-lminodiethanol [Diethanolamine]	9g
2,2′-lminodiethanol hydrobromide	1.5 g
l-Phenyl-3-pyrazolidone	0.5 g
Hydroquinone	6g
2-Aminoethanol	5g
Ethylene glycol	10 ml
FDC1, following ambiguity in Haist, had 'Water to make 1 liter.' This is wrong. The formula without water, represents the concentrate. Confusingly, the amounts given above do not provide a solution anything like a liter; rather, less than 100 ml by volume. Nevertheless, the patent indicates that to 1 liter of this finished product is added 0.25 g of Polyvinylpyrrolidone (PVP).	
Dilute 1:30 to 1:100 with water.	

The ethanolamine bromide and sulfite are powerful ammonia-based forms that are more active than the common forms. The PVP (which is the reason for the patent) helps prevent undesirable solvent effects (for instance dichroic fog) that could otherwise occur in a developer with so much ammonia. The result is a product which is more environmentally friendly than some, because the ammonia derivatives allow smaller amounts of the developer chemicals to be used. It is thus also less expensive to manufacture. It is remark ably stable on the shelf and after opening. HC-110 and Rodinal appear to be the most *stable* liquid concentrate developers ever formulated.

Although HC-110 is believed to have been introduced via a press release as early as 1962, there is little evidence it was actually available until the 1970s, and the patent dates from 1971. It is possible that it was announced prematurely and not actually released until a decade later.

Even with the PVP, HC-110 is a highly solvent developer. However, because it is used highly diluted, which minimizes solvent effects, it is generally perceived as a non-solvent developer, hence its inclusion in this chapter. It produces coarser grain than D-76, and is not as sharp as many high acutance developers (see sidebar p. 124). Nevertheless, it is convenient, economical, versatile, stable, and *reliable*. The long life of the concentrate has been much appreciated by professionals.

The patent examples do not mention pyrocatechin, though it is mentioned among the claims. The MSDS dated July 29, 2016 indicates the presence of pyrocatechin, though it does not list the PVP (nor is it legally obligated to do so). Also confusingly, the MSDS does not specify a 'diethanolamine sulphur dioxide complex' as the MSDS for TMAX Developer does, but rather splits it up, as follows, with a target pH of 9:

30–35% Diethanolamine
15–20% Sulphur dioxide

5–10% Hydroquinone
5–10% Diethylene glycol
1–5% Diethylenetriaminepentaacetic acid [DTPA] 1-<5% Potassium bromide
0.1–1% 1,2-Benzenediol [pyrocatechin]
0.1-<1% Ethylene glycol
0.1-<1% 3-Pyrazolidinone, 4-methyl-1 phenyl-[Dimezone-S]

The specific forms of sulfite and bromide in HC-110 are produced by piping sulfur dioxide and hydrobromic acid into diethanolamine. A similar technique is used in Ilford HC and Tetenal's Ultrafin Plus though Ultrafin Plus is not a high-dilution developer, and evidently contains about 50% water, which may limit its storage capabilities compared to HC-110. It has since been replaced by Ultrafin T-Plus.

Because HC-110 and TMAX developer both require the sulfur-addition product, which is manufactured by piping sulfur dioxide gas into diethanolamine, this kind of developer cannot be made in the home darkroom or small laboratory. A revised MSDS of February 2019 shows a slightly different formulation, with 20–30% methylethanolamine sulfur dioxide compound, 15–20% diethanolamine. 1–5% ethanolamine and 1–5% potassium bromide.

The use of pyrocatechin in this developer, first reported in FDC1, then disputed by many, but confirmed here in FDC2, is extremely unusual in a Kodak developer. HC-110 is probably the only commercial

The HC-110 technique of preparing a stable developer concentrate by replacing the water and sulfite with liquid organic amines and a sulfur dioxide addition product is described in Kodak Harrow's BP 958,678

(1964). To what extent does this help preserve Phenidone aginst degradation in liquid alkaline solutions? The answer may be, not much, since HC-110 now uses and probably always has, the more stable Dimezone-S. However, Phenidone remains less expensive and more soluble. Some approaches to stabilizing it in liquid are discussed in Haist, 525–529. The best way is to isolate the Phenidone in a separate concentrate. In one invention this solution contained 5 g Phenidone, 15 ml of lactic acid, and butyrolac-tone to make 50 ml. In another invention, the solution contained 95 ml glacial acetic acid, 5 ml water, and 20 g Phenidone. That is the time-tested technique used in some Kodak X-omat developers. But users prefer single solution developers. John & Field stated that a lactic or boric acid buffer produces more stable concentrates (BP 931,007, 1963). We think separate A+B solutions are best.

Kodak formula to use it, or to have ever used it. The question is *why*? It is most likely that Henn and his team found what Crawley and Lowe did: it is hard, though not impossible, to make a sharp developer with phenidone and hydroquinone alone. An additional agent is necessary to mediate or disrupt PQ's overactive regeneration kinetics. It is also possible that the pyrocatechin may help HC-110's noted stability, but its stability is probably mostly due to the absence of water in the concentrate.

Finally, we note that the main goal of HC-110 was to provide a modern concentrated liquid developer that had comparable stability and flexibility to Rodinal. However, it was found that this could not be achieved except through the use of powerful silver solvents, which can produce dichroic fog. Therefore, a chemical had to be added to counteract this undesirable effect. Philosophically, we might ask if Rodinal is not a preferable developer, since it avoids this chemical rigamorole? Decisions will ultimately be made on an aesthetic basis. Both these developers, one 50 years old, one more than a century old, have large followings among fine art photographers. **N.B**. PVP is now known to be an allergen.

HC-110's radical reformulation in 2019

HC-110 was reformulated in mid-2019. The hallmark DEA-sulfur addition complex, which conferred its great stability, has gone; it is now a conventional developer. We suggest the new formula should be called Neo-HC-110 or HC-110–2019 or even Non-HC-110. In this book, "HC-110" always refers to the pre-2019 product.

Ilford concentrated developers

It has been suggested online that Ilford DD-X is similar or even homologous to HC-110. These developers could not be less similar. DDX (and DD) are conventional PQ/borax developers with a moderate pH around 8.7. DD-X employes a high amount of potassium sulfite to aid concentratability. What makes DD-X unique is that while concentrated developers typically employ carbonate or hydroxide as alkali, DD-X uses a gentle borax-boric acid buffer. DD-X is an expensive developer to use, with a recommended dilution of 1:4 and a practical maximum not much higher, while HC-110 can be used up to 1:100. DD-X also does not have HC-110's long life. In other words, DD-X is a concentrated ID-68 or Microphen, the main difference being the use of potassium rather than sodium sulfite. At 1:4 dilution, potassium sulfite allows Ilford to use such a high level (around 400 g/L) that the sulfite content of the working solution is almost as high as full-strength ID-68 or D-76.

DD-X is the only concentrated liquid developer we know of based on a borax-boric acid buffer. This makes it interesting in its own right, and suggests further development along this line. We would propose a mechanism to moderate near-end-life phenidone regeneration, such as the PMQ combination Crawley found effective in this respect, the phenidone-glycin combination that worked in Unitol, or the PQ-pyrocatechin combination used in HC-110. (A stable phenidoneascorbate single solution concentrate does not appear to be an attainable goal: even two-solution concentrates have not been outstandingly successful.) For the special advantages potassium salts may confer on DD-X, see chapter 10.

A final question about HC-110. It has never claimed to have, nor has it been observed to have (in generations of use), a speed increase. But

why? Everything we understand about phenidone developers suggests there should be a speed increase of a third to two-thirds of a stop. Could the solvent action remove some developable silver, while the antistain agent prevents re-deposition? (Redeposition would cause a density increase.) Another possibility is that there isn't enough sulfite in the working solution: it is typically under 1 g/L. Crawley suggests that, in most cases, a dilute developer should have 4–5 g/L of sulfite to maximize speed. Adding 4 grams of sodium sulfite to a liter of Rodinal or HC-110 working solution might increase speed slightly. It seems likely that the high degree of physical development in HC-110 is what prevents this developer from showing a speed increase at normal contrast.

From the foregoing it should be clear that DD-X is a solvent developer. It is included in this chapter only because it fits into the discussion of Ilford concentrated developers.

On the other hand, Ilford's aptly named HC developer really is based on HC-110. It employs ethanolamines and an ethanolamine-sulfite product, just as HC-110 does, and it has similar dilutions. It should be noted that both Ilford DD-X and Ilford HC are fundamentally solvent developers. HC, like HC-110, can be used at high dilutions (1:50 or higher) where its solvent effect is minimal.

Agfa Rodinal

Although Agfa Rodinal was introduced in 1881, it was not until the 1950s that it was understood how well-diluted Rodinal can function as an acutance developer. Brett Weston and Henry Gilpin, among others, used it at 1:100 with Agfa 25. Today it is most popular with slow and medium speed films at 1:50 or 1:75.

Rodinal is both an Adox proprietary formula and a group of published formulas. Traditionally, it consists of a saturated solution of *p*-aminophenol hydrochloride, potassium metabisulfite, and sodium or potassium hydroxide. (Formula in Appendix I.) We call the traditional formula *Rodinal*; we call the commercial product *Adox Rodinal* (or in FDC1, *Agfa Rodinal*). There does not appear to be a significant difference between Agfa's many proprietary versions of Rodinal during its long history of manufacturing, and the basic version which has been known for nearly as long. However, 21st century MSDSs suggest that potassium rather than sodium hydroxide is now used, and that there has been some re-proportioning of the basic ingredients, and the addition of potassium bromide. There are in addition several other manufacturers with proprietary versions of Rodinal and these are almost certainly based on the formula we publish in Appendix 1, which also includes a wartime version which contains a desensitizer.

Agfa Rodinal no longer corresponded exactly to the traditional formula at the time of FDC1. It still contained *p*-aminophenol and potassium hydroxide, but in smaller amounts. Potassium bromide had also been added, which might not be necessary if *p*-aminophenol were still the sole developing agent. Some photographers preferred the traditional version; others the commercial version. Dr. Elie Schneour believed that the differences were not photographically significant. As currently manufactured by Adox, however, Rodinal is said to be extremely close to the

traditional formula. It has been suggested that one reason for Agfa's monkeying with the formula was that they were trying to get the solution to be completely clear.

Working characteristics of Rodinal

Normally an increase in film speed is expected from an acutance formula. However, the practical working speed of Rodinal is usually slightly lower than with D-76, according to Crawley, who stated that the probable reason is that the concentration of sulfite is too low. Film speed can be slightly increased by extending the development time, but overall image quality will suffer.

CLASSICAL HIGH ACUTANCE DEVELOPERS (WORKING SOLUTIONS)						
	BEUTLER	**FX 1**	**FX 1B**	**FX 2**	**WINDISCH**	
Metol	1	0.5	0.5	0.25	-	g
Glycin	-	-	-	0.75	-	g
Pyrocatechin	-	-	-	-	2	g
Sodium sulfite anhydrous	5	5	45	3.5	0.3	g
Sodium carbonate anhydrous	5.0	2.5	2.5	-	-	g
Potassium carbonate crystals	-	-	-	7.5	-	g
Sodium hydroxide	-	-	-	-	1.5	g
Potassium iodide, 0.001%	-	5 ml	-	-	-	
Pinacryptol Yellow, 1:2,000	-	-		3.5 ml	-	
Water to make 1 liter						

See Appendix II for detailed instructions on how to mix the stock solutions for FX 1 & FX 2; Appendix 1 forWindisch stock. FX 2

requires potassium carbonate crystals, not anhydrous: the crystalline grade contains some bicarbonate buffer.

FX 2 requires potassium carbonate crystals, not anhydrous: the crystalline grade contains some bicarbonate buffer.

Rodinal negatives possess a beauty and impact that is recognizably their own. Among commercially available developers Agfa Rodinal offers gradation that cannot be obtained otherwise. Many photographers prize it for this effect above all else. In practice, Rodinal-type formulas offer good, but not high, acutance.

The chart above reveals how FX 1 is descended from the Beutler developer, which was first published in the 1930s. To transform Beutler into a true high definition developer for post-war-era films, Crawley halved both the metol and the carbonate levels. He showed that the level of metol was too high for maximum definition, and the level of carbonate impracticably high. There has been endless speculation that the Neofin developers Beutler formulated for Tetenal in the 1950s and 1960s must somehow be equivalent to his early formula from the 1930s. This is not the case. The Beutler formula remains significant as a starting point for high definition developers. (Also see sidebar p. 71.)

Although acutance developers increase graininess, Rodinal can be used successfully with fast 35mm films as long as the cardinal rules of minimum exposure and minimum development are observed. It was most successful with Agfapan 400, a film that exhibited noticeably finer grain than Tri-X in its day.

Published formulas for high acutance developers

The only thorough published discussion of high acutance developers is the series of articles by Geoffrey Crawley published in the *British Journal of Photography (BJP)* where the FX developers were introduced.[2]

Shortly thereafter, Kodak scientists Henn (whose career was built around fine grain developers) and Altman published an analysis contrasting fine grain and high acutance developers.[4] This study was marred by the use of continuous agitation. As noted above and in chapter 4, continuous agitation causes a significant loss in edge effects resulting in a lower degree of sharpness. Richard Henry's otherwise meticulous research was also marred by this serious artefact.[1] We can categorically state that research on acutance developers which uses continuous agitation is of limited value.

Crawley appears to be the one of the few published researchers to have recognized as early as the 1950s that high acutance developers cannot be properly evaluated unless intermittent agitation is used. Unfortunately, little else has been published on the subject, aside from a few vague references in the literature.[5]

The chart above contains the more important published high definition formulas. The Windisch formula is discussed in Chapter 8.

Special additions to FX 1 and FX 2

FX 1 requires the controversial addition of 5 ml of a 0.001% solution of potassium iodide. According to Crawley, this "homeopathic" amount is vital in making the difference between FX 1's performance as a mere acutance

developer and a high acutance developer. This addition is not called for in FX 1b (originally published as FX 13), where, according to Crawley, it would not exert any visible effect due to the high level of sulfite.[6] A larger, but still minute amount of iodide is also used in Acutol (FX 14) as well as Acuspecial (FX 21).

Try replacing the potassium carbonate in FX 2 with approximately 1.5x the amount of sodium metaborate (Kodalk). Sharpness will not be as high, but this developer is tremendously flexible and provides enhanced midtones. We call this version FX 2K (for Kodalk). Alternatively, add a bicarbonate and citrate buffer as in Acutol and Acuspecial.

With FX 1, try using a 50/50 combination of sodium and potassium carbonate instead of straight sodium. Support for blending potassium and sodium alkali, which interested Crawley, can be found in Glafkides; see fuller citations in chapter 10.

Regarding the controversial iodide content, Ron Mowrey has proposed what he very carefully states is a *theory*: "Old emulsions have buried iodide, which is a powerful restrainer and induces edge effects. If added to a developer, iodide would instantly bind to the most numerous grains with the highest surface area (small grains). Due to developer induction, little happens while this adsorption takes place. Then development starts with the fine, iodide-rich grains, and releases iodide imagewise, promoting heavy edge effects. This released iodide readsorbs to the next greatest population of crystals, medium grain, and repeats the process, continuing to the coarsest grains. This provides the emulsion with enhanced edge effects and better sharpness. But if an emulsion has surface iodide (as in many modern tabular and mixed grain emulsions), these effects will not take place to such a great extent. That is why developers such as Acutol and FX 1 work best on traditional films." (An emulsion with surface iodide is often called "high iodide".)

With regard to FX 2, Crawley states that the desensitizer Pinacryptol Yellow offers slightly better fog-to-image discrimination than the usual antifoggants. It also helps prevent aerial fog, making FX 2 especially useful for sheet film development in trays.

Pinacryptol Yellow is expensive. But, since very little is used, it does not add appreciably to the cost of the developer. In addition, the stock solution of Pinacryptol lasts for years. Crawley suggests Pinacryptol need *not* be added to FX 2 when developing tabular grain films.[7]

TD-121	
Metol	0.7 g
Sodium sulfite anhydrous	5.0 g
Sodium bisulfiite	2g
Sodium carbonate anhydrous	3g
Water to make 1 liter	
A trace amount of iodide can be added, as in FX 1.	
Note: this suggested take on FX 1 comes from FDC1. We would now be more aggressive with the buffering, and might increase the metol slightly.	

Comparisons and modifications to FX developers

Though FX 1 and FX 2 were revolutionary when they were published in 1961, they have become the exemplars of modern high definition developers. No method to improve on the principles they codify has yet been found for conventional grain films. The main additions to the palette of published high definition developers are PMK (structurally related to FX 2); FX 37, which Crawley describes as a highly-evolved descendant of the Beutler formula; Pyrocat-HD; FX 21; and diluted Xtol.

Pinacryptol Yellow and other desensitizers used as antifoggants are most likely to be effective with older technology films and with hand-coated emulsions. Their effectiveness depends on the particular film and developer combination.

FX 1 is intended to produce maximum sharpness. FX 1 prints have stunning impact, but gradation is not as subtle as with other developers. FX 2 is designed for a more pleasing, pictorial gradation, with slightly less sharpness. Both developers are at their best with conventional films rated at ISO 200 or less. FX 2 and the related Formulary TFX-2 are both popular with tabular grain films. (TFX-2 is a liquid concentrate based on FX 2 with some proprietary refinements designed to provide

The reason I say FX 2 and PMK are related is that in each case (1) a valuable but slow developing agent has been combined with a small amount of metol to achieve better emulsion speed and increased stability; (2) the total weight of developing agents in each case is about 1 g/L; (3) the two-solution system is employed by both; (4) Gordon Hutchings told me that FX 2 was a primary inspiration to him in designing PMK. To my way of thinking, it makes sense that if I had wanted to create a modern pyro developer, I would have started with FX 2 as a model, replacing the glycin with pyro, adjusting the metol level down as Gordon did through experimentation, and reducing the sulfite to maximize image stain. I would have parted company with Gordon over the alkali, preferring a buffered carbonate system. But there is no doubt in my mind that one of the things that gives PMK its unique properties and special look is the metaborate he uses instead of carbonate as in FX 2. See chapter 8, especially the last page, where I present the reasons why Gordon's approach is probably best.

improved consistency and smoother gradation.) FX 1 may be suitable for tabular films when subject contrast is high.

FX 1, FX 2, TFX-2, and most other high definition developers, produce maximum adjacency effects, and therefore sharpness, when minimal agitation is used. Do not overexpose or overdevelop. Times for slow films, which are usually under 12 minutes, should be watched carefully. Agitating for only 10 seconds on every third minute increases sharpness but lengthens development times by about 50%.

TD-121 is a buffered version of FX 1 providing somewhat better gradation and finer grain, with the sacrifice of slightly less sharpness, and a little less speed increase.

FX 1b was Crawley's 1960 attempt to formulate a fine grain, high acutance developer. The method employed is to add 45 g/L of sulfite. This did not ultimately prove to be a successful approach, and the developer was dropped from the BJP listings after a few years. It is better to use one developer type, either fine grain or high definition. For situations when neither extreme is desired, use a moderately diluted fine grain developer such as D-76 or Xtol, 1:1 or 1:3. Adding sulfite to a high definition developer does not merely decrease grain by adding a solvent effect; it also preserves the developing agent so that fewer adjacency effects are formed. Adding 40–90 g/L of additional sulfite to a non-solvent developer has also been recommended for FG7 and Rodinal—in neither case do we regard this as a desirable approach.

FX 37 and tabular grain films

Most of the FX developers discussed here and in chapter 5 were formulated before the advent of tabular grain and other high-iodide films. Since then, Crawley formulated new proprietary developers for Paterson, and disclosed FX 37, a developer optimized for both T-Max and Delta films (BJP, March, 1996). Crawley makes it clear that FX 37 is not just for use with tabular films.

"This black-and-white negative developer is proposed for the processing of modern films, especially those using so-termed 'high-emulsion' [as used here, a synonym for high iodide] technology, such as T-Max and Delta. But it may be used for traditional type emulsions when the finest grain is not the prime requirement. It is an independent formula, not a substitute for any commercial product."[8]

FX 37 fully exploits Phenidone's speed-enhancing properties. For most films, true speed is a half to two-thirds of a stop more than the manufacturer's ISO.

Crawley made several interesting points about developing tabular films:

1. Traditional solvent developers such as D-76 do not work well unless diluted at least 1:1: "If grain is too fine, light scatter in the negative increases when a negative is enlarged, reducing edge contrast," resulting in decreased print impact. In Crawley's opinion, best results will be obtained by modifying a Beutler-family developer, rather than a D-76-family developer, and FX 37 can be seen as a highly evolved version of the Beutler developer optimized for modern films.
2. Nevertheless, Beutler-type developers have a tendency to compress tones excessively, especially when negatives are enlarged with a cold light head. Taking these two factors together, Crawley believed

that tabular films and even some of the newest conventional films should be developed for a denser negative than has been considered desirable in recent years, especially with 35mm film. Too thin a negative will give coarser grain with these films. Modern films give best printed results with a richer negative, and Crawley notes, "modest overexposure does not increase grain."

3. As regards pushing tabular films, Crawley's advice is identical to the latest findings at Kodak: the best technique is to dilute the developer even further. This is completely different from what has been found to work with Tri-X and D-76. "Dilution 1+5 can be used when it is necessary to uprate a film further, especially those of ISO 400 and over: 50% to 100% the normal time may be tried—up to 4x EI on suitable subjects." By suitable subjects, Crawley means those of inherently moderate contrast—for instance, those in diffuse light. On high contrast subjects, pushing will result in blocked highlights (though the aesthetic impact may be high).

> *In the 1960s, with FX 1, Crawley halved the developing agent and the carbonate of the Beutler formula to achieve maxiumum sharpness. In the 1990s, with FX 37, he increased developing agent and sulfite and lowered alkalinity to achieve best results with tabular films.*

4. Finally, Crawley noted that when tabular films came out in the late 1980s, there was a tendency to over-high contrast, especially with overdevelopment. Crawley thought this problem had been overcome in what he designated the second generation tabular films. However, he warned that because of the short toe typical of all tabular films, under-exposure latitude is still low compared to conventional films.

5. FX 37 uses the buffered carbonate-borax system Crawley has championed for decades. It also contains potassium bromide, which Crawley long maintained is essential to maintain sharpness in developers which contain borax. It is interesting to see the evolution of his thinking regarding benzotriazole, a chemical he did not think worked well with the films of the 1960s. Crawley was quick to realize that high iodide films have substantially different developing requirements from conventional grain films.
6. In summary, to quote Crawley again, FX 37 is "designed to produce enlarging quality, very sharp, tonally rich negatives on modern films, with an EI speed increase. It is not a fine grain developer in the old sense, and assumes that the fastest films will not be used when big [more than 12x] magnifications are required."

FX 37	**STOCK**	**1:3**
Sodium sulfite anhydrous	60	15 g
Hydroquinone	5	1.25 g
Sodium carbonate anhydrous	5	1.25 g
Phenidone	0.5	0.125 g
Borax	2.5	0.625 g
Potassium bromide	0.5	0.125 g
Benzotriazole 1%	5	1.25 ml
Water to make 1 liter		
Dilute 1:3. Diluting 1:5 will lengthen developing time and increase film speed.		
Development Time 4-8 minutes for most films		
A later version eliminated the benzotriazole which some users complained about sourcing, and increased the potassium bromide to 1 g (in the stock solution) to compensate.		

FX 37	STOCK	1:3

Experiment: Reduce the carbonate in the stock solution by a gram or two, which may allow you to omit the bromide and BZT. Try replacing the hydroquinone with glycin for better highlight control. Replace a few grams of the sulfite with bisulfite. Add a gram of metol and reduce the Phenidone by half. Instead of carbonate-borax try a meta bo rate-bisulfite buffer system.

Crawley's radical reassessment of the traditional suggestion for optimum negative density (thin as possible) takes both theorists and practitioners by surprise. Let it be noted that his language is moderate: he is talking about a small degree of density increase.

FX-39

FX 39 is the most recent of Crawley's proprietary developers, formulated in the mid 1990s and periodically adjusted until about 2006. Much of what has been said about FX 37 can be said about FX 39 but they really are independent formulas, and FX 39, which we cannot disclose, uses different methods to achieve optimum development for tabular and other modern high-iodide emulsions. FX 39 is currently

> *Around the mid-1990s Crawley started placing a dash rather than a space after F. We considered following his changing usage to be consistent with the historical source material. But we have chosen to keep to the space system.*

available as Adox FX 39 and represents Crawley's best effort to deal with modern films. Xtol is the only other developer we can compare it with, in the sense that both are successful developers specifically designed to provide optimal development of tabular grain emulsions. We do not think that Kodak Tmax developer, which is a modification of HC-110, succeeds in being even as good as HC-110 with modern films.

Buffered non-solvent developers

Kodak DK-50, D-61a (see Appendix I for formulas), and Unitol exemplify an historically important class of non-solvent developers which Crawley designated "buffered non-solvent developers." In these developers, it was seen to be desirable to move away from an alkali system based on straight carbonate or hydroxide, and move instead to one where, for example, the carbonate would be buffered with bicarbonate (including indirectly with bisulfite which creates sulfite and bicarbonate in solution), or with citrate, or with both. Sodium metaborate (Kodalk), which is functionally borax plus carbonate, is considered to constitute a buffer system, but it is possible to buffer it further with, for example, sodium bisulfite. Borax is loosely considered a buffered alkali but it is much more stable when it is truly buffered by, for example, boric acid. Above all, a buffered system results in more even pH throughout the developing cycle. These developers provide the best midtone and highlight separation for negatives of limited contrast range, such as controlled studio photographs. Generally, they work less well for long-scale natural light photographs. They are often extremely consistent and reliable.

Buffered non-solvent developers provide good sharpness (better sharpness than a fine grain developer, less sharpness than a high definition developer) and moderate grain (coarser grain than a fine grain developer, finer grain than a high definition developer), and snappy contrast. With the exception of Unitol, most of the developers in this category do not perform well with 35mm films, because graininess will be high without the compensation of enhanced sharpness. This is not a concern with larger film sizes.

The gradation of buffered non-solvent developers approaches as closely as possible straight-line characteristics without the high micro-contrast of high definition developers. As they do not exhibit compensating action, they

should not be used when under- or overexposure is suspected, or where a high contrast subject has been recorded.

DK-50 and D-61a were reliable professional stalwarts in the large format black and white studio photography of their era, roughly from the 1930s to the 1960s. With the decline of that kind of studio photography, these developers are no longer widely used. As a consequence, many photographers are unfamiliar with their qualities. Of well-known commercial developers, their characteristics somewhat resemble Rodinal at 1:25 or HC-110 dilution A, but they are by no means identical. Since they are less dilute, they are more consistent in use. Since their pH is moderate there is little risk of blistering damage to the film, especially when Kodalk is used.

D-165 (KODAK HARROW)	
Metol	6g
Sodium sulfite anhydrous	25 g
Sodium carbonate anhydrous	37.5 g
Potassium bromide	lg
Water to make 1 liter	
Specified dilution is 1:3, but for modern films, up to 1:10 could be used.	

Formulating buffered non-solvent developers

It is easy to construct a buffered non-solvent developer. All that has to be done is to modify the alkali of an unbuffered non-solvent developer. For instance, one could take a standard metol-carbonate developer, such as D-165. Several things could be done to turn this into a buffered developer.

KODAK	D-16	D-16R
Metol	0.31	0.3 g
Sodium sulfite anhydrous	39.6	40 g

KODAK	D-16	D-16R
Hydroquinone	5	9g
Sodium carbonate anhydrous	18.7	38 g
Citric acid	0.68	0.7 g
Potassium metabilsulfite	1.5	1.5 g
Potassium bromide	0.86	- - g
Water to make 1 liter		
From PCS. This early buffered tank developer and replenisher was recomended for motion picture positive film and also for negative development to medium or high contrast, for variable width sound negatives, and for both variable density and variable width sound prints. Add replenisher to make up for the developer carried out by the film. With its ultra-precise weights and its double buffer system, it shows an ancestral approach to some of the techniques Crawley would use years later in Acutol and Acuspecial. What we can learn from D-16 today is how buffers can help provide a consistent developing system when consistency is a high requirement.		

- Replace the carbonate with Kodalk, or a Kodalk/bisulfite buffer as used, for example, in Xtol.
- Create a carbonate/bicarbonate buffer system in either one of two ways: (1) Add 5 to 15 grams of sodium bicarbonate to the formula, (2) Replace some of the sulfite with sodium bisulfite, and raise carbonate to compensate. This will create bicarbonate in the final solution.
- Create a carbonate/bicarbonate/citrate buffer system as suggested by the example of FX 21. The potassium bromide can be reduced or eliminated. This might lower contrast and increase speed. Less bromide is needed when the developer is buffered, since the pH is lower, and the tendency to fog is not as great. On the other hand, in a buffered, lower pH, slower working formula, physical development may be greater. A small amount of bromide *may* help reduce physical development.

- If this developer is used with a very high speed film with a tendency to fog, it may be desirable to keep the bromide around 0.5 g/L, the same amount as in DK-50. In fact, the buffered D-165 developer is similar to DK-50, except that it contains no hydroquinone. This, in combination with a low sulfite level, results in a lower contrast developer. If developed to the same gradient as DK-50, there might be a slight gain in speed.

If you make D-165 with a carbonate-bicarbonate buffer (with the possible addition of acetate), you can make it up as a two-solution to maximize stability and customizability. To create the bicarbonate, acidify Solution A slightly with sodium bisulfite.

Buffered D-165 can be quite useful. Diluted it can function as an acutance developer. Indeed, if the sulfite is increased to 50 or 60 grams, and the developer is diluted 1:10, we have a high acutance developer almost identical to FX 1.

Various other modifications could be made:

BJP DILUTE DK-50 STOCK	
Solution A	
Metol	2.5 g
Hydroquinone	2.5 g
Sodium sulfite anhydrous	30 g
Potassium bromide	0.5 g
Water to make 1 liter	
Solution B	
Sodium metaborate (Kodalk)	50 g
Water to make 1 liter	

Working Solution: 1 part A, 1 part B, 3 parts water.
With current films, especially tabular films, we suggest 1 part A, 1

part B, 6 parts water. For higher sharpness, a dilution worth trying would be 1 part A, 2 parts B, 8 parts water.

- The bromide could be replaced with a small amount of potassium iodide (between 1/10 and 1/100 of the amount of bromide).
- Only with conventional grain films, a small amount of Pinacryptol Yellow or Green could be added to reduce aerial fog and possibly overall fog.
- The pH could be lowered further by replacing all the carbonate with sodium bicarbonate. The result would be a very slow working developer with finer grain than usual in a high definition developer.

BJP Dilute DK-50

Crawley's Dilute DK-50 is a special case in the buffered non-solvent category. It is balanced for one-shot, high sharpness use.

In this formula, DK-50 has been diluted 1:4, but the sodium meta-borate content has been kept the same as at full strength, to maintain reasonably rapid development times. With this developer it is possible to obtain good sharpness, and excellent gradation on nearly all films. Although sharpness is less than with FX 1 and FX 2, and there is no speed increase, it is possible to use this developer successfully with all fast conventional films, which is not generally the case with FX 1 and FX 2 or their more sophisticated commercial analogues, FX 14 and 21.

Crawley stated that this developer brings out a good balance of all the inherent qualities in a film, without giving emphasis to any one in particular. It is in roughly the same category (acutance, non-speed increasing) as Unitol and Rodinal and perhaps even HC-110. **Experiment:** It might improve sharpness and speed to replace the potassium bromide with one-tenth or less its weight of potassium iodide, or by lowering the pH and eliminating restrainer. Also try replacing the metaborate with a sodium carbonate/sodium bicarbonate buffer. For instance, instead of 50 g/L of

metaborate in Solution B, try 40 g/L of sodium carbonate and 10 g/L of sodium bicarbonate. **N.B**. Diluted DK-50 develops faster and more vigorously than we expected. Accordingly we suggest replacing some of the sulfite with sodium bisulfite, or diluting it even further. For example, 1 part A, 2 parts B, 7 parts water would create a sharp developer with less optimal midtones. But 2 parts A, 1 part B and 7 parts water should produce better midtones.

Buffers in perspective

Buffer systems were extremely important to Crawley. For conventional grain films, he discovered that there were two kinds of developer where tightly controlled buffering could help: (a) fine grain developers based on D-76 including those where the metol was replaced by Phenidone; (b) high definition developers based on unusually small amounts of developer agent. We emphasize that the ingenious discoveries he made apply primarily to conventional grain films. Tabular and mixed grain films, all with "high iodide" placement, tend to be less sensitive to these refinements. Fortunately, there are many responsive films still being manufactured, and of course these developers are desirable candidates for hand-coated emulsions. We hope that Crawley's insights into buffering will help those who create new developers or modify old ones.

NOTES

1. Henry.

2. Crawley 60/61.

3. T.H. James to BT, 1992.

4. J.H. Altman and R.W. Henn, *Phot. Sci. Eng.* 5:129, 1961. We can understand why Henry used continuous agitation: he wanted to test his results precisely against those of Altman and Henn. That leaves unexplained that Henn apparently deliberately sabotaged his results to look bad for acutance developers. Given that Kodak Harrow had a highly successful high definition developer and Kodak Rochester did not, it seems that politics may have played a part. It is also worth noting that in his test developers, Henn deliberately used a level of sulfite, 10 g/L, that was already known to be too high. Kodak Rochester would not claim a developer increased both speed and definition until Xtol was developed by an entirely separate team.

5. Thomas, *SPSE Handbook of Photographic Science and Engineering*, p. 956, references a modulation transfer study which shows vastly higher sharpness at all frequencies for DK-50 1:10 with no agitation compared to D-76 undiluted with continuous brush agitation.

6. The role of iodide in developers—as an antifoggant, a speed enhancer, and as used here, a sharpness enhancer—has not been adequately studied. Crawley clearly stated that this addition was only effective in dilute, low-sulfite metol developers. Confirmation was published by Arthur Kramer in *Modern Photography* 42, No. 10, Oct. 1978. This was contested by R. Henry who, however, did not test iodide in the kind of developer Crawley was using, because he was unaware of Crawley's published work at that time. What is clear today is that while the tiny amount of iodide may have a positive effect on conventional grain films, it has little on tabular and other high-iodide films.

7. Conversation with Crawley 2005.

8. Amateur Photographer, 17 Feb. 2007.

Chapter 7
SUPER-FINE GRAIN DEVELOPERS

Super-fine grain developers such as Adox Atomal 49, Kodak Microdol-X, Ilford Perceptol, Edwal 12, and the Sease series, still have loyal adherents although many technical problems arise when using them with modern films. In this type of developer the solvent effect is extremely pronounced, with loss of both speed and sharpness. If most of these developers are "pushed" to normal speed, the fine grain effect is lost, and sharpness little improved. In this chapter we will try to help you overcome these obstacles and find new ways to adapt super-fine grain techniques for modern films.

> *There are three types of super-fine grain developer that are versatile enough to be used at normal speed or a bit above. These are (1) the Atomal-F and Promicrol type; (2) FX 10 and related developers such as Adox Atomal 49; and (3) the Microdol type, when diluted 1:3. At normal speed, grain is fine but not super-fine, and sharpness approaches normal. When speed is halved, super-fine grain can be achieved. Along with the loss in speed, there is some loss of sharpness.*

We need to say upfront what has long been observed: super-fine grain developers always cost between 1 and 3 stops of film speed. Better results always occur when you use a slower film with normal development. If you use HP5 in a super-fine grain developer, you will be shooting at EI 50 or 100.

You will get finer grain and higher sharpness by using Pan F, at EI 50 or 80, and processing in a normal developer.

We also need to say that choosing super-fine grain development can be an aesthetic decision: in addition to looking for grainlessness, you may be looking for hazy, atmospheric negatives that do not produce an acute impression of sharpness.

Finally, when super-fine grain developers are used with large format negatives and only 2–4x enlargement, they may show adequate sharpness, as well as absence of grain. With an 8x10 contact printed, or enlarged to 16x20, you are going to achieve sharpness and fine grain no matter what film and developer you use. The real problems with super-fine grain development become most apparent when 10x and bigger enlargements are made from 35mm and roll film.

The practice of super-fine grain development belongs largely to the 1930s and 1940s when 35mm film became popular but films were still very grainy. As films have improved, this technique has become more historical. This chapter is history-heavy.

The “ancient” approach to super-fine grain developers

In the earliest super-fine grain developers, two approaches were taken to create a high solvent effect. Both were first disclosed in a paper by Lumiere & Seyewitz in 1904 (BJP 51, 866, hereafter L&S 1904). Little noticed at the time, it became influential in the 1930s and 1940s.

1. The use of a developing agent that has a high solvent effect, such as *p*-phenylenediamine (PPD).

2. The addition to a normal but low pH developer of a solvent such as ammonium chloride. In the 1930s ammonia derivatives such as the ethanolamines were investigated. Thiocyanate, a strong solvent without some of the disadvantages of the ammonia derivatives, was used in 1938 in Kodak DK-20, and subsequently in many transparency first developers for color and black and white, and by Crawley in the Aculux developers. A small amount of hypo (1–3 g/L) was investigated (Haist 372–374). The most simple and non-toxic of these additions was sodium chloride, which was only discovered by Henn in the 1940s and kept secret for decades. Before, it had always been thought that what was important in ammonium chloride was the ammonia component. Henn found out that the chloride component was the most valuable.

Both approaches shared disadvantages: two to six times normal exposure; loss of sharpness, long developing times, and the danger of dichroic fog even with the less sensitized films of the 1930s. The instruction sheet for Edwal 12 contained directions on removing dichroic fog by using a reducer, thereby decreasing density and sharpness even further.

A variation of the first approach was to fuse pyrocatechin with PPD. The proprietary agent Meritol was an equimolar mixture of pyrocate-chin and PPD said to avoid staining and toxicity. It had some vogue in Britain until the

1960s. (MCM–100, Appendix I) PPD was also simply combined with other agents, such as metol or glycin. But combining PPD with other developers increased grain, though it reduced speed loss.

A more successful approach was Agfa's 1935 use of the developing agent hydroxy ethyl-o-aminophenol in the developer Atomal, discussed later. In a 1952 patent, John and Field claimed a combination of hydroxy ethyl-o-aminophenol with glycin as a super-fine grain developer. The patent stated that whereas the aminophenol gave excellent fine grain images of good speed, the development time was inconveniently long. The addition of glycin was said to speed the development time without altering other characteristics. This combination is claimed to have characteristics similar to PQ developers (i.e., increased toe speed and contrast, with the straight line and shoulder portions of the film curve being of somewhat less contrast than an MQ developer). However, these effects are observed only when the negative is developed to a low contrast. Another advantage of the combination is lower fog than with PQ. The example patent formula corresponded to the proprietary May & Baker formula Promicrol which was, paradoxically, used as a speed-increasing developer with graininess comparable to D-76 (see chapter 5 for more information and the formula), and *not* for super-fine grain; it is also similar to Agfa Atomal F and Orwo A-49 from the mid-1950s up until c. 1990.

For a 2016 overview of the issues around PPD toxicity, see "paraphenylenediamine Containing Hair Dye: An Overview of Mutagenicity, Carcinogenicity and Toxicity", Chong et al., J Environ Anal Toxicol 2016, 6:5, available in full at researchgate.com.

Classical PPD developers

PPD is the foundational developing agent used in super-fine grain developers. With the right formula, the right film, and the right conditions, it can produce extremely fine grain negatives with beautiful gradation, and, on occasion, sharpness-enhancing edge effects.

SEASE SUPER-FINE GRAIN	
Water at 125F/52C	750 ml
p-Phenylenediamine (base)	10g
Glycin*	0-12 g
Sodium sulfite anhydrous	90 g
Water to make 1 liter	

* The amount of glycin in Sease 1,2,3 & 4 was, respectively, none, 1 gram, 6 grams, and 12 grams. As glycin is increased, speed goes up, but fine grain goes down. Develop 15-30 minutes at 68F/20C

L&S 1904 proposed a developer containing only 10 g/L of PPD and 60 g/L of sodium sulfite anhydrous (L&S 1904 PPD). Henn, writing in 1945 (Popular Photography Sept 1945 p. 41, hereafter Henn Pop Phot 1), stated that this first PPD formula was still acknowledged to be the finest grained of them all. It was indeed the gold standard. According to Henn, it was buried in the archives until the late 1920s and 1930s, when interest in fine grain developers and the adoption of the 35 mm camera simultaneously exploded (see Appendix IV).

Developers in the 1930s combined PPD with glycin or various other developing agents and other chemicals to try to overcome the obstacles of speed loss and long developing times.

Perhaps the best classical PPD developers were the four Sease formulas and two related commercial formulas, Edwal 12 and Super 20. All were called “compromise formulas” in the nomenclature of the day because they contained a second and sometimes third developing agent in addition to PPD.

The Sease formulas were published by DuPont in 1934. More elaborate Edwal developers such as 12, 20 and Super 20 followed. Super 20 was only discontinued around 2002.

EDWAL 12	
Water (distilled)	750 ml
Metol	6g
Sodium sulfite anhydrous	90 g
p-Phenylenediamine (base)	10g
Glycin	5g
Water to make 1 liter	
15-18 minutes at 70F/21C	

Ripening

PPD developers work best when they have been ripened, that is, aged or slightly used. The technique is to fog a roll of film by unwinding it and exposing it to light. Soak for half an hour in the freshly mixed PPD developer, then discard the film. You are now ready to use the developer. Every time you make a new batch, "season" it with about 5% of the old batch. This advice is based on years of practical observation by experienced PPD photographers. Crawley was the first to explain why this technique works: a partly exhausted or "ripened" PPD developer will slightly enhance sharpness through the formation of edge effects. (BJP 60/61)

EDWAL SUPER 20[1]	
Water (125F/52C)	750 ml
p-Aminophenol	2.62 g
Sulfuric acid 66 degree Baume	0.2154 ml
Sodium sulfite anhydrous	89.95 g
p-Phenylenediamine	9.59 g
Glycin	4.79 g
Water to make 1 liter	
Add each chemical slowly. Do not add until each one is dissolved completely. Mix slowly and gently for 30 minutes. Desired pH 7.6; Specific Gravity 1.080.	
12-15 minutes at 70F/21C.	
N.B.This differs from the formula in all previous printings of FDC. This is the version that was used after 1975 and seems to represent the best from all the possible choices.	
CAUTION: This formula is given for historical illustrative purposes only. Because of the dangers of working with sulfuric acid, it should not be mixed except by qualified chemists.	

The official formula for Super 20 has never before been published, though several popular authors have (incorrectly) claimed to know it. Please note that Edwal 20 is not the same as Super 20.

PPD toxicity

PPD and its derivatives are regarded in the photographic literature as allergenic, staining, and possibly more toxic than other photographic chemicals. On the other hand, PPD is used throughout the world in most permanent hair dyes. Some misinformation has been published, for example, that PPD was banned in Germany, France, and Sweden. The fact is that no EU country (or any other that we know of) has a PPD ban. Good hair dye is apparently not possible without it. The overall regulatory consensus is that PPD is safe in hair dye except for the estimated 1–1.5% of people who have contact allergy to it. It is often used at c. 3% in hair dyes which are applied directly to the scalp for 30 or more minutes. (The EU allowed a maximum of 6% as of 2019.) By contrast, a photographer using a PPD developer containing less than 1% of the chemical and wearing protective gloves, would have much less or no skin contact.

PPD derivatives

There have been many attempts to refine PPD. An early attempt was o-phenylenediamine, which had some limited hobbyist use. The exemplars of the modern PPD derivatives are mostly used in color developers including those used for developing chromogenic black and white films. These include:

Kodak CD-2: N,N-diethyl-2-methyl-*p*-phenylenediamine, monohydrochloride

Kodak CD-3: 4-(N-ethyl-N-2-methanesulfonylaminoethyl)-2-methyl-phenylenediamine sesquisulfate monohydrate

Kodak CD-4: 4-(N-ethyl-N-2-hydroxy ethyl)-2-methyl phenylenediamine sulfate

and many others—see p. 91 for CD-1 and variants.

The use of modern PPD derivatives is not common for the development of conventional black and white films. Nonetheless, useful developers could be formulated with these agents, with the potential to overcome some of the contrast problems tabular grain films exhibit. **Experiment**: As a starting point, any of the Kodak CD agents, or their equivalents, can be used to replace plain PPD in any of the old formulas. If, as may be likely, it is necessary to control dichroic fog, then we suggest adding dihydroxybenzophenone, as discussed later in this chapter. We suspect users will see lower micro-contrast than is common today. This will be especially useful for some kinds of photography, but may not be sharp enough for most negatives. As noted in chapter 3, Wella/P&G have recently developed less allergenic PPDs for hair coloring, and there may well be other PPDs used in other industries which could be adapted to photography. Home brewers could experiment with the dye concentrate component of permanent hair dyes. These usually contain a tube of dye concentrate that is mixed with a peroxide-based activator just before use. The dye concentrate typically contains PPD and aminophenol, along with ammonia and ethanolamine at a pH of 9–10, as well as sulfite. Could these work as film developers, perhaps at a dilution somewhere between 1:10 and 1:50?

When experimenting with hair dyes as film developers, NEVER use the peroxide (B) component.

Modern-era PPD developers

While Crawley noted the disadvantages of classic PPD solutions, he also believed that these developers might have some useful characteristics that could not be otherwise obtained.[2] He observed that the physical developers which were somewhat popular before WWII "…had the ability to preserve subject tones with exceptional faithfulness."

Crawley wrote about negatives that were "for no apparent reason just right … with an especial transparency and outstanding preservation of clarity in the highlights, together with exceptional retention of small tonal differences even in very minute areas of the negative…." He suggested that this effect could be encouraged by the use of very slow acting developers (developing times of 45 to 80 minutes) with at least some physical developing action. This effect would only be noted in photographs with intrinsically complex lighting effects, usually those taken by daylight, not tungsten or flash.

In particular, he recommended using FX 2 as a stand developer (chapters 4 & 6) but noted that the effect sometimes occurs with ripened PPD developers. In the course of this discussion, he makes some interesting remarks and speculations that deserve to be quoted in full.

> The other advantage claimed for pre-war physical processes [the principal advantage was fine grain, which Crawley found to be without much justification] was exceptional preservation of the subject tones; to some extent this seems justified, but also seems true of conventional developers under certain conditions. Since this effect apparently conflicts with rational sensitometry, some explanation is necessary. The characteristic curve of a developer is established of necessity by standardized exposure to a step-wedge, and subsequent analysis. In practice, however, an actual photograph consists of a kaleidoscope of areas of different illumination levels, sometimes hopelessly intermingled. On subsequent immersion in the developer, various factors come into play as this complex variety of contrasts builds up in density: superadditivity may cause various ratios of surface and depth development; presence or absence of a complex-

> forming solvent [such as sulfite] will cause various ratios of physical and chemical development; the presence of bromide formed during development may affect internal negative contrasts in various ways; agitation will be renewing supplies of developer which, mixing in the emulsion with the exhausted developer, will be forming differently composed formulae in various parts of the frame area. In fact each frame could be thought of as a separate chemical reaction proceeding according to its own internal dynamics, and the net result can be expected to give some falsification of the subject tonal values….

> *The quoted statement by Crawley, left was later partly confirmed by Mason, citing in part Barrows & Wolfe, Phot. Sci. Eng. 15, 472 (1971): "Although diffusion within the emulsion layer has little effect on development at the lower alkalinities on a macro scale, it can result in some important effects on the micro scale. These effects are all due to … the local exhaustion of the developer, but as this is manifest in several ways, several [adjacency] effects can be differentiated." (Mason, 114) Further, "When the rate of the overall development process is studied … it is the cumulative effect of several chemical and physical processes … not a straightforward chemical reaction. In applying the usual theories of chemical kinetics to the overall development reaction, this fact must always be considered, for the rate at any instant during development will be determined by the slowest process at that instant. This rate-controlling process need not be the same throughout the whole course of development, there being much evidence that the kinetics of the early stages differ from those of the later stages."*

Much of what Crawley has to say here is in the realm of speculative observation, and as he points out, conventional sensitometry is powerless to prove or disprove these observations. Yet the concept that a fairly dilute developer can, in some cases, adjust itself to each frame in a roll of film, is fascinating. As shown in the sidebar, he has support in the scientific

literature. These effects have also been reported by users of tanning developers (Hutchings, *Book of Pyro*).

Crawley then goes on to make the following points about PPD and PPD derivative developers:

1. Because of physical development, PPD-developed negatives have a brown tint with higher printing contrast than their visual appearance would suggest (use the blue channel of a color densitometer for accurate readings, as you would with tanned negatives).
2. To produce normal contrast with modern films, it would be necessary to formulate PPD developers with caustic alkali, but that would encourage dichroic fog and largely eliminate the fine grain effect.
3. When PPD is supplemented with another more active developing agent, that agent becomes almost entirely responsible for density. PPD is thus relegated to a minor role as a subsidiary solvent, along with the sodium sulfite. As a result the fine grain effect is lessened.
4. PPD itself cannot be used with chlorhydroquinone, as a precipitate invariably forms (this does not apply to derivatives).

(All quotations in this section from BJP 60/61)

	FX 9	**FX 10**
Sodium sulfite anhydrous	100	100 g
Genochrome or Kodak CD-2	7.5	7.5 g
Chlorhydroquinone	7.5	- g
Hydroquinone	-	6 g
Borax	-	4 g
Boric acid	-	4 g
Water to make 1 liter		

FX 9 and FX 10

After this preface we get to the PPD developers Crawley formulated for use with modern films. These developers employ some of the same PPD derivatives used in early color developers, plus a supplementary agent, HQ or CQ. Crawley states that the PPD derivative contributes significantly to image formation. Interestingly, a 30% increase in speed is claimed, and Crawley expressed the belief that these developers probably produced the optimum exploitation of the speed-grain relationship with modern films, the penalty being somewhat decreased sharpness. The achievement of good speed in a super-fine grain developer was a remarkable technical feat.

In 1960, Crawley chose to work with Genochrome (see next section), which is now hard to source precisely. In 1998 Crawley told us that Kodak CD-2 would be an acceptable substitute for those who want to experiment. FX 9 is said to offer "exceptional retention of detail on overexposure." On the other hand, FX 10 is said to be very sensitive to overexposure or overdevelopment, but also more "reliable in use."

These solutions were intended to be reused without replenishment. For each roll processed in a liter of solution, extend development time by about 5%. No more than 6 or 7 rolls should be processed per liter. No replenisher was designed.

> *Why are old-style highly solvent developers like Adox Atomal being used for tabular grain films today? Perhaps because PPD-derivative developers, like, for different reasons, tanning developers, offer a way to challenge the homogenous results high-iodide films are designed to produce.*

These two formulas were discontinued in 1971. With convenient development times of only 5 to 11 minutes (much shorter than classical PPD developers), they may be worth looking at again, perhaps diluted 1:3 with tabular grain films.

Discontinued and forgotten perhaps, but not by manufacturers. FX 10 has had a long afterlife. As can be seen below, it is closely related to today's Atomal A49 developer.

Modifying FX 9 and FX 10

If the solvent effect of these formulas is found to be too great, and dichroic fog results, the sulfite content can be lowered. Alternatively, the pH can be raised to decrease physical development. In the case of FX 9, a gram or two of sodium carbonate could be added. In the case of FX 10, the boric acid could be reduced, the borax increased, or both. Development times would be shorter.

If a finer grained effect is desired, with an inevitable loss in film speed, the pH can be reduced, and developing times extended, by adding a few grams of bisulfite to FX 9, or by increasing the boric acid in FX 10. However, this would also increase the chance of dichroic fog.

Probably the best way to prevent dichroic fog is to add 0.1 to 1g/L of benzophenone or twice that much of chlororesorcinol, as discussed later in the Microdol section. According to Henn, the use of CQ should also prevent dichroic fog, though not to as great an extent.

The source for the formula for Atomal-F/Orwo A-49, next page, is V. Mikulin, Photo Recipe Handbook, Moscow Art, 4th edition, 1972, citing a Czech publication. The source for the original Atomal formula is the Report on the Agfa Film Factory Wolfen, CIOS, Target No. 9/133, from 1945.

Commercial film developers with PPD derivatives

In Germany, PPD derivatives have been used in black and white film developers to a greater extent than elsewhere. Emofin from Tetenal was recently discontinued. Atomal A49 is currently manufactured by Adox. It is finding popularity used with contemporary films.

Both these developers appear to use, or to have used, the same chemical. However, there is confusion in the MSDSs as to what precisely this chemical is and what its CAS number should be. Haist II 546 definitively defines three related chemicals:

> *In 1937, just before Vittum showed why ammonium chloride should not be used in packaged developers, Edmund Lowe filed USP 2,164,280 (1939) for lower pH fine grain developers mostly utilizing ammonium chloride. Lowe's patent suggests there was then no knowledge within the industry of sodium chloride as a fine grain agent. Some interesting points: (1) the developer must be of low pH (7–7.8), using only sodium sulfite as accelerator; (2) all fine grain developers capable of enlargement from 20 to 60 diameters without appreciable graininess have these disadvantages: (a) flat negatives that require a one stop speed decrease, (b) tendency to blocked up highlights, (c) tendency to produce coarser grain if the negative has been overexposed, and (d) "the enlarged images tend to lack critical definition and the very large pictures produced do not faithfully record the surface texture of objects photographed." This last statement is notable in recognizing how*

definition and fine grain are antithetical goals, yet suggests aesthetic value in intentionally distorting surface detail.

1. *N,N,*-Diethyl-p-phenylenediamine monohydrochloride (Kodak CD-1, Johnsons Activol No. 6 formerly Activol H);
2. *N,N,*-Diethyl-p-phenylenediamine sulfur dioxide complex (BP 626,958) (M&B Genochrome. yielding sulfite *and* sulfate in solution);
3. *N,N,*-Diethyl-p-phenylenediamine sulfate (Johnsons Activol No. 7 formerly Activol S; Ferrania S-28).

CD-1 was an early color developer which is now obsolete for color. Chemicals 2 and 3 were later improvements. The predominant drift of the MSDSs indicates that Chemical 3 was used in Emofin and is now used in Atomal A49, except that it is sometimes identified in MSDSs as CD-1, which it is not, though it is close.

Emofin was a two-bath developer with metol as additional agent. Adox Atomal A49 uses HQ as the additional agent. It is thus similar to FX 10 and may even have been based on that developer. Older Atomal developers were quite different. They utilized a HEAP-based developing agent, described in the next section, that has not been commercially available since before the 1990s.

Non-PPD approaches to super-fine grain

During the 1930s and '40s, there were alternative schools to those trying to improve the 1904 Lumiere developer. Their goal was to avoid PPD completely, and so be rid of toxicity and staining problems.

Avoiding PPD by finding an alternative solvent developing agent

By far the most successful PPD-alternative solvent developing agent of the 20th century was hydroxy-ethyl-o-aminophenol (HEAP). It was synthesized and patented by I.G. Farben in 1929 (BP 295,939) with the claim that it was a particularly fog-free developing agent. It was then used from 1935 in Agfa Atomal. The formula for Atomal was published in 1945. Around that time it was investigated by John and Field at May & Baker. They concluded that much superior results would be obtained by using glycin as the superadditive agent. The resulting formula was Promicrol, sold from the mid-1950s. Around this time, Agfa reportedly adopted the M&B approach, and issued Atomal-F, which is almost the same as the patent example for Promicrol (chapter 5). Orwo called this A-49.

	Atomal	Atomal-F
Sodium sulfite anhydrous	100	100
Hydroxyethyl-o-aminophenol	6	6
Pyrocatechin	10	-
Hydroquinone	4	-
Glycin	-	1.2

	Atomal	Atomal-F
Sodium carbonate	25	10
Potassium bromide	1	0.5
Sodium metaphosphate	1	-
Distilled water to make 1 liter; all quantities in grams		

Around the 1980s, HEAP ceased to be synthesized either in Germany or Britain. At this time, Atomal-F became Atomal-FF, an ordinary PQ developer. At some point, Promicrol was similarly reformulated as a PQ-carbonate-citrate developer of no great distinction. According to Mirko Böddecker, Atomal-F was the best developer of its time in Germany. It was extremely compensating, had good speed, fine grain, high sharpness. He believes that the current Atomal A49, based on a PPD derivative (see previous section), maintains all those qualities except sharpness.

Avoiding PPD by using an alternative chemical solvent

The search for alternative silver solvents began with the same paper, L&S 1904, which had recommended ammonium chloride as an effective fine grain agent.

EX. 5 FROM USP 2,466,423	
Metol	5 g
Sodium sulfite	100 g
Ethylene diamine sulfate	12 g
Sodium metaborate	4 g
Potassium bromide	0.25 g
Sodium chloride	20 g
Water to make 1 Liter	

In the 1930s, the Kodak chemist Paul Vittum, who would later gain fame (and infamy) for leading the development of Kodak's monopack color films, became interested in ammonium chloride. His USP 2,053,516 (1936) discusses ammonium chloride as a fine grain agent. Typical example formulas include D-76 with the addition of 50 g/L ammonium chloride. Decreasing this amount increases graininess, but going above 50 g/L does not materially decrease graininess. The patent also covered the addition of TEA.

A practical problem with ammonium chloride developers was pointed out by Vittum in USP 2,113,312 (1938): loss of ammonia on aeration. Vittum's solution was to claim "a salt of a primary, secondary, or tertiary aliphatic amine" such as, for example, ethanolamine hydro-chloride. It was still thought that it was the ammonia part of the compound which assisted fine grain, more than the chloride component. But it was already clear that chloride should preferentially be present. There is no evidence that an ethanolamine was ever used in a black and white developer product of that period, but it would later be used in color developers that Vittum was responsible for.

Would it have been possible to patent solely the sodium chloride addition? Henn Pop Phot 1 suggests a reason why not: Lowe had already published using sodium chloride as an addition to a PPD developer. (Henn does not source this article, and we have not found it independently.) Henn suggests that Lowe was only interested in chloride as an adjunct to PPD developers. Since Lowe was also interested in low pH metolsulfite developers, he was perilously close to discovering the Micro-dol secret. But he never did. It was too audaciously simple to occur to him.

Continuing Vittum's line of work, Henn's USP 2,466,423 of April 1949 claims, for fine grain, a soluble amine and a soluble chloride or compound which yields chloride ions in concentration in excess of the molar

concentration of the amine. Specifically, among several examples, the patent claimed a single powder developer shown in the sidebar on this page.

The patent shows that adding ethylenediamine to a developer reduced graininess on an empirical scale by 7 points. But adding 10 to 50 grams of sodium chloride could reduce graininess by 9 to 15 points. Misleadingly, the patent implies that it is the amine which is reducing graininess, that the chloride is there to accelerate the amine's action.

This patent was applied for in May, 1945, just a few months before Microdol was introduced. Although it is sometimes described as the foundational Microdol patent, its purpose is to mislead. It is the first patent to identify sodium chloride as a fine grain agent. But it doesn't disclose that *sodium* chloride, *alone*, could excel as a fine grain agent.

This patent is for a developer that was never made. But Henn knew by 1945 that sodium chloride, alone, was the most generally useful adjunct to super-fine grain development other than sodium sulfite. The proof is that Kodak introduced Microdol in the autumn of that year. The patent covered it, without anyone being able to figure out what was in the product. Only if you subtract the amine, the metaborate, and the bromide, do you get Microdol.

Why do D-23 and D-25 contain 7.5 g/L of metol while Microdol and many other example formulas given in patents, use 5 g/L or less? I believe the answer is that D-23 and D-25 are intended for amateur use, and the additional amounts represent the kind of idiot-proofing that was always a part of Kodak's philosophy. When you consider also that developers at that time were often used for long periods, and stored for long periods, having an excess of developing agent makes sense.

One thing is clear: there was an enormous amount of research by Kodak and others which came out of the L&S 1904 ammonium chloride suggestion. But few if any of these developers were ever made. By contrast, Agfa's

Atomal-F, Orwo's A-49, and M&B's Promicrol were highly successful. One reason may have been that the HEAP-glycin combination allowed them to be used either as sharp speed-increasing developers with graininess comparable to D-76, or, with overexposure, as super-fine grain developers with better sharpness than PPD types. HEAP really was an outstanding developing agent. Efforts to synthesize it today have so far been too costly. Yet, the Atomal-F/Promicrol type of developer was so much more versatile than the directly competing super-fine grain developers, including those we come to next.

Richard Henn, D-25, Microdol, metol and super-fine grain developers—the modern approach

Already in 1938, Richard Henn had published the developer which heralded his career-long interest in simple metol-sulfite developers (JPSA 4, Fall & Winter 1938; BJP 86, 3, 1939). DK-20 was Kodak's first successful answer to achieving super-fine grain without PPD. The technique was to use a simple metol-sulfite developer and add a small amount of potassium thiocyanate. This was one of the first published developers to incorporate thiocyanate, which would also go on to be used in color developers through to the end of the 20th century. DK-20 can be seen as the parent of the D-23 line which would come in 1944. The formula is printed in Appendix 1. DK-20 was manufactured for some decades. It claimed to produce substantially finer grain than D-76 with a one-stop loss in speed. Dichroic fog was a problem which dogged this developer, especially when not used with fresh film. When Henn patented antistain (anti-dichroic fog) agents in the 1960s, discussed later in the Microdol-X section, he recommended them for DK-20. For a more modern use of thiocyanate in concentrated developers, see chapter 5 on Crawley's Aculux.

> *Henn compared D-25 to the Lumiere & Seyewitz PPD formula, the gold standard for fine grain development. But this was in the 1940s, before the study of acutance and MTF. The advantage the PPD developers have is that after ripening, they produce sharpness-enhancing adjacency effects through exhaustion. This doesn't happen in D-25 type developers. So while grain may be comparable, sharpness may not. At*

this time, image evaluation was still primitive. In spite of all of this, Henn's published prints appear to show that D-25 is sharper than L&S 1904 PPD.

Henn's approach to the formulation of super-fine grain developers became even more elegant. He started by formulating the simplest moderate fine grain developer of all, Kodak D-23, which contains only 7.5 grams of metol and 100 grams of sodium sulfite to a liter of water.

To convert D-23 into a developer with graininess approaching PPD developers, but with less inconvenience, less toxicity and better overall quality, he reduced D-23's pH to 7 by adding 15 g/L of sodium bisulfite. The resulting formula was D-25. The lower pH means lower activity and reduced graininess through two mechanisms: less "clumping" and more solvency (because the film spends more time in the sulfite-rich solution). Developing time was 30–40 minutes but could be reduced to the same as D-76 by elevating temperature to 77F/25C. By adding even more bisulfite (Henn did not specify how much) for a developing time

To obtain best performance with D-25, adjust the bisulfite level for the particular film you use. If you notice dichroic fog, cut back on the bisulfite until you reach a safe level. Or add benzophenone.

of 3 hours, Henn achieved even finer grain than L&S 1904 PPD.

This was the discovery Henn published in 1944.[3] He refined his approach in the commercial developer Kodak Microdol and its successor, Microdol-X. The *stated* advantage of Microdol over D-25 was the same super-fine grain but *half* the developing time. Although the formula for Microdol has never been published by Kodak, it consists of D-23 (with 5 grams of metol instead of 7.5) and the startlingly simple addition of a small quantity of sodium chloride (common salt). Salt has the ability to decrease graininess without

the penalty of increased developing time. This is the "secret" behind Microdol and Microdol-X. The original Microdol formula is believed to have contained 5 grams Metol, 100 grams sulfite, and 30 grams sodium chloride to a liter of water.[4, 5, 6]

The increased solvent effect of developers with common salt is proportional to exposure, since salt primarily affects silver that has been exposed. Many other compounds have been studied for obtaining reduced graininess but no one seems to have found a simpler way of designing super-fine grain developers than Henn.

> *Data from Altman and Henn in 1960, and Henry in 1986, show that for achieving the best balance of speed, grain, and sharpness, D-25 was the best developer to use for Kodak Panatomic-X. D-25 was not widely used throughout the period from 1960 to the present, but is now enjoying popularity as a developer for tabular films, often diluted 1:3. Whether this indicates the resiliency of the developer or that of the tabular grain films, we are not in a position to say. Long developing times may be reduced by raising the temperature a few degrees, as with Microdol-X at 1:3. The fine grain effect of D-25 is largely lost at 1:3. At that point it has become a buffered, lowpH, mildly solvent to non-solvent developer.*

Hints of Microdol in Kodak patents in the 1950s

Various formulas similar but not identical to Microdol or Microdol-X (that is, sodium chloride is mentioned in the claims but not in the examples) crop up in Kodak patents relating to the use of phthalates and anhydrides as preservation agents for packaging chemicals. (Of all these chemicals, boric anhydride was found by Kodak to be the most useful. US Patents 2,606,188

(1952), 2,592,366 (1952) and 2,682,464 (1954) discuss boric anhydride in single powder developers or fixers.)

Why does sodium chloride work?

When Microdol was released in 1945, it was clear that Henn had known for some time *that* sodium chloride was a valuable fine grain enhancer. But for *how* it worked we have to turn to van Veelen and Peelaers of Agfa-Gaevert in 1967. This paper,[4] cited by Haist and Mason, examined the addition of sodium chloride to a simple metol developer and its effects on several different kinds of emulsions. They stated,

> Sodium chloride, added in a high concentration [i.e. 50 g/L] to a developing bath of low activity dissolves silver bromide or silver iodobromide, when the silver chlorobromide complexes are quickly removed. This can be attained by adding active colloidal silver nuclei to the emulsion whereupon these complexes will be reduced. In the absence of nuclei practically no solvation of the silver halide is observed.
>
> In the case of exposed emulsions the latent image can act as active nucleus. In Metol developers of low pH this reduction can be more important than the chemical development and compact silver with brown image tone will be formed."

In other words, *sodium chloride only works on exposed film.* This may explain why it took so long for its usefulness to be discovered: the earlier researchers may have measured silver solvency on unexposed emulsions.

Henn's metol-sulfite developers usually contain 5 to 7.5 g of metol, which seems an excessive amount but does provide a safety factor. The US Navy had a more prudent approach. Its little-known N-2 negative developer contains Calgon 0.5 g, Metol, 2 g, Sodium sulfite 100 g, to a liter of water. (JSMPE, 44, no. 4, April 1945, L.M. Dearing, "Processing of Combat Films")

Haist goes on to observe (379), "Solution physical development was thought to be the cause of the compact silver particles and the brownish tone of the developed silver. When the concentration of the sodium chloride was 50 g/liter of developing solution, the developer produced filamentary silver particles that had been thickened by the solution physical development."

There is also the implication that silver will be preferentially dissolved in areas of high exposure—just where graininess is most acutely perceived.

At around the same time, Willems patented emulsion additions and gave as an example a Microdol-type developer composed of Metol 4.5 g, Sodium sulfite 90 g, Sodium chloride 30 g, boric acid to bring the pH to 7.8, and water to a liter. (USP 3,523,797, 1970)—illustrating that within the industry, the formula for Microdol was known by then. This patent notes that some speed-increasing accelerators to be incorporated into emulsions are only effective when slow-working fine grain developers are employed. This is a remarkable instance of Agfa-Gaevert researching ways to doctor films so they could be developed optimally in Microdol or Perceptol.

Sodium or lithium chloride were referred to as "a graininess reducing salt" in USP 3,865,591, which may be the only time the quoted term has been used.

One thing to consider when comparing D-25 and Microdol-type developers to PPD developers is that Henn's developers are designed never to exhaust in normal use. Thus adjacency effects are minimized. By contrast, a ripened PPD developer will, under ideal circumstances, partially exhaust, giving rise to sharpness-enhancing adjacency effects. It is clear from the entire trajectory of Henn's career that he was not interested in working with developers where planned exhaustion was part of the system. One might go so far as to say that he fought them.

The 1960s, Microdol-X, agents to prevent dichroic fog

In the 1960s, film emulsions became more subject to dichroic fog. Haist 258 observes that "Dichroic fog is very easily produced on modern high-speed photographic films.... Apparently, certain speed-increasing emulsion addenda provide or are instrumental in forming nucleation centers for the formation of a scum of metallic silver on the emulsion surface. Manufacturers of photographic film often warn against the use of solvent developers for processing such films." This statement applies to the films of the 1970s. Their increased tendency to dichroic fog in highly solvent developers mandated the change from Microdol to Microdol-X, which took place in the mid-1960s. The change was the addition of what Henn called an "antistain" agent.

Henn's antistain patents

Still of some practical value to us today are Henn's patents for what he called "antistain" agents. What Henn refers to in his earlier patents, correctly, as "dichroic fog", he refers to later as "stain". This is not a conventional usage, and Henn was obliged to define "stain" in his subsequent patents in the same words that he had formerly used to describe dichroic fog.

US Patent 3,161,513 (1964) discloses Henn's use of 2,4-dihydroxybenzophenone as an antistain agent in fine grain film developers. That the developer may include sodium chloride or ammonium chloride is stated in the claim, but no specific example is given. The preferred usage range is 0.1–1.0 g/L.

MICRODOL-X EQUIVALENT	
Water at 125F/52C	750 ml
Metol	5 g
Sodium sulfite anhydrous	100 g
Sodium chloride	20–30 g
2,4-dihydroxyb enzop henone	0.1–1.0 g
Sodium hexametaphosphate	0.2 g
Boric anhydride	0.2 g
Water to make 1 Liter	
Develop undiluted 10–15 minutes	
Desired pH of 7.7–7.9 may require adding boric acid. (Microdol MSDS 5/2003 and USP 3,523,797,1970).	
N.B.The boric anhydride should be omitted. It is there only to ensure stability of single-powder packaging. See USP 2,606,188 (1952), 2,592,366 ((1952), and 2,682,464 (1954). The Calgon may also be omitted with discretion, or it may be replaced with DTPA. Depending on the film, more-or less-ofthe benzophenone may be needed.	

Important practical observations Henn makes about “stain” or “scum” in his vocabulary, or dichroic fog in ours, include: **(1) it is most likely with high speed films, but it is possible with all films when a highly solvent developer is used; (2) it is more likely to be produced in used solutions than in fresh solutions; (3) it is more likely to be produced when using aged films rather than fresh films**.

US Patent 3,161,514 is similar to the previous patent but discloses the use of chlororesorcinol instead of benzophenone. Here the recommended amounts were between 0.2 and 2.0 grams per liter. A pertinent observation, in both patents, is that smaller amounts of the antistain chemical will reduce stain, but larger amounts will eliminate it.

Henn observes that resorcinol and chlorhydroquinone also possess about the same antistaining properties as each other, but much less than

chlororesorcinol. This may help explain the success of some super-fine grain developers of the past that contained CQ.

Henn stated that his antistain compounds would work with any known developer. However, later, when he formulated HC-110 (see chapter 6), he discovered that these compounds were not preventing dichroic fog. For that developer only, he discovered that PVP was the only compound to work.

Henn's antistain compounds should be useful to those trying to get PPD or its derivatives to work with modern films. They may also help those who are working with multi-hour stand development, and with all other processes that have a tendency to produce dichroic fog.

Nobody has yet proposed an explanation as to why Henn's antistain compounds work. Questions abound: are they effectively anti-silvering agents? But if so why don't anti-silvering agents prevent dichroic fog?

There is some dispute as to whether Microdol-X used benzophenone or chlororesorcinol as "antistain" agent. Haist believed the former, Mowrey believed the latter. Henn patented both in 1964: USP 3,161,513 and 3,161,514. It is possible that, at different times, Micro-dol-X has used both of these, but probably not together. Henn also discovered that when highly solvent research developers employ CQ, that chemical itself operates as an anti-stain agent. Some unpublished work by J. King now held at George Eastman House represents one of the few known times that Kodak considered using CQ in a modern-era product.

Using Microdol-X

Microdol-X at full strength requires an extra stop of exposure, but speed becomes normal when it is diluted 1:3. There are two reasons why *diluting* Microdol-X increases speed.

1. At full-strength the solvent effect is great enough to dissolve away so much of the latent image that some of it is lost altogether. But when the developer is diluted, the solvent effect is not as great.

2. When a metol developer is diluted, highlight development is restrained more than shadow development. This gives the shadows a chance to catch up with the highlights.

Microdol-X may be replenished when used full strength. Negatives have a typical brownish cast in areas of high exposure, indicating that physical development due to chloride occurs preferentially in the highlights. However, Microdol-X is more commonly used at the 1:3 dilution. This less solvent dilution results in a higher degree of sharpness.[7] Speed becomes normal, although developing times are quite long, and Kodak recommends processing at 75F/24C to keep times manageable.

Microdol-X equivalents

Ilford Perceptol is formulated to be used at the same dilutions and times as Microdol-X. It has some working properties in common with Microdol-X, is marketed as an equivalent, and appears to be chemically close to Microdol.[8]

Finally, D-23 plus 7.5 grams sodium bisulfite has been incorrectly published as being equivalent to Microdol-X.[9] As we have seen, a developer closer to Microdol-X is D-25 which contains twice as much bisulfite. However, there are long-standing recommendations to make D-25 with half the bisulfite, in order to gain emulsion speed and faster processing time, when the finest grain is not required. Some contemporary users of D-25 have found it too soft. The reason is probably that they aren't developing long enough. D-25 times will always be long: Henn suggests they are usually at least twice those for Microdol. Kodak positioned D-25 as the home-brewer's alternative to Microdol but, given the unique way sodium chloride works in Microdol, the two developers are not directly comparable. Graininess may be comparable. But there is more to image quality than that.

FX 5

In 1960, Crawley published FX 5 as a Microdol-X equivalent. Instead of sodium chloride, Crawley uses additional sulfite to obtain a greater fine grain effect. “In FX 5 an attempt has been made to retain the maximum definition that is compatible with true fine grain.” Speed loss is one stop compared to D-76. At that time, like everyone else except a few at Kodak, Crawley was unaware of the sodium chloride technique used in Microdol. Nevertheless, FX 5 does produce similar negatives, even down to the brown hue.

FX 5	
Water at 125F/52C	750 ml
Metol	5 g
Sodium sulfite anhydrous	125 g
Borax	3 g
Boric acid	1.5 g
Potassium bromide	0.5 g
Water to make 1 Liter	
Develop undiluted 10–15 minutes	

The future of super-fine grain

FX 5 was one of the last super-fine grain developers to be formulated based on the D-23/D-25 technology of the 1940s. Crawley does not appear to have thought this line of developers could be exploited further. It might be possible to tweak FX 5 to work better with a given film by making fractional modifications to the proportions. But for those interested in modern super-fine grain developers, we think that experimentation with PPD derivatives would be more rewarding. We suspect they might prove particularly valuable with tabular grain films. Ammonia derivatives are tricky to work with because though highly solvent, they do not necessarily result in finer grain. We also believe that sodium chloride has not been sufficiently researched as a super-fine grain enhancer.

Experiment: Make up the suggested Microdol-X equivalent, omit the antistain agent and vary the amount of sodium chloride between 10 and 50 g/L.

Experiment: It is interesting to note that two commercial super-fine grain developers still available, Microdol-X and Perceptol, do not use Phenidone. Try adding 30 grams of sodium chloride to PQ or phenidone-ascorbate formulations. However, unless the developer is formulated for low activity the physical development component may not be large. Phenidone's fast induction period may prevent the chloride from being as effective as it is with metol.

Experiment: Make up FX 2 as directed in Appendix 2. For solution B, use 150 grams of sodium metaborate per liter of water instead of potassium carbonate. You will not need Solution C. Make a working solution consisting of 75 ml A, 75 ml B, and water to make 1 liter. Add 30 to 60 grams of sodium chloride. This is a starting point for a compromise developer with very fine

grain *plus* enhanced adjacency effects. The results could be comparable to those obtained with ripened PPD.

Experiment: As Henn pointed out, the practical maximum super-fine grain effect can be achieved by adding additional sodium bisulfite to D-25 such that developing time will be three hours. But there are other approaches. For example, instead of adding BZT to a Microdol-like developer, add 15 grams of sodium bisulfite to bring the pH down to 7.2 or even 7.0. Developing times will be considerably increased, but grain will be finer. The risk of dichroic fog will be high, depending on the film and its age but can be circumvented with an "antistain" agent.

See Appendix IV for Henn's suggestions for using BZT with Microdol to enhance fine grain.

One cat that keeps on chasing the super-fine grain mouse is dichroic fog: DK-20 worked well with the films of the 1930s, but produced dichroic fog on the films of the 1940s, hence D-25. D-25 caused dichroic fog on the films of the 1950s, hence Microdol. Microdol caused dichroic fog on the films of the 1960s, hence Microdol-X. Since then, we've had a truce. Things haven't gotten worse, but they haven't gotten better. Super-fine grain myths remain tenacious: some distinguished photographic textbooks written in the 1980s still recommended DK-20, a developer which had not *then* been usable for forty years. We'll need clear eyes and meticulous testing to bring the practice of super-fine grain development into the 21st century.

Could DTOD be the answer?

DTOD (discussed in chapters 3, 5 and 14) was suggested for use in photography as early as the 1960s by Ron Mowrey. It has value both as a fixer additive and as a solvent in fine grain developers. It is believed that DTOD is now used instead of thiocyanate in the E6 First Developer. In chapter 5, we have suggested replacing thiocyanate with DTOD in an Aculux-type developer. Could DTOD be applied to super-fine grain developers, presumably at higher levels? Well, the fact is that in an Aculux-type developer, the solvent (traditionally, thiocyanate) is already at the highest level it can be that will not create dichroic fog. The same may be true of DTOD. This indicates that it would not be possible to decrease apparent graininess further unless exposure and development are adjusted to downrate the film by 1–3 stops. One significant thing about DTOD is the observation that it does not impair sharpness the way thiocyanate and other solvents do. So it might be a good choice for those who want super-fine grain but don't want mushiness.

The best way to get super-fine grain

The best way to get super-fine grain is to use a slower film. A slower film will almost always give better results than a higher speed film that is processed in a speed losing super-fine grain developer. Kodak's advice when Panatomic-X was discontinued is a reminder that pull processing is not the same thing as losing speed through super-fine grain development: pull process TMAX 100 for results similar to Panatomic-X. (While we do not accept that statement as 100% true, and would much rather have Panatomic-X available, we do admit that there is some truth in it.)

> *A mercapto compound was used as the anti-silvering agent in ID-11 Plus, a modification of D-76 formulated by Peter Krause and introduced by the US branch of Ilford in the 1980s. Apparently its main purpose was to eliminate sludging in automatic processors, but many photographers thought it produced better sharpness as well as lower fog. It was quietly taken off the market for reasons that have not been verified to our satisfaction. It has been reported in a newsgroup post by Sil Horwitz, Technical Editor of the PSA Journal from 1970 to 2002, that, according to information he received from Ilford, the agent was cinnamic acid disulfide, and that it was found to cause unacceptable speed loss with some new technology films. This is a good illustration of the way that products or techniques may have to be discontinued when new films are introduced.*

In the 1920s, Berenice Abbott used a PPD developer for some of her Paris portraits (Abbott to BT). But I doubt anyone would be able to tell in which

of her photographs some softening is due to the developer, the Hermagis lens, or some other factor.

Research on super-fine grain developers was concentrated in the years between 1904 which brought Lumiere and Seyewitz's foundational suggestions for fine grain, and 1964, which brought Henn's patents on how to avoid the dichroic fog that these developers tend to produce. For much of this time films were slow and grainy. But advances in sensitization from the 1940s onwards brought great reductions in grain. Image evaluation was in its infancy. But already in 1939, G. Higgins had written in the Journal of Applied Physics (10, 18, 1939) that when slow fine grain emulsions are developed in MQ borax developers, graininess is similar to that obtained by developing faster emulsons with speed-losing super-fine grain developers.

Should ‘antistain’ agents be used at all?

What Henn, in both his Microdol-X and HC-110 patents called ‘anti-stain agents’ raises a question: Isn’t the fact that one needs such an agent an indication that the silver solvent level is too high? Wouldn’t it be better to reduce the solvent level rather than add offsetting chemistry? This was Crawley’s approach in the Aculux series. In HC-110, it isn’t possible to reduce the silver solvent level because the developer’s long bottle life depends on it. Analogous advice came from Haist: ‘If you need an antifoggant, your alkali is too high.’

However, there is no doubt that antistain agents can be used to make highly solvent developers practical for everyday use. This applies both to experimenting with the old formulas and coming up with new ones.

Would an antistain agent be necessary if DTOD were used as the solvent?

Recreating history

It now seems clear that historically, where super-fine grain development was most successful was not with 35mm, where it was most needed, but with large format negatives, often contact printed, where the definition-obliterating effects were less noticeable. The heyday of super-fine grain developers was the 1930s and 1940s. Not coincidentally, this was also the last period when pictorialism was still popular. But who can say when it will next come into vogue?

The question arises, might some of the old super-fine grain formulas be useful with handmade emulsions?

For someone whose main goal is to recreate an historical process, it seems a valid procedure. But given the trouble and expense of working with handmade emulsions, we would be more inclined to use less finicky, more predictable developers. Super-fine grain developers belong to a time when film was plentiful and cheap, and when expectations of image quality, particularly sharpness, were not as high as they are today. They were only popular for a few decades in photographic history. We doubt they were used in the Hollywood glamour photography of the 1930s and '40s, which depended on realistic sharpness and the skillful obliteration of unwanted details through hand retouching. Of all the super-fine grain developers worth trying with handmade emulsions, we would choose Adox Atomal 49 as the most likely to produce good results. Not coincidentally, it is the last of its class still being manufactured. Best of all, it means we don't have to weigh out PPD from scratch.

What I take away from the history is that PPD super-fine grain developers are likely, as Lowe pointed out, to reproduce texture imperfectly. And I like the idea of that look! Whenever I see an old picture with imperfect texture, I ask myself, was that the effect of PPD? Can I replicate it? What kind of

picture would I use it for today? The D-25/Microdol kind of developer is more clinical, and really does, as Henn claimed, preserve texture better.

Evaluating super-fine grain negatives before printing

Any super-fine grain developer may produce a brownish negative. This indicates physical development, and that your processing really is working to produce super-fine grain. Such negatives may look unacceptably flat. But, as with tanned negatives, printing contrast is greater than you would think. As with tanned negatives, use the blue channel of a color densitometer to provide more accurate readings. Not all of the developers mentioned here will produce this brownish tinge, or produce it all the time.

NOTES

1. Disclosure to SA from Falcon Safety Products for the formula in FDC1 1st and 2nd printings; disclosure to BT from Bob Schrader for the post-1975 formula in FDC1 3rd printing.

2. Crawley 60/61.

3. R.W. Henn & J.I. Crabtree, "An Elon-Sulfite Developer and an Elon-Sulfite-Bisulfite Fine-Grain Developer", *J.PSA* 10:727 (1944).

4. G.F. van Veelen & W. Peelaers, "Formation of Compact Silver in Metol Developers of Low Activity Containing Sodium Chloride", *Phot. Korr.* 103:107 (1967).

5. Edgar Hyman, "Microdol", *35mm Photography*, 8 (1):10 (1965).

6. Kodak MSDS for Microdol.

7. This conventional wisdom is contradicted by Richard Henry's meticulous granularity and acutance tests in *Controls in Black and White Photography*. He found no significant difference in granularity or acutance ratings between Microdol-X used either full strength or at 1:3, with Tri-X and Pan-X. We cannot explain his findings. Dickerson and Zawadzki inform us that Henry's numbers run counter to what they have found over decades of research: almost without exception, dilution increases sharpness and speed. On balance, we must conclude there was an artefact in Henry's measurements.

8. Ilford Catalogue 12866, 10/1997.

9. Patrick Dignan, *150 Do-it-Yourself Black and White Photographic Formulas*, 1977, Dignan Photographic, Inc.

Chapter 8
TANNING DEVELOPERS

We use "pyro" to refer only to pyrogallol. We use "pyrocatechin" to refer to the chemical also called "catechin", "catechol" and "pyrocatechol".

Pyro was widely used from the late 1800s up until the 1920s. There are many reasons for the decline of pyro's popularity, not least its unreliability, toxicity, and tendency to oxidize rapidly. The discovery of more reliable agents such as metol, hydro-quinone, and p-amino-phenol presented the photographic industry with an easy choice: it could not have grown without these other agents.

Pyro and pyrocatechin are mythical developing agents in the jargon of black and white photographers. Pyro is the best known, possibly because it is the oldest developing agent still in use, possibly because of the recent popularity of PMK and, earlier, WD2D. WD2D and PMK were the first pyro developers for modern films based on extensive research and testing.

Properly formulated tanning developers, based on either pyro or pyrocatechin, produce gradation and sharpness effects no other developers can rival. Tanning also offers a potential chemical mechanism to improve the micro gradation of tabular films. As modern high-iodide films become more resistant to developer variations, tanning developers provide the most effective technique for subverting manufacturers' efforts to impose uniformity. We acknowledge the scientific and engineering brilliance of the

films that even out differences between developers. But we don't applaud it, as it decreases our artistic choices.

Pyrocatechin has never been popular in the US. Yet it is a more reliable developing agent, with many of the strengths claimed for pyro, without most of the weaknesses. But no important pyrocatechin formulas had been introduced in decades at the time of FDC1. That has changed.

What is tanning?

Tanning is the hardening of the film's emulsion, rendering it insoluble and difficult to damage.[1] Tanning hardens in proportion to the amount of silver deposited during development. This causes the film to dry at different rates, according to the image density. The result is an adjacency effect unique to tanning developers which increases sharpness.

A secondary effect of tanning developers is staining of the image with a permanent dye created by the reaction products. Although staining goes hand-in-hand with tanning, it is a separate phenomenon.

There are two types of staining by tanning developers. One is *proportional* to the density of the silver image. It provides extra density and contrast *without increasing grain*. The second is a *general stain*, unrelated to the image, which has to be printed through as if it were fog. Not all films accept stain to the same degree.[2] Although many developing agents will stain and tan film, the two most important are pyrogallol (pyro) and pyrocatechin.

QUICK GUIDE RECOMMENDATIONS

- The best tanning developers for modern films are PMK, Wimberley WD2D+ and Pyrocat-HC. All are available from Photographers' Formulary and other suppliers, or can be mixed from raw chemicals.

Developing agents which tan

R.B. Pontius investigated the tanning capabilities of several developing agents. ('The Action of Developers as Tanning Agents', Phot. Sci. & Tech., PSAJ., 19B (9):76 (1951)) He classified the agents as follows:

TANNING OF DEVELOPING AGENTS

Strong	Weak	Ineffective
Pyrogallol	Amidol	Glycin
Catechol (pyrocatechin)	Metol	*p*-Phenylenediamine
Hydroquinone	*p*-Aminophenol	Most *p*-Phenylenediamine derivatives
Aminocatechol	Ortol (n-methyl-*o*-aminophenol)	
Aminopyrogallol	Eikonogen	
Chlorocatechol	*o*-Aminophenol	
Chlorohydroquinone	Ascorbic acid	
Bromohydroquinone		

> *"With conventional developers, it is extremely difficult to render important atmospheric effects such as fog or mist convincingly in a print. Even prints from 8x10 negatives have a flat, slightly granular look. A stained pyro negative, because of the continuous tone effect of the stain, prints fog like a cool liquid—a seamless water-color effect that ba±es the senses, as real fog does."*
>
> —GORDON HUTCHINGS THE BOOK OF PYRO

Haist (515) has several unreferenced comments: Combining a developing agent with a compound that is a tanning agent which possibly has developing activity as well, may increase the effectiveness of the tanning development. Metol-pyrogallol or Metol-tannic acid developers were

especially effective in promoting a strong tanning development. Metolpyrogallol gives considerably greater speed than pyrogallol alone. Metol, a weak tanning agent alone, is an active developing agent whose oxidized forms can cause tanning development by an auxiliary agent which may not even be a developing agent, for example when combined with tannic or gallic acids. The addition of Phenidone to a pyrogallol or catechol developer appears to operate in a similar manner, considerably increasing the rate of tanning development.

Mason (170–172) points out that hydroquinone or glycin can reduce the tanning action of pyrogallol. Mason, citing Tull (J. Phot. Sci. 11, 1 (1963)) continues, "It has long been known that an oxidising stage after development enhances the tanning effect of those developing agents which exhibit tanning during development, but more recently it has been shown that this after-treatment produces tanning when certain developing agents were used which showed no tanning without the oxidation step." This has been termed "latent tanning" and is seen with the substituted paraphenylenediamines used in color development. "The best oxidising bath found was 10% potassium ferricyanide, a typical processing sequence being 2 minutes development, 1 minute wash, 1/2 minute oxidation, followed by a wash-off in warm water." The developer is normally simple, with high pH and little or no sulfite.

Printing with tanning developers

The yellow, yellow-green, or brown stain of a tanned negative has high printing contrast. A properly developed stained negative appears flatter than an unstained negative. According to Gordon Hutchings, a correctly developed pyro negative "will appear murky, low in contrast, have translucent highlights and in general, will seem unprintable."[2]

Because the color of the stain blocks blue light, to which enlarging papers are most sensitive, use the blue channel of a color densitometer for accurate

readings.

Tanned negatives work with graded paper like ordinary negatives. The dye density blocks light as effectively as silver. But, with variable contrast papers, dye density acts like a color mask that reduces printing contrast proportionately. The effect is greatest in the highlights.

Negatives with a high stain density have a reduced Callier effect. This minimizes (though it does not eliminate) the contrast differences between point source, condenser, and cold light enlarger heads.

Tanned negatives print with even higher density when the light source is ultraviolet, explaining their popularity with alternative historical printing processes which require a higher contrast negative.

> *"After years of printing conventional negatives we grow accustomed, perhaps unconsciously, to what can and cannot be successfully photographed and printed. Pyro will free the photographer to think and see in new ways. Its great sensitivity to minute differences in light values will capture subtle values and details not possible with conventional developers."*
>
> —GORDON HUTCHINGS

Before using a tanning developer

Test before using pyro or pyrocatechin developers with modern films. Unpredictable results can occur due to interactions between the developer and the hardening chemicals in the film or for other reasons.

For example, contemporary users of pyrocatechin and pyro sometimes notice a reticulation or mottling effect that cannot be eliminated by omitting the stop bath and substituting a water rinse. The effect is not seen with other low-salt, high-alkali developers such as Rodinal. The effect should disappear if distilled or deionized water is used for both development and in a water

bath prior to fixing. If your water is exceptionally hard, use distilled/deionized water even in the fixer. Tap water can be used for washing after fixing.[3]

Sulfite inhibits stain. For maximum stain, keep sulfite in the formula to the practical minimum. Kodak D-7, a pyro-metol formula, uses 14 grams of sulfite in the working solution, and produces no visible stain. Kodak SD-1 uses a mere 1.4 grams and creates substantial stain.

Since desirable stain continues to form after the development process, sulfite should be minimal even in post-processing. The fixer should contain little or no sulfite, and bisulfite stop baths should not be used. Hypo clearing agents, which contain sulfites, should not be used.

The stain effect can also be neutralized by the acids in typical stop baths and fixers. To maximize stain and adjacency effects, use a plain running water rinse for one minute in place of a stop bath, followed by an alkaline fixer low in sulfite (chapter 12).

Unless otherwise specified, pyro should always be mixed and used between 65F/18C and 70F/21C.

Both pyro and pyrocatechin stain skin. They may also be, according to Hutchings, the most toxic chemicals in the darkroom. However, he goes on to add that "a few drops of the chemical on the skin during safe processing procedures is no cause for concern."[2] Always wear gloves and a dust mask when mixing the dry powders, and *always* wear gloves when immersing your hands in the liquid solution.

Pyro

Pyro is one of the most fickle developing agents. It tends to produce low speed, high fog, poor grain, and stained fingers. The working solutions are unstable, and even the stock solutions have to be carefully formulated to obtain any useful life. Nonetheless, the romance of pyro, photography's

eldest developing agent, never seems to fade. Hardly a year passes without someone rediscovering an old pyro formula or inventing a new one.

Due to its unique tanning and staining action, pyro can provide acutance and gradation effects that no other developer can, except pyrocatechin. Its ability to separate nearly adjacent tones, particularly in the highlights, is legendary. To counteract speed loss and increase stability, pyro is often combined with metol in modern developers. This combination does not decrease pyro's desirable properties.

Tonal separation effects may be less with some modern films, particularly tabular films.

Pyro oxidizes quickly in all alkalis. For this reason stock solutions are often designed so the A part containing the pyro is acid. The alkali and sulfite are contained in the B, and sometimes a C, solution. The working solution is mixed immediately before use.

See the section 'Modern PPD Developers' in chapter 7 for discussion of some points raised by Crawley and Mason that are pertinent to better understanding high acutance developers such as many pyro and catechol developers.

All stock solutions of tanning developers lose some potency immediately after mixing. PMK is claimed to stabilize after a few days and to be reliable after many years of storage. The same should be true of WD2D. But for formulas like ABC, which don't contain a subsidiary agent, maximum film speed is achieved when it is freshly mixed.

Note: Most tanning developer formulas are given as stock solutions. It is possible to gain approximately a half stop of speed and eliminate some of

the inconsistency problems in old formulas such as ABC by mixing the formulas fresh each time as working solutions.

Developing with pyro

The most common problem experienced with pyro is aerial oxidation. Aerial oxidation is a general fog or veiling of parts of the negative exposed to air during development. There are many situations in which aerial fog can occur (e.g., adding formaldehyde to a developer for warm weather processing), but the most common in modern day practice, is premature exhaustion of the developing agent combined with exposure of the partially developed film to air before development is complete. This can occur with both tray and rotary processing.

Because pyro is a very energetic developing agent it rapidly exhausts in solution, which is why it is important to begin development as soon after mixing the working solution as possible. When the film is exposed to air during shu±ing, or during the rotation out of solution with a Jobo processor, aerial oxidation can occur.

Tray development with pyro

For tray processing develop a maximum of 4 sheets of 4x5-inch film in 1 liter of developing solution (or 6 sheets in 1200 ml). Shu±e through the negatives no more than once per minute, followed by a one-minute rocking cycle; lift one corner of the tray, lower it; lift the center, lower; lift the right corner; lower. Do not rush either the shu±ing or the rocking. Take as much time as needed. This method may require adjustment of the overall development time due to the reduced agitation.

Note: Add one negative to each shu±e count so that the bottom negative ends on top. For example, if you are developing 4 negatives, shu±e as if you

have 5, etc. Always wear protective gloves when tray developing with pyro.

> *The ideal way to tray-develop multiple sheets with pyro is to use a tray insert, p. 42, if you can find or make one. The tray insert keeps all sheets separated and since the entire insert is covered with developer, aerial oxidation cannot occur.*

Rotary processing with pyro

Rotary processing encourages aerial oxidation, which must be avoided when developing with pyro. One solution is to add 30% or more of the solution containing the pyro than called for by the formula. This will help ensure that the developing agent is not fully exhausted by the time the process is complete. You may need to adjust the development time due to the increase in both water and developing agent. Rotary processing is sub-optimal for all development processes where highly dilute or fragile developers are being used, and that applies to all tanning developers.

Tank development with pyro

For all films, develop no more than 160 $in.^2$ per liter. 80 $in.^2$ per liter is preferable. Modern pyro developers, like high definition developers, are low in developing agent and sulfite, so similar precautions apply. Pyro's instability makes the problem worse. For general tank recommendations see chapter 4.

WIMBERLEY WD2D

WIMBERLEY WD2D	
Metol	0.14 g
Sodium bisulfite	0.45 g
Pyrogallol	1.36
Sodium carbonate anh.	1.55 g
Benzotriazole	1.82 mg
Water to make 1 liter	
This is the 1977 version.	

Tank agitation with pyro

We agitate pyro developers once every minute for 10 seconds. Hutchings recommends two vigorous inversions every 15–20 seconds. If a particular film gives problems with pyro, try the Hutchings technique.

Modern pyro developers and PMK

Little postwar research was done on pyro in photography, except in relation to the Technicolor process. The first modern pyro developer for black and white was John Wimberley's WD2D formula, which created quite a stir when it was published in 1977. Key points are: low total quantity of developing agent; the insight that metol should be about a tenth the quantity of pyro; very low sulfite; some buffering of the carbonate with bisulfite. Two results are better speed and less grain than older formulas. It was revised in 2003 to remove the BZT, which allowed the quantities of developing agent to be reduced by about 30%.

WIMBERLEY WD2D +	

WIMBERLEY WD2D +	
Metol	0.1 g
Sodium bisulfite	0.3 g
Pyrogallol	1 g
Sodium carbonate mono	1.6 g
EDTA	0.7 g
Water to make 1 liter	

See Appendix 1 for stock solutions.

This is the 2003 revision, which brought the formula considerably closer to PMK; see Appendix 1 for stock solutions.

Meanwhile, Gordon Hutchings was working on a similar formula with a radical difference: he replaced the carbonate with metaborate. PMK was first published in 1991. However, it was not until the 1992 publication of *The Book of Pyro* that the pyro revival gained traction. We recommend *The Book of Pyro* to everyone interested in working with pyro.[2] As can be seen by comparing the working solution formulas to the right, PMK is very similar to WD2D+; the important difference is in the choice of alkali.

In formulating PMK Hutchings had four main goals: batch-to-batch reliability, full emulsion speed, maximum image stain, and minimum general stain.

The PMK formula has several interesting points:

- No restrainer. Nearly all previous pyro developers contain a restrainer to reduce fog. Restrainer may impair sharpness and speed, and indicates too high a pH, which in turn can drive fog up.
- Lower pH. Virtually all previous pyro developers relied on unbuffered or slightly buffered carbonate to produce a high pH and a rapid development time. This sometimes caused fog and general stain rather than image-specific stain. PMK uses sodium metaborate (Kodalk) for a pH of 9.6, approximately one unit less than earlier pyro developers. The

results are reduced fog and graininess, enhanced stability, and enhanced image-specific stain.

- The amount of developing agent is correct to maximize image-specific stain, minimize general stain, maintain the film's inherent granularity, and enhance sharpness through controlled exhaustion/adjacency effects. (PMK has approximately the same total weight of developing agent as FX 2—see chapter 6).

PMK	
Metol	0.1 g
Sodium sulfite anydrous	0.2 g
Pyrogallol	1g
Sodium metaborate	6 g
Water to make 1 liter	

See Appendix 1 for stock solutions.

PMK is stable in two different ways: the stock solutions are stable because of careful formulation; the working solution is more stable than most other pyro formulas because the pH is lower, one result of Hutchings's choice to use Kodalk rather than carbonate as the main alkali. We point out that a carbonate-bicarbonate buffer to the same pH would have the same effect on stability. Generally speaking, many of the observations here regarding PMK can be applied to WD2D+. In spite of the exceptional stability of these stock solutions, Gordon Hutchings told me in 2019 that he now prefers to mix PMK from powder just before developing. This confirms what Steve Anchell and a few others have always said, that despite the convenience of stock solutions, nothing beats a pyro developer mixed fresh just before using. A small speed increase is usually recorded, but I think there may be other advantages, harder to qualify.

Using PMK

The stock solutions for PMK are given in Appendix 1. The standard dilution is 1 part A, 2 parts B, 100 parts water. Though many photographers regard this (or any other) dilution as written in stone, it is not, and Hutchings advises creatively altering the dilutions as necessary to meet special circumstances. PMK should be used immediately after mixing the working solution. Right after mixing, the solution should change color from grey green to pale amber. If this does not happen, the solutions may not have been correctly mixed, or may have become contaminated.

Temperature

Hutchings has given much study to temperature differences. His standard times are for 70F/21C. He states that with PMK, development time should be decreased by about 4% for each degree the temperature is raised. We prefer not to process film above 75F/24C.

PMK and Jobo processors

Jobo processors have two problems when it comes to PMK: (a) the revolution rate is too high; and (b) the motor is too weak to rotate when the drum is filled to capacity with developer, as it should be with PMK. The result with a partially-filled drum is excessive oxidation of the developer, which can "bomb out" prematurely. There are two techniques for dealing with these deficiencies: (1) add 0.3 g/L of sodium sulfite (about a pinch) to each liter of PMK working solution; or, better, (2) use 30% more of stock solution A when making up the working solution. We recommend the

second technique. Later in this chapter we discuss developers which are intended specifically for Jobo processors. However, two facts stand in the way: (1) pyro is an agent which is particularly subject to aerial oxidation; (2) roller processing is a technique which exposes films to a lot of air.

Pyro post processing

Hutchings recommends fixing PMK negatives in TF-4 alkaline fixer. Directly after fixing, Hutchings advises a two-minute alkaline after-bath to induce further stain formation. This after-bath can consist either of the used developer (which can be used for this purpose, but not to develop further films), or a 2% solution of sodium metaborate. Agitate every 30 seconds.

The negatives are now ready to be washed. Hutchings advises a full 20–30 minute wash, to intensify the pyro stain still further. However, even though tanned negatives are hardened, we think this step may allow too much swelling, depending on how highly the film was hardened during manufacture. Hutchings recommends filtered water for washing especially of smaller negatives.

Classic pyro developers

Several older pyro developers are worth examining. Each imparts its own unique "look" to negatives. Although they do not have the reliability, speed, and high image-specific stain/low general stain characteristics of PMK and WD2D+, they have stood the test of time. The main feature of the pre-PMK pyro developers is the use of carbonate rather than metaborate, a complex issue we discuss in more detail at the end of this chapter.

ABC PYRO WORKING SOLUTIONS			
	1:1:1:7	**1:1:1:71:1**	**1:1:1:14**

ABC PYRO WORKING SOLUTIONS	1:1:1:7	1:1:1:71:1	1:1:1:14
Water at room temperature	750	750	750 ml
Sodium sulfite anhydrous	11.5	8.2	6.6 g
Pyro	6	4.3	3.5 g
Potassium bromide, 10%	10	7	6g
Sodium carbonate monohydrate	9.0	6.5	5.2 g
Water to make 1 liter			
See Appendix I for stock solutions and the Edward Weston variation.			

See Appendix 1, p. 166, for the Edward Weston dilution, and our philosophy of dilution.

Kodak D-1 (ABC Pyro)

The classic pyro formula, Kodak D-1, which dates to the 19th century, is the oldest published developer formula still being used. It is known as "ABC" because it has three stock solutions. There are several minor ABC variations (Ansco 45 and Defender 1-D), and different opinions as to the best ratio of the three solutions.

ABC still works well with modern films though, in a break with tradition, we recommend using the 1:1:1:11 dilution for tray development with times between 6 to 10 minutes at 68F/20C, and the 1:1:1:14 dilution for tank development with times between 8 to 12 minutes at 68F/20C.

KODAK SD-1

KODAK SD-1	
Water (68F/20C)	750 ml
Sodium sulfite anhydrous	1.4 g
Pyrogallol	2.8 g
Sodium carbonate monohydrate	6.2 g
Water to make 1 liter	
Develop 5 to 10 minutes at 68F/20C	

Kodak SD-1

In the 1930s Kodak designed SD-1 to provide maximum image-specific stain while minimizing general stain with the films of the day. Like PMK, SD-1 does not use a restrainer. The formula is published as a working solution. Post process as for PMK. According to Hutchings, this developer as published has low energy, resulting in a low EI, and a very flat characteristic curve (which might be useful for very long scale subjects). For modern films we suggest diluting 1:3 but doubling the carbonate—which brings SD-1 closer to Bürki's formula, below.

BÜRKI'S PYRO DEVELOPER	
Pyrogallol	0.75 g
Sodium sulfite anhydrous	0.75 g
Sodium carbonate monohydrate	24 g
Water to make 1 liter	
Develop 6 to 7 minutes at 68F/20C.	
See Appendix 1 for stock solutions	

Bürki's pyro developer

This developer was published in the 1950 *American Annual of Photography* and probably earlier in Europe. It is one of the few formulas, before FX 1 in 1960, or the 1945 Fox developer (p. 73) to have specified less than 1 g/L of total developing agent.

Since the amounts of sulfite and pyro are so low, a very large amount of carbonate is required. The lack of restrainer is notable in a pyro developer of this vintage. It produces a high degree of stain, high sharpness, and moderate speed. We suggest adding 0.1 g/L of metol or 1/20th that much phenidone to help stabilize this formula and increase speed, and halving the carbonate for modern films. Another possible modification would be to buffer with bicarbonate. Of all the known pyro-only formulas, this is the one most likely to work well with modern films. Post process as for PMK. It is essential not to use an acid stop bath with a developer that contains so much carbonate.

PYROCATECHIN (CATECHOL)

Pyrocatechin stains and tans as well as pyro. It is generally considered to be more stable and reliable. It was said to be used, at some point, in Neofin Blue (chapter 6), and is still used today in HC-110 though not for its staining properties. As a developing agent pyrocatechin has been more widely used in Germany than the US or UK.

Below we describe the one historic pyrocatechin developer that was still in use at the time of FDC1. We follow with our own suggestions for pyrocatechin developers, slightly modified from FDC1. Then we discuss some post-PMK tanning developers. Sandy King's contemporary work with pyrocatechin is described in the section after that.

> *This formula is listed in some BJP Annuals as a high acutance developer with the ba±ing title "Windisch Pyrocatechin Developer (USA)", although Windisch was a German who first published the formula in German. For many decades it was the only developer formula that would allow the successful photography of scenes with a brightness range greater than 10 stops.*

The Windisch developer

The reputation of pyrocatechin in the US and UK was based for years on the compensating formula published by Hans Windisch in the 1930s. This developer was championed by Ansel Adams in various editions of *The*

Negative,[4] but was never printed even approximately correctly in that book until the last printing of the last edition.

The Windisch developer has been claimed over the years to have an extraordinary compensating action, suitable for photography of very wide range subjects, such as a bare bulb filament. It is worth noting that, despite these claims, this developer has never been taken seriously in the technical literature, and is not mentioned in Levy's[5] or Shepp and Kammerer's[6] surveys of low contrast developers.

There are several reasons for this. First of all, pyrocatechin, closely related to hydroquinone, is known to be a high contrast developing agent. Second, it is a tanning developer—the density-increasing stain increases contrast further. Therefore, on the face of it, pyrocatechin is a high contrast developer, and has been specified for this purpose in formularies by Agfa, a company which knew a thing or two about developers.

WINDISCH COMPENSATING DEVELOPER

	DIL. A	DIL. B
Sodium sulfite anhydrous	0.3	0.5 g
Pyrocatechin	2	3.2 g
Sodium hydroxide, 10% solution	15	10 ml
Water to make 1 liter		
Develop 12-15 minutes at 68F/20C		
Windisch published two dilutions for this developer. We prefer dilution A; Ansel Adams preferred dilution B. See Appendix I for the stock solutions.		

On the other hand, it appears that, with the correct formulation, even a high contrast developing agent can be made to perform as an effective low contrast developer (chapter 3).

We believe that the Windisch developer is too alkaline for modern films, tending to create unnecessary fog; we also suspect that a high degree of

fogging may be partly responsible for its reputation as a low contrast developer to begin with. Maxim Muir published a variant which uses carbonate instead of hydroxide, which drastically changes the working properties of this developer (Appendix I). We have long believed that carbonate is the most rational alkali to use with pyrocatechin and modern films. A developer formula should not have to depend on fog to create low contrast.

Ideal post-processing for pyrocatechin is the same as for pyro: a one minute running water stop, followed by an alkaline fixer.

The Photographers' Formulary Modified Windisch formula reverses the proportions of sulfite and pyrocatechin in dilution A. It produces a low contrast, high definition developer with heavy stain and some fog. Negatives look very dense, but are printable without excessive grain, and the results can be very appealing. Use distilled water.

Caution: read Appendix III before using sodium hydroxide.

TD experimental pyrocatechin formulas

The experimental formulas below, which are disclosed for non-commercial use only, may be useful starting points for those who wish to find an ideal modern pyrocatechin developing formula. According to traditional research, pyrocatechin, like pyrogallol, should not be used with borate alkalis, a finding which is more true for pyrocatechin than for pyro, see p. 112. Pyrocatechin is believed to be subadditive with metol, and is seldom used in combination with any other developing agent.

TD EXPERIMENTAL PYROCATECHIN FORMULAS

	TD-101	TD-102	TD-103
Sodium sulfite anhydrous	4	1	1
Pyrocatechin	0.5	2	0.25

TD EXPERIMENTAL PYROCATECHIN FORMULAS			
	TD-101	**TD-102**	**TD-103**
Sodium carbonate anhydrous	14	10	15-20
Distilled water to make 1 liter. All weights in grams. Multiply to make stock solutions.			
Develop for 10-15 minutes at 68F/28C; prefer distilled water			

TD-101 is a normal to low contrast high definition developer. TD-102 produces high contrast without excessive grain because much of the highlight density comes from stain, not silver density. TD-103 is designed for very low contrast and can be used with document films.

Reducing the sulfite in any of these formulas to a half or even a quarter of the amounts specified will increase the tanning and sharpness, but may also decrease speed.

All these formulas have the grain structure typical of carbonate high definition developers. This could be moderated by buffering with one gram of sodium bicarbonate for every two grams of sodium carbonate. However, the lower alkalinity will result in longer development times and may necessitate adding more pyrocatechin to compensate.

These experimental formulas can easily be made up into stock solutions. To make stock solution A, simply multiply the amounts of sodium sulfite and pyrocatechin by 10 and add to one liter of water.

Although pyrocatechin is a highly toxic chemical in large amounts, Japanese researchers have found that the minute amounts of catechin and related chemicals that are naturally present in green tea appear to have anti-mutagenic and anti-carcinogenic effects. Pyrocatechin is also a constituent of human urine. How and why the human body manufactures pyrocatechin is something we will leave to future

generations of scientists—or theologians. At the time of writing, there was no shortage: 20 million kg of pyrocatechin are produced annually for a wide variety of non-photographic uses. Incidentally, pyrogallol was found to be a good preservative for fats in foods and cosmetics in the 1940s. A related compound, propyl gallate, is still widely used for those purposes today.

Working solution will be 100 ml to a liter of water. To make stock solution B, make up a 10% sodium carbonate solution: 100 grams of sodium carbonate to a liter of water. Use 10 ml for every gram of sodium carbonate you want in the working solution. For instance, to get 14 grams of sodium carbonate per liter of working solution, use 140 ml. These stock solutions should keep for at least six months but, as with all stock solutions, should be used as soon as possible. The keeping qualities of the A stock solutions can be improved by using sodium bisulfite instead of sodium sulfite. This will create a small amount of bicarbonate buffer when the two stock solutions are combined to make the working solution.

As with all developers containing pyrogallol or pyrocatechin, use distilled or deionized water for the stock and working solutions to avoid mottling. Post process as for pyro developers.

In light of what we have learned about Crawley's more advanced buffer systems as used, for example, in Acuspecial (chapter 6), we emphasize the advice we gave above, to try buffering the carbonate. We might also suggest adding a tiny amount of potassium iodide. **N.B**. These two suggestions are primarily for conventional grain films. They would be less likely to have a large effect on tabular or mixed grain high-iodide films. And we emphatically note that it is possible to prefer the behavior of the unbuffered developer, depending on what ultimate image characteristics work best for the picture.

Post-PMK pyrogallol and pyrocatechin developers

Since the publication of PMK and FDC1 which provided guidelines for possible future developments, there have been several tanning developers of note. Interestingly, the goal of many of the developers has been to improve the performance of staining developers in rotary processors. Because of the sub-optimal way rotary processers agitate (rotary rather than vertical; continuous rather than intermittent; small total developer volume; excessive exposure to air), it was found that many highly dilute developers, especially tanning developers, showed artefacts such as uneven development, excessive general stain, streaking, premature oxidation, and aerial fog. Nevertheless, we appreciate that there are those who are wedded to rotary. The developers designed for rotary processing are worth trying for conventional processing as well.

Max Pyro

In 2008, Hutchings introduced this proprietary developer, an evolution of PMK, for Bostick & Sullivan. It is said to be ideal for first-time users, to offer good film speed, fast development times, and absence of streaking.

Rollo pyro

Harald Laban's popular ABC+, generally called Rollo Pyro (see DCB4 for the formula), appears to have been the first staining developer formulated specifically to address the problems of rotary processing with pyro. It is an evolution of PMK, adding ascorbic acid, EDTA and bromide to the pyro-metol mix, and retaining the metaborate alkality that is one of the fingerprint characteristics of PMK development.

In addition to Rollo Pyro, Harald Leban has more recently formulated a developer called Beutler Pyro.

DiXactol

This commercial formula by Barry Thornton has many admirers. It utilizes the pyrocatechin/glycin combination which Crawley had experimentally found to be potentially valuable (Crawley 60/61). Other ingredients include sulfite, bromide, and potassium hydroxide. The presence of potassium bromide suggests that the formula is too alkaline.

For those interested in pursuing the pyrocatchin/glycin combination on their own, we suggest carbonate instead of hydroxide, possibly buffered with bicarbonate or citrate or both.

Sandy King's pyrocatechin developers

In the history of tanning developers, the predominant technique has been to use a single developing agent. The main exception has been a line of pyro-metol developers starting well over 100 years ago.

However, there has been little use of pyrocatechin with other developing agents. There has also been little use of Phenidone with tanning developers, though Russian research in the 1960s showed that Phenidone may "accelerate the tanning by hydroquinone or catechol [pyrocatechin]." (Mason 171; hydroquine, in low-sulfite solutions, is also a tanning agent, though the effect is not as pronounced.)

Inspired in part by FDC1—we are grateful for his acknowledgement—Sandy King took a logical next step by combining pyrocatechin with Phenidone. The result has been a popular family of developers. The original Pyrocat-HD is still the most widely used, but King's experiments with pyrocatechin and several other chemicals are worth investigating.

> *The combination of pyrocatechin and metol has been observed to be sub-additive. But that doesn't mean it is necssarily a poor choice for development, only that it is an expensive one. Subadditive combinations may provide new avenues for shaping the characteristic curve.*

Going further with the King developers

The most successful of the King developers is the first, and this is because Phenidone is known to aid tanning in pyrocatechin and probably is the most effective agent to do so. How could this developer be improved or evolved? Our suggestion is, just as it is for the simple pyrocatechin/carbonate developers we proposed earlier, further buffering, taking suggestions from the working solution of Acuspecial (chapter 6). The slight lowering of the pH by buffering would probably remove the need for the bromide. We would also suggest replacing the Phenidone with Dimezone-S, but because Part A is slightly acid, Phenidone should be reasonably stable in it.

PYROCAT-HD	
Part A	
Distilled water (68F/20C)	750 ml
Sodium metabisulfite	10g
Pyrocatechin	50 g

PYROCAT-HD	
Phenidone	2g
Potassium bromide	1g
Distilled water to make 1 liter	
King gives alternate directions for Part A where the water is replaced by propylene glycol, resulting in a stock solution of great longevity.	
Part B	
Distilled water	750 ml
Potassium carbonate	750 g
Distilled water to make 1 liter	
Working solution: 1A + 1 B + 100 water.	
Extensive instructions and suggestions for working with this developer are available in the article'An Introduction to Pyro Staining Developers' available at www.sandykingphotography.com	

Sulfite-less formulas to go forwards?

An interesting recent pyro formula is Hutchings's 'Simple Pyro' published in DCB4. This refers to a 1960s Paul Farber formula which contains only pyrogallol, TEA and water. TEA has also been used by Jay de Fehr, in 510-Pyro, another sulfiteless developer. His Hypercat developer, employing pyrogallol, Phenidone, and ascorbic acid, likewise contains no sulfite.

While tanning and staining should theoretically be at their maximum possible with sulfite-less developers, this is not a line of development we promote. We think tanning developers should contain a small amount of sulfite.

We also note the appeal of TEA as a stable alkali and chemical solvent, but we don't like its silver solvent effect on

> *According to Sandy King, the problems encountered when using pyrogallol in roller processing can be substantially alleviated but not eliminated when using Rollo Pyro. In his view, streaking and pressure marks can only be eliminated by switching to pyrocate-chin as principal tanning developing agent. Many advantages are recorded, including higher speed. Pyrocat-HD's resistance to streaking problems is so high that it has been found possible to use it with the minimal agitation and stand techniques that were previously recommended mainly for FX 2.*

film. HC-110 is the outstandingly successful developer based on ethanolamines precisely because it employs an effective "antistain agent" (chapters 4 and 6).

Or have we already got the ideal tanning formulas?

We used to think the ideal pyrogallol formula would look like PMK, except replacing the Kodalk with a carbonate/bicarbonate buffer. However, Hutchings experimented with many ratios of such a buffer. But he never found he could reach the image quality of PMK, perhaps for the reasons discussed in the next, last section.

So what could possibly improve PMK? Pyro-phenidone, or pyrometol-phenidone, could theoretically enhance tanning via several different modalities, and might permit a lower pH. However, we doubt a better pyro formula than PMK will be appearing anytime soon.

Pyrocatechin is the most stable of the common tanning developing agents. We think Pyrocat-HD is a rational and valuable evolution of the more traditional simple pyrocatechin/carbonate developers we have advocated for in the past.

Pyro, pyrocatechin, and borates

PMK was the first developer employing either pyrogallol or pyrocate-chin, to use a borate alkali. The reason for this is that the technical literature warns about this combination, which was known to be problematic by the beginning of the 20th century.

Haist (244) states, "… Borates … should not be used with developing agents having two hydroxy groups ortho to each other, as in catechol or pyrogallol. Borates react with o-dihydroxybenzene compounds to produce a reaction product that has very low developing action."

Mason (34) states, "Developers based on borates often give results which differ greatly in many respects from developers of the same pH based on other buffer systems. Most of these differences can be attributed to the ability of the borate ion to form stable molecular complexes with compounds containing hydroxyl groups on adjacent carbon atoms. Thus catechol and pyrogallol or certain of their derivatives should not be used in developers based on borates."

A little more detail may be helpful to those who may be formulating with these developing agents in the future.

Borates can chelate with catechol to such an extent that the developing agent is unavailable. However, whether the chelation is complete or not depends on conditions and pH. The chelation is greater the lower the pH. (R. Pizer & L. Babcock, Inorg. Chem. 1977, 16, p. 1677.) Because catechol has 2 OH groups but pyrogallol has 3 OH groups, with pyro there will still be one group that will not be chelated and so can act.

PMK has been a popular and influential developer for almost 30 years. It illustrates how breaking the rules can lead to success. The unique kinetics of PMK come from the way borate alkali may *partly* disable pyro's activity. Because this chelation is pH dependent, local rises in pH may restrain highlight development, which may help *partly* explain PMK's unique highlight handling.

However, we would not try a borate with pyrocatechin.

NOTES

1. L.F.A. Mason, *Photographic Processing Chemistry*, Focal Press, Boston & London, 1974.

2. Hutchings. Our thanks to the author for permission to quote from *The Book of Pyro.*

3. Grant Haist has speculated both to BT and Gordon Hutchings that the relatively open molecular structure of both pyro and pyrocatechin allows these chemicals to react readily with water impurities—much more than other common developing agents do. This theory is supported by the observations of BT and Hutchings that the use of distilled or deionized water with either pyro or pyrocate-chin seems to eliminate the problem.

4. Adams, *The Negative.*

5. Marilyn Levy, "Wide Latitude Photography", *Phot. Sci. and Eng.*, 11: 46 (1967).

6. A. Shepp and W. Kammerer, "Increased Detectivity by Low Gamma Processing", *Phot. Sci. and Eng.*, 14: 363 (1970).

Chapter 9
SPECIAL DEVELOPERS

This chapter covers several developer types that do not readily fit into our other categories: two-bath, water bath, high and low contrast, and ascorbic acid developers.

TWO-BATH DEVELOPERS

Two-bath developers give excellent results with almost all films at a fixed time and temperature. It is almost impossible to overdevelop with two-baths, and it takes an effort to underdevelop. They are ideal for photographers who want quality negatives but are not interested in obsessing about developers.

Although Zone-style control is not possible with two-baths, this is not a real limitation with modern films.

In two-bath developers, the A bath contains the developing agent *with no alkali except sulfite*, so minimal development takes place. The film is immersed in this bath primarily to absorb the developing agent.

The B bath contains the alkali activator. In the B bath the developer is quickly exhausted in the highlights, making overdevelopment difficult. This also improves shadow contrast and increases definition. Agitation may be continuous without impairing image quality, ensuring even development with no streaking, mottling, or air bubbles. Two-baths are thus a tenable choice for Jobo rotary processors. However, as noted in chapter 4, it is exceedingly important to break up the directional flow during agitation, particularly during continuous agitation.

Two-baths can be used for virtually all films except document films. Since time is fixed, development is automatic, typically resulting in:

> *It would not be impossible to design a two-bath specifically for document films, but we don't know of any and are inclined to think such a developer would be problematical.*

- normal emulsion speed, or slightly higher

- good acutance with moderately fine grain
- long scale gradation, with some highlight compensation, allowing high contrast scenes to be photographed without special adjustments
- good economy

Storage and capacity of two-baths

The stock solutions of most two-baths will keep for 6 months in tightly sealed bottles. Solution A can be used for up to 20 films. The inexpensive, replaceable Solution B should only be used for 10 rolls of film. After 10 rolls, discard and make a fresh solution. Unlike re-used or replenished single bath developers, there is almost no compromise in quality when the two-bath is reused.

Low contrast scenes

Although two-bath developers are not ideal for very low contrast scenes, moderately low contrast scenes can be printed on a high grade of paper. In any case, extended development, which was routine in the early days of the Zone System, fails with modern films. Today, expansion (i.e. high contrast) is best obtained by using a special high contrast developer (see below).

> *"My approach to a sea shell is exactly the same as to a human being or to a leaf. I see everything as being connected."*
>
> —RUTH BERNHARD

D-23 two-bath developers

Many two-bath developers use a Solution A similar to D-23, along with a plain alkaline Solution B. A potential problem with plain alkali B baths is that they contain no preservative to prevent staining or streaking, and no salt to prevent film swelling, which should be avoided whenever possible. Adding 50 g/L of sulfite will solve both problems. However, if you want to use less sulfite to improve acutance, add only 5 to 10 g/L of sulfite plus 40 g/L of sodium sulf*ate* to decrease swelling.

The table below lists some of the D-23-type two-baths, and our own versions, TD-200, and TD-201, which is particularly recommended for tabular films.

Note: In the Dalzell modification of the Stoeckler developer, sulfite has been reduced to 75 grams to increase sharpness. In this developer do not add additional sulfite to the second bath.

Experiment: To increase the fine grain effect of the two-baths below, add about 30 g/L of sodium chloride (common salt, but use a laboratory grade) to the A solution—or to both. The result would be something like a two-bath version of Microdol, which would eliminate the need for sodium sulfate in the second bath. The two-bath formulation and relatively short developing time might solve some of the problems encountered with Microdol-X over the years.

Directions for all two-baths

Do not presoak. Temperature may be between 65F/18C to 75F/24C.

1. Pour Solution A into the tank.
2. Agitate continuously for 3 minutes.
3. Pour Solution A back into its storage container.

Note: Do not rinse between solution A and B. This would wash out the developing agent.

4. Pour Solution B into the tank.
5. Agitate continuously for 3 minutes.
6. Pour Solution B back into its storage container.
7. Stop or rinse, fix, and wash the film.[1]

D-23 TWO-BATHS:	STOECKLER	DALZELL	ADAMS	LEITZ	TD-200	TD-201
Solution A (quantities in grams)						
Metol	5	5	5	5	3	5
Sodium sulfite anhydrous	100	75	100	100	100	100
Water to make 1 liter						
Solution B						
Borax	10	10	-	-	-	2
Sodium metaborate	-	-	10	-	-	5
Sodium carbonate anhydrous	-	-	-	15	10	-
Sodium bicarbonate	-	-	-	-	3	-
Sodium sulfite anhydrous	-	-	-	-	6	6
Sodium sulfate	-	-	-	-	40	40
Water to make 1 liter						

VESTAL'S DIVIDED D-76

VESTAL'S DIVIDED D-76	
Solution A	
Metol	2g
Sodium sulfite anhydrous	50 g
Hydroquinone	5g
Water to make 1 liter	
Solution B	
Borax	2g
Sodium sulfite anhydrous	50 g
Water to make 1 liter	

Divided D-76

The problems of swelling and preservation in the second bath were recognized in 1933 by Russell in his two SD developers (below). A modern developer where this problem was solved (by accident) is David Vestal's version of divided D-76. He couldn't remember if the sulfite should go in the A or the B bath, so he split it evenly between them.

Many other two-bath versions of D-76 have been published, but we think Vestal's is the best. We suggest omitting the hydroquinone, boosting the metol to 3 grams and the borax to 5 grams. Directions are the same for other two-baths except that Vestal recommends 5 minutes in each bath instead of the usual 3, for most films—but upping the borax as we suggest should solve that problem.

A popular variant by R.J. Starks is usually called Farber's split D-76 after the writer who made it popular. The reason we prefer Vestal's formula is that the alkali in Farber's formula is too high, requiring the addition of bromide to solution A. The point of D-76 is that it has been carefully balanced so as not to require bromide. This formula could be improved by halving the amount of borax and omitting the bromide. An article on this

developer by Neil Lipson was published in *Darkroom and Creative Camera Techniques*, Nov/Dec 1988.

FARBER'S SPLIT D-76	
Solution A	
Metol	2g
Sodium sulfite anhydrous	100g
Hydroquinone	5g
Potassium bromide	1g
Water to make 1 liter	
Solution B	
Borax	60 g
Water to make 1 liter	
Develop 3 minutes in Bath A followed by 2-4 minutes in bath B.	

Kodak SD-4 and SD-5

H.D. Russell introduced two excellent formulas in the 1930s that never received the attention they deserved, Kodak SD-4 and SD-5. The sugar in these formulas was added to suppress development in the A Bath.

Two modern variations, TD-144 and 145, are an attempt to provide subtle improvements in image quality. TD-145 produces slightly higher sharpness, with slightly coarser grain than TD-144. However, the practical differences between the two developers are small.

	SD-5	TD-145	SD-4	TD-144
Solution A (quantities in grams)				
Metol	7	5	5	5
Sodium sulfite	10	10	100	100

	SD-5	TD-145	SD-4	TD-144
Hydroquinone	-	-	2	-
Sodium bisulfite	2	6	5	5
Granulated sugar	100	100	100	100
Solution B				
Sodium carbonate	10	14	14	10.0
Sodium sulfite	25	100	100	10
Sodium sulfate	-	-	-	40
Potassium. iodide	-	0.01	0.01	0.01
Potassium bromide	-	-	0.5	-
Water to make 1 liter	-	-	-	-

Sugar may well have suppressed development in SD-4 and 5 with the films of the 1930s. Whether this would happen with contemporary films, we do not know. We also don't know how valuable the effect is.

Nearly all two-bath developers are based on metol—testament to this most generally useful developing agent. One exception to prove the rule is Harold Baumann's Diafine, a two-bath which had limited popularity in the 2nd half of the 20th century. It was generally considered inferior to Acufine. Diafine was a high-sulfite PQ developer with two unusual ingredients: trisodium phosphate as the primary alkali, and citric acid as, we would guess, a phenidone preservative in the first solution. It is possible to create two-baths based on phenidone. An advantage is that the A solution pH could be neutral to slightly acid, enhancing phenidone's stability in solution. As a starting point, create a Solution A from your favorite phenidone developer, but don't include the alkali,

and do replace some of the sulfite with bisulfite. For Solution B, you will need a multiple of the alkali. The kinetics of MQ and PQ development are quite different. Phenidone's fast induction period may cause too much development to occur in the first bath unless pH is carefully controlled.

Water bath developers

Water bath development is a cousin to two-bath development. Generally, film is immersed in the developer for two or three minutes, then in plain water and left motionless for two or three minutes. These steps are usually repeated several times. Ansel Adams used a water bath for his famous 1936 picture *Moonrise Over Hernandez*, but later repudiated the technique for contemporary films because it causes streaking.[1]

Nevertheless, it is possible that the streaking problem could be cured, just as it was for two-bath developers, by using a 3% sodium sulfite solution instead of plain water for the "water" bath. There will be somewhat less compensation as a result, but this is of minor importance, considering that streaking ruins the negatives completely. It is important to transfer the film between the developer and water solutions as quickly as possible to avoid aerial fog. A glycin developer might work well for this process, perhaps double-strength FX 2.

Although we have suggested a way to make water bath development work with modern films, we agree, on balance, with Adams, that it is no longer a viable technique.

N.B. We recommend a running water bath for 1 minute in place of an acid stop bath (chapter 12). This is in effect a very mild form of water bath development. It does not cause streaking, because the time in the water bath is short, because the developer/water bath cycle is not repeated, and because it occurs *late* in the development process, when streaking is unlikely to occur. (In chapter 4 we reference Zawadzki's hitherto unpublished

observation that visible defects due to uneven development will typically occur in the first 30 to 60 seconds of development, and will magnify as development proceeds.)

LOW AND HIGH CONTRAST DEVELOPERS

Low and high contrast development was a cornerstone of photographic technique from the 1930s to the 1960s (N– and N+ in ZoneSpeak). It was particularly important to Zone System photographers who often recorded high contrast landscape scenes. But with today's films, low and high contrast development is hard to achieve, and Zone System photographers now rely more on multiple grades of paper than they did in the past. In the foundational days of the Zone System, effective and consistent graded papers were hard to find, and good variable contrast papers were not yet available. There were practical reasons to produce negatives that would print on the normal contrast papers of the day.

Until the late 1970s, most quality photographic papers only came in two or three grades, and variable contrast papers were not highly thought of by experienced printers (with the glorious exception of DuPont Varigam, which was discontinued in the early 1970s.)

Today, the Zone System idea of arriving at the perfect negative that will print on Grade 2 paper is not a practical necessity but a philosophical choice. However, the problem remains for those employing alternate process printing

Low and high contrast development lives on in the maxim "Expose for the shadows, develop for the highlights." This does not work as well as it used to, because with modern films, you cannot change the way highlights develop without changing the way shadows develop. That was probably true of older films as well. The maxim dates from a period when sensitometry was inexact.

Depending on how flexible both the film and the developer are, you can usually change contrast by at least a "zone" (one stop) in either direction, by

changing development time. Diluting the developer with more water for lower contrast, or with less water for higher contrast, is also effective. While changing development time will change contrast, it will also usually change *speed.*

> *A system for two bath development using Pyrocat-HD (chapter 8) has been proposed by Sandy King. See "Two-Bath Development with Pyrocat: A Simplified Methodology of Exposure and Development of Black & White Film for a Digital Work-Flow", August 2014 (use google to find). This system is geared to a workflow where negatives will be scanned and digitally printed, but it could perfectly well be used with graded or MC paper as well. Bypassing the complexities of the Zone Systems, King takes an incident meter reading in the darkest area where shadow detail is desired. Films are then developed for five minutes in each bath. Solutions A and B are diluted 1+15. Contrast is adjusted during the digital workflow. Or, as we suggest, in an all-analogue workflow, by choice of paper grade. King points out that definition will be highest and grain lowest when all films are developed to a fairly low contrast. King suggests that with two-bath development, presoaking for three minutes may be desirable with modern ultra-hardened films, to aid absorption of the first solution of a two-bath.*

What constitutes a low or high contrast developer?

The first component to consider is the developing agent. All developers oxidize (exhaust or decompose) as they are used. As they do, reaction (oxidation) products are formed. These oxidation products are not neutral in effect. They can either accelerate or decelerate development. This has a

marked effect on contrast, because the effect is *not* just one of faster or slower development.

Oxidation products are formed most in areas where there is much exposed silver—the highlights, and less in areas where there is little exposed silver—the shadows. If the oxidation products *accelerate* development, contrast will be *increased*, because the rate of development in the highlight areas will be increased, while the rate of development in the shadows remains normal. But if the oxidation products *decelerate* development, contrast will be *decreased*, because the rate of development in the highlights is decreased, while development in the shadows again remains normal.

The oxidation products of metol, Phenidone, and the PPD family decelerate the rate of development. The oxidation products of most other developers accelerate the rate of development. The situation can get complicated when you combine developing agents.

Formulating low contrast developers

The first thing to do when formulating a low contrast developer is to select one of the agents whose reaction products decelerate development. The next is to formulate the developer so that a controlled amount of oxidation takes place during development. There are three ways of doing this:

- lowering the concentration of the developing agent
- lowering the concentration of the preservative
- a combination of both approaches

To achieve a dramatic effect, use a specially formulated low contrast developer. A good starting point for those interested in experimenting with low contrast developers would be T/O XDR-4 and the other developers in chapter 11.

Agitation technique for low contrast developers is critical. Agitate little, so exhaustion products around the highlights will have a chance to

accumulate. We recommend ten seconds every two or three minutes, after continuously agitating for the first minute (chapter 4). Ideally, developing time should be at least 12 minutes. Minimal agitation is not appropriate for development times under 8 minutes.

> *One of the best tricks for increasing contrast through development is to use a carefully formulated, reasonably fog-free staining developer. Staining should be proportional to density: The greater the density, the more the stain. Such developers often increase contrast dramatically, without increasing silver density or apparent graininess. A suitable agent is pyrocatechin. The TD-102 formula in Chapter 8 is a good starting point. Alternatively increase only the amount of developing agents in PMK or Pyrocat-HD.*

Formulating high contrast developers

Formulating high contrast developers is similar to formulating low contrast developers, except that you choose a developing agent where the reaction products accelerate development. An ideal developer would be hydroquinone in a low sulfite formulation. Such developers have been used in many industrial applications for high contrast images. However, in a full tonal scale photograph, there are other variables to maintain: sharpness, fine grain, and speed..

With modern films, developers such as full strength DK-50 or D-61a produce fairly high contrast by the time development has gone on long enough to reach normal film speed. Even D-72 or Dektol could be used for extreme expansion. But the problems with all these particular suggestions include low speed, low acutance, and coarse grain.

Ascorbic acid and ascorbates

Photographic research on l-ascorbic acid (vitamin C) has been ongoing since 1935 when Mauer and Zapf identified it as a developing agent. Since that time, numerous articles have appeared in photographic publications and ascorbic acid formulas have been used in the motion picture industry. Research intensified in the 1990s, and dozens of patents have recently been granted for ascorbic acid developers.[2] With the introduction of Kodak Xtol in 1996, still photographers became aware of ascorbic acid's potential as a low toxicity developing agent.

Ascorbic acid and ascorbates appear to be useful replacements for hydroquinone in developers where hydroquinone is used as the secondary agent, usually in combination with metol or Phenidone. However, our concept of what usually constitutes a primary and what a secondary agent in a formula may be in need of refining. Silvia Zawadzki, the formulator of Xtol, believes that the ascorbate in that developer is, in fact, the primary agent. Most valuable is Zawadzki's observation that the ascorbate can provide a half stop speed increase over hydroquinone in similar formulations.

> *Ryuji Suzuki helpfully characterizes ascorbate as follows: "It is a strong reducing agent but does not act directly at the latent image center. Phenidone is a weak reducing agent but it sticks onto the crystals and is very effective in bringing ascorbate's (or HQ's) reducing action to where the action needs to happen. That is the mechanism of superadditivity. Metol is similar. It is a weak reducing agent but it sticks to where the action needs to happen."*

Ascorbic acid has been confusingly characterized as both a weak and a strong developing agent. It has been said to have a tendency to high

contrast, and to require high alkalinity to be active on its own. Moderate alkalinity is apparently sufficient when it is used as a secondary agent. It is superadditive with Phenidone and metol, and is currently being used as a more environmentally friendly replacement for hydroquinone in some new formulas. However, some developers, for example Ilford Ilfosol-S, used sodium ascorbate in addition to hydroquinone. There is no environmental or health benefit with this approach: ascorbates are simply being used to enhance the photographic properties of conventional chemicals.

It has been thought that, because ascorbic acid is an antioxidant, it could partially replace sulfite as a preservative. As a practical matter, this does not seem to be the case. Even formulations with large amounts of sulfite are difficult to preserve.

Based on present information, ascorbic acid cannot be used as the sole developing agent unless fairly high contrast (approximating D-72) is desired. The only practical developer we know of which at one time claimed to use an ascorbate as the sole developing agent was Agfa Neutol Plus, a print developer. A sparse 1998 MSDS does not reveal the presence of any developing agent at all. A 2006 MSDS is even less informative, listing only potassium carbonate. We believe this developer contained Dimezone-S.

MYTOL	
Distilled water (80F/27C)	750 ml
Sodium sulfite anhydrous	60 g
Sodium metaborate (Kodalk)	4g
Sodium ascorbate	12 g
Phenidone	0.15 g
Sodium metabisulfite	3g
Water to make 1 liter	
At 1:2; 8-13 minutes at 68F/20C	

A good starting point for information on ascorbic acid is US Patent 5, 756,271 (1998) which discloses the technology behind Kodak's Xtol

developer, discussed in more detail in chapter 5.

Many formulas which include an ascorbate have been published. Paul Lewis's Mytol is a formula similar to Xtol but uses more readily available chemicals.[3] It is recommended full strength or 1:2. In fact it can be used at any dilution Xtol is used at. Functionally, it is very similar. But it would need DTPA to be reliable (chapter 5).

D-96A a dead end or a starting point?

Kodak D-96A is an ascorbic acid formula which Kodak at one time in the 1990s, but no longer, recommended for motion picture film. Though Kodak has never promoted it for still photography, it should work equally well with all black and white films. Times should be shorter than for D-76. (To use borax decahydrate in this formula, substitute 5 grams for the 3.8 grams of pentahydrate.)

Experiment: Instead of regarding this developer as a curious dead end that was probably the result of environmental concerns on Kodak's part, I prefer to think of it as a springboard for further experimentation with the D-76 type of developer.

1. Eliminate the pH rise problem most borax developers have (chapter 5) once and for all by using the superior buffer system of Xtol (Kodalk-bisulfite).
2. Eliminate the Calgon and replace with DTPA, which would protect the ascorbate against iron and copper impurities.
3. Eliminate the bromide, lowering borax if necessary.
4. Instead of ascorbic acid use 12 g/L sodium isoascorbate, the amount chosen for Xtol.
5. For a possible speed increase under some conditions replace the sodium sulfite with potassium sulfite. The discussion of Ilfotec DD-X in chapter 10 provides a rationale for this.

KODAK D-96A	
Distilled water	750 ml
Calgon	1g
Sodium bromide	0.35 g
Sodium sulfite anhydrous	15 g
L-Ascorbic acid	2g
Metol	1.5 g
Borax pentahydrate	3.8 g
Sodium sulfite	60 g
Water to make 1 liter	

TD-96 TRIAL	
Distilled water	750 ml
Metol	2g
Potassium sulfite	75-90 g
Sodium or potassium metabilsulfite	3.5 g
Sodium isoascrobate	12 g
Sodium metaborate	4g
DTPA	1-3 g
Water to make 1 liter; pH 8.3	

The TD-96 trial in the sidebar tries to do many things. First and foremost is to eliminate the pH elevation problem most borax-only developers have. If that was the only change we made, we would have arrived at a D-76-type developer that had a reliable and repeatable pH. But I want to experiment with techniques to enhance speed. The small amount of ascorbic acid in D-96A probably only has a slight effect. The 12g/L of sodium isoasorbate in TD-96 Trial is enough to provide some real development activity. But we don't yet know how superadditive ascorbate and metol are, compared to phenidone and ascorbate. As discussed in chapter 10, two techniques which

may amplify the latent image slightly are using ascorbates, and using predominatly potassium salts in the developer. Taking the final step to increase speed, replacing metol with phenidone, we would simply arrive at the formula for Xtol. With TD-96, we want to see if we can gain some of the improved Xtol image quality but with greater reliability, albeit with a possible loss of Xtol's speed increase. However, if, as in Xtol, the ascorbate in TD-96 were to serve as the primary developing agent, then the same occasional risk of sudden death would exist. On the other hand, if the effect of the ascorbate is small, and metol is the primary developing agent, then this may prove to be a reliable developer. It may be necessary to adjust the ascorbate so that its effect is small; in that way, if it were to fail, we might still have enough energy from the metol to complete development, which is not the case with Xtol.

> *Ryuji Suzuki points out that ascorbate developers are more likely to oxidize without color change when the pH is low, as in Xtol. He has also observed that when ascorbate oxidizes, it may take down the other developing agents that are present.*

Thinking of Crawley's work with the PMQ combination, makes us wonder if the PM-ascorbate combination might prove to be more reliable than phenidone-ascorbate alone? However, there is no evidence Crawley experimented with this combination.

Ascorbic acid in the future

Progress in photographic chemistry has always been slow: it has taken chemists 50 years to begin to become comfortable with Phenidone and its derivatives. Knowledge and use of ascorbates is still in its infancy.

Unfortunately, this coincides with a time when not only is developer research on hold but major photography companies are actually destroying earlier research. Yet there is a need for more research. Certainly not from the photographic point of view: we have enough to play with there. But from the point of view of human and environmental health, we need better and safer chemicals.

Photographic chemicals, when handled with reasonable precautions, do not, in the view of some manufacturers in the fairly recent past, appear to pose a health hazard greater than many common household cleaning solutions or cosmetic products such as hair dyes. Yet there is a continual desire by educators, who wish, for example, to teach black and white processing to children, for chemistry that is entirely safe. This desire is complicated by our imperfect and constantly evolving knowledge of toxicity. Phenidone and its derivatives are an example: it was thought, until recently, that the oral toxicity of the Phenidones was very low. Recently, however, animal data suggest that Phenidone may be more dangerous than hitherto supposed—when ingested. It is not yet known whether these data are applicable to humans. Even vitamin C is coming into question. Dr. Linus Pauling's well-publicized advocacy of massive dosages of vitamin C on a daily basis may not be as safe as has been supposed for several decades (see Appendix III). Nevertheless, ascorbates are the safest developing agents both for humans and the environment yet discovered.

Chapter 5 discusses practical solutions for dealing with the occasional and unpredictable stability problems of ascorbate developers. Will research in the 21st century finally answer the questions that have been raised by Xtol's success?

NOTES

1. Adams, *The Negative*. Adams includes two additional techniques for obtaining yet more compensation from two-bath developers which interested readers can consult, but we are reluctant to recommend them.

2. The best sources for information on ascorbic acid are patents, which can easily be located on the internet. All references below happen to be US patents. A fundamental patent is 2,688,549. Other important patents include: 5,766,830 (1998), 5,766,832 (1998), 5,756,271 (1998), 5,702,875 (1997), 5,648,205 (1997), 5,578,433 (1996), 5,503,965 (1996), 5,503,966 (1996), 5,384,233 (1995), 5,278,035 (1994), 5,264,323 (1993), 5,236,816 (1993), 5,217,842 (1993), 5,196,298 (1993), 5,098,819 (1992), 4,038,080 (1977), 3,942,985 (1976), 3,938,997 (1976), 3,658,527 (1972), 3,649,280 (1972). There are many others worth exploring.

3. Paul Lewis, "Don't Forget Your Vitamin C," Maxim Monochrome, Volume II, No. 2, March/April 1997.

Chapter 10
INCREASING FILM SPEED

QUICK GUIDE RECOMMENDATIONS

- The maximum true speed increase that can be obtained through development is 60% to 100%. For slow and medium speed conventional films, preferred speed increasing developers are high acutance types such as FX 1, Acutol or Acuspecial. For all films we recommend Ilford DD-X, FX-37/39, and ascorbate-based developers such as Xtol, FX 50 and FX 55.
- For low light photography, Delta 3200 and Tmax P3200 are the available ultra fast films.
- A good technique for *moderate* pushing of all films is diluted Xtol (1+1 to 1+3) with extended times. For *extreme* pushing with Tri-X and HP5, undiluted D-76 has long been championed but Ilford DD-X 1+4—the standard full-strength dilution containing about 100g/L of sulfite—may now be a better choice. Tabular films respond less well to extreme pushing.
- Green light latensification is a technique worth trying with all films, particularly conventional grain films.

True speed increase versus pushing

A film's speed rating measures its ability to record shadow detail. A *true speed increase* therefore means that the film can record shadow detail with less exposure. It is almost impossible to achieve more than a one stop true speed increase over a manufacturer's ISO rating, in spite of claims by countless products. The simple reason is that film manufacturers use every technique possible to increase the speed of their films. There is not much more that can be done! There are, however, three traditional methods for increasing speed with modern films:

- hypersensitization before exposure
- latensification after exposure
- special developer techniques or additives

Pushing film means underexposing and overdeveloping. Overdevelopment produces greater density in the midtones and highlights, but little increase in the underexposed shadows. The result is:

- a maximum one stop increase in shadow density
- a 1 to 4 stop increase in midtone and highlight density
- greatly increased grain and contrast

There are two reasons to push film:

(1) aesthetics and (2) pushing lets you make tenable handheld exposures in low light situations. For example, if your meter reads f/3.5 at 1/8 of a second for a normal exposure, you may choose to underex-pose by two stops to make a handheld exposure at f/3.5 at 1/30 of a second to avoid camera shake. With the correct pushing formula, the shadow areas will be underexposed by only one stop instead of two.

We call a 1–2 stop push a *moderate* push, and a 3–4 stop push an *extreme* push. Anything beyond that is unrealistic.

Overdeveloping results in printable midtones. Highlight detail will often be blocked (how much will depend on the nature of the highlights) but can often be brought out through printing techniques. The increased grain and contrast can result in prints with high graphic impact, an effect that makes pushing a viable aesthetic choice.

Films for pushing—then and now

Nearly all films can be given a moderate push of 1 to 2 stops. For extreme pushing, the most popular film was Tri-X, from the 1940s to the early 2000s. Its reformulation in 2007 achieved remarkably low grain and high resolution at EI 400 to 800, but the film lost its flexibility when attempting to push process.

The late 1980s brought tabular grain films including Tmax P3200 from Kodak and Delta 3200 from Ilford. These are EI 800 films which are claimed to be pushable to EI 3200 and beyond. P3200 was discontinued in 2012 but brought back in 2018.

> *"Latitude is what you can get away with."*
>
> —DAVID VESTAL

The first tabular grain films pushed poorly because they had a tendency to block highlights beyond anyone's ability to recover them in printing. The latest films from Kodak and Ilford are more flexible. Moderate overdevelopment *in a dilute developer* (Xtol 1:1 to 1:3 or FX 37 1:5) works well—but only for a moderate push. It remains true that if you want to get the best out of tabular films, you *pull* process rather than push process them.

Even Kodak itself has recommended pull processing P3200 to EI 400 for greater image quality.

Our recommendation is to use Ilford HP5 for extreme pushing to EI 3200, especially with 35mm film.

Developers for moderate push processing

Many phenidone-based developers increase speed by 60%, including Xtol, FX 15, FX 37, FG7, Acufine, Acutol, DD-X and Microphen. This true speed increase is *only* evident when negatives are developed to normal contrast. These developers usually do not *push* underexposed film as effectively as undiluted MQ-based D-76, once considered to be the best developer for pushing. But modern films, especially tabular, have different requirements for moderate pushing. In the 1990s both Crawley and Zawadzki found that best moderate pushing of tabular films occurs when modern developers (Xtol, FX 37/39) are diluted by half or more. One reason this technique works is that dilution helps minimize highlight blocking with tabular films.

For moderate push processing using *undiluted* developer, increase development time by 25% for a one stop increase; by 50% for a two stop increase.

Using *diluted* developer, the general guide is: dilute the developer with twice the amount of water you would use for normal development, then increase time by 50–100% for a one to two-stop push.

As always when diluting, use less film per liter of developing solution (chapter 4).

Developers for extreme pushing

For extreme pushing we recommend Ilford HP5+ at EI 2400 or 3200, processed in Ilford DD-X 1+4 for 18 minutes at 75F.

Why does DD-X work better for extreme pushing?

I was ba±ed as to how DD-X could, chemically speaking, be a discernibly superior pushing developer to D-76. DD-X is parenthetically described in chapter 6. It looks like a PQ variant of D-76—in other words, a concentrated variation of ID-68 or Microphen, employing a large amount of potassium sulfite (about 400 g/L instead of the 100 g/L of sodium sulfite in D-76; at the usual 1:4 dilution this results in working solutions of about 80 g/L of sulfite). Potassium sulfite is more soluble than sodium sulfite, hence its use in concentrates, though it is more expensive.

At 1:4, DD-X has about the same sulfite concentration as D-76 undiluted. In the past, it has never been found that any PQ developer, undiluted, was superior to D-76 for *extreme* pushing. What had changed? Keeping in mind that sulfite is a significant part of the alkali system in DD-X, I could only think of one possible answer, going back to Glafkides (p. 63), who states:

> *Possible mechanisms we know of for amplifying the internal latent image through development are three. One is to use a high sulfite developer like D-76. It is thought that the solvent action may uncover latent image centers that would not otherwise be available for practical development (Haist). Another is to use Xtol. T.H. James in his well known early patent on ascorbate developers (USP 2,688,549; 1954) proposed that a phenidoneascorbate developer may amplify the internal latent image. Finally, there is the mechanism described in the DD-X section of this chapter, where it is thought that a developer high in potassium ions may help amplify the latent internal image. All of these being possible, might we not go a step further and prepare Xtol with potassium sulfite? We would then be employing all three techniques. Would it be possible thereby to tweak another couple of percent in speed? For moderate pushing, we would suggest diluting Xtol-potassium; for extreme pushing we would suggest using it undiluted.*

> The potassium alkalis, although having similar properties to the sodium compounds, alter the developing properties of the solution. *The K+ ions are photographically more active than the Na+ ions, particularly towards the internal latent image of the silver bromide grains. The emulsion sensitivity is increased.* (emphasis added) The simultaneous presence of K+ and Na+ ions increases the efficiency of anti-fogging compounds.

Glafkides cites three little-known French sources for this information: Lous-Labetoulle L.[sic; the initial should be A]: *Sci. Ind. Phot.*, 1946, 65; Sauvenier H.: *Sci. Ind. Phot.*, 1951, 41; Gauvin [H.]: *C.R.*, 1953, 807–809. These papers are little known. The choice of sodium or potassium salts is usually made on cost (sodium wins) or in rare cases, concentratability (potassium wins). Rarely, if ever, is the choice made based on the reasoning outlined here.

Though obscure, these papers are respectfully discussed by Haist (254) with additional citations. He focused on Gauvin's finding that "the potassium salt developer has a greater capacity to neutralize the acid formed *during* development" (emphasis added), and Mme. A. Lous-Labetoulle's finding that "A developer containing both [mixed] sodium and potassium ions was more active than a solution having only sodium ions." This point was also made by Crawley (60/61) who suggested mixed sodium/potassium carbonate for concentrated developers. Crawley did not provide citations but these papers appear to be his sources. Mason (33–34) also cites Glafkides on this issue, focusing on the suggestion that potassium salts may result in a small increase in the development of the internal latent image. He adds, "Against this small advantage must be considered the much greater cost of potassium compounds and the somewhat deliquescent natures of potassium carbonate and potassium sulfite."

It is noted that developing solutions made with potassium salts are more susceptible to fog formation if the developer is contaminated with sodium thiosulfate from the fixing bath.

More about DD-X and potassium rich developers

USP 5,210,010 (1993) by Ross Fielding at Ilford describes a developer concentrate that is thought to correspond fairly closely to DD-X. The patent compares it to a formula of the HC-110 type based on DEA-sulfite, noting that the DEA causes much higher granularity. The developer in this patent (B) is shown to produce finer grain than (A). Speed measures as about the same when film is developed to a normal gradient, and we accept that. But when a potassium-rich developer of this type is used for extreme pushing, there is a surprising, perceptible gain in speed over traditional developer formulations.

DD-XTYPE DEVELOPER (B) COMPARED TO HC-110 TYPE DEVELOPER (A)		
	A	**B**
DEA H_2SO_3 (15% SO_2)	980 g	---
Pot. sulfite (65% w/v/)	---	548 ml
Water	205 ml	380 ml
Digol [diethylene glycol]	---	45 ml
Hydroquinone	44 g	44 g
Dimezone-S	1.2 g	1.2 g
DATPA	4.8 g	4.8 g
Borax	---	23.5 g
Water to make 1 liter		
Both developers are stated to have a pH of 8.5 when diluted 1+4, at 25C. From USP 5,210,010..		

It seems likely that the choice to use potassium sulfite in DD-X was made solely for reasons of concentratability. There is no explicit indication that the formulator knew of the French research we have discussed. Thus, like so much in photographic engineering, its value was serendipitous.

Experiment: We would suggest experimenting with formula B. Alternatively, try any of the PQ solvent developer formulas in chapter 6, simply replacing the sodium sulfite with potassium sulfite. Our observations supporting the practical value of the French research raise this and other possibilities: D-76 undiluted might show improved push-ability if the sodium sulfite is replaced with potassium.

For high definition developers (which should not be used for extreme pushing), we would recommend experimenting with potassium rather than sodium alkalis if you want a *little* more speed.

N.B. We recommend thoroughly rinsing films processed in a potassium rich developer so potassium is not carried over into the fixer.

USP 5,210,010 notes disadvantages to concentrated developers using an alkanolamine sulfite, that is, the HC-110 and Ilford HC type. The patent states they cause "a build up of image density with a reduced contribution from physical development. This tends to produce an image which is more grainy than an image obtained in the absence of an alkanolamine." Additionally, the high viscosity, or "syrupiness", presents formulation problems. DAPTA is specified in the formula but elsewhere in the patent, DTPA is stated to be preferred. Also, Phenidone is specified in the formula but the text underneath specifies that Dimezone-S should be used. See chapters 4 and 5 for references to Haist on diethylamino-ethanol (diethylethanolamine or DEAE) & dicyanamide.

Hypersensitization and latensification

Photographers and scientists have long sought techniques to increase film sensitivity before development. There are two broad categories:

Hypersensitization The film is treated *before* exposure to increase its sensitivity.

Latensification The film is treated *after* exposure but before development. The aim here is not to increase the film's *sensitivity*, but to increase the *developability* of the least exposed grains, which would not develop with normal processing.

These techniques were popular prior to the 1960s, when films were slower. However, they can still be useful for "available darkness" photography. Their advantage over push processing is that they produce image quality which approaches the results of normal processing.

Note: Hypersensitization and latensification work best with slower films. Results are often negligible with fast films, which are treated by the manufacturer to obtain every nuance of speed. These techniques also exhibit the greatest effect with exposures longer than one second. With both hypering and green light latensification some fog rise and loss of contrast is inevitable. Even so it is best to use normal developing times and print on a higher grade of paper if necessary.

Increasing speed *before* exposure: hypersensitization

The traditional methods for hypersensitization do not appear to work well with modern emulsions.[1] The one successful method employed more recently is hydrogen gas hypersensitzation, often called "gashypering" or just "hypering", first published by Everhart in 1981.[2]

Gas-hypering was dramatically successful with Kodak 2415 (Tech Pan) and other monochrome and color films of the 1980s and 90s. Before exposure, the film is soaked in a forming gas mixture of 92% nitrogen and 8% hydrogen for several hours. The hypersensitization effect can last for years if the film is properly stored (earlier hypersensitization techniques only worked for a few hours). Astronomers, working with exposures which may run into the hours, reported reliable and dramatic speed increases as well as

reduced reciprocity failure with long exposures. For example, a night sky photograph that would formerly take four hours could be made in 30 minutes or less with gas-hypered film. With conventional exposures, shorter than one second, the maximum speed increase you can usually expect is one stop. The vendor which formerly sold hypered films no longer does, but procedures for this technique can be found.[3]

Increasing speed *after* exposure: latensification [4]

The best method of latensification requires no chemistry, just a darkroom safelight. The safelight should have a broad area of coverage. A 7.5 or 10 watt *incandescent* bulb with a dark green No. 3 safelight filter is required.

> *Farber's use of latensification with Tri-X is described in chapter 5, in the sidebar near the heading "Other solvent developers using phenidones," p. 59. Haist approvingly quotes Farber's conclusion that latensification may well be the best way to achieve a true speed increase of a full stop.*

After exposure, the film is taken to the darkroom, unwound, and taped to a wall ten feet away from the safelight. The film emulsion should face the safelight. The film is exposed to the safelight for between 15 and 40 minutes. Expect a one stop speed increase from Tri-X. Slower films may yield a two stop increase. It is not known how well tabular grain films work with green light latensification.

Note: This recommendation is only for panchromatic films. We do not know how well it works for extended red, ortho, or infrared films.

Levy's guanidine carbonate technique

Haist describes Marilyn Levy's 1959 invention, US Patent 3,005,710. After exposure, film is bathed in a 0.5 to 5 molar solution of guanidine carbonate for between one and twenty minutes. The film is then developed, with or without rinsing, as usual. Increasing the time of immersion results in increased film speed. As tested, the increase in fog is either none or minimal.

Increasing speed *during* exposure: concurrent photon amplification

Concurrent Photon Amplification requires a specially modified camera fitted with small LEDs in front of the film plane.[5] According to Schwalberg, this is the most effective method for increasing film speed for exposures shorter than one second, with no loss of image quality. Scholarly articles and theses discussing the technique can be found on the internet.

Increasing speed *after development:* hydrogen peroxide

Unlike hypering and latensification, sensitizing with hydrogen peroxide takes place *after development, before fixing*. The technique is to "steam" the film in pressurized hydrogen peroxide fumes just after development. This technique can measurably increase shadow detail with conventional film that has been "pushed" two to three stops in D-76 or Xtol. The results are grainy but have a unique quality that often complements low light photography aesthetics.

According to Bob Schwalberg, the best normal developing time for Tri-X (EI 400) in D-76 1:1 is 8 to 10 minutes at 68F/20C. To push one stop (EI 800) he recommended undiluted D-76 for 9 to 10 minutes. For pushing two stops (EI 1600) he recommended at least 12 minutes and found development beyond 15 minutes useless. These recommendations contradicted Kodak's. A contemporary Data-guide recommended 9 minutes for normal time processing of Tri-X in D-76. In Schwalberg's system that amounts to a one–stop push. Schwalberg's thirty year dispute with Kodak over development times was legendary. According to Schwalberg, Kodak's longstanding policy was to build a safety factor into development times to prevent accidental underdevelopment. Kodak ardently disputed this. After one of his articles on this subject appeared, Schwalberg received an anonymous postcard postmarked Rochester, which bore the words "You are right." Schwalberg believed it came from Haist (in his opinion, the only incorruptible scientist at Kodak). But Haist denied it, when I asked.

1. Place either two 35mm reels or one 120 mm reel, as a spacer, and eight ounces of over-the-counter 3% hydrogen peroxide in a *metal* tank of at least 1 liter. With the lid on, place the tank in a water bath of 105F/40C to 110F/43C. Bring the peroxide to this temperature.

2. Develop the film by push processing with D-76 (undiluted), FX 37 or Xtol.

3. After development rinse the film with plain water at the temperature of the developer. *Do not use acid stop bath at any time during this process.*

4. In total darkness transfer the film to the tank holding the peroxide and the spacer reels. Never allow the peroxide to touch the film. Place the lid on firmly—the tank must be airtight so pressure can build up. Leave the film to "steam" for ten minutes, maintaining a water bath temperature of 105F/40C. During this period, it is safe to turn on the lights. Once every minute the tank should be gently swirled (not inverted!) for ten seconds, being careful not to splash the peroxide onto the film.

5. At the end of 10 minutes, turn the lights off. Carefully remove the lid. Transfer the film to a dry tank (metal or plastic). Cap the lid tightly. Let stand for 5 to 10 minutes.

6. Rinse the film in plain water at the original processing temperature by filling and emptying the tank at least five times. Fix and wash as usual.

Increasing speed through developer additives

Various proprietary additive products have been marketed over the years. They may contain development accelerators such as hydrazine or ethanolamines, and a highly active developing agent, such as Pheni-done, that is likely to increase the activity of developers that do not already contain Phenidone. Two of the most popular are Formulary Excel and Crone-C. There is not, in the entire photographic literature, a single scientific study showing that these developer additives increase speed beyond the maximum 60% of most solvent phenidone developers. These additives are believed to include Phenidone, so when added to an MQ developer such as D-76, there will indeed be a slight increase of speed, but there will be no improvement in pushability. There is also unlikely to be any improvement if they are added to developers that already contain Phenidone. When used with an MQ developer, these additives will also accelerate the *rate* of development.

Apart from these two products, the literature of the 2nd half of the 20th century, including patents, offers many possibilities for using chemical additives to increase speed. One such is the Haist and King dicyanamide technique discussed in the D-76 section of chapter 5. Many more, if not all, are covered in Haist. By and large, not a single one of this vast number of inventions has found its way into a commercial product. What sometimes happens is that when a chemical sensitization technique is discovered, it is incorporated into the film itself. Many of the chemical additives proposed have been far from safe to use in the ordinary darkroom.

CAVEAT

Latensification and hypersensitization have shown real if limited success in the past—though not, necessarily, in combination. They may not work well, or at all, with some modern films. One reason may be that modern films have been super-sensitized to an extent not possible before the 1990s. However, for the less sophisticated films still available today, these techniques are likely to be effective. And for the simple emulsions used for hand-coated films or plates, these techniques should be quite effective. With simpler materials, even the older hypersensitization techniques covered in Haist, 468–480, should show value.

INTERESTING HISTORICAL SPEED DEVELOPERS

We include here formulas for two developers which were widely used for speed increasing: Perfection XR-1, which has long been available from a patent, and Crawley's Acuspeed, which is published here for the first time.

FX 20 (Acuspeed)

Acuspeed, or FX 20, was introduced around 1968 and discontinued 30 years later in 1998 when it was replaced by Varispeed. We have not been able to locate a formula for Varispeed but we do have a formula for Acuspeed, and reproduce it both as an historical curiosity and because several notable photographers have used it in the past, particularly with Tri-X. That said, Acuspeed uses an older approach to the problem of increasing speed, and we believe Crawley took a different approach with Acuspeed.

There are many interesting things about this developer, but first let us address the problem of the two columns. We take this from a page dated 15 June 1967 and printed in proportionally spaced Helvetica. Thus, the page was probably prepared decades later, on a computer, although there is a small chance it could have been prepared in 1967 on an IBM Executive typewriter, which has proportional spacing, or an IBM Composer. The second column is handwritten. In our experience, in Crawley's notebooks, when two formulas are presented in aligned columns, the 1st column is usually the latest formula, while the 2nd is usually an older version. However, in this case, we suspect that the 2nd column may be the later formula. Manufacturers sometimes make a formula just slightly stronger than it has been tested at, to compensate for shelf storage. Could that be what the B formula is?

ACUSPEED (FX 20) 15 JUNE 1967		
	A	**B**
Sodium sulfite anhydrous	70	77.5 g
Sodium carbonate anh.	22.5	25 g
Sodium metaborate	22.5	25 g
Glycin	22.5	25 g
Hydroquinone	12	13.3 g
Phenidone	1.25	1.4 g
Sodium bisulfite	1.25	1.4 g
Potassium hydroxide	10	11g
Sodium hydroxide	10	11g
Potassium thiosulfate (powder)	5.25	6g
Potassium bromide	1.25	1.4
Water to make 1 liter		
We have not included the solvents Crawley used, so this concentrate may have to be made up at, for example, 1/2 strength.		
pH betweem 10.9 and 11		
Dilution 1+9 (?)		

The formula is also interesting in its use of the PQ-glycin combination that Crawley also employed in the first high speed formula he published in1961, FX 11. However, FX 20 is much more alkaline and it also includes a surprising silver solvent, potassium thiosulfate. (For the use of sodium thiosulfate as a solvent for fine grain developers in the first half of the 20th century, see Haist, especially 372–375.) Note the use of mixed sodium and potassium hydroxide: the Lous-Labetoulle technique, p. 123.

PERFECTION XR-1		
	A	**B**
Metol	0.25 g	0.25 g
Sodium sulfite anhydrous	30	30 g

PERFECTION XR-1		
	A	**B**
Hydroquinone	0.5 g	0.25 g
Phenidone	1.5 g	1.75 g
Borax	0.75 g	0.5 g
Water to make 1 liter		
Instructions available on the Internet, see unblinkingeye.com (2019).		

There isn't anything quite like FX 20 in the photographic literature. Unfortunately, we haven't yet located Crawley's later thoughts on this type of developer.

It is significant that FX 11 only claimed a one stop speed increase. With FX 20, the manufacturer's claim is that films such as Tri-X and HP5 can be exposed up to EI 1250 without appreciable loss of shadow detail, and higher if some loss of shadow detail can be tolerated. Crawley positioned FX 20 as a valuable standby, to produce usable negatives from underexposed films where conventional developers would fail.

Perfection XR-1

Another speed-increasing developer that earned considerable cachet and a cult following was Perfection XR-1. I used it to process my negatives of the art critic Edit Deak, rating Tri-X at 1600. Bob Schwalberg wanted to publish them as a textbook example of why speed increasing developers don't work (extreme grain, soot and chalk gradation, no shadow detail, blocked highlights, reticulation from high temperature). However, the pictures were Deak's favorite portraits of herself. With pushing, you are always going to … lose shadow detail and block highlights. The trick is to make that work for you aesthetically, as many low-light photographers have done.

Perfection XR-1 was patented. There are two examples in the patent, USP 4,083,733. Bill Anneman, its author, told me that one of them corresponded to the manufactured product. Readers who are interested in this curious developer will have to experiment with the two formulas given here, which are not radically different. What is essential about making this developer provide its typical quality is to follow the temperature recommendations: 86F/30C and 92F/33C.

The formula is interesting for its use of the rare PMQ combination, for its simplicity, and for its fairly low pH. A pushing formula usually needs energy, and this is often provided by high alkalinity, as in FX-20. Anneman's idea was to obtain the energy from elevated temperatures instead. This brought considerable risks with the less hardened films of the developer's heyday, but these temperatures should be fine with contemporary 3G-hardened films.

Were I making this developer up today, I would trial half, or a quarter as much Phenidone.

Can we do more?

Have we really reached the maximum speeds the development process is capable of? Grant Haist told me he thought that investigating naphthalene developing agents could bring great advances. We are only at the beginning.

NOTES

1. Haist, Clerc, and Jacobson.

2. E. Everhart, *Sky and Telescope*, 1981.

3. A vendor for gas-hypered films *was* Lumicon at the time of FDC1. Astronomers have since mostly moved to digital sensors, and hypering is now a DIY affair. The technique is well-described by Everhart, above, and by Wallis & Provin, *A Manual of Advanced Celestial Photography*, and Reeves, Wide-Field *Astrophotography*. Internet searches may provide helpful information.

4. Haist.

5. Bob Schwalberg, *Popular Photography*, June 1976.

Also see Mitsuo Kawasaki and Yoshiaki Oku, "Characterization of High-efficiency Hypersensitization of AgBr Emulsion by Gold(I) Thiocyanate. Solution", *J. Photogr. Sci.*, Vol. 43, No. 4, pp.122–130, 1995.

Chapter 11
DOCUMENT FILMS

Document films—also sometimes called "high contrast copy films"—are slow, ultra sharp, ultra-fine grain, ultra-high contrast emulsions. Yet when processed in special low contrast developers, they can produce negatives that have almost normal gradation with amazingly fine grain and high sharpness. They can rival the grain and sharpness of large format films, even though they can never possess the microtonal subtleties which keep large format popular. Nevertheless, truly spectacular results can be achieved with document films at enlargements of 20x or more.

Document films can be used to photograph low contrast subjects successfully. But scenes of normal (7 stops) or higher contrast will show impaired highlight rendition. Even so, with the right developer, it is possible to record a 12-stop range.

Since the contrast range of document films is limited, exposure is critical. Traditional Zone System methods for determining film speed should *not* be used. With the Zone System, the first usable density is taken to be 0.1 above base+fog. In fact, the *minimum printable density* is usually about one exposure stop *below* this point. With document films processed in developers which produce high toe contrast the first printable density can be as low as 0.03 above base+fog.[1]

QUICK GUIDE RECOMMENDATIONS

- Use Xtol 1:5, POTA or a variant, Formulary TD-3, or a Spur developer with document films.
- POTA-type developers produce exceptionally even density growth over their useful range but have an abrupt shoulder after eight stops (zones). No further highlight detail is available above that point. Developers based on Beutler technology such as TD-3 have choppier density growth but a much gentler shoulder with an overall printing range as high as 10 stops.

Document films past, present, and in between

In the 1960s, the document films of choice for making continuous tone pictures were Agfa Copex-Rapid and Kodak High Contrast Copy Pan. HCCP was discontinued when Kodak Technical Pan came out in 1977 and there was no replacement when Kodak stopped selling Technical Pan in 2004. But Copex-Rapid continued to be manufactured until about 2019. This film was marketed by scores of small manufacturers all claiming their product to be unique. Frozen stock should be available for some years to come. A document film that is still being manufactured is sold by Adox as CMS 20. It is finer grained than Copex-Rapid, but slower, with an effective ISO speed of about 20. We suspect that some of the hypersensitzation and latensification techniques discussed in chapter 10 could increase the speed of this relatively simple film by 2–4 times.

Frozen stock of Kodak Technical Pan (Tech Pan), an extended red panchromatic film, is scarce and expensive. Old stock of Agfa Ortho 25 is occasionally available under a bewildering variety of trade names.

Agfa Ortho 25 is not as fine grained as the two other films, and is not a true document film. But it is high in contrast and sometimes processed like document film, so is included here. Other films in this category are available and attract attention from time to time. One example is Eastman 5369, a specialty film used in the motion picture industry that is expected to be available indefinitely. Its major problem is slow speed.

> *"Fog? What is fog? You just print through it!"*
>
> —MARILYN LEVY

Low contrast developers for document films

Although the chemical mechanism of low contrast developers is not well understood, they have been around since the 1960s. The first developer to be widely used for this purpose was the famous POTA formula of Marilyn Levy, published in 1967.[2] (POTA stands for Photo-Optics Technical Area at the Fort Monmouth military installation where Levy worked.) A precursor 'extended range developer' (Levy's term for a very low contrast developer) was the Windisch pyrocatechin developer discussed elsewhere in this book.

Developing time for Tech Pan and other document films is about 15 minutes with 10 seconds agitation each minute, and about 6 minutes with continuous agitation in a tray for sheet films. POTA may be used with normal contrast films when extremely low contrast is desired. A range of 20 stops can then be recorded *with normal film.*

POTA	
Sodium sulfite anhydrous	30 g
Phenidone	1.5 g
Water to make 1 liter	
Use IMMEDIATELY after mixing.	

Superficially, this developer resembles D-23, with the metol replaced by 20% of its weight of Phenidone and the sulfite reduced by 70%. However, its results are quite different, and cannot be duplicated by any known metol formulation. The pH of POTA mixed with distilled water is about 8.7. The pH of the sulfite solution alone is about 9.8, which indicates the importance of sulfite in POTA as an alkali.

POTA problems and modifications

POTA is distinguished by the fact that it is in a state of exhaustion from the moment it is prepared, because straight Phenidone is not well preserved in sulfite. This can be seen by observing the typical orange color of the POTA solution. If hydroquinone were added, the orange discoloration would disappear. Because the oxidation products of Phenidone in POTA retard development, less development will take place in areas of high density, where more developer is being used, and more oxidation products are being created. This is probably the main mechanism which makes POTA such a low contrast developer.

Interestingly, these oxidation products do not obviously stain the film. Unfortunately, considerable *streaking* can result. The streaking may be due to oxidation, but it has been theorized that it may also relate to a physical development effect that takes place with POTA.[3] The streaking problem most obviously affects large areas of uniform density, such as cloudless skies. It is an intermittent problem.

Marilyn Levy noticed these problems in 1967. They were not considered critical as the large aerial films for which POTA was originally intended were commonly given continuous brush agitation, which minimized the effect. However, brush agitation is impractical with 35mm film, and irksome with sheet film. In any event document films should have intermittent agitation to produce the desired contrast and definition characteristics.

One way to minimize the problems associated with Phenidone oxidation is to modify the formula. A simple way to minimize oxidation with only a small rise in contrast is suggested in Levy's earlier paper on Phenidone-pyrogallol developers.[4] If a small amount, about 0.25 grams, of either hydroquinone or pyrogallol, is added to the solution, the result is good preservation of both agents, with a surprisingly small rise in contrast compared to plain POTA.

There are two other factors to consider. The first is that Phenidone is hard to dissolve at the pH of POTA. With another developing agent present there is no reason to use 1.5 g/L; 0.5 g/L would be a good trial amount.

The second is high fog, a problem with Phenidone and pyro developers. It is desirable to have a low fog level if this can be achieved without spoiling

other characteristics of the developer.

Levy did not employ antifoggants in POTA because they would have reduced speed and increased contrast. They could also have other unpredictable effects on image quality. However, as T.H. James specifically noted to us in this connexion, one of the problems with fog, despite the famous quote on the previous page, is that its growth is never even or predictable, which can cause subtle degradation in image quality.

Part of the fogging problem found with POTA may be due to the level of sulfite. In POTA sulfite is the main alkali. Reducing sulfite will also reduce the pH, which is the best way to reduce fog. Early work at Kodak by Crabtree indicated that a low level of sulfite (such as 10 g/L) had a minimum tendency to fog. Although it is unwise to generalize from this kind of early experimental information, 10 g/L would be an appropriate level of sulfite for trial.

There is another good reason for lowering sulfite when a document film is used. Sulfite at *any* level has a solvent action which initiates solution physical development. The finer grained the film, the more pronounced this action. Document films are exceedingly fine grained. Sulfite should be reduced to a minimum on the assumption that doing so will improve image quality. (Some document films are so sensitive to sulfite that they are fixed in several minutes in a 10% sulfite solution. POTA was not designed for such fine-grained films.)

MODIFIED POTA

Hot water (150F/65C)	
Sodium sulfite anhydrous	10g
Phenidone	0.5 g
Pyrogallol or Hydroquinone	0.25 g
Cold Water to make 1 liter	

MODIFIED POTA
Add borax or bicarbonate as desired to control time, contrast, and speed. Hot water helps the Phenidone to dissolve, but the solution should then be cooled to working temperature as soon as possible. Develop for 11 minutes as a trial.

The formula to the right is a trial modification in which we try to optimize POTA for document films. Because sulfite has been reduced, the pH of the developer may not be quite as high. But developing times should be shorter than the 15 minutes generally used with POTA and variants, because of the superadditive activity of the combined developing agents.

This formula contains less of the difficult-to-dissolve Pheni-done. It is also more stable, and less expensive. Raising the pH with a small amount of bicarbonate or borax will enable you to fine-tune the results. Yet another possibility to obtain higher overall image quality is to add metol, a technique Crawley found useful with Phenidone developers. A half gram of metol could be added to the Modified POTA formula above, or could replace the pyro or hydro-quinone for a less superadditive effect.

POTA modifications with glycin

As stated, the problem with adding a second agent to POTA is that the better it stabilizes the Phenidone to prevent streaking, the more it raises contrast. Probably the most stabilization with the least rise in contrast will be obtained with glycin. This technique is thought to have been used in H^W Control developer. Because of its resistance to oxidation, glycin permits adding the lowest practical amount of sulfite. The trial formulas TCLC-101 and 102 can be used as starting points.

	TDLC-101	TDLC-102

	TDLC-101	TDLC-102
Sodium sulfite anhydrous	4	4g
Phenidone	0.1	0.25 g
Glycin	0.5	0.25 g
Sodium bicarbonate	20	5g
Water to make 1 liter		
Develop Tech Pan for 15 minutes.		

Another possible addition to these formulas is a small amount of potassium iodide as an antifoggant, and possibly as a speed accelerator (0.001–0.01 g/L). Isopropyl alcohol could also be added (50 ml per liter). This will increase speed slightly, and preserve the solutions better when stored. For more compensation, use a small amount of a stronger alkali such as metaborate or carbonate to replace the bicarbonate.

The Delagi POTA modification

Other problems with POTA formulas are slow speed and, according to R. E. Delagi, a metallurgist, poor edge sharpness. A modification by Delagi published in an article by Bob Schwalberg in Popular Photography in 1982, was said to increase sharpness and acutance dramatically. This is an overoptimistic claim which reflects the inherent variability of POTA formulas, as well as batch-to-batch variations in Tech Pan that are due to its complex manufacturing process.[5] In the original publication a 2% BZT solution was given in error; it should have read 0.2%, as published here. Borax has been added to boost activity pre sumably lost through the BZT addition. Kodalk (sodium metaborate) boosts activity and contrast even more. Formulators normally use potassium bromide rather than an organic antifoggant in low to medium pH Phenidone developers. BZT has little antifoggant effect at these pH levels. It is still better to avoid using an

antifoggant if possible. Usually the best way is to lower the alkalinity. This developer may well have value, but if so it is not for the reasons stated.

DELAGI-8	
Sodium sulfite	25 g
Phenidone	1.4 g
Borax (decahydrate) or Kodalk	2g
Benzotriazole, 0.2%	15 ml
Water to make 1 liter	

Other low contrast developers

Stepping away from the abyss of Phenidone and its problems, Shepp and Kammerer at Polaroid formulated Developer T/O XDR-4, using the MQ combination.[6]

Like POTA, this is a simple and ingenious formulation. TDLC-103 is more likely to give good results with document films, and as an extreme low contrast developer for today's normal contrast films. Since its first publication in FDC1, we have noticed that some manufacturers are supplying TDLC-103.

T/O XDR-4	
Metol	1g
Potassium sulfite	25 g
Hydroquinone	1g
Potassium bicarbonate	10g
Water to make 1 liter	

There is no apparent need for HQ in either formula at this pH. Contrast with this formula and T/O XDR-4 is somewhat higher than POTA. Most

importantly, the Phenidone streaking problem is eliminated. The 1g/L of metol called for in the T/O XDR-4 may not be low enough. I have modified TDLC-103 to use 0.25 to 1 g/L of metol. I reduced sulfite as well: 25 g/L could be too solvent for some document films. By allowing more oxidation of the metol, the lower level of sulfite should also result in more controlled highlight gradation, and more adjacency effects.

TDLC-103	
Metol	0.25-1 g
Sodium sulfite anhydrous	5g
Sodium bicarbonate	10g
Water to make 1 liter	
Feel free to use potassium salts or mixed sodium & potassium salts, see ch. 10, p. 123.	

Actually, most developing agents can be used for document films, if the amount of the agent is low enough. Formulas with metol, metol-glycin, or pyrocatechin can be prepared with carbonate as alkali. Such developers are similar to the traditional high acutance compensating formulas, except that the amount of developing agent is approximately half, and the carbonate is proportionately higher.

The technique is to keep the total amount of developing agent between 0.15 and 0.3 grams per liter of solution. This assumes rather high carbonate alkalinity. With this in mind, either FX 2 or PMK could be used with one-half to one-third their standard A solution and twice their standard B solution. However, in light of later experience, we would also look at buffering the carbonate, and adjusting the amount of developing agent slightly upwards if necessary.

LOW CONTRAST DEVELOPERS	
Metol or Pyrocatechin	0.15-0.30 g

LOW CONTRAST DEVELOPERS	
Sodium sulfite anhydrous	1-5 g
Sodium bisulfite	0-2 g
Sodium carbonate anhydrous	10-15 g
Distilled water to make 1 liter	
Reducing the sulfite to a half or even a quarter of a gram will increase the tanning and hardening effects of the pyrocatechin, as well as sharpness and contrast for both pyrocatechin and metol. A bicarbonate or bicarbonate-citrate buffer, Crawley-style, may provide some control in shaping the characteristic curve to your particular needs.	

The table to the right shows suggestions for low contrast developers based on metol and pyrocatechin. The pyrocatechin developer is very sharp, has good speed and gradation, and a tanning effect. Develop for 10 to 15 minutes, depending on the film and desired effect. Agitation is an important factor with all such developers. Minimal agitation—10 or 15 seconds every 3 minutes—helps to increase the speed by suppressing highlight development, without affecting shadow development (see chapter 4).

As with all carbonate developers, use a buffered stop bath of pH 4.5–5.5, or a 5% sodium sulfate solution, or a plain water rinse for one minute. Follow with an ammonium thiosulfate fixer. However, determine clearing time in advance. Although clearing time for Tech Pan is not unusual, clearing time for Copex-Rapid-type films is extremely rapid. Overfixing *must particularly* be avoided with document films, so be sure to move to a water rinse with agitation immediately after fixing, or better yet, use an alkaline fixer.

The speed of these dilute high alkali developers can be expected to be as much as twice that of POTA, while still maintaining low fog levels. This can amount to a working speed of EI 50 or even higher.

Variants of some commercial developers have been used to achieve low contrast. One is FX 14 (Acutol) at 1:20, another is Microdol-X at 1:10. Even

D-76 has been successfully used full strength, but the developing time of one minute or less is too difficult to practice reliably, and there is undoubtedly speed loss with this procedure. (D-76 has also been used at 1:10.) Xtol 1:5 for 12.5 minutes at 70F/21C, is recommended by Kodak. We suggest trying Xtol at 1:10 and adding 1g/L of sodium metaborate to keep developing times reasonable. This may produce a small increase in speed.

All of these variants will produce noticeably different gradation characteristics. Different developers will give infinitely more variety of response than "normal" developers give with "normal" films. This extraordinary measure of tonal control makes experimenting with document film developers a fascinating experience.

HQMS, tanning, buffering

HQMS (hydroquinone monosulfonate) is beginning to get a fairer slice of mindshare. Because its regeneration kinetics are weaker than and different from HQ when working with the phenidones, it is a natural candidate for making innovative phenidone-plus-some-other-agent developers for document films. In the TDLC developers given earlier in this chapter, HQMS could be used instead of glycin, although the quantity of HQMS would probably have to be higher.

For those who want to explore a tanning developer for document films, we suggest Formulary TD-3 or Pyrocat-HD at 1/2 strength (1:1:200 or even 1:1:300).

Another suggestion for all carbonate-based developers being used for document films is to try the Crawley technique for buffering with bicarbonate or bicarbonate-citrate (chapter 6). This will provide some control in shaping the characteristic curve of document films. We emphasize that the curve shape of document films is easy to change dramatically.

Low contrast developers based on PPD derivatives

Grant Haist has suggested that it should be possible to formulate low contrast developers valuable for both document films and tabular grain films by adapting techniques used for developing color negative films. We hope this suggestion will be addressed by researchers in the future.

Commercial low contrast developers for document films

The only low contrast developer from a major company was Kodak Technidol, a variation on POTA. It shared POTA's faults and provided no advantages. Offerings from small companies are continuing to evolve.

> *USP 3,772,019 (1972) for the H^W developer contains much useful information. It is claimed that in prior developers, Phenidone is used in small quantities to activate a primary developer such as HQ, ascorbic acid, etc. In this developer Phenidone is said to be the primary developing agent, and the superadditive agent is secondary.*

A developer which alleviates the streaking problem is Photographers' Formulary TD-3.[7] This developer has a different characteristic curve from POTA derivatives, with a short toe, exceptionally marked shadow and middle-tone contrast, and a long shoulder which gives a characteristic pearly appearance to high tone values.

TD-3 produces speed approximately double that of POTA types while significantly lowering granularity, perhaps through a physical development action which T.H. James thought was occurring.[5] However, it can be more difficult to print than POTA. The best overall results are obtained when

contrast is high enough to require grade 1 paper with a condenser enlarger or grade 2 paper with diffused light.

The first commercial document developer, H&W Control, is no longer available; neither is Tetenal's Neofin doku.

USP 3,77,.267 (1973) by Simeon Braunstein for the USAF shows a technique for using a Phenidone/glycin developer to achieve wide range and high speed on normal films.

In the 21st century, the Spur company in Germany has been active in promoting document films and their proprietary chemistry. The Spur developers often utilize the phenidone-HQMS model, which we think is a good approach. Though claims for the products can seem exaggerated, the Spur products have been successfully used for over two decades and have won a loyal following. Other companies that market their own special developers include Adox and Rollei.

Adox's Adotech IV is a developer designed specifically for Adox CMS 20 II. Generally speaking it uses the Spur technique, with every effort made to optimize the formula for this particular film.

All the developers we have discussed represent the intelligent adaptation of known photographic science to the obstinate problem of producing low contrast developers. We are still waiting for a breakthrough in low contrast development—a technique that would not rely on developer exhaustion.

Low contrast developers with normal films

All the developers mentioned in this chapter can be used with normal films when it is necessary to photograph scenes of extreme light range (over 10 stops). It is crucial to test individual developers beforehand since it is

impossible to predict exactly how each will behave with a given film. We are inclined to think, for extremely long-range subjects, that a pyrocatechin tanning developer, used 1/2 to 1/3 strength, is likely to produce the best pictorial results. However, a POTA-type developer is more likely to provide a smoother characteristic curve. We expect that results will be better with conventionl grain films.

A perspective on document films and fine negatives

Some photographers expect to obtain the quality of 8x10 sheet film with 35mm or 120 document films. The reality is that no matter what developer is used, document films will never have either the micro or the macro contrast range of 8x10 Tri-X or HP5. Unless this is understood results with document films will be disappointing. Exposure must be determined much more carefully and bracketing of important exposures is recommended where possible (a stop either way should be adequate). Furthermore, it is important to study the spectral sensitivity of the document film you are using so that you know where it deviates from conventional panchromatic.

Speed for document films must be determined either by experience, or on a scientific basis by the fractional gradient point Jones method or the fixed point gradient method of Nelson and Simmonds,[1] which allow speed to be accurately determined at any gradient.

OTHER CONCERNS WITH DOCUMENT FILMS

Camera and lenses

An attraction of using document films is that they can be enlarged 20–40x and still maintain excellent sharpness. 20X enlargement from a 35mm negative is equivalent to a 20x30–inch print. 40X enlargement would be equal to a 40x60–inch print. To accomplish this while maintaining excellent sharpness requires much care.

Magnifications of this size require excellent lenses, clean and in good condition. Lens faults you were unaware of will become obvious with 20x enlargements.

It is important to avoid camera motion. Hand-held exposures should be made in good light or with flash. For maximum sharpness use a tripod and cable release at any speed below 1/125. If possible, pre-release the mirror at least 10 seconds before exposure.

> *Depth of field is different with document films. In some pictures, there may be noticeable areas which are obviously not quite in focus but which yet seem not to be completely out of focus either. This seems to be due to a complex relationship involving depth of field calculations, film resolution and granulaity, viewing distance, and lens bokeh.*

Use the lens's sharpest aperture, usually 2–4 stops down from wide open. Depth-of-field indicators on lenses should be regarded as optimistic if you

plan big enlargements. If you use very small apertures to obtain great depth of field, you will notice a falloff in lens sharpness. That falloff is often masked by the grain of conventional and tabular films, but not with document films.

All filters impair lens definition to some extent. If used with document films, filters should be of the highest quality, and in perfect condition. Only filters made of optical glass should be used.

Finally, document films can be more sensitive to static electricity than other films. Handle film slowly and carefully, especially when rewinding.

Enlarging document films

Just as it is important to avoid camera shake in the field, it is important to avoid vibration during enlargement, especially during the long print exposure times which are often required for big enlargements. Moving around the darkroom while the print is being exposed may lead to unsharp prints.

It is essential that your enlarger be in perfect alignment. Even professional enlargers fall out of alignment. Misalignment becomes more obvious when extreme enlargements are made.

Negative carriers should have an adjustable masking device to reduce flare.

Some document films have polyester bases with a particular tendency to curl. To minimize film curl with all films, dry the film with weights and store flat.

Tiny micro-abrasions can be caused by excessive handling. They may not be noticeable with normal enlargements, but can become evident when the negatives are enlarged 20 or 40x.

Enlarging lenses

Almost all enlarging lenses for 35mm film are optimized for maximum sharpness at 10x magnification (just as most camera lenses, except macro lenses, are optimized for maximum sharpness at infinity or a middle distance). However, with document films, there is often the desire to make 20x and greater blowups. With 40x to 100x blowups, a top quality camera lens mounted on the enlarger may give better results than many enlarging lenses. An exception is the Schneider 45mm Apo-Componon which can be used to 30x.

> *These recommendations also apply to conventional films when extreme enlargements are planned.*

There is also a series of Schneider G-Componon lenses designed for 20x and greater magnifications (a similar range is available from Rodenstock). For general use, a 28 or 35mm enlarging lens can be used if only a small part of the negative is being used. Care should be taken to center the part of the negative being enlarged. Unfortunately, most of these lower focal length enlarging lenses are optimized for 10x. Exceptions are the 28mm Schneider Componon and Rodenstock Rodagon which are optimized for 20x.

Use all lenses at their optimum aperture—usually 2 to 3 stops down from their largest opening. For critical corner-to-corner sharpness, a glass carrier should be used, although this creates other problems. When using a glassless carrier the lens may have to be stopped down to f/11 to obtain corner to corner sharpness. This is not the ideal aperture for a good 50mm lens and the difference may well be visible.

Increasing speed with document films

Tech Pan was often used by astronomers and photographers interested in capturing nighttime scenes. For very long exposures, the speed of Tech Pan could be increased up to 10x by gas hypering. All document films should be responsive to any of the hypersensitization and latensification techniques discussed in chapter 10. These processes also often reduce contrast and alleviate reciprocity failure with long exposures.

Suggestions for the future

We would suggest looking at some of Crawley's highly buffered non-solvent developers. Acuspecial is a developer of known stability that would probably work well with document films, though it may have to be diluted further. It is possible that the minute amount of iodide may have a sharpness-increasing effect when used with the comparatively primitive document films that are available to us today. As mentioned, we believe some dilution of Pyrocat-HD should work. It may be that the developer would need to be modified. For example, keeping dilutions the same, the amounts of the developing agents would need to be halved. But just about the same effect could be obtained by using the developer at 1:1:200 and adding a gram of sulfite. It is also possible that the accelerator would need to be higher: for example, 1:2:200. We would also suggest experimenting with buffering the accelerator solution. Buffering will, however, bring the pH somewhat lower, thereby reducing activity somewhat. This may require a small weight increase for the developing agents, although simply developing for a longer time may also provide the adjustment.

Phenidone-ascorbate developers for document films

At the time of FDC1, phenidone-ascorbate developers were just becoming popular. Zawadzki and Dickerson have suggested that Xtol is a good

developer for document films at 1:5 and we suggest experimenting with dilutions up to 1:10. There may be room for improvements in finding the ideal phenidone-ascorbate developer for today's document films. If perfection seems elusive, rebalancing the ingredients to meet the requirements of the particular film may be required at greater dilutions.

> *When using phenidoneascorbate developers such as Xtol at very high dilutions, it may be necessary to add more DTPA—chapter 5.*

For example, the Kodalk(sodium metaborate) level may have to be raised if development times get too long. If contrast still seems too high with the film you are testing, decrease the amount of ascorbate.

Philosophical caution

When we use a document film for normal range photography, just as when we use a normal film for wide latitude (over 10 stops) photography, we are using the film in ways it was never designed for. In both cases, we seek developers that are useful for a short period just before they reach the point of total exhaustion. This is a far riskier technique than normal development of normal films. If you are willing to take risks and suffer an occasional disaster, fine. But if you need to play the photographic process as predictably as possible, document films are probably not for you.

Why we use document films

What we find most exciting about working with document films is *not* the ability to make huge enlargements. Indeed, for many reasons, best print size

will often be found to be 8x10 or less. For us, what makes working with document films so rewarding is their ability to produce unusual tonalities through unusual characteristic curve shapes. They add to our palette.

NOTES

1. For a technical explanation of this point, see L.A. Jones and M.E. Russell, "Minimum Useful Gradient as a Criterion of Photographic Speed, *Phot. J.*, 75:657 (1935); L.A. Jones "The Evaluation of Negative Film Speeds in Terms of Print Quality, *J. Franklin Inst.*, 227:297, 497 (1939); L.A. Jones, "Photographic Film Speeds as Evaluated in Terms of Print Quality, *British J. Phot.*, 87: 191 (1940); and C.N. Nelson and J.L. Simonds 'Simple Methods for Approximating the Fractional Gradient Speeds of Photographic Materials', *Journal of the American Optical Society*, 46: 324 (May 1956). These classic articles form the cornerstone for all speed determination methods right down to the present. Though crystal clear, they have been radically distorted by most subsequent commentators claiming expertise in sensitometry. One exception is Stephen Benskin, 'The New ISO Standard', *Darkroom & Creative Camera Techniques*, Sep/Oct 1995.

2. Marilyn Levy, "Wide Latitude Photography", *Phot. Sci. and Eng.*, 11: 46 (1967).

3. T.H. James & M. Levy to BT.

4. Marilyn Levy, "Superadditivity of Phenidone/Pyrogallol Developers", *Phot. J.*, 105: 303 (1965)

5. Henry. Sylvia Zawadzki has found that the original POTA formula is sharper than any of the variants based on it (SZ to BT, 1998).

6. A. Shepp and W. Kammerer, "Increased Detectivity by Low Gamma Processing", Phot. Sci. and Eng., 14: 363 (1970).

7. R. Bender, *Darkroom Photography*, May/June 1984.

See also:

A. Shepp, W. Kammerer, and R. Shuman, "Extended Dynamic Range Processing", Technical Operations, Inc., AFCRL-67–0633, Air Force Cambridge Research Laboratory, Bedford, Mass., November 1967. R. M. Shaffer and D. M. Dutton, "Wide Latitude Processing of Tri-X Ortho Oscillographic Film", EG&G Report 1183–1465, Tech Report No. L-9, 15 January 1970.

Chapter 12
AFTER DEVELOPMENT PROCESSES 1

QUICK GUIDE RECOMMENDATIONS

- Kodak research established that a conventional stop bath does not stop development rapidly. The industry mainly supported stop baths because they prolong the life of acid *hardening* fixers. However, since these are rarely used today, conventional stop baths have little point.
- Conventional indicator dyes should not be relied on.
- For all modern films and papers we recomming using a *running* water stop bath and an *alkaline* fixer. An alkaline fixer allows much shorter washing times, potentially less swelling of the emulsion, and eliminates silver image loss (bleaching) when fixing for extended periods. An all-alkaline-to-neutral process, from development to final rinse, provides greater image integrity, greater archival stability, and *substantial water conservation.*
- Kodak's recent E-6 processes don't use a stop bath. For years, Ilford has been recommending a *running* water rinse after film development. One result is improved sharpness.

STOP BATHS: ACID VERSUS WATER

The main function of an acid stop bath is to stop development as completely and quickly as possible. This is most desirable with development times under 10 minutes, when a small error can make a significant difference in negative quality. One advantage of long developing times is that timing errors must be much greater to have any visible effect.

The secondary function of an acid stop bath is to prepare and condition the film for immersion in a hardening acid fixer. Such fixers are less often used today but when they are, it is essential to keep the pH within a narrow range to avoid sludging of the hardener in the fixer.

Although there are advantages to acid stop baths, there has been a shift away from them, to running water baths, notably in Kodak's current (and high precision) E-6 system.

One disadvantage of conventional, unbuffered stop baths (a 1–2% solution of acetic acid) is that when the film developer contains carbonate, irreversible blistering may occur (Haist 243). Another is the occasional possibility of reticulation (Mason 207). A third disadvantage is smell, though this is really only a concern where open trays are used. Finally, and most important, as shown below, a *conventional* stop bath does not stop development rapidly. To stop development instantly, a *buffered stop bath* is required. A buffered stop bath will also (a) minimize swell (because of higher salt content), and (b) minimize or eliminate the possibility of blistering with carbonate developers (because of higher pH). See "Avoiding Swell" in Appendix 1.

Using a neutral water stop bath in place of an acidic stop bath creates a different set of circumstances. When film is placed in water, the developer does not immediately cease to work; it is merely diluted. Since it is so dilute in the water stop, it will rapidly exhaust in the highlights, but continue to

develop in the shadows for a few moments. At the same time, valuable sharpness-enhancing adjacency effects occur.

Using acid stop baths

To use an acid stop bath, drain the film for 10 seconds after development and move to the stop bath as quickly as possible. Agitate continuously for 30 seconds, drain for 10 seconds (the optimum draining time for photographic solutions[1]), and then move the film to the fixing bath.

> *Ron Mowrey notes that acid stop baths promote the removal of metol, a potential advantage when processing times are very short.*

The temperature *must* be the same as the developer.

Using water stop baths

Using a "slow stop" water bath system necessitates slightly shorter developing times. Our recommended system for tank development is:

1. Pour the developer out of the tank and drain for ten seconds.
2. Immediately refill the tank with fresh water at the *same temperature* as the developer. Agitate for ten seconds, then pour out the water.
3. Repeat the sequence for four more cycles, which will take 1–2 minutes depending on your fill/empty times.
4. Pour the fixer into the tank and agitate 30 seconds.

With tray development of sheet film we recommend a *running* water tray setup, such as the Paterson High Speed Print Washer.

Wash the film for *one full minute*. Drain for ten seconds before moving it to the fixer.

The takeaway from the Kodak research on stop baths is the finding that except when absolutely fresh, conventional stop baths stop development so slowly that one might as well use water. Their value is in helping to prolong the life of acid fixers, particularly acid hardening fixers. Related-ly, it became apparent that conventional indicator dye encourages the use of conventional stop baths long after they have lost what little effectiveness they had in the first place. It is significant that in 1938, when PCS was published, Kodak recommended acetic acid stop baths mainly for prints, not negatives. To add a further wrinkle, PCS advised, "Stop baths should always be used with discretion … otherwise an excess of acid is carried over into the fixing bath which in turn causes sulphurization."

COMPOSITION OF ACID STOP BATHS

Most commercial and published formulas for stop baths are based on acetic acid, the acid in common vinegar. The working solution is usually between 1% and 2% in water. It is cheap and plentiful and "does not precipitate sulfur or interfere with the hardening of the fixing bath" (Haist 548; E. Weyde, BJP v. 82 p. 326, (1935)). The only other ingredient sometimes added is a pH indicator dye for "indicator" stop baths.

Household distilled or 'white' vinegar for table use is usually 5% acetic acid and could be used as an emergency stop bath diluted with water 1:1 or 1:2. In some countries stronger vinegar, which must be handled with great care, is available.

Objections to this typical bath are its odor, low buffering capacity, excessively low pH (2.9) when first used, and inability to stop development in under 10 seconds except when used the first one or two times. Even so, acetic acid stop baths are still preferable to those based on bisulfites and most other acids. Sodium bisulfite eliminates the possibility of blistering (PCS) because of higher pH, but is too weakly acidic to be a preferred chemical.

The pH of a fresh acetic acid stop bath is 2.9. The pH of an ideal stop bath is 4.5. The ideal stop bath is an approximately 10% buffered equimolar solution of acetic acid and sodium acetate as in the TS-7 formula. Capacity: at least 40 x 80 square in.[1]

TS-7 BUFFERED STOP BATH	
Water at 125F/52C	500 ml
Acetic acid 28%	120 ml
Sodium acetate	80 g

TS-7 BUFFERED STOP BATH
Cold water to make 1 liter

In this bath the pH is raised but the *total acidity* is increased. As a surprising result, this bath will stop development more quickly than a conventional stop bath (3 seconds as opposed to 30 seconds), prevent blistering (because of moderate pH), and prevent reticulation and swelling (because of its high salt content). It will also have maximum compatibility with acid fixing baths. (Think of pH as measuring strength, and total acidity as measuring stamina.)

As pointed out earlier, a plain acetic acid bath promotes swelling. However, the high salt content of TS-7 minimizes swelling. We strongly recommend a formula of this kind whenever an acid stop bath is used.

Some pros and cons of alternate acids to acetic are discussed in Haist, PCS and Crabtree, Muehler and Russell, "New Stop Bath and Fixing Bath Formulas and Methods for Their Revival", JSMPE 38:352 (1942).

Odorless stop baths

An adequate, not excellent (because unbuffered) stop bath can be made with 3% to 5% boric acid in water. Unlike most other acids, boric acid does not interfere with metal hardeners used in acid hardening fixers. To make, add 50 grams of boric acid to one liter of warm water. Boric acid does not go into solution easily. Use a grade intended for photographic use. The solution should become clear after 24 hours. If it does not, add more water until it does. Capacity is about 10 times 80 inches^2.

Citric acid odorless stop baths; other solid organic acids

Haist (547) states, "Solid organic acids such as citric, diglycolic, tartaric, maleic, malic, or oxalic, may be suitable to stop development in the stop bath but if carried over into the fixing bath, these acids may form complexes with the metal ions of the hardening agents, thus weakening the hardenining properties of the fixing bath."

> *If citric acid is to be used, (1) it should never be used where a hardening fixer is used and (2) it should be highly buffered with sodium citrate, analogously to TS-7.*

Citric acid stop baths are becoming more popular, probably because they are easier to ship in many areas. In the past, citric acid has only been used when acetic acid was unavailable, for example due to wartime restrictions. One reason not to recommend citric acid is that it hasn't been studied as well as acetic acid. So, for example, we don't know, as we do with acetic acid, how quickly an unbuffered citric acid bath would stop compared to a buffered citric acid bath. A typical formula is Kodak SB-7, 15 g citric acid to 1 liter of water.

Since the best reason for using a stop bath is to prepare the film to be immersed in a hardening fixer, and since citric acid impairs that, we don't see value in using it for tank developing. For film and paper developed in open trays, its lack of odor provides a more compelling argument.

pH indicators for stop baths

The ideal pH range of a stop bath is between 4 and 5, with pH 5 the safest maximum. If you do not have a pH meter, a narrow range indicator strip is

the most convenient way to check pH. Indicator paper can be unreliable, but so can uncalibrated pH meters. If you use a meter, calibrate it often with reference solutions.

The commonly used indicator dye is bromocresol purple. It is yellow at pH 5.2 or below, and purple at pH 6.8 or above. In other words, it is useless, since the stop bath will have been almost inactive long before the dye color changes.

Bromocresol green is preferable. It is yellow at pH 4 or below, green at just above pH 4, and blue at pH 5 or above. The bath is still good when green, but should be discarded very soon after it turns blue. Haist (545) strongly recommends a few drops of a **0.5% alcoholic solution of bromocresol green** in stop baths for film processing.

When using a highly buffered stop bath such as TS-7, pH will remain consistent for *much* longer than might be expected.

Neither borate nor citrate should be used for color stops baths. In black and white, most acids other than acetic cause compatibility problems or are suboptimal for other reasons, not excluding cost.

STOP BATHS AND TANNING DEVELOPERS

More developers form colored oxidation products—brownish stains—and various scums, than is commonly realized, because acid baths (conventional stop or fix) remove them. Thus where oxidation stain is desired, such as when using a pyro or catechol tanning developer, keep the film processing alkaline or at least neutral from start to finish.

This fact has often been overlooked, which has led to some of the disappointments experienced by those using pyro or other tanning/staining developers. A water rinse, in place of an acid stop, should be used with all tanning developers.

Grant Haist speculated that when a film is moved from an alkaline developer into an acid stop bath, enough molecular heat could be generated to cause structural changes in the negative. I got into trouble when I included this remark in FDC1. I should have pointed out that Grant's theory has not been established. On the other hand, anything Grant said (or speculated) was worth listening to. The quotation from Mason (p. 207) to the right, about how immersion of film in a dilute acid bath can cause reticulation, supports what Grant was saying. Haist gave over an entire page (544) to a photograph illustrating the problem.

AVOIDING RETICULATION OR "EXCESSIVE GRAININESS" DURING WASHING

A frequent question is *'why is my negative so much grainer than usual*?' Mason gives the definitive answer:

> Reticulation … is an irregularity of the surface of the gelatin, caused by stresses in the gelatin parallel to the support. As only the surface layers can move to relieve this stress, the effect is confined to the surface layers of gelatin. Stresses giving rise to reticulation are produced by alternate treatment in baths promoting swelling and shrinking of the gelatin. A common cause in normal processing is the use of wash water at a higher temperature than the processing baths. It can also be produced by immersion in dilute acid baths. In severe cases of reticulation, some movement of the image silver may tend to migrate to the ridges of the relief pattern, and hence an optical mottle pattern is superimposed upon the mechanical relief pattern. When this happens, the graininess is very much worse than would normally be expected. (Mason, 207)

We would add, when using a water stop, don't let the film dawdle. Shorter times will minimize swelling. Haist observes that "fine ruptures" can occur even during a water rinse. Keep times short, and keep the temperature of the rinse water the same as the developer. If there is something about your process that still obstinately causes reticulation, the ultimate cure is to use a stop or water bath that contains 5% sodium sulfate (not sulfite), which will keep swelling down to a safe point.

HARDENING STOP BATHS AND PRE-HARDENERS

The various approaches to hardening stop baths are discussed in the second half of Appendix 1. Hardening stop baths and prehardeners are important for all films or plates which do not use modern 3G hardening processes during manufacture, and for films or plates which must be processed at very high temperatures.

NOTES

1. The source for this information is R.W Henn and J.I. Crabtree, *Effects of (a) Degree of Acidity and (b) Total Acidity on Neutralization Time*, PSAK., 17B:14(1951). Is this research still true half a century later? Ron Mowrey tells us that an unpublished study was made more recently which confirmed these findings but indicated that stop times are now somewhat faster with some materials. Mowrey also points out that generally speaking, development will be stopped more rapidly with films based on bovine gelatin rather than porcine gelatin. Regardless of these points, a sodium acetate buffered stop bath will stop faster and minimize swelling.

Chapter 13
AFTER DEVELOPMENT PROCESSES 2: FIXING, WASHING AND DRYING

> *An alternate definition of fixing is given by Mason (183): At the end of the development process there are, in addition to the developed image, some residual silver halides. If these are not removed or converted into more stable compounds, they will decompose over time into metallic silver. The removal of the silver halide is achieved by converting it into a soluble complex, which is subsequently washed out of the emulson. This process is known as 'fixation'. If the residual silver halides are converted into more stable compounds and left in the emulsion layer, this process is known as 'stabilization'.*

After the developer, film is placed in a stop or water bath to stop development and condition the film for the next step: the fixing bath, usually called the fixer. Fixing removes the unused silver salts from the emulsion layer. These salts are opaque. Removing them makes the developed image appear transparent on the film or plate base. Another reason why these unused silver salts must be removed is that they are still light sensitive, and would darken when exposed to light. After fixing, washing is necessary to remove harmful residual compounds. An optional step is archival protection, covered in chapter 15. Finally, the film is dried.

Clearing time

Clearing time is the time it takes for the fixer to visually ‘clear’ the film, that is, to turn the undeveloped areas, such as the edges, or the film leader, from opaque to transparent. Fixer is usually discarded when clearing time doubles.

FIXERS: SODIUM VERSUS AMMONIUM THIOSULFATE

In the 1980s almost all research into the nature of the fixing process and image permanence came to a halt. At that time, new findings suggested (a) that sodium thiosulfate fixers were not adequate for modern films and papers and (b) that some residual thiosulfate in films and papers could protect them from atmospheric attack (see chapter 15). Some Kodak researchers went so far as to suggest that thiosulfate should be replaced by more stable chemicals, but layoffs ended further investigation. Grant Haist had already stated (p. 589), "Ammonium thiosulfate fixing baths are relatively insensitive to increasing amounts of iodide up to certain limits. **For modern bromoiodide films, rapid fixing baths containing ammonium thiosulfate are more suitable than those that contain sodium thiosulfate, whose fixing times increase when small amounts of dissolved iodide build up in solution.**" (emphasis added.) Iodide levels have increased in both films and papers since Haist wrote this in 1979.

QUICK GUIDE RECOMMENDATIONS

- Researchers have known since the 1950s that all-alkaline (or near alkaline) processing, from developer to fixer, may be the best way to process film and paper for permanence.

Acid sodium thiosulfate fixers

Increased iodide is the main factor working against sodium thiosulfate fixers,[1] but new sensitizing dyes and tabular grains may also play a part.[2]

> *Iodide levels in films and papers increased in the 1980s when manufacturers refined the ways iodide could be used to improve speed, tone, and sharpness. When Ilford's 30-second ammonium thiosulfate archival print fixing technique was introduced for fiber papers in 1979, Ilford specific-ally warned, and independent tests confirmed, that the system could not be used with some Kodak papers. The reason, not then generally known, was that Kodak was the first to elevate iodide levels in enlarging papers. Later, other manufacturers would take advantage of research in iodide epitaxy and other techniques, such as precision iodide placement.[2] Progress was fast. By the 1990s, Ilford was no longer recommending the 30-sec. fix, even for its own papers. [Some of this material is in C.W. Kennedy, Popular Photography, Jan 1981.] The Ilford rapid sequence was the work of LFA Mason. His technical paper describing the process was distributed to technical writers but was not published in a scientific journal. Ilford no longer seems to have this paper. The system is still of value for fibre-based papers that use little iodide.*

When sodium thiosulfate fixers are fresh, they *will* fix adequately, but with modern materials, they will exhaust much sooner.

Although we no longer strongly recommend sodium thiosulfate fixers with modern films, they can be used as long as you keep an eye on clearing time. The gold standard formulas are Russell's F-5 and F-6 for Kodak, especially F-6 (Appendix 1). The commercial equivalent to F-5 is "Kodak Fixer" which has long been the standard for commercial sodium thiosulfate fixers. Expanded coverage of most of Harold Russell's Kodak fixers is included in Appendix 1. In particular we note the combined ammonia-salt/sodium thiosulfate fixers, F-7, 8 and 9. These are intermediate in speed

between sodium and ammonium: about twice as fast as sodium, while pure ammonium thiosulfate fixers are about four times faster. These may also turn out to be the most economical of rapid fixers, depending on relative prices of the chemicals in your area. Furthermore, these formulas can easily, if the alum hardening component is dispensed with, be adjusted to near-neutral or alkaline pH. Above all, the ammonia-sodium fixers can safely be recommended for modern high iodide films because the ammonium component should be sufficient to prevent fixing times increasing excessively as iodide builds up during the life of the bath.

Exception: for old technology and hand-coated emulsions, it has been found that sodium thiosulfate hardening fixers *must* be used, and F-5 is the safest choice. Since potassium alum (but not chrome alum) increases washing times, use a hypo clearing agent. For very soft emulsions, it may be necessary to harden with a chrome alum stop bath. In some cases, it has even been found necessary to harden the material before development, either in a (fresh) aldehyde or (fresh) chrome alum hardener. Much more on this in Appendix 1.

To use sodium thiosulfate fixers safely with modern films: Observe and record clearing times throughout the life of the fixer, especially after the middle of the fixer's expected life, when iodide buildup is likely to occur. The higher the iodide levels in the film or paper, the less will be its life. Times for tabular films may be very long. Discard the fixer when clearing times double, which may be sooner than you expect. Appendix 1 includes a formula for an alkaline sodium thiosulfate fixer.

Acid ammonium thiosulfate "rapid" fixers

If an acid fixer is to be used, we prefer "rapid" fixers based on ammonium thiosulfate. (To avoid the possibility of bleaching during long fixing times with rapid fixers, use a neutral or alkaline fixer instead.) Check clearing times often during the lifetime of the fixer. Several commercial acid rapid

fixers, all similar, are available. The standard is Kodak Rapid Fixer. The optional hardener which comes with most rapid fixers is no longer necessary except with processing temperatures over 80F/27C (see Appendix 1) or with soft emulsions.

Few formulas for acid ammonium thiosulfate fixers have been published. It is simpler and usually more economical to buy them ready made. The first formulas were published by Alnutt in 1943,[3] reflecting that ammonium thiosulfate had just become available cheaply and in quantity for the first time. His best is ATF-1, which is the granddaddy of all subsequent formulas. Other Alnutt formulas are given in Appendix 1. ATF-1 is a great formula for 1943, but today we would expect a higher degree of buffering.

ATF-1 RAPID FIXER	**Working Solution**	**Stock Solution**
Water	700 ml	-
Ammonium thiosulfate, 57-60%	185 ml	740 ml
Sodium sulfite anhydrous	12 g	48 g
Acetic acid glacial	9 ml	36 ml
Boric acid	7.5 g	30 g
Water to make 1 liter. To use the stock solution dilute 1:4.		

A superior formula for this type of fixer, because of its moderately high level of buffering, is incidentally presented in Kodak's US patent 5,026,629. It doesn't look like the formula for Kodak Rapid Fixer (Appendix I). It is better buffered, and may be more expensive to produce. It may be intended for industrial use.

OPTIONAL HARDENER	
Aluminum chloride, hexahydrate	50 grams
Water to make 100 ml.	

OPTIONAL HARDENER

If desired, add 25 ml of the hardener solution to 1 liter of fixer working solution. Note that since the time these formulas were published, it has become common industrial practice to acidify the hardening solution with sulfuric acid. As a result they should be handled with extreme care.

The good amount of buffering (2.5% acetic acid working solution balanced with sodium hydroxide to create sodium acetate; metabisulfite; borax) results in moderate total acidity. Development should be stopped quickly even if film is placed directly from the developer into the fixer—see buffered stop baths, chapter 12—and the fixer should always be at optimum pH in normal usage. In that sense, this is the best formula we have seen published for an acid ammonium thiosulfate fixer with optional hardener. Ideally, we would prefer total acidity to be twice as high.

FORMULA FOR RAPID FIXER FROM KODAK USP 5,026,629

Demineralized water	125 g
Glacial acetic acid	98 g
Sodium hydroxide 50%	41g
Sodium metabisulfite	24 g
Sodium tetraborate pentahydrate (borax)	45 g
Ammonium thiosulfate 57%	986 g
Total quantity will be just over a liter.	

FORMULA FOR RAPID FIXER FROM KODAK USP 5,026,629

Note that the liquids are measured by weight. The method for mixing this fixer, according to the patent, is as follows, and includes the optional hardening component:

"In a first container, about 125 grams of demineralized water, about 98 grams of glacial acetic acid, about 41 grams of a 50% solution of sodium hydroxide, about 24 grams of sodium metabisulfite, about 45 grams of sodium tetraborate-pentahydrate and about 986 grams of a mixture of 57 weight percent of ammonium thiosulfate and 4 weight percent of ammonium sulfite, the balance being water are intimately mixed together at about 80° F. in order to give a solution having a pH of about 5.1.

"In a second container is mixed about 948 gramsofa 25% by weight solution of aluminum sulfate in water, about 148 grams of 93% sulfuric acid and about 206 grams of cold tap water.

"About 250 milliliters of the solution from the first container is mixed with 28 milliliters of the solution from the second container and this mixture is diluted with water to provide one liter of fixer solution."

Use extreme caution when handling glacial acetic acid, sodium hydroxide, and the optional sulfuric acid component.

Directions for using all acid fixers

Before using an acid fixer, films should be either immersed in a fresh acid stop bath with continuous agitation for 30–60 seconds, or rinsed in running water for 60 seconds. Fix for two times the clearing time; with modern technology films preferably three times the clearing time. This will usually be a minimum of three minutes even with rapid fixers. *Do not overfix.* After fixing, rinse the film in fresh water for one to two minutes, agitate continuously in a fresh hypo clearing bath for one minute and wash for 5–10

minutes in running water with occasional agitation. Without hypo clear, the washing time will be 20–30 minutes.

Hypo clearing agent

Hypo clearing agent (HCA; formula on the next page) is *only* recommended when an acid fixer is used. It is particularly advised when the material has been hardened in potassium alum. HCA saves time and water, and by decreasing the time spent in water, helps keep swelling lower than it otherwise would be. The bisulfite in the formula overleaf is added to minimize swelling. If swelling is not a concern, omit it, and hypo reduction will be greater and faster. A sequestrant can be added to prevent the precipitation of sulfite by calcium ions in the water supply. (Haist 651) The bisulfite also has the effect of minimizing precipitates in cold water if you are not using a sequestrant.

Chrome alum fixers, stop baths and pre-hardeners

The use of chrome alum fixers, stop baths and pre-hardeners has been deprecated for some time. However, there is renewed interest in them now that photographers are hand-coating emulsions. Chrome alum has two advantages: better hardening and less hypo retention than potassium alum (Mason, 205). However, as Haist warns, "the use of strong alkali also destroys chrome hardening, presumably by forming the less soluble hydroxide of the chromium" (p. 556) [this applies to chrome alum *pre*-hardeners], and as Mason warns, the aldehyde hardeners have their own set of problems. Ron Mowrey has pointed out that chrome alum appears to be the ideal hardener for hand-coated emulsions on glass plates. In his experience, subsequent processing in developers up to carbonate alkalinity has not caused problems. See Appendix 1 for detail and formulas.

HYPO CLEARING AGENT	
Water at 125F/52C	750 ml
Sodium sulfite anhydrous	200 g
Sodium bisulfite	15 g
Cold water to make 1 liter	
Dilute 1:10 to make working solution.	

Alkaline fixers

Although it may be more convenient to use acid fixers, as they are more readily available, film processing should ideally take place in high salt solutions at or near the pH of the developer.

There are several advantages to using an alkaline fixer:

1. Alkaline fixers do not dissolve (or bleach) image-bearing silver. (This was first discovered as early as 1932 [JSPME 18, 371] by Russell and Crabtree.) Therefore, there is little danger when over-fixing (for example, when trying to remove residual dye from tabular films). Bleaching is greater the lower the pH and the finer the grain of the film or paper.
2. Alkaline fixers allow much shorter washing times and therefore substantial savings in water usage. Removal of hypo is much faster even than when an ordinary fixer plus a hypo clearing agent is used. Film fixed in an alkaline fixer does not require hypo clearing agent: hypo is down to archival levels after 40 seconds of washing (Haist II 203). But film should be washed a total of two minutes to ensure all developer residue is removed, and there is little harm, if running water is plentiful, in extending the time to three or four minutes. Wash in running water. When times are as short as a

minute or two, agitation should be continuous. When water must be conserved, use Levenson's system (see Washing overleaf).

3. Keeping the entire system either neutral or alkaline, from alkaline developer, neutral water stop, alkaline fixer, neutral final wash (without HCA), will improve the permanence of all films and papers because the thiosulfate does not mordant or bind to the silver image or base. This is particularly valuable with papers.
4. Alkaline fixers have longer tray and storage life; when compared to acid hardening fixers with a sludge point, their capacity can be greater since there is no sludge point with alkaline.
5. Alkaline fixers are easier to formulate and more stable as thiosulfates are more stable in an alkaline solution.
6. Alkaline fixers can be formulated to have low odor.

TF-3 ALKALINE FILM FIXER	
Ammonium thiosulfate, 57-60%	800 ml
Sodium sulfite anhydrous	60 g
Sodium metaborate	5g
Water to make 1 liter	
Working solution: Dilute 1:4 with water	

Although alkaline fixers have been used for years in research labs, and in several automated and rapid access systems, the only commercially available alkaline fixer available at the time of FDC1 was Formulary TF-4. There are now several others, though we don't know enough about any of them to make specific recommendations. (See chapter 14 for a little more detail.) For those who wish to mix their own we are disclosing, for non-commercial use only, the formula for TF-3. TF-3 has higher alkalinity than TF-4, which means it has a faint ammonia odor. That makes it less suitable than TF-4 for film or print fixing in open trays. Because of its alkalinity and low sulfite content, TF-3 is particularly recommended for PMK and other staining/tanning developers.

> *Photographic film fixed in an alkaline solution is known to wash more quickly than film fixed in an acid fixing bath .... Thus, it is to be expected that monobath-processed film would require only a short wash in water to free the emulsion layer from residual chemicals. According to A. Green and M.G. Rumens (J. Phot. Sci. 19:149–150 (1971)), it was necessary to wash monobath-processed films only 40 sec. in tap water at 12˚C in order to remove the thiosulfate to the level required for archival permanence. It was found necessary, however, to wash 60 sec. at 12˚C in order to remove residual hydroquinone to prevent staining.*
>
> —HAIST, V.2, P. 203

To use TF-3 or TF-4 immediately follow development with a sixty-second running water wash or a minimum of five full changes of water, and agitation for the first 15 seconds of each cycle. Fix the film for three times the clearing time—usually 3 to 5 minutes. HCA is not required.

The pH of TF-3 can easily be lowered by replacing a proportion of the sulfite with sodium bisulfite or adding some boric acid, but don't go below pH 7.5. At this near-neutral pH, odor should be at its possible minimum.

Experiment: For maximum image stain with tanning developers, reduce or eliminate the sulfite in TF-3. If you do this, the life of the working solution cannot be guaranteed beyond a day, but you will achieve the maximum imagewise staining a tanning developer is capable of.

Acid stop baths and alkaline fixers; alkaline stop baths

Some users may want to use an acid stop bath followed by an alkaline fixer. In that case, rinse the film in running water for 30 seconds *after* the stop bath but before the fixer. This will keep acid from being carried over into the fixer. Alkaline stop baths are still experimental. See Appendix 1 for suggestions.

DETERMINING FIXING TIMES AND CAPACITY

Ideally, *fixer clearing time should be tested before each use.* From a practical standpoint, testing every third time should be adequate. Keep in mind that *clearing times are different for every film.* So if you are checking clearing time throughout the life of a batch of fixer, make sure you use the same kind of film each time to do the checking. You want to know what clearing time is for Film A when the fixer is absolutely fresh, and you want to know when clearing time for Film A doubles.

> Author's Note: *Haist told me that the material summarized above was all he was permitted to state regarding alkaline fixing because the technique, discovered by H.D. Russell, was still regarded as a trade secret. It is now evident that other companies were not aware of its benefits. BT*

Determining clearing time: With the lights on, place 1–2 inches of 120 film or the 35mm leader in fresh fixer. With gentle agitation observe how long it takes the film to become completely transparent, or clear. This is the clearing time. Multiply the clearing time by two (conventional advice) or three (our advice) for your total fixing time.

As the fixer is used the clearing time will increase. Test whenever convenient. When the clearing time doubles from the fresh test, discard the fixer. It is best practice to use fixer for no more than 20 8x10 square inches of film per liter.

The working solution of a fixer should never be kept for more than two months—two weeks if the ambient temperature is over 85F/29C. Stock solutions of commercial ammonium fixers should not be kept for more than a year. When storage for more than a month is contemplated use a container filled to the top and tightly capped. Alkaline and neutral fixers can be formulated to have much longer storage life.

Discard any fixer the moment it turns yellowish *and* cloudy. This is a sign of sulfur precipitation. This is yet another reason not to use a conventional indicator stop bath. The indicator dye may be carried over into the fixer, disguising sulfur precipitation.

Techniques for extending the life of fixers with replenishment and silver recovery can be found in Haist and Mason.

Determining clearing time: wet or dry?

Clearing time should be estimated using wet film, as clearing time can be slower with dry film. As Baines observed (J. Phot. Sci. 3 (6), 175 (1955)), photographic scientists before 1943 "fell into the error of assuming without question that what happens with dry film in a laboratory will happen with wet film in a darkroom." (See also Alnutt, footnote 3, the first to discuss this issue.) Use a small piece of film that has been soaked in water for several minutes. The important thing is not to use dry film. (Mason 187)

All of that said, Ron Mowrey's recent practical experience is that with *modern* films, the difference between wet and dry *can* be negligible. One reason may be that for various reasons, some modern films swell more rapidly.

Haist (564) observes, "The concept of clearing time, although difficult to estimate accurately, has been used as a handy measure of the effectiveness of silver complexing agents and the fixing baths that contain them." It still is.

WASHING

When possible film should be washed in a running water bath. Films fixed with an acid fixer followed by a one minute hypo clearing bath should be washed for 5–10 minutes. Film fixed in an acid potassium alum hardening fixer without hypo clear needs 20–30 minutes. Film fixed in an alkaline fixer does not need a hypo clearing bath and only needs to be washed for two or three minutes. Research has indicated that films processed in alkaline fixers may be archivally washed in as little as 38.5 seconds, but we prefer to err on the conservative side (p. 146). Also, it requires 60 seconds to remove hydroquinone.

When water is in short supply an alternate water saving method can be used with film in spiral tanks. A non-hardening fixer must be used and the washing temperature kept between 77F/25C and 68F/20C. This method was devised by Kodak Harrow's celebrated G.I.P. Levenson and published in 'The Economics of Photographic Washing', Brit. Kinemat., 30: 95 (1957), a paper cited by Haist extensively, and also by Ilford's own chief researcher L.F.A. Mason.

1. Process the film in a spiral tank and fix in the normal manner.
2. After fixing, fill the tank with water at the same temperature as the processing solutions, and invert it 5 times. **Let the tank sit for 5 minutes**.
3. Drain the water and refill. Invert the tank 10 times. Let the tank sit for 5 minutes.
4. Drain and refill for the third time; invert the tank 20 times. Let the tank sit 5 minutes. Drain the water.

Kodak was sufficiently concerned about tabular film dye stain to research a solution. US Patent 5,026,629 (1991) discloses a little-noticed method where, preferably, 15g/L of an imidazole is added to the working solution of an ordinary ammonium thiosulfate hardening fixer of pH 5.1. There are two extraordinary results. (1) residual thiosulfate levels with most (not all) films are reduced to 1/10 what they would normally be; (2) dye staining from sensitizing and antihalation dyes is markedly reduced, though not completely eliminated. Both results occur even with very short processing times. We don't know if this technique has been used commercially. If it had been, it would likely have been in automated processing solutions. We don't know what downside or undesirable side effects there may be. Nor does the patent suggest any reason why this chemical reduces residual thiosulfate so markedly. The patent highlights the element of serendipity that has often characterized photographic research.

5. A final rinse of water to which a few drops of wetting agent have been added will aid rapid and uniform drying.

This method is particularly effective when used with an alkaline fixer. **Note the instructions to invert**.

Note: This method has been published elsewhere (by Ilford) **without** the five minute waiting time between steps. This is **incorrect** and directly contradicts what Mason, Ilford's most prominent scientist, says about washing (Mason 201–207). Ilford has admitted that it does not possess a shred of scientific evidence to support leaving out the waiting time, but continues to suggest it.

We note two publications—'Processing KODAK PROFESSIONAL Black-And-White Films' and 'How to Process and Print Black-and-White Film - Eastman Kodak', both available as pdfs from Kodak's website (Google

“kodak film washing times”)—that give ambiguous advice on washing when continuous running water is not available. They recommend *ten* complete changes of water for film but do not make clear that these changes must take place with agitation *after* film has been treated with hypo clearing agent.

Washing tabular grain films

Without special sensitizing dyes, all films would only be sensitive to blue light. Because tabular grains have a large surface area, they require more sensitizing dye, and this in turn needs more time to wash out. The dye (usually magenta) is hard to wash out, and manufacturers have had conflicting advice as to whether the dye actually needs to be washed out or not. Our present understanding is that the dye is not readable as density by any current printing papers, and should therefore have no photographic effect. Nor does there appear, at present, to be any archival concern. However, even if these beliefs are borne out by time, it is both psychologically and visually unpleasant for photographers to have this residual dye left in tabular grain films. Tri-X now has this dye.

For a time, extended fixing, which is manifestly an improper processing procedure, was recommended as a cure. In addition, many fixers have claimed to be able to remove the dye, but we have not seen any that actually do. What we have found is that three intermittent soaks in standing water will often remove the dye. After fixing, rinse films for a minute in running water. If an acid fixer is used, place the films in HCA for a minute with continuous agitation. If an alkaline fixer was used, no HCA is required. Fill the tank or wash chamber and leave the film to stand in fresh water. After 3 minutes change the water completely. Allow the film to stand for another 3 minutes. Repeat a third time for complete removal of the dye. If the film was processed in an acid fixer, wash for an additional ten minutes in running water. If the film was processed in an alkaline fixer, wash only for one additional minute in running water. The problem with this method is that

because of the extra time spent in water, swelling will increase, but the concern is usually minimized by the extra hardening typical of most tabular films.

Alternatively, some have found that over-fixing, for about six minutes in a rapid fixer, removes the dye. It is essential to state that **when deliberately overfixing, only an alkaline fixer should be used**.

> *It is sometimes stated that a magenta cast need only be of concern when it is excessive. But what is excessive? There are no straightforward answers. A little seems to mean a slight magenta cast, and a lot seems to mean a heavy magenta cast. If there is a heavy magenta cast, that may be a clue that either fixing or washing was not adequate. The fixer may be exhausted or you may not have fixed long enough. Check clearing times always! Kodak has also recommended longer periods in HCA, as sulfite is thought to destroy the dye. If the dye is still oppressive after washing, try another period in HCA with agitation, followed by a wash of at least 1 minute with agitation.*

Otherwise, density will be lost. There is no known downside to moderate over-fixing in an alkaline fixer.

Our recommendation is not to worry about the dye, because techniques to get rid of it may cause more harm than good.

Wash water temperature

A frequently asked question is, to what extent is washing affected by temperature? The answer is that nobody knows for sure. Haist gives two contradictory findings: (1) “A value of 2.3 times faster for a 10°C/18°F rise in wash water temperature has been reported”; (2) “washing at 80°F is 30%

faster than at 40˚F." All we know is that washing is faster when water is warmer, and slower when it is cooler. **For many reasons, it is best to ensure that wash water is at the same temperature as all the other processing solutions, which should usually be 68F/20C**. In the section below, Mason notes that a common cause of reticulation is washing at a higher temperature than processing, and this may sometimes also occur when the wash water is too cool. If it is absolutely obligatory to process at higher temperatures, then additional hardening may be required. Haist notes that for washing *papers*, a slightly warmer temperature of 70 to 75˚F is advised. Washing of papers is definitely lengthened when the temperature is below 65˚F.

Wash water quality

In many parts of the world, acquiring clean water, or any water, can be a daily problem. Haist states (666–667) that "pure water [i.e. distilled water] makes a poor washing medium." By contrast, good tap water is superior: "Hard water with dissolved salts, especially bicarbonates, or soft water with sodium bicarbonate present at a fraction of a gram per liter, is superior to pure water in washing power, especially after fixing with an acid hardening bath containing potassium alum. Chlorinated water has been claimed to have some thiosulfate-eliminating action." Haist then discusses problem water: "Water for washing may contain mineral matter (sand or rust, for example), vegetable matter (wood particles), sulfurous gases, or other undesirable impurities. Wash water should be filtered to remove any particulate matter that might adhere to a soft gelatin emulsion layer, especially small-size film negatives or color materials. Dissolved sulfide gases may be removed by boiling the water. In this era of increasing pollution of water supplies, the suitability of water for washing should be carefully assessed and assumptions of purity should be avoided."

Avoiding reticulation or "excessive graininess" during washing

Or, *'why is my negative so much grainer than usual*?' We repeat from chapter 12 Mason's advice on this topic, which applies both to the stop and wash stages:

> *Films and papers can be washed in sea water, which helps lower hypo levels, but must have a 5-minute final rinse in fresh running water or 2 changes of 2 minutes each in fresh water (Haist 650; JSMPE 40, 380, 1943).*

> Reticulation … is an irregularity of the surface of the gelatin, caused by stresses in the gelatin parallel to the support. As only the surface layers can move to relieve this stress, the effect is confined to the surface layers of gelatin. Stresses giving rise to reticulation are produced by alternate treatment in baths promoting swelling and shrinking of the gelatin. A common cause in normal processing is the use of wash water at a higher temperature than the processing baths. It can also be produced by immersion in dilute acid baths. In severe cases of reticulation, some movement of the image silver may tend to migrate to the ridges of the relief pattern, and hence an optical mottle pattern is superimposed upon the mechanical relief pattern. When this happens, the graininess is very much worse than would normally be expected. (Mason, 207)

Wetting agents

A wetting agent (chapter 3, p. 37) is a purified low-foaming detergent which allows water to run off the film quickly and easily, preventing water spots. To use a wetting agent, soak the washed film in a solution of water (preferably distilled) and wetting agent. It is essential to mix the wetting agent working solution carefully: this is a case where less does good but more does harm. We recommend using less than the amount the

manufacturer recommends. Just one ml per liter seems to work well. Use fresh solutions of wetting agent. Don't keep wetting agent overnight as sludge and algae may build up and adhere to the emulsion.

Agitate for 30 seconds, drain, and hang the film to dry.

Only wetting agents designed for photography should be used.

After hanging, remove excess water from the film's surface. A *one-sided* soft rubber squeegee, dipped in wetting agent (working solution) and held at a slight angle so the blade runs behind, works well. Wipe each side of the film only once. This method works equally well with sheet film.

Never wipe film with a sponge or any tool that squeezes the film on both sides. Even an apparently non-abrasive sponge can make micro-scratches in the negative which, though invisible to the naked eye, could degrade image quality. This is especially true with document films.

DRYING

Hang film in a dust-free place with weights attached to the bottom of roll and 35mm film. Whenever possible use a drying cabinet. Even if film appears to be dry wait several hours before printing or filing it in archival pages. We recommend avoiding plastic storage pages that do not allow atmospheric moisture to escape.

With the exception of a dust-free, temperature controlled drying cabinet, avoid quick drying. Many chemical techniques have been proposed,[4] but all of them may cause irreparable damage to negatives. Tetenal has a product which dries film in 2–5 minutes called Drysonal, available only in Europe. We are concerned by cautions such as "Flecks may appear after drying if the film has not been wiped evenly and not all of the Drysonal has been caught."

If you absolutely must dry film in a hurry, the safest method is to blow gentle heat over the film, at less than 100F/38C. In an emergency you can use a blow dryer at its lowest heat setting. Hold the dryer at least three feet away. It is slower, but safer, to use a fan without heat. *Dust spots are bound to result.*

Mason is as thorough on this subject as on all others, and devotes four pages (207–211) to drying, for those who wish to know more. One interesting matter he raises is density change. Summarizing papers from the 1930s through the 1960s, he writes:

> During drying, changes in image density may occur, due to changes in the photometric equivalent of the image silver. The extent of these changes depends on the drying conditions, in particular the use of drying air of high humidity results in an appreciable increase in density. For this reason the drying conditions should not be suddenly altered when a film or plate is partly dry. Another manifestation of this effect is the change in density if part of a negative is wetted and redried.... Two processes affecting photometric equivalent appear to take place during the drying operation, these having opposite effects on it. As the gelatin begins to dry down, the image grains tend to re-

> orientate so that the plate-like grains lay more parallel to the support. In this way more efficient use is made of the diminishing gelatin volume. The result of this rearrangement is to increase the cross-sectional area of the silver grains when viewed perpendicular to the support. As the drying proceeds to completion, the formation of new hydrogen bonds across the gelatin chains results in some compression of the silver grains, thus causing a reduction in their cross-sectional area. Both these processes are occurring to some extent during the whole drying time, but during the early stages the effect of the former process far exceeds the effect of the latter process, but in the final stages of drying, the reverse is the case. The relative contributions of each process depend upon the history of the gelatin layer as well as upon the drying conditions. Any treatment which will tend to inhibit the formation of hydrogen bonds between gelatin chains during drying, will result in increased covering power when dry. Such treatments include high temperature processing, soaks in gelatin denaturing agents or drying at high humidities. For accurate and consistent results, the drying conditions must therefore be strictly controlled.

This may seem like excessive detail but we hope it will serve readers who may have encountered processing anomalies that may now be explained.

NOTES

1. Haist; see also W.E. Lee et al., “New Procedures for Processing and Storage of Kodak Spectroscopic Plates”, *Journal of Imaging Technology*, Vol. 10, no. 1, Feb. 1984.

2. US Patent 5,061,616 (1991) is one of many which provides some insight into the process of precision iodide placement, and some history. Fuji has also been active in this research. For dye layering, see US Patent 6,143,486; for dye layering with low stain, see 6,787,297.

3. Donald B. Alnutt, “Some Characteristics of Ammonium Thiosulfate Fixing Baths”, *JSMPE*, 41 300 (1943).

4. C.I. and R.E. Jacobson, *Developing*, 18th edition revised, Focal Press, 1978.

Chapter 14

AFTER DEVELOPMENT PROCESSES 3: ADVANCED FIXER TOPICS

NEAR-NEUTRAL AND SUPERADDITIVE FIXERS

When I formulated, with the encouragement and advice of Grant Haist and Harold Russell, TF-4 for Photographers' Formulary, it was the first alkaline fixer ever offered for sale as such. Now that they have both passed on, I can happily disclose that it was not *my* idea to come out with an alkaline fixer, it was theirs. There was considerable mystification and hostility at the time, but TF-4 was gradually accepted, and now has imitators. Harold Russell started at Kodak in the late 1920s. When I was introduced to him by Grant Haist more than 60 years later, he was still going strong, and had a photographic memory. Russell was responsible for most of the published and proprietary Kodak fixers over the length of his career, which covered the early hardening fixers such as F-5, up to alkaline fixers he devised for the Xomat and Versamat processes of which he was architect. At the time he and Haist believed that the supreme benefit of alkaline fixing was drastically reduced washing times. However, I learned from Ron Mowrey that the color researchers at Kodak had found that this benefit may extend down to about pH 6.5, or near neutral. It is at this point that fixers such as the Kodak C-41 and E6 fixers are formulated, for a number of reasons. Haist and Russell thought alkaline fixers should be well above neutral, but odor evolution can then become a problem. Practically speaking, the most odorless fixers are those closest to neutral.

Note: In the C-41 and E6 processes, a stop bath is not used anymore. Rather, a water rinse of 30 seconds is specified for E6 (C-41 uses an acid bleach). This is in line with what we have long advocated for black and white films. The two major reasons for this are faster processing times and better adjacency effects.

In addition to a near-neutral pH for rapid washing and no hardener, Ron Mowrey's Superfix and the C-41 fixer, both printed on the next page, introduce an important concept, that fixing agents can be super-additive. The preferred combination, for economy, is ammonium thiosulfate and ammonium thiocyanate (formerly known as ammonium sulphocyanide). We use the term superadditive here but the combination is not of the order of magnitude of increased activity which occurs, for example, with the PQ combination. Nevertheless, the combination of these agents is superadditive. They account for the brief fixing and washing times seen in the C-41 RA process.

KODAK C-41 RA FIXER	
All numbers in grams per liter of final solution	
Ammonium thiosulfate	112.85
Ammonium sulfite	8.99
Sodium sulfite	14.00
Ammonium thiocyanate	90.00
EDTA, dihydrated sodium salt	1.20
Glacial acetic acid	0.77
pH adjusted to a value of	6.20
Water to make 1 liter of working solution. Adjust pH to 6.20 with ammonium hydroxide or sulfuric acid at 24C.	
Use only with films intentionally hardened for use with thiocyanate.	
Source: US Patent 6,649,331 (2002)	

One fly in the ointment is highlighted by Haist (596) who notes that thiocyanates cause softening of black and white films. While color films are designed and manufactured to be used at high temperature and with thiocyanate, this has not been a requirement of black and white films. Haist warns that only films and papers hardened for use with thiocyanate should

be used, as does Mason (183). Mowrey has discussed the use of 3G hardeners (e.g. BVSM) by Kodak and Fuji, but we do not know which of their black and white films or papers use these hardeners.

An incentive for using Kodak C-41 fixer for black and white is that in some areas it is the most economical fixer that can be bought.

According to Mowrey, clearing times for black and white films and papers in Superfix should usually be 30 seconds or less. Fix for twice the clearing time. Washing times of 1 minute for film and 2 minutes for paper are recommended to bring them to archival standards. It is always best practice to test for retained hypo and retained silver. But a test for retained thiocyanate is not yet part of standard darkroom practice, nor do we know precisely what levels provide a protective effect against pollutants.

RON MOWREY'S SUPERFIX 6

Ammonium thiosulfate 60%	100 ml
Ammonium thiocyanate	60 g
Ammonium sulfite	12 g
Disodium EDTA	3g
Waterto 190 ml	
Adjust pH to 6.5 with glacial acetic acid and then top up to 200 ml with water.	
Dilute to 1 liter for film or paper.	
Use only with films intentionally hardened for use with thiocyanate.	
This formula is for Superfix 6. Superfix 7, which adds thiourea, is published as an APUG/Photrio resource. Superfix 8, containing additional ingredients, has not yet been published. 1 prefer version 6 because 1 would not want to work with thiourea.	

Note: Where Superfix (or any other fixer) is capable of clearing a particular fiber-based paper in 15 seconds or less, allowing a total fixing time of 30 seconds, paper washing will be the most rapid it can be because there

is minimal penetration of the fixer into the baryta and paper fibers: this is one of the principles governing the (now generally obsolete) Ilford rapid paper processing sequence of the 1980s.

Archival stability with ammonium thiocyanate

A disincentive to use thiocyanate is that the stability of black and white images fixed in such fixers has not been well studied. Given how astonishingly difficult it has turned out to be to make defini tive recommendations for archival processing using only thiosulfate, it is impossible to endorse any other fixing agent for archival processing.

A question still unresolved a century after it was raised by Piper (BJP 61, 511 (1914)) concerns the extent to which insoluble thiocyanates may be formed in the gelatin layer. Today, the indications are that residual thiocyanates may protect against environmental pollutants. For example, thiocyanate was the original (and ultimately problematic) stabilizing agent in Agfa's Sistan product, discussed in chapter 15.

Additional superadditive fixing agents

Mowrey observes that thiourea and DTOD are also known to be superadditive both with thiosulfate and thiocyanate. Thiourea is probably best kept out of most darkrooms, because it fogs unexposed materials and, as Grant Haist has remarked, once it is in a darkroom, it is very hard to get out.

The swelling that thiocyanate causes helps it penetrate film more rapidly. The trick in formulating with thiocyanate is to provide enough to provoke the desired amount of swell but not so much that reticulation occurs. That could mean different amounts for different films.

Grant Haist often spoke of his desire that the issue of hardening during processing would be eliminated by hardening black and white materials to the same extent that color materials are hardened. He was ba±ed that

it wasn't done. There has been some progress, but we don't know for certain how much. Test before using a process that may soften films or prints. Mowrey tested Superfix 6 on many contemporary black and white materials before publishing it. It is significant that the thiocyanate level he chose is only 6%, compared to 9% for C-41 RA. This confirms Piper's finding in 1914 that solution of gelatin by thiocyanate is gradual below 10% but very rapid above 10%.

One of the interesting things about DTOD is that it apparently doesn't cause swell, as thiocyanate does. A fixer containing DTOD and ammonium thiosulfate should have low swell compared to one made with thiocyanate and thiosulfate. Although the thiocyanate/thiosulfate combination is not strongly superadditive, the thiosulfate/DTOD combintion appears to be highly superadditive. Only 5g/L of DTOD needs to be added to an ammonium thiosulfate fixer, Mowrey suggests. DTOD can also be added to sodium thiosulfate fixers, and may prove to be a valuable adjunct for softer emulsions.

For maximum speed, all four of these agents could be combined, but the cost would be prohibitive.

It may be found that swell is a limiting factor in achieving faster fixation with these chemicals.

ALTERNATIVE FIXING AGENTS

Until the mid-1980s, there was much research to try to find new fixing chemicals. There were many reasons for this. One was that it was believed that the stability problems with photographic materials were caused by thiosulfate residues. But at that time, it was discovered that thiosulfate residues could actually exert a stabilizing effect on photographic materials—under *just* the right conditions. The problem was that it was virtually impossible to process photographic materials so that just the right amount of thiosulfate was left. It was deemed better to remove as much thiosulfate as possible and subsequently to process with a stabilizing agent—issues covered in the next chapter.

Grant Haist spent much of his career investigating mercaptans as fixing and stabilizing chemicals. One result of this line of research was an enlarging paper which incorporated a monobath. Processing wet in a simple alkali bath for a few seconds, plus a few more seconds of washing. resulted in an archival print. A later version used only heat, no chemistry (Haist V2, 256–261). Haist 602–605 discusses some of the work done on mercapto acid fixing. Unfortunately, Kodak placed strong limits on what he could say.

> *Unmentioned in the literature is the homely fact that Haist's monobath papers were coated in a light-tight garage using wallpapering equipment.*

According to his book, the amino acid cysteine is one of the most rapid mercapto acids for fixing, at pH 10.5. In 2005, Ron Mowrey and I prepared such a solution, and in our experiments found it caused the film emulsion to

reticulate. However, we were using an old-fashioned film by Efke which was the only film we had available for experimentation that day. Subsequently a collaborator tested cysteine with Tri-X and had positive results, although clearing time was not appreciably faster compared to ammonium thiosulfate. Cysteine is cheap for a specialty chemical, but expensive compared to thiosulfate.

> *Sodium sulfite will fix films if the solution is strong enough and the time is long enough. We have found that some document films can be fixed in 10% sulfite in a few minutes.*

Another important fixing agent found by Kodak in the 1980s was HTTT, or, as denominated by Kodak, tetrahydro-5-(2-hydroxyethyl)-1,3,5-triazine-2(1H)-thione, EC number 248-140-3. This was believed to be an extremely rapid, desirable chemical for fixing. Its value was discovered by Keith Stephen but after his untimely death in 1995 most (but not all) work on this chemical's use in photography ceased. Patent searches reveal there is still a trickle of activity.

But will they last?

Scientists working on alternative fixing agents widely assumed that the compounds they were studying would produce more stable silver images than thiosulfates. This may indeed be true, but there is no published evidence to document it. Is it possible that silver photographic materials processed in alternative fixing agents such as mercaptans, or HTTT, may still require sulfiding treatment, discussed in the next chapter, to acquire archival stability? Or could that have an adverse effect? There is much room for future research.

"There was never anything by the wit of man so well devised or so sure established, which in continuance of time hath not been corrupted."

BOOK OF COMMON PRAYER, 1549

PROBLEMS WITH POTASSIUM SALTS

When potassium ions from a developer or stop bath enter the fixer, they may partially convert the ammonium or sodium thiosulfate to potassium thiosulfate in solution (Haist 605–6). Potassium thiosulfate is less active compared to the ammonium or sodium salts (Haist 566). Regardless of the exact mechanism, it has been observed that when potassium ions enter a fixer, they may cause increased clearing time, premature exhaustion, or incomplete fixation.

That potassium thiosulfate is "almost ineffective" has been widely believed by nearly all photographic scientists. (Haist 566, citing Frank and Schramm). An alternate view is presented in a handful of papers and patents, for example USP 5,358,832 (1992). It is possible that there is some variable, at present unknown, which would account for these contradictory findings. For example, potassium thiosulfate may perform reasonably well when fresh but may exhaust at an earlier point than would be expected, or it may be harder to wash out than expected. It may be more sensitive to iodide. Nobody yet knows with certainty.

Chapter 10 notes some potential benefits in using potassium-rich developers.

At present, it is prudent to avoid carrying potassium salts over into the fixer by observing the following precautions:

1. Avoid stop baths based on potassium metabisulfite or another potassium salt.
2. When using a developer high in potassium salts, if using a water stop, make sure the film is well rinsed, at least 60 seconds with running water, or five complete changes, before placing it in the fixer. If using an acid stop bath, replace it often to avoid buildup of potassium salts.

Fuji's US patent 3,565,621 (1971) describes this problem, and suggests compounds to ameliorate it.

Ilford's USP 5,358,832 (1992) mentions environmental reasons to avoid ammonium salts. Surprisingly, the patent goes on to state that a fixer containing a mixture of sodium and potassium thiosulfate will fix faster than either sodium or potassium thiosulfate alone, though not as fast as ammonium thiosulfate. This is reported to be true even when tested with a film containing a large amount of iodide. This product was apparently never commercialized. That could have been due to the high cost of potassium thiosulfate, or to some undesirable behavior that might have been discovered in subsequent testing.

Chapter 15
AFTER DEVELOPMENT PROCESSES 3: IMAGE PERMANENCE

QUICK GUIDE RECOMMENDATIONS

- The Image Permanence Institute's published IPI Polysulfide Toner should be used on all negatives and prints that you wish to preserve archivally. It can be used at any time, long after negatives and prints have been processed. It is very easy to mix.

PROCESSING FOR PERMANENCE

K.B. Hendriks wrote that "Recent studies have shown that toner treatments should be considered mandatory for contemporary films and paper if permanent photographic images that are resistant to chemical changes are to be obtained."[1]

There are a few indications that if film is processed correctly in the conventional manner, the limiting factor in its life is the film base, not the silver image. But the great weight of available evidence shows Hendriks was right. There can be no doubt that increased environmental pollutants are posing new challenges in photographic preservation. The best information available since Hendriks's death in 1997 suggests that toning, following the protocols established by the Image Permanence Institute (IPI), should be performed on all silver photographic materials new or old.

There are three categories of post-washing stabilizing product: (1) proprietary formulas with completely unknown contents, (2) proprietary toners where the contents are approximately but not exactly known, and (3) published formulas (usually toners) that the user will make from scratch. For reasons that will become clear in this section, we can *only* recommend published formulas. We will only recommend manufactured products when, or if, the manufacturer has made a 100% disclosure of the manufacturing formula. We hope this will happen in the future.

Stabilizers with unknown composition

At the time of writing there is only one product in this category, Adox Adostab (Sistan-New). It seems to have been formulated in response to problems that were emerging with Sistan (Old) over time. (APUG/Photrio is

a source of information on this topic.) We have been unable to discover what the product is, and the MSDS is not informative. We can speculate that Adostab (Sistan-New) is an excellent product and does not have some of the annoying odor problems of the older polysulfide toner formulas, but we need to see solid published research using methodology comparable to that established by the IPI, and complete disclosure of its formula before we can recommend it. All photographic manufacturers without exception have poor records for providing reliable archival stabilization solutions.

Proprietary stabilizers with partially known composition

Sistan

Sistan was a stabilizer originally intended to protect RC prints. It was formulated by Agfa and later made by a successor company, Adox. It was claimed to work equally well with fiber base prints and negatives to protect the silver in the image. It has no toning effect on film or paper. The theory is that a very small, controlled amount of potassium thiocyanate is left in the material, where it will exert a stabilizing effect. The product was apparently composed of 70–75% water, 15–20% of potassium thiocyanate, and 5–10% of Triton-X 100 (the detergent that is the principal ingredient of Photo-Flo) circa 1998. There seems little doubt that an effective substitute for the product could be made from these indications. This was an easy and fast method of treating film for permanence.

The earliest MSDS for Sistan we know of gave 5–10% Triton-X as wetting agent/spreader. Later MSDSs show a bactericide based on

methylchloroisothiazolinone (MCI; CAS 55965-84-9) but no Triton. If there was no effective spreading agent present, the problems that emerged with Sistan in recent years might be explained by this later reformulaton.

Caution: As has been extensively documented on APUG/Photrio, severe staining problems have emerged with Sistan. The problems may be related to uneven application and removal with a squeegee. Regardless, we cannot possibly recommend a technique that is uncertain in application and result. If thiocyanate has any future in archival photographic stabilization—which we doubt—improved application and dosing processes would have to be devised.

Ag-Guard

Ag-Guard was a product introduced in 1984 by Fuji. Fuji stated it contained a 'very stable sulfur compound' which MSDS research revealed to be 2-(Amidinothio)ethanesulfonic acid, CAS 25985-57-3, at 0.5 to 1.5%, in water. It was tested extensively in 1988 by Jim Wallace, Director, Office of Printing & Photographic Services, Smithsonian Institution. He compared it to Kodak Rapid Selenium Toner (KRST). He concluded that the product showed promising potential but that its usefulness depended heavily on the specific product it was used with. We believe Ag-Guard is no longer available. The chemical itself appears to have several manufacturers. Because Ag-Guard only works well with some materials, and because testing it is expensive, we don't regard it as a successful product or one that anyone should worry about acquiring.

Jim Wallace's paper is available on the internet. The title is 'An examination of the effectiveness of Ag-Guard protecting silver halide photographic emulsions', Topics in Photographic Preservation, Volume 2, pages 69–91.

Kodak proprietary toners used as stabilizers and the reason why no proprietary product should ever be used for image permanence unless the manufacturing formula has been 100% disclosed, and all changes in production are disclosed

Kodak Rapid Selenium Toner can be used immediately after washing, or the film can be rewet after it has dried. The wet film should be toned for three minutes in a 1:29 solution at 68F/20C, with frequent agitation. Washing film for 20 to 30 minutes after toning has been recommended, as KRST contains thiosulfate. However, since the solution is alkaline, two minutes for films and ten minutes for paper should be adequate washing time. Immerse for one minute in working solution wetting agent and then hang to dry.

The full story of the problem with changes in KRST is told in 'Stability of Black-and-White Photographic Images, with Special Reference to Microfilm,' Reilly, Nishimura, Cupriks and Adelstein, 1988, presented at the 'Conservation in Archives' Symposium, National Archives of Canada, May, 1988. At the time of writing it was available at the cool.conservation-us.org site. Given the importance of micro-film in preserving and disseminating material that would otherwise be lost, it is astonishing that it took 30 years, from the 1960s when problems were

first reported, until the problem was finally addressed. And then it was solved not by any manufacturer, but by an independent research organization.

Caution: KRST was for some time, partly because of W.E. Lee's important work at Kodak in the early 1980s, the favorite stabilizing process of the image preservation community. Until, one day, it wasn't. In 1987–88, IPI had been testing Kodak Rapid Selenium Toner as a stabilization material for microfilm. Even at this late stage of microfilm manufacturing, widespread stability problems were being experienced by archives, and not just for microfilms but for other negatives and prints. It was then believed that KRST might be the best for stabilizing these films and by extension all black and white photographic materials. To their astonishment, the IPI team found that KRST

> … failed to provide protection against redox blemishes, when used as suggested. If highly concentrated solutions were used, the level of protection increased, but was not complete. Such concentrated solutions are impractical for reasons of cost, excessive contrast buildup, and excessive image color change …. This finding conflicted with numerous published results from Kodak [footnotes 17, 20, 21 in the paper]; when we spoke with Kodak personnel, they confirmed that in their own recent peroxide testing with microfilm, the selenium toner was depositing selenium, but not preventing oxidant attack, which it had done in tests performed as recently as one year ago. They suspected that small changes in formulation made by the manufacturing area were responsible, but were not clear on exactly why. It is our strong feeling that the changes in formulation that suddenly rendered dilute selenium toner ineffective relate to the sulfiding action of minor constituents.

This was a watershed moment. The team knew they could not work with commercial products whose properties could materially change without notice. Eventually, they would formulate their own toner.

Another problem the IPI discovered with KRST was that high density areas of materials convert readily to silver selenide and are well-protected, but areas of lower density don't convert as well and are left vulnerable.

An important finding by IPI concerned *Kodak Gold Toner GP-2*. Kodak had recommended this expensive solution for years to help preserve microfilm and most or all other black and white photographic materials. Many institutions and individuals couldn't afford to use it. Yet with all its research might, Kodak failed to discover what IPI did, that *GP-2 works just as well whether it contains gold or not*. The important chemical in the toner turned out to be inexpensive thiourea, a known sulfiding agent. In other words, neither gold nor selenium themselves were important in providing image stability. It was other chemicals in these formulas that provided the desired sulfiding reaction.

The IPI was unofficially informed that Kodak Brown Toner contains approximately 245 g/L of sulfurated potash and nothing else. The 2007 MSDS reveals it also contains 5–10% sodium carbonate.

IPI found that *Kodak Brown Toner* (which is functionally similar to the published Kodak T-8 formula) was a more satisfactory commercial product, even when used at dilutions as low as 1 part toner to 200 parts water. However, as Kodak would not disclose the precise manufacturing formula for the product, and for other reasons, it could not ultimately be considered a satisfactory solution. This paper stated in summary,

> It is characteristic of the sulfiding approach that only a small amount of sulfiding agent is needed. For example, sodium sulfide solutions of 0.1 g/L (about 1/100 of [one] percent) are completely effective. However, for reasons of diminished odor, toxicity of the bulk substance, and shelf life of the solution, the polysulfides are preferable in practice to straight sodium sulfide. We have shown that Kodak Brown Toner does its work of protecting the silver image without significant change of density or image hue. The method of treatment is simple: processed microfilm of any age can be immersed in the solution for a few seconds (shorter immersion times require slightly higher concentrations than longer times), then washed and dried.'

IPI followed up with the work discussed in the next section.

Stabilizers of known composition

These encompass many of the known brown and polysulfide toning formulas. Many of these will provide image protection, but none are ideal for that purpose. They were, after all, formulated, in their day, exclusively for aesthetic purposes. IPI concluded that none of the traditional toning formulas offered the level of performance IPI was after. To solve this problem IPI formulated and published its own toner in a long process described in 'Sulfiding Protection …' cited to the left.

> *The basic source for the IPI toner and the most authoritative information available on the permanence of silver halide materials is "Sulfiding Protection for Silver Images: Final Report to the Office of Preservation, National Endownment for the Humanities,'" J.M. Reilly and K. Cupriks, 1991, available online at the IPI website. It contains a wealth of information that is vital to all photographers who want to preserve their work. In effect, it is a bookend to the great papers by Loyd Jones in the 1940s which defined speed determination, exposure, and tone reproduction as we understand them today. Jones made it easy to expose pictures reliably. The IPI papers have symmetric stature in showing us how to preserve those images.*

The IPI polysulfide toner formula: today's standard

Here we quote and summarize a fraction of 'Sulfiding Protection …'. First, the IPI Toner formula:

1) Make a very strong concentrate [of] 495 g of solid sulfurated potash up to 1 L with deionized water, and stopper the solution well.

2) Add 20g/L sodium [tetra]borate decahydrate to each liter of concentrate.
3) Do not dilute this concentrate more than 1:25 in compounding working solutions.
4) Do not expose the concentrate or the working solutions to unnecessary aeration, and discard [if] any signs of decomposition such as scums or strong odors are present.

All these aspects will ensure that the optimum equilibrium among polysulfides is present in solution, thus controlling the toning reaction kinetics. No discolorations will result, the extent of conversion will be high, and the contrast of the residual sulfide image will be close to that of the original.

Use IPI polysulfide at a dilution of 1:25 (1 part concentrate to 25 parts water).

[C]oncentrated polysulfide solutions have a pH of ca. 13. The diluted working treatment solutions for photographic film have a pH of ca. 11. [Because the composition of sulfurated potash is so variable, it has sometimes been found necessary to adjust the pH downwards with 60% citric acid solution. This must be performed by a professional chemist in a fume cupboard, as hydrogen sulfide is released.]

Use fresh concentrate, keep the concentrate well stoppered, and avoid unnecessary aeration of either the concentrate or the working solution. Replenishment tanks containing treatment solution should have floating lids.

> *"Old photographers never die; they just stop developing."*
>
> —Donna D. Conrad

Treatment can be done either in-line (as part of original processing) or later on, using a dedicated processor. In the case of in-line processing, two extra tanks will be required: one for the polysulfide solution, followed by one for the final wash. If using a dedicated processor to treat film some time after original processing, it is not necessary to pre-wet the film before it enters the toner tank.

Treatment temperatures and processor speeds can vary within broad limits. A recommend starting point is 80°F for 30 seconds. Higher temperatures, longer treatment

> times, and more vigorous agitation will result in higher levels of conversion to silver sulfide. [Consult the full paper for Quality Control tests and replenishment.]
>
> In general, the toning capacity of the solutions at 1:25 dilution is very large, so it is likely that factors other than solution exhaustion (for example, aeration) will end the useful life of the solution. In other words, it is more likely the solution will decompose than to lose its capacity to convert silver to silver sulfide. When dark field yellowing appears in the peroxide immersion test, the solution should be entirely discarded and a fresh one provided. Likewise, when signs of decomposition such as increasing odor or sludgy precipitates appear, it is time to discard the solution.

Sulfurated potash has CAS no. 39365-88-3. Potassium (poly)sulfide, liver of sulfur, has CAS no. 37199-66-9 and is specifically given for Kodak Brown Toner. "Sulfiding Protection ..." states that these two compounds are essentially the same.

Note: the IPI Toner does not protect against nitrogen dioxide, a pollutant which is rising in many cities. Nor does it protect against ozone. There is urgent need by photographic archivists to research these problems.

Summary: There is less and less reason to believe that properly fixed and washed negatives and prints will be archivally stable for the life of the film or paper base. The overwhelming weight of published research shows that silver negatives and prints should be toned in a polysulfide toner. The best choice is the IPI Polysulfide Toner. Tenable second choices may be Kodak Brown Toner or Kodak T-8 toner. We hope the future will bring improvements in techniques to preserve and maintain silver-based photography. However, future claimants will have to meet the high bar of the testing procedures established by the IPI.

We *don't* think it possible that any proprietary stabilizing product will ever be trusted again. Formulas for this kind of product must be fully disclosed and rigorously tested.

Caring for the negative

Even a small amount of fixer spilled and not wiped up may become chemical dust. Once airborne it can deposit on materials at random. Even trace amounts of fixer on your hands or clothes and subsequently transferred to a negative, can undo all your efforts towards permanent processing. There is no point in processing films for permanence if the next minute they are stained by hypo-laden hands.

The darkroom, measuring room, and drying room should be thoroughly aired and vacuumed as often as possible. Hands should be washed with soap and water and thoroughly dried before handling a negative.

Last thoughts on image stability

The issue seems simple: Do you want your work to last? Today you may not care. Ten years from now, you may.

Fortunately, you don't have to make up your mind every time you develop and print. Stabilization with the IPI toner is a thing you can do in a great batch, once a year.

But the existence of the IPI toner is not a reason to fix and wash carelessly. It will not cure problems caused by inadequate fixing (such as insufficient time in the fixer, or using exhausted fixer). Nor will it cure gross hypo retention caused by inadequate washing. Always process films and prints the best you can.

The IPI toner is not a bulletproof vest. As noted, there are pollutants we still don't know how to protect against. But the IPI toner is the best archival protectant we have.

NOTES

1. *Focal Encyclopedia 3*, page 380.

Most citations for this chapter are contained within the text.

Appendix 1
REFERENCE FORMULAS AND ADDITIONAL INFORMATION

Where given below, the developing times come from a variety of sources and should only be used as approximate starting points. Mostly they are given for medium speed films. You will usually have to develop a third less for slow films, and a third more for fast films, but there are no hard and fast rules. All amounts are in grams, unless otherwise specified, and all are to make 1 liter. All development times are 68F/20C unless otherwise noted. Sodium sulfite and sodium carbonate are always anhydrous unless noted.

> *"I drifted into photography as one drifts into prostitution. First I did it to please myself, then I did it to please my friends, and eventually, I did it for money."*
>
> —PHILIPPE HALSMAN (GLOSSING FERENC MOLNÁR)

Agfa/Ansco film developers

	14	17	17A	17M
Metol	4.5	1.5	2.2	1.5 g
Sodium sulfite	85	80	80	80 g
Hydroquinone	-	3	4.5	3 g
Borax	-	3	18	- g
Sodium metaborate	-	-	-	3 g
Sodium carbonate monohydrate	1.2	-	-	- g
Potassium bromide	0.5	0.5	-	0.5 g
Water to make 1 liter				

Agfa 14 is somewhat related to D-76, but the carbonate results in coarser grain, and necessitates bromide restraint. The Agfa 17 family is similar to D-76, but somewhat less solvent: results should be coarser grain and higher sharpness. 17A is the replenisher for 17; 17M is the metaborate version.

Ilford film developers

Historically, most published Ilford film developers have been either generic or Kodak knockoffs. Greater innovation set in after Ilford perfected the manufacturing process for Phenidone in 1951. ID-68 is the most representative formula of this era. Another published developer of this era has no number, but is known to have been designed by Axford and Kendall, Ilford's principal chemists at that time. It was assumed by Dignan, among others, to correspond to Microphen. That it was intended for professional use is indicated by the target pH indications which, as Grant Haist often remarked, should be specified for every developer. However, the pH

specifications to two decimal places are a fussy absurdity: few pH meters are capable of reliably measuring to two decimal places. There are two replenishers for this developer; one is for the topping up system; the second is for the bleed system. We like this developer better than ID-68 because the pH is lower.

ID-68	
Sodium sulfite	85 g
Hydroquinone	5 g
Borax	7 g
Boric acid	2 g
Phenidone	0.13 g
Potassium bromide	1 g
Water to make one liter	

ILFORD REPLENISHING DEVELOPER			
		TOPPING UP	**BLEED**
Sodium sulfite	100	100	100
Hydroquinone	5	8	6.25
Borax	3	9	4
Boric acid	3.5	1	2.5
Potassium bromide	1	-	-
Phenidone	0.2	0.24	0.22
PH	8.95	9.28	9.09

Water to make 1 liter; all other quantities in grams.

Nearly all PQ developers provide a 30–60% speed increase over D-76 when the film is developed to normal contrast. However, sharpness and photographically acceptable gradation are hard to obtain. The published and proprietary developers in Crawley's FX series were the first Phenidone developers designed specifically for the perfectionist photographer.

KODAK DK-50	
Metol	2.5 g
Sodium sulfite	30 g
Hydroquinone	2.5 g
Sodium metaborate	10 g
Potassium bromide	0.5 g
Cold water to make 1 liter	

Once Kodak eventually made up its mind to use phenidones, it produced, after much research, innovative developers such as HC-110 (chapter 6) and Xtol (chapter 5). It is worth noting again that phenidone developers with a shelf life greater than one year are almost impossible to prepare (except with the HC-110 technique), especially if they must be packaged in polyethylene plastic rather than glass. Derivatives of Phenidone have proved more stable, but shelf life remains a concern. For this reason Xtol is sold as a two-package powder.

As to replenishing systems: where volume is so high that a replenishing system is required, we suggest Kodak Xtol, based on the evidence available at this time.

KODAK DK-40	
Metol	1 g
Sodium sulfite	30 g
Hydroquinone	4 g
Sodium metaborate	20 g
Potassium bromide	0.5 g
Cold water to make 1 liter	
Originally for MP positive films	

Kodak Developer Formulas

DK-20 is given for historical reasons only. It represents an interesting attempt by Kodak in the 1930s to achieve super-fine grain without employing phenylenediamine. It continues to be cited in contemporary publications for its historical interest, but cannot actually be used on contemporary films with satisfactory results. Sharpness will be poor and dichroic fog likely. For those determined to try DK-20 with modern films, we suggest reducing the thiocyanate by at least 50%, and adding a Hennian antistain agent. This might be a gram or two of benzophenone or chlororesorcinol. Another possibility would be to replace the thiocyanate with about 1/10th as much DTOD. Crawley's Aculux formulas show how thiocyanate can be incorporated into developers for modern materials, and the Ektachrome First Developer formulas can also be adapted for use with black and white. See chapters 5 and 7.

KODAK DK-20	
Metol	5 g
Sodium sulfite	100 g
Sodium metaborate	2 g
Sodium thiocyanate	1 g
Potassium bromide	0.5 g
Water to make 1 liter	

KODAK DK-60	
Metol	2.5 g
Sodium sulfite	30 g
Hydroquinone	2.5 g
Sodium metaborate	20 g
Potassium bromide	0.5 g

KODAK DK-60
Cold water to make 1 liter
For rapid machine development of roll films and film packs

DK-20 was the first in Kodak's long line of developers based on D-76 which attempted to provide finer grain than D-76. It was replaced by D-25 and Microdol in the 1940s, and Microdol-X in the 1960s. See chapter 7. Other related developers include FX 5 and Perceptol. Kodak's most recent solvent developer, Xtol (chapter 5), has finer grain and greater sharpness than D-76, but is not a continuation of this line of thought.

D-61A is an early buffered MQ developer that does not rely on borates. For this reason, and because of its widespread use for many decades, it is an important milestone in developer chemistry. For old films the directions were: for tray use take 1 part of the stock solution to 1 part of water. Develop for about 7 minutes at 65F/18C. For tank use take 1 part of the stock solution and 3 parts of water. Develop for 10 minutes at 68F/20C. See also D-16, chapter 6, for an early developer with a double-buffer system.

DK-50 and variants were other important KRL buffered developers.

KODAK D-61A	
Metol	3 g
Sodium sulfite	90 g
Sodium bisulfite	2 g
Hydroquinone	6 g
Sodium carbonate mono	14 g
Potassium bromide	2 g
Cold water to make 1 liter	

D-76 variations—MQ fine grain developers

The most interesting variations on D-76 are the ones discussed in the chapter on solvent developers. However, a significant formula not mentioned there is Kodak D-89, which contains no hydroquinone, and pointed the way for future development of D-76 type developers.[1]

KODAK D-89	
Metol	3 g
Sodium sulfite	100 g
Borax	5 g
Pinacryptol Green 1:500	5 ml
Water to make 1 liter	

This formula was stated to be similar to D-76. It was intended for development of motion picture films by inspection when sampling of strips could not be done. Directions for the films of the 1930s were to develop for one minute in total darkness, then inspect with a two cell flashlight fitted with a 3.8 volt bulb and a Series 3 dark green filter. Two thicknesses of medium weight paper should be placed between the filter glasses to reduce the light further. The desensitizing action of the bath is said to decrease with age, whether it is used or not. (Crawley notes that the action of pure Pinacryptol Yellow solutions may increase with age—this may not happen when it is combined with a developer.) As noted in chapter 5, an improved form of D-76 can be prepared by increasing the metol or borax slightly, and omitting the hydroquinone. In D-89, where metol is 3 g/L, some loss of energy is probably due to the desensitizer. The effects of these desensitizing chemicals on modern films, particularly tabular grain types, is not known. The formula reflects the knowledge that because of pH rise activating the HQ, D-76 becomes a more reliable developer for motion picture film (or any other film) when the HQ is omitted.

Of the conventional D-76 variants, only the Adox formula, with somewhat less sulfite and the addition of bromide, was of interest to Crawley, who studied these formulas carefully. See chapter 5, p. 54 for the

formula. What interested Crawley was that in his microdensitometer and visual tests, he found the Adox formula sharper than D-76. He speculated that careful balancing with bromide removed a sheen from borax that impaired definition. He utilized this technique in the early FX solvent developers.

When some D-76 variation has the difference of 98 g of sulfite instead of 100, or 4 g hydroquinone instead of 5 g, this is absolutely insignificant—in the former case, the difference of two percent is within allowable measuring error; in the latter, since the hydroquinone is not active at the target pH, it makes no difference at all. In a PQ developer, where the interaction between the two developing agents is more complex, a 20% difference in the weight of the hydroquinone would have greater effect, even at a pH lower than 9.

The real problem with the Adox formula is that it didn't use buffering to fix the pH rise problem, see page 54 for related detail.

Pyrogallol formulas

The most famous of all pyro formulas is Kodak D-1, affectionately referred to as ABC for its three solutions. The formula is discussed, and the working solutions are given, in chapter 8. Here we give the stock solutions and briefly discuss the famous Edward Weston dilution. We also provide here the stock solutions for the Bürki developer discussed in chapter 8.

ABC PYRO STOCK	
Solution A	
Sodium bisulfite	9.8 g
Pyrogallol	60 g
Potassium bromide	1.1 g
Distilled water to make 1 liter	
Solution B	

ABC PYRO STOCK	
Sodium sufite anhydrous	105 g
Distilled water to make 1 liter	
Solution C	
Sodium carbonate mono	90 g
Distilled water to make 1 liter	

The Edward Weston dilution; dilution philosophy

The standard ABC dilutions are 1:1:1:7 and 1:1:1:11. Weston's dilution is different: 3:1:1:30. Weston believed this dilution resulted in a better tonal scale with less risk of aerial oxidation. Weston was using films that have little relation to the working characteristics of today's films. Other dilutions might be found which work better with contemporary films. The lesson to take away from the Weston dilution is not the diluton itself, but the idea that adjusting dilution is a valuable creative tool we photographers have at our disposal. Experimenting with different dilutions of single-solution developers such as Rodinal, D-76 or Xtol, is a good way to increase your palette and skill. When you come to the two- and three-solution developers, such as ABC, PMK, FX 1 and 2, and Pyrocat-HD, the possibilities for creative modification are limitless.

BÜRKI PYRO STOCK	
Solution A	
Pyrogallol	15 g
Sodium sulfite anhydrous	15 g
Water to make	250 ml
Solution B	
Sodium carbonate mono	100 g

BÜRKI PYRO STOCK	
Water to make	4 liters
To make 1 liter of working solution, add 50 ml of Solution A to 950 ml of Solution B.	
Develop 6 to 7 minutes at 68F/20C.	

Pyro-metol formulas

Pyro-metol is generally considered to be more useful than pyrogallol alone. The metol compensates for pyro's loss of speed, without spoiling the qualities for which pyro is prized. The table contains three formulas: BJP Pyro-metol, Wimberley WD2D in its latest incarnation (which no longer contains benzotriazole), and PMK. PMK stock solutions have, according to their formulator, exceptional shelf life. "Partially filled and stoppered bottles will last 10 years or more …. After a week or two, the color of stock solution A will turn a pale yellow color. This is the equilibrium point and no further change will occur." This makes them amongst the most useful of all photographic stock solutions. WD2D and WD2D+ should have the same shelf life.

One of the oldest pyro-metol formulas is the venerable British Journal of Photography formula. With old films, it produced a greenish-brown stain. By today's standards, there is too much metol, and the bromide is probably unnecessary. The weakest dilution given for this formula was 1:1:6. To be usable with modern films, 1:1:20 would be a more realistic starting point. (The original formula calls for potassium metabisulfite rather than sodium bisulfite. The substitution should not have any observable effect.)

	BJP	WD2D+	PMK
Solution A			
Distilled water	750	750	750 ml

	BJP	WD2D+	PMK
Metol	8	6	10 g
Sodium bisulfite	20	20	20 g
Pyrogallol	9	60	100 g
EDTA tetrasodium salt		5	
Water to make	1	1	1 liter
Solution B			
Distilled water	750 ml	750 ml	1400 ml
Sodium metaborate	-	-	600 g
Sodium carbonate mono.	65	110	- g
Water to make	1	1	2 liters

Directions for mixing PMK

These directions are quoted directly from *The Book of Pyro*.
Caution: Hutchings advises extreme caution when mixing any developer containing either pyrogallol or pyrocatechin. It is particularly important to avoid contact with the skin, eyes, and lungs. Since pyrogallol is crystalline, dust is not a major problem, but gloves should be worn when handling the dry chemical and when tray developing. See Appendix III for further safety recommendations. See *The Book of Pyro* for further safety recommendations specific to pyrogallol.

Stock Solution A

1. It is best to use distilled or deionized water for stock solution A, but high quality filtered tap water can be used. Mix the solution with water at room temperature. Maximum solution purity and stability is obtained at this temperature.

2. Weigh out the sodium bisulfite first. From this quantity, take a small finger pinch of it and add it to the water for the A solution. Set the rest of the weighed sodium bisulfite aside.
3. Add the metol to the A solution and stir until it is *dissolved completely*.
4. Add the remaining sodium bisulfite and stir until dissolved.
5. Weigh out the pyrogallol and add it to the stock solution *outside or under a ventilating hood*. See *Toxicity* in the *Appendix* [of *The Book of Pyro*] before handling.

Stock Solution B

1. Distilled or deionized water must be used for solution B. It is highly concentrated and a considerable quantity of the sodium metaborate may eventually precipitate if the water is not pure.
2. Dissolve the sodium metaborate in room temperature water. Best solution purity and stability will result at this temperature. It may be difficult to dissolve completely at this temperature, but any residual amount will dissolve by itself over a 24-hour period. The small amount of residual chemical will not affect the solution activity even if it is to be used immediately. The chemical will dissolve much more readily if the water is above 100°F, although upon cooling, a cystal precipitate may form.

JACOBSON PYROCATECHIN

Stock Solution A	
Sodium sulfite	40 g
Pyrocatechin	20 g
Water to make 1 liter	
Stock Solution B	

JACOBSON PYROCATECHIN	
Potassium carbonate	120 g
Water to make 1 liter	
Working solution: 1 part A, 1 part B to 8 parts of water.	

Be sure to label all solution bottles. The shelf life of the stock solutions is exceptional. Partially filled and stoppered bottles will last 10 years or more. Clear glass is fine for PMK, if solution A is kept out of strong light.

After a week or two, the color of stock solution A will turn a pale yellow color. This is the equilibrium point and no further change will occur. (The PMK solutions can be used immediately after mixing.)

Working solutions of PMK

1 part A + 2 parts B + 100 parts water

Example: 10 ml A + 20 ml B + 1000 ml of water make approximately one liter of working solution (1030 ml). Measure the quantity of water and add the A and B stock solutions. It does not matter which is added first. *Note:* When the PMK working solution is mixed together, it will immediately proceed through color changes from grey-green to pale amber. This is an important visual check of solution activity. If there is no color change, something is wrong! Recheck stock solutions for correct formulation and the working solution for correct dilution.

WINDISCH PYROCATECHIN COMPENSATING	
tock Solution A	
Water (room temperature)	750 ml

WINDISCH PYROCATECHIN COMPENSATING	
Sodium sulfite	12.5 g
Pyrocatechin	80 g
Water to make 1 liter	
Stock Solution B	
Cold water	750 ml
Sodium hydroxide	100 g
Water to make 1 liter	

Pyrocatechin formulas

In the Jacobson developer, the grade of potassium carbonate is not specified, but it can be assumed to be anhydrous. Better results may be obtained with the crystalline grade because of buffering.

There is probably not a well-known developer that has been mis-printed as frequently as the Windisch Pyrocatechin developer. It has been printed in dozens of books with substantial errors. This is the definitive formula with the definitive dilutions—we think.

There are two basic dilutions for the Windisch developer. The first, which we prefer, calls for 25 ml A plus 15 ml B plus water to make one liter. The second, preferred by Ansel Adams, calls for 40 ml A plus 10 ml B. Development times should be 9 to 12 minutes with modern films.

Caution: do not use pyrogallol, pyrocatechin, or sodium hydroxide without reading Appendix III on Safety thoroughly and taking the precautions advised.

MUIR PYROCATECHIN COMPENSATING	
Solution A	
Water (125F/52C)	500 ml

MUIR PYROCATECHIN COMPENSATING	
Sodium metabisulfite	20
Pyrocatechin	80
Cold water to make one liter	
Solution B	
Sodium hydroxide	100
Cold water to make one liter	
Working solution: 10 ml A, 5 ml B to 1 liter of water; develop 6 to 8 minutes at 70F/21C for slow films	

Maxim Muir has been active in reworking some of the old pyrocate-chin formulas. For his developer, Muir advises presoaking the film for 2 to 5 minutes in either plain water or water with Edwal LFN added per directions. We do not recommend presoaking or the use of wetting agents during development.

As can be seen, the stock solution is almost identical to the Windisch formula, except that 20 g of metabisulfite replaces Windisch's 12 g of sulfite. What is more significant is Muir's recommended dilution, which results in a more moderate developer. The working solution is:

Pyrocatechin 0.8 g	Sodium metabisulfite 0.2g	Sodium hydroxide 0.5 g

This is a very dilute developer, capable of heavy tanning and staining.

For low contrast, Muir recommends an alternate solution B: instead of 10% sodium hydroxide, 10% sodium carbonate anhydrous. Muir believes this will allow N-2 and N-3 contractions with the following working solution: 10 parts A, 40 parts B, to a liter of water; 8 minutes at 70F/21C with slow films. Muir notes that N-2 and N-3 development result in "inevitable" film speed loss and midtone compression. While we agree that highly dilute developers compress midtones, if the developer is correctly balanced, there should not be a speed loss, but a speed gain. **We strongly recommend making the**

stock and working solutions of all pyrogallol and pyrocatechin developers with distilled water.

HÜBL PASTE	
Hot water (130F/54C)	500 ml
Sodium sulfite	165 g
Glycin	135 g
Mix well, and add gradually:	
Potassium carbonate cryst.	625 g
Water to make 1 Liter	

Glycin developers

Glycin developers were among the first real high definition developers, especially when used as so-called stand developers: with developing times of about an hour and no agitation (chapter 4). The most famous photographer to use this kind of developer was Atget. A typical developer of the early 20th century is Hübl Paste, a highly concentrated suspension with excellent keeping properties. Indeed, this may be the most highly concentrated of all developer formulas. The potassium carbonate should be crystalline.

Shake well before use. The normal dilution suggested for turn of the century films was 1:12. As a guide for modern films, Paul Lewis suggests 1:35, developing Agfa APX 100 for 11 minutes. With all pure glycin developers, a speed loss of about one stop can be expected.

TD-107	
Metol	1 g
Sodium sulfite	25 g
Glycin	1 g
Sodium bisulfite	1 g

TD-107	
Sodium metaborate	1 g
Water to make 1 liter	

The paradigmatic modern glycin developer is FX 2 (chapter 6). It remains the best glycin developer yet published. Chapter 11 contains some suggestions for low contrast Phenidone-glycin developers for document films. But what about glycin and tabular grain films? Could this agent be advantageous? Crawley thought so. For those willing to experiment, we propose TD-107 as a starting point. For more sharpness but coarser grain, replace the metaborate with 1 gram of sodium carbonate anhydrous.

MCM 100

MCM 100	
Water (125 F/52C)	750 ml
Sodium sulfite	88 g
p-Phenylenediamine	7 g
Pyrocatechin	9 g
Borax	2.3 g
Trisodium phosphate, cryst.	6.9 g
Potassium bromide, 10%	2 ml
Cold water to make 1 liter	
Do not use the monohydrate of trisodium phosphate.	

This formula originally required Meritol, a developing agent that was the reaction product of an an equimolar admixture of p-phenylenediamine and pyrocatechin. After Meritol was no longer available, the formula was revised to provide the same functional results with the two chemicals split up. We

publish the formula because, unlike most PPD formulas, it can work with some modern films, due to its high alkalinity and the high energy of pyrocatechin, which accounts for most of the development. It may be worth trying with modern films, even tabular films. The alkali system may need to be modified. This formula illustrates how useful phosphate alkalis can be. MCM 100 is said to offer normal emulsion speed. On older films developed in MCM 100, the emulsion side of the film had the appearance of being so highly polished that it was difficult to distinguish from the base side.

Presoak the film in water or a 5% solution of sodium sulfite for 2 to 3 minutes to remove the anti-halation coating which may restrain development. Use a running water stop bath with this developer and fix in an alkaline fixer.

N.B. It is essential not to use an acid hardening fixer with any developer containing any form of sodium phosphate.

Traditional Rodinal

TRADITIONAL RODINAL	
Solution A	
Water (125 F/52C)	750 ml
p-Aminophenol hydrochloride	100 g
Potassium metabisulfite	300 g
Cold water to make 1 liter	
Solution B	
Cold water	300 ml
Sodium hydroxide	200 g
Cold water to make	400 ml

There have been hundreds of unauthorized publications of the “original” Rodinal formula. All of the most authentic ones consist of 100 grams of *p*-

aminophenol hydrchloride and 300 grams of potassium metabisulfite in a liter of water. To this is added a 50% solution of sodium hydroxide, drop by drop, until only a few crystals of precipitate are visible. All classic Rodinal formulas *must have* a crystal or two of precipitate at the bottom of the container. If they do not, the developer will not work well and the concentrate will not keep. The best instructions for making this formula were given to us by Dr. Elie Shneour: **Caution**: When making up the 50% solution of sodium hydroxide heat is generated. The solution must be cooled before adding to the developer. Add a small amount of sodium hydroxide to the water, let dissolve, check heat, then add a little more. Never add water to the sodium hydroxide. Only add hydroxide to the water. **Use gloves and protective eye goggles, and carefully read the additional information in Appendix III regarding sodium hydroxide**.

Note: Although it is sometimes considered acceptable to substitute sodium metabisulfite for potassium metabisulfite, the substitution is not successful in this formula.

Allow Solution A to cool. A precipitate of p-aminophenol hydrochlo-ride will form. Place Solution A in an iced water bath and, with continuous mixing, slowly add 280 ml of Solution B. Then very slowly add additional Solution B until a sudden darkening in color takes place. Finally, add, drop-by-drop, Solution B until only a few crystals remain.

The developer will, in time, turn dark brown. The stock solution will last for several years. Some Rodinal experts believe that Rodinal-type formulas should be used within a few weeks for optimum and consistent results. Others believe that it improves with age. Although its characteristics do change with age, the change is not dramatic, and the developer remains viable for an astonishingly long time.

This formula can be used at dilutions ranging from 1:25 to 1:200. The most frequently used in continuous tone photography are 1:50, 1:75 and 1:100. Developing times published for Adox Rodinal can be used as a starting point.

Windisch Film Developers

The Windisch metol-sulfite formula is identical to D-23 except that metol is exactly at one-third and and sulfite exactly one-fourth. Functionally, then, it is D-23 1:2. Some photographers have been reporting promising results with tabular grain films. Developing times will be on the long side, certainly over ten minutes. Although state-of-the-art tabular grain developers such as Xtol and FX 37 are likely to give more satisfactory overall results, we believe this formula (or D-23 1:3) should be investigated further. Experience indicates that tabular grain films seem to work best with a developer that contains less than 35 g/L of sulfite per liter of working solution, as this one does.

WINDISCH METOL-SULFITE	
Metol	2.5 g
Sodium sulfite	25 g
Water to make 1 Liter	

Windisch's more famous developer, the pyrocatechin formula, is listed two pages back and is also discussed in chapter 8. Windisch's other famous formula was a super-fine grain developer based on ophenylenediamine. It can be found in *The Darkroom Cookbook*.

One of the most authentic versions of Rodinal is in the 1945 Report on the Agfa Film Factory Wolfen, CIOS, Target No. 9/133. This states the formula as follows: "Rodinal (concentrated single solution developer, for 600 litres). Dissolve 34 kilos of para-aminophenol in 340 litres of water. Add 558 kilos of a 30% solution of potassium sulphite at 55°C followed by 50 kilos of a 34% potash solution, then 5.52 kilos potassium Bromide in a little water, followed by 42 grms. P.1347. Filter and allow to stand 14 days." The compound B. 1347 is defined as: "Anthraquinone-1.2 triazole sodium sulphonate." This may correspond to "1,2

triazoleanthraquinone-3-sulfo acid" mentioned in USP 2,265,138 as a desensitizer for film developers. After 1–2 minutes, film could be developed by light green or yellow darkroom light. It appears that this vintage of Rodinal contained a desensitizer. It isn't known if it would work with modern films. This formula was obtained under duress. How accurately it reflects what Agfa was really making we cannot say. Anthraquinones have been used in emulsions to suppress fog.

Monobath Formulas

In a monobath, development and fixation both take place in the same solution. For those who wish to experiment, here are two formulas. To use either formula, agitate continuously for the first thirty seconds, then for 10 seconds every 30 seconds thereafter. At 75˚F the film should be fully developed in less than three minutes, and will develop no further. However, due to the relatively low concentration of hypo, fixing usually takes from 4 to 7 minutes. If you remove the film from the solution prematurely it will have a milky-white appearance. Don't panic. Simply place the film back in the solution, continue agitating as you would for normal fixation, and the fixing process will continue.

Phenidone is often difficult to dissolve except in highly alkaline solutions. With these formulas, using sodium hydroxide as the alkali, start with water at room temperature and dissolve the sulfite. Do not use water over 75˚F, as the hydroxide may heat up and spatter. After the addition of the Phenidone, add a pinch of hydroquinone followed by the sodium hydroxide. The Phenidone will dissolve completely; the small amount of hydroquinone will help prevent oxidation of the phenidone. Then add the remainder of the hydroquinone and other chemicals in the order given. **Read the cautions regarding sodium hydroxide in Appendix III. Wear gloves and protective eye goggles**.

G.W. CRAWLEY FX 6-A (BJP ANNUAL, 1964)	
Water at room temperature	750 ml
Sodium sulfite	50 g
Phenidone	lg
Hydroquinone	12 g
Sodium thiosulfate	70 -125 g
Sodium hydroxide	10g
Water to make	1 liter

KODAK RESEARCH LAB (PHOTO. SC. ENG. 5, 198 (1961))	
Water at room temperature	750 ml
Sodium sulfite	50 g
Phenidone	4g
Hydroquinone	12 g
Sodium thiosulfate	no g
Sodium hydroxide	4g
Water to make 1 liter	

UPDATE: Donald Quall, devised an amonium thiosulfate monobath by combining HC-110, Ilford Rapid Fixer, and ammonia. For more, see covingtoninnovations.com/hc110. What is particularly appealing about this technique is that the antistain agent in HC-110 (assuming it is still present) may prevent dichroic fog problems that could otherwise arise. The solution should be used immediately, due to the volatility of the ammonia. FURTHER UPDATE: HC-110 as of mid-2019 is a completely different type of developer (chapter 6). The Quall technique would now have to be investigated using Ilford HC. N.B. All photographic solutions employing ammonia should be used immediately after mixing.

Of these two formulas, we prefer the BJP version by Crawley. They are very similar, but note that the Kodak formula calls for 4 grams of Phenidone,

which is very hard to dissolve, as opposed to the 1 gram in Crawley's formula, which uses more sodium hydroxide to compensate. In Crawley's formula, the precise amount of thiosulfate is left open. This is an underlying principle of all monobath formulas. The precise amount of thiosulfate required depends on how quickly the particular film being used fixes. Slower, finer grained films have a faster clearing time, and therefore need less thiosulfate. Faster films, especially tabular grain films, will need the maximum amount of thiosulfate.

Washing time after monobath processing is exceedingly rapid because the solution is alkaline. No more than five minutes is needed for a wash to archival standards. However, as sodium thiosulfate is now less recommended for fixing films, it is harder to recommend the use of these traditional monobath formulas unconditionally. We have seen no successful formulas published for ammonium thiosulfate monobaths. Development would have to be exceedingly rapid.

Although it has been demonstrated that unique sharpness-enhancing adjacency effects can be produced with monobaths, it was a struggle to rival the image quality of conventional processing with D-76.

Later monobath technology It will be seen that monobath formulation only took off after the use of phenidone became widespread. Phenidone's extremely rapid induction period is an essential component of the sodium thiosulfate monobath's heyday, in the late 1950s and early 1960s. From the 1960s, research focused on non-thiosulfate fixing chemistry. Ultimately, the technology led to extremely rapid monobaths and then to monobath-incorporated films and papers. Haist V2 covers these developments in the chapters on Monobath Processing and Stabilization Processing. We tend to think of stabilized prints as temporary unless they are subsequently fixed and washed. However, Haist devised and described monobath-incorporated papers (some activated by simple alkali, others activated by heat) which he suggested formed images of great and even archival stability.

ACID STOP BATHS

Chapter 12 makes clear that we favor all-alkaline film processing without acid stop baths. It contains our best suggestion for using an acid stop bath today: a buffered acetic acid stop bath, as described by Crabtree and Henn in 1951. That is the single important publication on stop baths in the entire history of photography. It is not a topic that has attracted much research. The various stop baths in old formulas don't seem to us worth reprinting. Stop baths are indeed the neglected step child of photographic processing.

ALKALINE STOP BATHS

Alkaline stop baths have not yet gone beyond the experimental stage. The approach that has been taken experimentally is to use a high concentration of an antifoggant, such as 5–10% potassium bromide, 0.5–1% benzotriazole, or 0.05–0.1% 1-phenyl-5-mercaptotetrazole. Sodium sulfite should be added as a preservative to help prevent swelling and oxidation staining. Between 2 and 5% is a suitable amount. A buffering system should be used to keep pH within the desired range. A combination of sodium metaborate and sodium bisulfite may be suitable for trial.

Moving from F-5 to its commercial equivalent, the single-package dry powder 'Kodak Fixer', was not an easy process for Kodak. Some steps along the way are indicated in various patents such as US 2,378,248 (1945), US 2,548,552 (1951), (which addresses caking problems) and US 2,543,086 (1951) (which describes a heating process to reduce or eliminate dust).

SODIUM THIOSULFATE FIXER FORMULAS

KODAK SODIUM THIOSULFATE FIXERS				
	F-5	F-6	F-10	F-24
Sodium thiosulfate pentahydrate	240	240	330	250 g
Sodium bisulfite	-	-	-	25 g
Sodium sulfite anhydrous	15	15	7.5	10g
Boric acid crystalline	7.5	-	-	- g
Sodium metaborate (Kodalk)	-	15	30	- g
Acetic acid 28%	48	48	71.25	-ml
Potassium alum	15	15	22.5	- g
	Water to make 1 liter			

The table above lists some of the traditional Kodak sodium thiosulfate fixers. These are better formulated than any other competing published formulas. Kodak was indeed lucky to have H.D. Russell in charge of their development over a 40-year period.

The historical value of F-5 and Kodak fixer cannot be overstated. Before Russell formulated these in 1933, there was no way to prepare a robust hardening fixing bath. Without the borate, an alum fixing bath must be formulated and kept near pH 4. The pH can't be lower or the thiosulfate will decompose. Yet the aluminum begins to hydrolize at pH 4.2 and sludges at pH 4.8. The addition of the borate raises the sludge point to pH 6 or a little higher, extending the hardening life of the fixer by a remarkable three to four times. Boric acid had been tested many times before Russell and found to be useless. Russell explained to me that the difference was that he slowly titrated the challenge alkali solution of developer into the fixer (as in normal

processing), rather than dumping it all in at once, and that was the key to his discovery.

Note on optimal hardening with Kodak fixers: Although F-5 and Kodak Fixer can be used over a wide pH range, that is from pH 4.2 to about 6.2, Haist points out that *maximum hardness will occur at pH 4.5*, at the nominal isoelectric point of cow gelatin. This indicates the wisdom of using a well-buffered stop bath such as TS-7 when this kind of fixer is to be used. Will this maximum point of hardness change if the nominal isoelectric point is altered, as is routine today? We don't know.

All of the formulas above are rated to be able to fix about 20 to 25 rolls of 35mm, 36 exposure film (80 square inches) *without replenishment*. F-5 is the standard sodium thiosulfate-based formula. The commercial product known as Kodak Fixer is functionally identical, one difference being that the acid is in solid form.

Reducing odor

Most acid fixing formulas produce strong odors caused by sulphur dioxide emanating from the reaction of acid and sodium sulfite. In F-6 and F-10, odor is substantially reduced. However, while F-5 has just about sufficient acidity to be useful to exhaustion even if a stop bath is not used, F-6 and F-10 *require* an acid stop bath to be used if the fixer is to be used to maximum capacity.

Kodak's non-hardening fixer

The non-hardening formula, F-24, has been recommended for use with tanned negatives, such as those developed in pyro or catechol, as it is less acidic than the hardening formulas. However, it is still too acidic, and too high in sulfite, to be ideal for processing tanned negatives.

Alkaline sodium thiosulfate fixers

TF-2 ALKALINE FIXER	
Water	750 ml
Sodium thiosulfate	250 g
Sodium sulfite anhydrous	15 g
Sodium metaborate	10g
Water to make 1 liter	

It is simple to construct an alkaline sodium thiosulfate fixer. One formula is TF-2. Although this fixer will wash out of negative and print materials more rapidly than any acid fixer, we give this formula for users who are determined to use sodium rather than ammonium thiosulfate and who would like a formula superior to the traditional acid hypo fixers. It would be appropriate to use for negative or print materials that contained little or no silver iodide, such as hand-coated materials. If sodium thiosulfate is used to fix contemporary print or negative materials, be sure to fix for *three times the clearing time*, rather than the traditional recommendation of twice the clearing time, and discard the fixer when clearing time doubles. That will alleviate concerns about the ability of sodium thiosulfate to fix iodide-containing materials adequately. As with all alkaline fixers, washing is very rapid and hypo clearing agent is not necessary. For films, a two-minute wash in running water should be archivally adequate. That time can be extended to five minutes for peace of mind, but will not bring residual thiosulfate levels appreciabily lower. Fiber-based prints should be washed for at least 30 minutes. As there is no ammonia, this formula will have no odor. Capacity is the same as for F-5. **N.B**. Excessive iodide buildup will not occur when sodium thiosulfate fixers are not used to their maximum capacity.

SODIUM THIOSULFATE FIXERS WITH AMMONIUM ION

Ammonium thiosulfate was not available in commercial quantities until the 1940s. However, it was known by some that ammonium thiosulfate was more much more rapid than sodium. (Not every old authority agreed: for example, Eduard Valenta's authoritative 'Photographische Chemie' of 1899 stated there was no advantage to ammonium thiosul-fate at all.)

There was an easy and inexpensive way, however, to obtain a good proportion of ammonium thiosulfate in solution, and that was to add ammonium ion to the sodium thiosulfate. Practically speaking, this meant either ammonium chloride, ammonium sulfate, or a mixture of both. Agfa was the first company to figure this out on a commercial basis, and in 1906 patented their Rapid Fixing Salt (British Patent 25,869). One example in the patent is, 30 parts of dessicated sodium thiosulfate, 10 parts of ammonium chloride, 2 parts of sodium bilsulfite to acidify. To use, dissolve 10 parts in 50 parts of water. Another example is, in 100 parts of water, dissolve 24.8 parts sodium thiosulfate (cryst.), 5.3 parts ammonium chloride, and 6.6 parts of ammonium sulfate. Or to prepare as a solid, 3 parts of sodium thiosulfate (anhy.), 2 parts ammonium chloride, and 0.3 parts of sodium bisulfite.

The patent notes, "… when mixing sodium hyposulphite with a suitable ammonium salt, such as ammonium chloride or ammonium sulphate, the ammonium salt may be taken in excess so that the fixing bath contains an ammonium salt besides the ammonium hyposulphite formed by the reaction. On the other hand the fixing bath or the fixing agent in the solid state should not contain less than such a proportion of the ammonium salt as will ensure the presence of at least one molecular proportion of ammonium hyposulphite for each molecular proportion of sodium hyposulphite."

Even in 1906, Agfa was aware that "The new fixing agent has the advantage that when it is used, the fixing operation occupies only one half the time consumed when sodium hyposulphite is used; moreover, when several plates are fixed in succession in the same bath the duration of the fixing remains unaltered, whereas in a sodium hyposulphite bath the duration of the operation becomes much longer after a few plates have been fixed." In other words, the clearing time is reached much later, and capacity is greater. And that is still true today.

It is interesting to note that there is no hardening mechanism proposed by Agfa. The necessary developments in practical hardening chemistry would come from Kodak (JSMPE 21, 137, 1933).

This technique did not have widespread use until it was re-approached by Russell at Kodak in the 1940s and rationalized (JSMPE 38, 353, 1942). In these fixers, a simple ammonium salt is added, partially converting sodium to ammonium thiosulfate. The result is fixation which is about twice as fast as a conventional sodium thiosulfate fixer though only about half as fast as an ammonium thiosulfate fixer. These fixers are therefore about exactly intermediate in speed between conventional sodium and conventional ammonium fixers.

These fixers have largely been passed by, but it is possible they will become of interest again, if supplies of cheap ammonium thiosulfate dry up, as has been predicted by some.

Two special points in these fixers' favor: they are more suitable for high-iodide modern films and papers than sodium thiosulfate fixers, and their capacity will be as much as 50% greater.

KODAK SODIUM THIOSULFATE FIXERS WITH AMMONIUM ION

	F-7	F-9

KODAK SODIUM THIOSULFATE FIXERS WITH AMMONIUM ION			
Sodium thiosulfate pentahydrate	360	360	g
Ammonium chloride	50	-	g
Ammonium sulfate	-	60	g
Sodium sulfite anhydrous	15	15	g
Boric acid crystalline	7.5	7.5	g
Acetic acid 28%	48	48	ml
Potassium alum	15	15	g
	Water to make 1 liter		

General notes: F-7 has a tendency to 'attack and pit certain types of stainless steel, such as contained in tanks, trays, clips, hangers and other processing equipment. Stainless steel of types 302 and 304 was atacked but type 316 was not.' (Haist 586) Hence F-9, which has no more tendency to pit stainless steel than sodium thiosulfate fixers without ammonium ion.

Variation: It would be easy to convert these fixers to neutral or alkaline pH, but only if the alum hardener is dispensed with. One way of doing this would be to dispense with all the acid ingredients. Another would be buffer with a mild or moderate alkali.

Caution: Haist repeats a warning present in some form in all the Kodak publications which described this type of fixer: "Caution: With rapid fixing baths, do not prolong the fixing time for fine-grained film or plate emulsions or for any paper prints; otherwise the image may have a tendency to bleach, especially at temperatures higher than 68F/20C. This caution is particularly important in the case of warm-tone papers." **Cure**: if it is possible to do without alum hardening, then the pH can be adjusted to neutral or alkaline, and the danger of bleaching will be eliminated.

ATF-2 RAPID CHROME ALUM FIXER	
	Working Solution

ATF-2 RAPID CHROME ALUM FIXER	
	Working Solution
Water	700 ml
Ammonium thiosulfate, 57-60%	185 ml
Sodium sulfite anhydrous	15 g
Sulfuric acid 5%	80 ml
Potassium chrome alum	15 g
Water to make1 liter.	
"Dissolve the chemicals in the order given.To make sulfuric acid 5%, add 5 ml of C.P. acid to 95 ml of cold water slowly with rapid agitation." "Formula ATF-2 was developed to produce a fixing bath whose hardening action could keep pace with its fixing action. It is well known that chrome alum gives not only extreme hardening of gelatin emulsions, but that this action is relatively rapid when it is used in a bath whose acidity is properly adjusted. This bath produced satisfactory hardening with the time necessary for it to clear most types of emulsions. In common with most chrome alum acid-hardening fixing baths, the service life of this bath is short and it has poor keeping qualities."	

Hardening: Alnutt states, in the paper referenced in the next section, that, as regards F-7, “ammonium chloride seems to decrease the hardening action of such baths.” He also notes that the hardener is effective at a higher pH: “The commonly used hypofixing baths appear to lose their hardening action when the pH has been raised to between 5.5 and 5.8, although their fixing power may still be good; an ammonium thiosulfate aluminum salt bath will retain satisfactory hardening action up to a pH of 6.5 to 7.”

ACID AMMONIUM THIOSULFATE FIXER FORMULAS

On the callout of this and the following page, we give some hard-to-find formulas that aren't included in the main text, namely Alnutt's ATF-2 and ATF-5, which Haist reproduces. ATF-3 and ATF-4 are dry-package formulas utilizing anhydrous ammonium thiosulfate. Only a few commercial products utilize the anhydrous, because of its cost and its tendency to take on water from the atmosphere. These formulas can be found in JSMPE (Journal of the Society of Motion Picture Engineers) v. 41, 1943. p. 300. It is clear that Haist did not reproduce them because he thought they were impractical.

KODAK RAPID FIXER	
Ammonium thiosulfate	40-45%
Sodium actate	5-10%
Acetic acid	1-5%
Boric acid	1-5%
Ammonium sulfite	1-5%
Sodium bisulfite	0.1-1%
pH 5	

Kodak Rapid Fixer

This fixer is of particular interest as it has long been considered the standard of quality for rapid fixers. One MSDS we have seen for it (5–2019) gives the weight percentages in the callout. As will be seen, this is close to the Kodak

patent formula in chapter 13, except that it seems to be somewhat weaker and less highly buffered.

> *Sulfuric acid has been almost universally used in the hardener concentrate that accompanies acid ammonium thiosulfate fixers, resulting in a highly acid pH of 1. However, Tetenal and some others have chosen a more moderate technique. For example, Tetenal's Hardener for Fixers and Stop baths contains 10–25% acetic acid and 10–25% aluminum sulfate, resulting in a slightly less hazardous pH of 2.*

Acid ammonium fixer hardeners

Ammonium thiosulfate fixers are often formulated as a concentrate, which will be diluted 1:3 or 1:4 for film and, conventionally speaking, 1:7 or 1:8 for papers, although it has been found advantageous to use "film-strength" rapid fixer for papers. In such a case, they are usually supplied with an optional "B Solution" of hardener.

According to Mason, this hardener should be a concentrated solution of either aluminum chloride or aluminum sulfate, plus enough acid to keep them clear. The final fixer should contain about 5 g/L of aluminum chloride (or sulfate, and as *anhydrous*) per liter. The acid used is usually sulfuric.

Note that the Alnutt hardener in Chapter 12 is without sulfuric acid.

ATF-5 GENERAL PURPOSE RAPID HARDENING FIXER	
	Working Solution
Water	700 ml
Ammonium thiosulfate, 57-60%	200 ml
Sodium sulfite anhydrous	15 g

ATF-5 GENERAL PURPOSE RAPID HARDENING FIXER	
	Working Solution
Acetic acid 28%	55 ml
Potassium alum	15 g
Water to make 1 liter	
"Dissolve the chemicals in the order given. Dissolve the boric acid in a small volume of hot water before adding to the bulk of the solution." Haist continues, "The loss of silver image during fixation is directly proportional to the acidity of the bath. [Russell & Crabtree, JSMPE 18 p. 371 (1932)] Ammonium thiosulfate fixing baths have greater reducing action than sodium thiosulfate baths at the same pH. Films or plates should not be allowed to remain in [acid] ammonium thiosulfate baths more than twice the time to clear. Photographic paper prints are especially susceptible to the destruction of their finely divided silver image. No noticeable reduction of a silver image of a photographic film was observed by Alnutt during a 10-min immersion in ammonium thiosulfate baths containing 150g/ liter of the thiosulfate salt. With baths containing 200g/liter... marked image reduction was noticed after 8 min immersion. Prints fixed in this or similar ammonium thiosulfate rapid fixing baths should not be immersed in the solution for more than 4 minutes."	

When Alnutt published his formulas in 1943, it was still early days for commercial ammonium thiosulfate fixers. The need to acidify the hardening concentrate was probably discovered only later on. Of the hardeners Alnutt tested, he preferred chloride for best and most rapid hardening. However, things have evolved since then, and Kodak seems to have preferred the sulfate. According to the MSDS of 4-5-2011, Kodak Rapid Fixer hardener contains by weight

Aluminum sulfate 15–20%
sulfuric acid 10-<15%
pH 1

Caution: See Appendix 3 for cautions about sulfuric acid.

Choosing which acid hardener to use

Mowrey prefers simple hardeners in this order: 1st, potassium alum; 2nd, aluminum sulfate; 3rd, aluminum chloride. Alnutt preferred chloride for speed and degree of hardening, but in the light of later experience sulfate appears to be preferred for liquid hardeners.

Other addenda to acid hardening fixers

Smaller manufacturers, seeking some advantage real or imagined, have added some unconventional ingredients to their rapid fixers from time to time. One example is Frodex (corn syrup solids) in Edwal Quik-Fix; another is magnesium sulfate in Acufix. Perhaps the most unexpected (yet longstanding) addendum is sodium thiosulfate. Harold Russell told me that he added a small percentage of sodium thiosulfate to the ammonium thiosulfate fixers he formulated for Kodak because he had discovered it improved stability. The only fixer we know of that employs this technique is Kodak's X-omat fixer. The MSDS indicates ammonium thiosulfate at 10–15% and sodium thiosulfate at 1–5%. It appears that this is still Russell's formula, more than half a century later.

Many other additives have been suggested to improve ammonium thiosulfate hardening fixers. Some are mentioned in Haist, and the patent literature is full of them. To the best of our knowledge, none of these were ever used in commercial products. The sole practical exception is ammonium thiocyanate, as discussed in chapter 14.

CHROME ALUM STOP BATHS AND FIXERS

Chrome alum hardens much better than potassium alum (and aluminium sulfate and chloride) but its use has been deprecated for many decades because it is so much harder to work with than potassium alum, aluminum sulfate and aluminum chloride, and because films have themselves become harder over the years. The best point about chrome alum is that it hardens films so well that the gelatin is insoluble in boiling water. No other commonly available or reasonably safe hardener has such properties.

Working with chrome alum is much more challenging than using simple and almost foolproof formulas like Kodak Fixer and Kodak Rapid Fixer. Careful pH control of the chrome alum bath, over a quite narrow range, is essential to success.

Because chrome alum is still in occasional use today, and because authoritative information about it is scarce, we will quote extensively from Haist, who covered this chemical in great detail, and from his sources. Haist's material on chrome alum is based almost exclusively on what remains the foundational paper, Crabtree and Russell's "Some Properties of Chrome Alum Stop Baths and Fixing Baths (Part I)" JSMPE, 14:483 (1930), Part II p. 667. Our direct quotes in this section are all from that paper. We will further indicate this by the abbreviation (JSMPE 14). A great deal of this material was also summarized in PCS, which we will cite as such.

When would we need to use a chrome alum stop or fix today?

With the most modern films from the main manufacturers, hardening is not needed even at 100F/38C processing. With softer films, chrome alum should only be needed when processing temperatures are high (80–100˚F). However, with hand-coated and other soft emulsions, chrome alum hardening may be desirable even at normal processing temperatures.

According to PCS, it was conventional at the time (late 1930s) to use a chrome alum stop bath for films and plates. Acetic acid stop baths were only preferred for prints.

Should we choose to pre-harden, stop or fix with chrome alum?

Hand coated glass plates should probably be hardened before development. However, there is the possibility of the material losing hardening when placed in a highly alkaline developer. Therefore, such materials should probably *also* be hardened in a chrome alum stop bath. We do *not* recommend chrome alum *fixers*, because they cannot be reliably kept for more than a day without pH control. Instead, we recommend a potassium alum hardening fixer after the chrome alum stop bath. Haist supports this view: "**Probably the best choice would be a chrome alum stop bath followed by a potassium alum fixing bath**. This would provide a more reliable and uniform degree of gelatin hardening with use than would be provided by a chrome alum fixing bath with a high concentration of alum." (Haist 581) This technique does add three or four minutes to the overall processing time.

Warning 1: Haist observes (581), "At normal temperatures of processing, chrome alum baths may provide almost too much hardening, so that a thin, upper layer of the gelatin is highly hardened but the underlying gelatin is unhardened. This case hardening of gelatin by chrome alum has resulted in some spectacular disasters, as the gelatin layer of the emulsion can slide off the film base. For example, in his book, *The Photographic Negative* (Vol. 2, p. 345), Herbert C. McKay mentioned that 'The memory still lingers of sixteen hundred feet of chrome-hardened motion-picture emulsion slipping from the celluloid base into a mass of sludge in the bottom of the tank.'"

Additional warnings: (restated and amplified from (JSMPE 14))

1. upon storage, chrome alum baths may lose the ability to harden even if they have not been used, especially when stored at high temperatures [this is contradicted a few years later in PCS, p. 146, which states "A plain solution of chrome alum retains its hardening properties indefinitely." We are unable to resolve the contradiction, but would advise always mixing chrome alum stop baths fresh.];

2. as the pH rises with excess alkaline developer, chrome alum stop baths may precipitate a scum or sludge that adheres very strongly to the film surface;

3. at high temperatures, chrome alum baths may stain gelatin green, though no staining is evident at regular processing temperatures if high concentrations (greater than 3%) are avoided;

4. Chrome alum must be added to water at a temperature below 150F or hydrolysis will cause lowered pH and decreased hardening. For various reasons, the preferred mixing temperature is 70F/21C.

5. Wipe or squeegee the surface of the film before drying to remove any possible traces of chromium scum; once dried it is almost impossible to remove. [Mowrey recommends common synthetic sponges; PCS recommends "wetted cotton" which probably means soft muslin but could also mean wetted cotton balls, in which case, it is important not to leave cotton tendrils on the film.] The scum can sometimes be removed by immersing the material in 5% potassium citrate but this causes the film to soften and destroys the hardening. *Chromium scum does not usually occur if the chrome alum bath is fresh and the films or plates are agitated for the first 45 seconds.*

Advantages of chrome alum are its ability to render gelatin insoluble even in boiling water, and its efficiency.

Additional points:

Gelatin hardening occurs more rapidly in a stop bath than in a fixing bath, so the swelling in the emulsion layer is inhibited before it occurs.

Haist quotes verbatim this section from JSMPE 14:

1. "plain chrome alum solutions are more suitable for hardening motion picture [and other] film than those containing acid [keep in mind that this recommendation is for the softer films of the 1930s];
2. "The addition of developer decreases the acidity and the hardening properties;
3. "The acidity or pH value of a chrome alum solution must be maintained at a value of 4.0 for neutral film rinsed in water for 15

minutes after development [which we do not recommend] and between 3.8 and 3.0 for alkaline film if the maximum degree of hardening is to be obtained. The hardening properties are constant, irrespective of the concentration of chrome alum above 0.5% when the pH is adjusted to these values;
4. "Sulfuric acid is the most suitable acid for maintaining this activity; and
5. "The hardening properties of a bath containing an excess of developer decrease with age."

Practical exhaustion tests with and without revival with acid with 2% and 3% chrome alum baths have shown that:

1. as the degree of exhaustion increases, the acidity and hardening properties decrease;
2. the addition of sulfuric acid at regular intervals increases the hardening properties and prolongs the life of the bath;
3. with a 3% chrome alum bath more uniform hardening properties are obtained with use than with a 2% bath; and
4. more uniform hardening properties are also obtained at 85F/29C than at 70F/21C

Based on these findings **Kodak SB-3 Stop Bath** was published. This is simply chrome alum 30 grams in a liter of water.

USE: "The chrome alum should be dissolved in water at a temperature lower than 150F/66C, otherwise the solution will tend to become more acid due to hydrolysis and its hardening properties will be affected.

"After development, immerse for three minutes … taking care to agitate the film for 30–45 seconds. This will tend to prevent blisters, streaks, and chrome alum stains."

If the bath is not replenished with [sulfuric] acid, discard it when its original color of blue-violet turns to yellowish-green, as the bath has lost its hardening properties.

"If the film is not agitated as above, the alkali in the developer is apt to precipitate a sludge of chromium hydroxide on the film although with developers which do not contain more than 2% of sodium carbonate no trouble is usually experienced."

"A less expensive bath may be compounded by using a 2% solution of chrome alum in place of the 3% solution above. This has less tendency to give blisters or green stains at high temperatures, but its life is much shorter than that of the 3% bath."

"The baths will keep indefinitely without use but with use the hardening properties fall off as a result of the addition of developer carried over by the films and in the case of any bath containing a given quantity of developer the hardening properties continue to decrease as the bath ages. In most cases, however, the hardening properties of fresh or old baths which have been impaired by the addition of developer can be restored by the addition of a quantity of sulfuric acid necessary to bring the pH value (degree of acidity) to 4.0 for neutral film and between 3.0 and 3.8 for alkaline film."

Few developers today contain 2% carbonate. It can be seen that with the less alkaline developers that are more common today, there will be fewer problems with chrome alum baths.

"Blisters may tend to form if the film is swollen on immersing in the bath, as a result of the decomposition of the carbonate in the developer by the chrome alum which is normally acid, but agitation will tend to prevent their formation." (JSMPE 14) [Blisters should not form with developers whose main alkali is Kodalk or borax, or those based on the ethanolamines.]

If necessary, swelling can be further decreased by adding to SB-3 60g/L of sodium sulfate (anh.), at which point it becomes **SB-4**. The pH of SB-3 is approximately 3.2, so it is ideal when fresh.

To extend the working life of SB-3 in use, it is necessary to replenish with sulfuric acid, but this technique is not recommended today, not least because

sulfuric acid is a dangerous and unpleasant chemical to work with but also because the process requires constant pH monitoring. Today, on the few occasions when a chrome alum stop is needed, it should be made up fresh, used within hours and then discarded.

However, should a vast amount of film need to be run through a chrome alum bath over a period of time, close pH control and topping up with sulfuric acid is the preferred technique.

Hardening life of baths without revival: 'The life of a 2% bath without revival with the D-16 developer is about 200 feet [about 36 rolls of 35mm film] of motion picture positive film per gallon, that is, the bath will continue to harden the film so that it does not melt at a temperature below 212F/100C up to this point. The life is only 100 feet per gallon over a period of use of two weeks. [In other words, the life of a fresh 2% chrome alum bath is about 9 rolls of 35mm film or 9 times 80 in^2 per liter of hardener.]

"If revival with acid is not possible or desirable, a 3% bath is to be preferred in view of its longer life which, with the D-16 developer, is equal to 300 feet per gallon in a fresh bath and 200 feet per gallon during a period of use of two weeks. [A 3% bath has about 50% more capacity, fresh, and not kept longer than a day, than a 2% bath.]

"Since the gelatin coating of negative motion picture film absorbs about twice as much developer as that of positive film the life of the stop baths when using negative film is proportionally less. The lives of the baths can, of course, be prolonged by rinsing in water previous to immersion in the stop bath but usually this is impractical. [Mowrey believes this statement does not apply to modern positive and negative films.]

"With the D-76 developer the life of the baths is about one-half of that with D-16 when fresh and the hardening properties fall off more rapidly on keeping." (JSMPE 14)

Summary: It is clear the simplest way to use chrome alum is as a freshly-made stop bath, using the simple formula 2–3% chrome alum in water. If there is only a small amount of emulsion to harden, this can be 2%. Discard when the color turns from blue-violet to yellowish-green.

It is evident that the life of such a fresh chrome alum bath can be considerably extended by rinsing the film in running water for a few minutes with agitation between the developer and the stop bath. However, this will allow much-diluted development to continue (which might be desirable) and will allow swelling to increase (which is not desirable).

We still don't understand why D-76 reduces the life of a chrome alum bath compared to D-16.

As stated elsewhere, in an acid stop or fixer, the preferred acid is acetic, except when chrome alum is employed *for revival*: in that case sulfuric acid *must* be used. But sulfuric acid can and should be avoided in chrome alum stop baths, by simply using them fresh and discarding when the color changes.

Chrome alum fixers

We have made clear that we are not in favor of chrome alum *fixers*.

Those who feel it is necessary to employ one (for example, those coating their own glass plates) should read PCS and JSMPE 14 on this subject.

ALKALINE HARDENERS

For much of the 20th century, formaldehyde hardeners have been recommended when hardening is necessary from the very beginning of film processing. For a typical formula, see IH 5 in the last section in this appendix. However, the preferred hardeners of this type are glutaralde-hyde and succinaldehyde. Glutaraldehyde is more readily available. It hardens best at a pH of about 10, near the pH of sodium metaborate, according to H.D. Russell.

TH-5 HARDENER

Water	750 ml
Glutaraldehyde 25%	30 ml
Sodium sulfite	20 g
Sodium metaborate	2g
Water to make 1 liter	

Caution: all aldehydes are now considered hazardous, including by inhalation. In recent decades, aldehyde hardeners have come to be seen as more hazardous than was ever understood before, when they were commonly used in photographic processing. If gloves are warn while handling, apparently the greatest risk is chronic inhalation. I personally am comfortable using aldehydes occasionally, in a well-ventilated area, for tank processing. My exposure to the vapor is thus minimal. I would be much more concerned if someone needed to be exposed to the aldehydes for hours on end, day in day out. If you choose to use them, make yourself aware of the potential hazards. The internet is a good place to start.
Formaldehyde is still used in so many industries and for so many household products that exposure is difficult to avoid.

TH-5 HARDENER

At this time, glutaraldehyde is considered to be less hazardous than formaldehyde. For example, glutaraldehyde is reported to be non-carcinogenic, unlike formaldehyde. Inhalation danger is thought to be substantially less for gluataralde-hyde than for formaldehyde. Glutaraldehyde is on the World Health Organization's List of Essential Medicines.

Succinaldehyde, favored by some photographic chemists in the postwar period, is now little used due to rarity and cost.

For the use of bisulfite-aldehyde adducts, favored by Haist, see USP 3,451,817 (1966), which points out that formaldehyde, like chrome alum (see our Warning 1, p. 178), can over-harden the surface of materials, resulting in reticulation problems.

A 25% solution of glutaraldehyde is readily available. TH-5 should not be kept for more than a week once mixed. This formula can be used as a prebath for 2 minutes, before development, when it is necessary to process at high temperatures. Glutaraldehyde can also be added to one-shot developers if desired—again, 30 ml of the 25% solution can be added to virtually any developer when extra hardening is needed.

Theoretically, glutaraldehyde could be used not just to harden films but to harden prints. However, as there is some tanning action, depending on the strength of the solution and how long the material is processed, there is also potential for some darkening of the material. We have experimentally used TH-5 on some papers for two minutes and have not found visible darkening of the whites. But we have not conducted aging tests and would not advise treating prints with aldehydes until more research is done.

Acid post-hardeners

Acid hardeners such as chrome alum and potassium alum are no longer recommended in fixers because they must be used in acid solution and thus

directly and indirectly cause longer washing times. However, where it is necessary to harden films or prints, potassium alum can be used *after* washing. An excellent acid hardener can be made by mixing all of the ingredients of F-5 or F-6 except the sodium thiosulfate. After neutral-to-alkaline fixing, wash the film in running water with continuous agitation for 1–2 minutes. This will bring residual thiosulfate to archival levels. Then place the material into the hardener for 3–5 minutes with continuous agitation for at least the first 45 seconds. After hardening, wash the film for a further two or three minutes, rinse in wetting agent, and dry. A typical usage scenario for this kind of acid post-hardening would be when washing must take place at temperatures above 75F/24C.

AVOIDING SWELL

Hardening of the gelatin is desired for two main reasons: to avoid swell during processing, and to prevent damage when the dried material is handled. It is widely agreed that swelling of the emulsion should be minimized to the greatest practical degree during photographic processing. The best way to do this is to harden the gelatin during manufacture. At last, well into the 21st century, third generation (3G) hardeners are now used in some black and white films made by some major manufacturers. But we don't know which ones. That is due to manufacturers' traditional secrecy over emulsions. One clue is, if the film is recommended for processing at 100F/38C, without further hardening during processing, then it is probably 3G-hardened.

> *3G hardeners were used much earlier in color films, once high temperature rapid processing became the norm.*

Smaller manufacturers may not yet use 3G hardeners; neither do makers of hand-coated emulsions. (3G hardeners are hard to work with, and hazardous to handle.) So swell is an ongoing issue. Those who use non-3G materials need to consider swell during processing.

> *With regard to high temperature processing, acid hardeners have been recommended for use when temperatures above 80˚F cannot be avoided. But they can only be used after the stop bath stage, yet hardening is needed at the developing stage too. This is why aldehydes have been*

used before or during development Alternatively, Ron Mowrey has encouraged the use of chrome alum as a pre-hardener, particularly with hand-coated glass plates. A highly alkaline developer (above around pH 10.5) should not be used with materials that have been pre-hardened in chrome alum. Because alkaline development will cause some weakening of chrome alum hardening, such materials should be further hardened with a chrome alum stop bath for 3–5 minutes. For processing between 80 and 100°F, additional hardening should not be needed provided the film was hardened with a 3G hardener.

Controlling swell via pH

In general, swell should be least when the gelatin is being processed in a solution at a pH close to the gelatin's isoelectric point. For bovine gelatin (used in most modern films) this is around pH 4.5 while with porcine gelatin it is around pH 7 to 9. However, the isoelectric point of gelatin can be changed at the designer's will during manufacture, so origin is not a reliable guide.

Moreover, although swelling is theoretically least at the gelatin's isoelectric point, that is only a relative quality. A film with an isolectric point of pH 4.5 that goes from a high-salt developer into a low-salt typical acid stop bath, even if the pH has been adjusted to 4.5, will swell considerably. "An emulsion layer still containing developing solution may swell to a dangerous extent when immersed in a strong acid bath of low salt content." (Haist, 543; his term "strong acid bath of low salt content" means a standard acetic acid stop bath when fresh.)

Controlling swell via salt content

There is a consistent rule of thumb we can use as a guide: swelling will always be least when the material is in a high-salt solution. Examples are developers with high sulfite content, such as D-76 or Xtol, highly buffered stop baths such as TS-7, and many fixers.

Immersion in an acid rinse bath should, in general, produce lower swelling than immersion in a neutral or alkaline bath. In practice, swelling

depends most on the salt content of the solution, and the length of time it spends there. That is why we recommend a high-salt-content stop bath when a stop bath is used (chapter 12).

Haist (577) shows how swell is moderate in developer or fixer, but doubles in a rinse or wash bath. He uses a figure which indicates how swell increases with temperature, and with time. The amount of *time* a material spends in solution is thus important in considering how to control swelling. The figure also indicates that salt content of the solution is more influential over swelling than pH.

Haist believed that, taking all these factors into account, the minimum possible trauma to materials would be achieved with all-alkaline processing at a fairly consistent pH. By this he did not mean that swell would reach possible minima. He meant that keeping processing at a consistent pH would promote a *consistent* state of swell. As a result, possible damage to the emulsion at both a gross physical level and at a molecular level would be minimized.

There is an observable problem point in the Haist-like processing we have advocated: when a film is placed into a water rinse between the developer and the fixer, swelling will increase, unless the rinse contains a salt, such as 2–5% sodium sulfate or even sodium chloride (common salt). To minimize this swell point, a water rinse should be achieved as quickly as possible (about 60 seconds), in running water, or with continuous agitation or with both, if the the tank or tray allows it.

A distinct advantage to Haist-like processing is that washing time after fixation is only a minute or two, compared to the 15–30 minutes it would otherwise take. Swelling increases little in this short time.

Alkaline fixing achieves minimum swell by reducing the time of the final wash from 15–30 minutes (during which swelling greatly increases) to 1–2 minutes (during which swelling increases little).

Sodium sulfate as anti-swelling agent; formaldehyde prehardening

If a film or plate is so fragile that a running water rinse would cause excessive swelling, either at normal or elevated temperatures, then it may need to be hardened before development.

The traditional agent used to control swelling in so-called tropical processing is sodium sulfate. I had always understood that sodium sulfate worked because it lessened swelling just as any other salt would, the difference being that it was considered to be photographically inert. However, Ron Mowrey notes that it was generally recognized by KRL to have additional anti-swelling properties of its own. Depending on the conditions, sulfate has been used at levels of 2 to 15 percent. Some lengthening of expected processing times is reported in the older literature, because "the developer does not penetrate the gelatin film as rapidly and the developing activity is lowered." (PCS, 181)

For high temperature processing Mason (211) recommends first a 3-minute immersion in a formaldehyde hardener such as IH 5. [We prefer this formula to Kodak SH-1 because of its anti-swelling sulfite content.] Follow by a short wash (for example 30 seconds in running water with continuous agitation) and then development. After development rinse for 2–3 seconds in water (PCS) and then immediately follow with a fresh 3% chrome alum solution (Mason) or Kodak SB-4 (3% chrome alum with 12% sodium sulfate cryst.) (PCS). "Agitate the material for 30 or 40 seconds when first placed in this bath, in order to minimize the tendency for the formation of blisters, streakiness and chrome alum stains. If the film or plate is not rinsed slightly and agitated, the alkali in the developer is apt to precipitate a sludge of chromium hydroxide on the film which is difficult to remove." (PCS 183) Follow with a hardening fixer, which will probably be of the F-5 or F-6 type.

IH 5 HARDENER

Water	750 ml
Formaldehyde 40%	25 ml
Sodium sulfite CRYST	200 g
Sodium carbonate ANH	4.6 g
Water to make 1 liter	

IH 5 HARDENER

Caution: all aldehydes are now considered hazardous, including by inhalation. See the caution notes under the TF-5 Hardener formula on p. 182.

From Mason 211; "A 3 minute immersion should be given, followed by a short wash, before development is begun.This bath should only be used as a pre-development bath. If used at later stages in the processing, it may cause reticulation."

Caution: all aldehyde hardeners are now considered hazardous, including by inhalation. See notes under formula TH-5 on p. 182.

Photographers who need to process hand coated or other soft emulsions at high temperatures should consult the relevant pages in PCS, which can now be read, or “borrowed”, at the internet library at archive.org. The relevant articles on chrome alum can be found in JSMPE v. 14, which can be downloaded freely from archive.org.

For modern materials from the major manufacturers, hardening during processing at normal temperatures should not be necessary. When in doubt, test.

Our dilemma in discussing alkaline hardeners is considerable, given the recent insights into aldehyde toxicity. We can no longer recommend these chemicals for casual use as was done by earlier photochemists. But we know of no other alkaline hardeners suitable for photographic processing.

NOTES

1. PCS (Crabree and Matthews, *Photographic Chemicals and Solutions*, American Photographic Publishing Co., Boston, 1939); Improvements in Laboratory Apparatus", C.E. Ives, A.J. Miller and J.I. Crabree, *J. Mot. Pict. Eng. 17*, 26 (1931).

Appendix 2
MIXING SOLUTIONS

When mixing solutions, especially those intended for storage, all operations should be slowly and gently carried out, so that no air is introduced into the solution. Concentrated liquid developers keep well until oxidation begins. Once oxidation begins, it proceeds very quickly.

All developers will oxidize when exposed to air. MQ and PQ developers containing high concentrations of sodium sulfite are slow to oxidize. High-energy developers containing caustic alkali, developers containing pyrogallol, amidol, and many others, oxidize rapidly, and should be used immediately after mixing the working solution.

Sequestering agents

Sequestering agents (chapter 3) are used in virtually all commercial developers to deal with water quality problems in some areas. For mixing formulas from scratch, sodium hexametaphosphate or sodium polyphosphate (the product Calgon before it was re-formulated to remove phosphates) was the first to be widely used. Later EDTA (ethylene-diamine-tetraacetic acid) was more often recommended. Manufacturers today prefer an EDTA relative, DTPA (diethylenetriamine-pentaacetic acid, sometimes as pentasodium salt).

Crawley did not recommend the use of sequestering agents in most developers, particularly high definition developers although he had to use them in his commercial developers. We recommend not using sequestering agents when possible. It is usually economically feasible to use distilled or deionized water for mixing stock and working solutions of developers, which obviates the need for sequestering agents.

Sequestering agents are not photographically inactive! Mason discusses sequestering agents at length (55–62) and Haist (272–4) takes much of his discussion from that material. An important objection to the EDTA/DTPA type of sequestrant is that they are silver solvents, capable of promoting physical development and dichroic fog. See chapter 3. Gordon Hutchings has reported that using greater than 0.05 g/L of EDTA in PMK working solution results in loss of desirable stain. Nevertheless, he recommends the use of this chemical to smooth out uneven development "when all attempts to vary agitation patterns still yield uneven development."

The best practice is to mix your own chemicals, use deionized or distilled water, and thereby safely avoid sequestrants.

Mixing and scales

Most of the formulas in this book are available in kits with each chemical pre-measured from Photographers' Formulary and various similar suppliers throughout the world.

> *"Around 1955, Marlene Dietrich came to George Hurrell's studio for a sitting for the first time since the 1930s. Dietrich was known among photographers as the only actor who could 'read' a contact sheet. When leafing through them, she observed, 'Gee George, you don't take pictures like you used to.' Hurrell replied, 'But Marlene, I'm 20 years older!'"*

If, like many, you prefer to mix from scratch, you will need a good scale.

Today, many scales are available for weighing chemicals. Digital scales are now the most widely used. The important thing to understand is that *if* you will be working with chemicals like Phenidone, which is often specified in quantities less than a gram, you will probably need two. A typical scale type is one that reads to about 400 grams (the highest weight most photographers will need) and has readability to 0.1 grams. As a general rule, the accuracy of digital scales is half the value of its readability. So in the case of a 400 gram capacity scale with readability to 0.1 gram, accuracy should be within 0.05g.

A problem arises when you need to measure quantities of 2 g or less accurately. Then you will need a microgram scale, one with readability of 0.001 grams, and with a maximum capacity around 20 to 50 grams.

The accuracy, consistency, and reliability of cheap scales are unlikely to be high. There are three broad price ranges for scales: the $5–20 range is the cheapest. Scales in the $40–100 range are intended for and typically used by schools. Scales costing in the hundreds or even the thousands are the most reliable of all. It is best to buy from a specialist laboratory equipment supplier you can trust. Get the best scales you can afford. If your scale uses batteries, make sure you don't leave them in long enough to corrode.

Make sure your scale can be calibrated. Ideally it should come with calibration weights. If it doesn't, acquire some. Calibration weights will pinpoint issues that are more likely to arise with less expensive scales. Many inexpensive scales today *can* be calibrated.

Doing without scales

If you are primarily going to mix simple developers like D-23, and simple stop baths and fixers, then it is acceptable to use the teaspoon and cup method. *The Darkroom Cookbook* has conversion tables in its appendices.

Working with the chemicals

A convenient method for weighing small amounts of chemicals is to place them on pre-cut pieces of paper. Write the name and weight of each chemical on the paper, and arrange the chemicals on the mixing bench in the order of use. In this way they can be checked before mixing to avoid errors. For amounts over 20 grams, use a small Dixie Cup instead. Polystyrene weighing dishes are very convenient. They can be washed and reused. They are available from chemical and laboratory suppliers.

Dissolve each chemical thoroughly before adding the next. Stir gently, to reduce the introduction of air into the solution, and never shake to dissolve the ingredients.

Use glass, enamel ware, hard rubber, or plastic containers to mix the solutions. Metals such as tin, copper, or galvanized iron will react with the ingredients of the developer to create fog and other unpredictable effects.

For most developers the sulfite should be dissolved first in order to retard the oxidation of the reducing agent when it is added. The exception is metol which does not dissolve in a *strong* solution of sulfite. Because metol oxidizes slowly it is acceptable to dissolve the metol first then immediately

add the sulfite. A common method is first to dissolve a pinch from the total sulfite, then follow with the metol, then the rest of the sulfite.

Unless otherwise recommended use water at about 125F/52C. There are several exceptions to this. The first is when mixing caustic soda: sodium or potassium hydroxide. Both produce considerable heat when added to water. They should always be dissolved separately in cold water and then slowly stirred into the rest of the developer. Intense heat is also generated by combining sulfuric acid and water. Always add the acid to the water, and never the reverse, or serious injury may result from spattering. Add the acid slowly, or the sudden heat may break the container if it is glass. **See the precautions in Appendix III before using hydroxides or strong acids**.

Another exception is any developer which contains pyro or amidol. Hot water accelerates their already too rapid rate of oxidation.

Note: Although 125F/52C is the almost universal recommendation for mixing photographic solutions in the US, in the UK, temperatures of 75–80°F (24–27°C) are commonly used. The idea is that, though mixing may sometimes be more difficult, there is less likelihood of agent decomposition. For most formulas the lower temperature works well.

Unless called for, filtering is not necessary if the water is clean. Any ordinary sediment will be precipitated out if the solution is allowed to stand without agitation until cooled. If filtering is necessary it is usually sufficient to filter through absorbent cotton or fine cloth that has been washed to remove any sizing matter it might contain. In FDC1, we recommended Bounty Microwave towels, but these are no longer available. Melitta coffee filters are an acceptable substitute. Filtering through tightly woven paper or fabric is a slow process. It should be avoided as it exposes the solution to the air, causing oxidation.

Special considerations

A few chemicals sometimes require special treatment to make them easily dissolve in water.

1. Phenidone tends to cake when added to water. It can be crushed in the bottom of the solution by using a clean, non-reactive stirring rod or substitute. Dissolving Phenidone in a little alcohol first often helps. For some grades, dissolving Phenidone at 150F/65C is helpful. The solution should be cooled as soon as possible to avoid oxidation. Although weighing out small amounts of Phenidone is difficult, using a stock solution of this chemical is not advised, as no solvent is known in which Phenidone is stable, although many recommendations have been published (see chapter 3. sidebar, p. 30).

In addition, Phenidone does not have a long shelf life in dry form. The chemical should not be used for film developers if it has been kept for more than six months, though it can work acceptably in print developers after that point.

2. Sodium carbonate can clump or lump together while dry, forming hard crystals which are difficult to dissolve. Usually it is easy to break it up while still dry, using a stirring rod or some other clean, non-reactive object, before adding it to the solution.

3. Boric acid is always hard to dissolve, even at concentrations less than 5%. Use photo grade or better and in difficulty, leaving the solution overnight will usually work. If not, it may be necessary to weaken the solution with more water.

Storing stock solutions

Aeration, or oxidation, is the primary cause of developer deterioration. Most developers prepared with water that has been boiled to remove the gases and allowed to settle, or with distilled or deionized water, will keep well for at least three months if stored in a filled and stoppered glass bottle. Many stock solutions will last much longer than this. Rodinal and PMK are particularly noted for long life. Developers that contain Phenidone are

difficult to keep long, so the simplest thing to do, if you need to keep a stock solution for months or even years at a time, is not to use Phenidone. Dimezone-S is more stable.

Oxidation occurs in proportion to the amount of air in the container and is often apparent by a change of color of the developer. However, many developers can oxidize without a change of color. Today, devices to exclude air from opened wine bottles, such as the Vacuvin, can be adapted to photographic solutions stored in glass. When available glass should be used in preference to plastic containers.

Removing air from the developer (or fixer) container can extend the life of solutions by 2 to 4 times. Tetenal's Protectan Spray is a compressed gas heavier than air, a mixture of butane, propane, and isobutane. It is sprayed onto the surface of the solution, driving away the air, and the bottle is sealed until the next use. Since this mixture is flammable, keep such containers away from any source of ignition. At the time or writing, Protectan is only available in Europe.

Nitrogen gas is not flammable and is safe so long as concentratons in ithe atmosphere are low. It is widely used in food packaging. A small amount of nitrogen is squirted into the container, displacing air; then it is sealed.

Finally, argon gas, though expensive, is widely available for preserving opened bottles of wine, and can be used to preserve photographic solutions in containers. However, only products containing 100% argon gas should be used. Avoid any products containing carbon dioxide. Argon gas is also widely used to preserve food.

AN EXAMPLE OF IDEAL MIXING PRACTICES

Although it is not necessary to mix all developers in the stringent manner recommended below by Crawley for FX 1 and FX 2, his instructions for mixing and storing make an excellent guide for those who wish exact control over the variables in the process. These methods may be used with other developers as desired.

These stock solutions were designed with considerable care, and if stored properly, may be kept six months without deterioration, particularly the very stable FX 2.

FX 1 STOCK SOLUTIONS	
Stock Solution A	
Metol	5g
Sodium sulfite anhydrous	50 g
Potassium iodide, 0.001%	50 ml
Water to make 1 liter	
Stock Solution B	
Sodium carbonate anhydrous	25 g
Water to make 1 liter	
Working Solution: 1 part A, 1 part B, and 8 parts of water. Stir gently for two minutes, and allow to stand for a minute more. Discard after use.	

FX 1 STOCK SOLUTIONS

Mixing stock solution A

Boil the water (you will need just over 2 liters for both solutions) for three minutes, then cool to about 86F/30C. [Skip boiling if you are using distilled water.] Place 500 ml of water in a container. Stir in a pinch of the sulfite. Then gently stir in the metol, until dissolved. Follow with the sulfite, and finally the potassium iodide solution. Add water to make 1 liter. Filter, through additive-free coffee filter paper. [If you are using distilled water and your chemicals are of high quality, filtering won't be necessary.] Fifty ml of the water can be replaced with isopropyl, ethyl, or methyl alcohol to improve keeping qualities and avoid precipitation in extreme cold. Store in securely capped, filled, glass bottles.

The stock solution will keep for a year unopened, or until discoloration is evident. A faint yellowish tint can be ignored, but anything deeper means the solution must be discarded.

Mixing stock solution B

Pour 500 ml of water in a container, stir in the carbonate, and stir gently until dissolved. Stir in water to make 1 liter. Store as above. This solution should be stored in plastic if it is to be kept for more than a few weeks, as it might etch glass. It lasts indefinitely in completely full bottles. In partially full bottles it should be replaced after two months to maintain consistency.

Single Solution Concentrate: The chemicals in solutions A and B may be mixed together in a single solution to make 1 liter. Again, alcohol may be

used. Discard when discolored. The working solution is prepared by adding 100 ml of stock to 900 ml of water. This solution is not as stable.

FX 2 STOCK SOLUTIONS

Mixing stock solution A

Boil slightly over 1 liter of water for 3 minutes and cool to about 86F/30C. [Skip boiling if you are using distilled water.] Use clean mixing and storage containers. Measure out 800 ml of water, and gently stir in a pinch of the sulfite. Next add the metol, then the rest of the sulfite, and finally the glycin, making sure that each chemical is fully dissolved before the next is added. Stir gently with a rod, trying not to aerate the solution. If the glycin fails to dissolve, either add a pinch of carbonate (from the 75 grams) or, preferably, add 50 ml of isopropyl, ethyl or methyl alcohol, which will improve keeping qualities and resistance to precipitation in the cold. Add water to make 1 liter.

FX 2 STOCK SOLUTIONS	
Stock Solution A	
Metol	2.5 g
Sodium sulfite anhydrous	35 g
Glycin	7.5 g
Water to make 1 liter	
Stock Solution B	
Potassium carbonate crystals	75 g
Water to make 1 liter	
Stock Solution C	
Pinacryptol Yellow 1:2000	

FX 2 STOCK SOLUTIONS
Working Solution: 100 ml A, 100 ml B, 3.5 ml C; water to make 1 liter of working solution.

Filter the solution if necessary, and pour into bottles filled to the top, and seal securely. The solution keeps for a year unopened. It is a clear golden tint when fresh, and should be discarded when it discolors to a deep yellow, or a shade noticeably darker.

Distilled water is not necessary but is preferred. Even if distilled water is used, filtering may be necessary. But don't filter if you don't see the need. If there is no visible precipitate, filtering isn't necessary. Use a good grade of sulfite, and really fresh glycin.

Mixing stock solution B

Boil slightly over 1 liter of water for 3 minutes and cool to about 86F/30C. [Don't boil the water if using distilled.] Dissolve the carbonate in 800 ml of water. Add more water to make 1 liter. This solution maintains activity indefinitely in a full bottle. However, renew a half-used solution after two months to maintain consistency. As with the FX 1 carbonate solution, keep in plastic rather than glass if you plan to store for more than a few weeks. All other photographic solutions should be stored in glass.

Stock solution C

Preferably, obtain this as a prepared solution at 1:2000 dilution. If you must mix it, dissolve the Pinacryptol Yellow first in a little alcohol, then in distilled water to make a 1:2000 solution. It keeps indefinitely away from

strong light. However, after two years, an increase in activity may occur, and it should be discarded.

Most other developers can be mixed using these guidelines.

Appendix 3
CHEMICAL SAFETY

The way we think about safety has evolved dramatically in recent decades. Safety guidelines are, rightfully, much more stringent than ever. Yet experienced chemists often wonder if we have not gone too far in the other direction? If metol were discovered today it would probably not be approved by any regulatory authority. Indeed, all developing agents used today, except ascorbic acid (vitamin C), are toxic by today's standards. Yet, to place the application of the word "toxicity" in some perspective, many of the developing agents considered the most toxic are present in such common cosmetic products as permanent hair dyes, and powerful alkalis such as sodium and ammonium hydroxide are used in many common household cleaning products.

Even vitamin C is under a cloud of doubt as of 1998. Multigram daily supplements of vitamin C have been widely recommended for over two decades. Yet researchers have recently found that ingesting as little as 500 mg per day can cause measurable genetic damage in humans in as little as six weeks. Large vitamin C supplements apparently have oxidant, as well as antioxidant, effects. The vitamin C naturally present in food is said not to have these oxidizing effects.[1]

In spite of all these dangers, a recent 31-year study of photographic processors (i.e., photo lab workers working with both black and white and color films and papers) exposed to photographic chemicals full-time, on a daily basis, over most of their working lives, shows that *photographic processors have a lower mortality rate* when compared either to the general

population or to all hourly workers. Nor was there any evidence of any increase in any particular cause of death. Commenting on these data, the Encyclopedia of Occupational Health and Safety concludes that "Based on available epidemiological information, it does not appear that photographic processing presents an increased mortality risk, even at the higher concentrations of exposure likely to have been present in the 1950s and 1960s."[2]

Although we are now accustomed to thinking of most chemical substances, including vitamins, as potentially toxic, it appears, in the ordinary black and white darkroom, that if we exercise ordinary prudence with chemicals, including not eating them, we are unlikely to suffer ill effects. Based on the available literature, ordinary prudence appears to mean taking reasonable precautions against chemical exposure to the skin, the respiratory system, and the eyes.

General guide to chemical safety

The *Focal Encyclopedia of Photography*, 3rd edition, contains an article entitled "Chemical Safety" by Grant Haist.[3] We reprint this section, with Dr. Haist's permission, in its entirety as a guide:

> Safe handling of chemicals and solutions simply involves preventing any contact with human skin, eyes, or respiratory system or internal ingestion. Safety glasses or shields, an apron or laboratory jacket, and keeping the hands away from the face and mouth, will greatly minimize some of the potential dangers. Not smoking or eating candy or food in work areas will also help to eliminate possible mishaps. A workplace with adequate ventilation, or the use of a respirator, will limit the inhalation of air contaminated with dust, gases, vapors or fumes.
>
> Good laboratory and darkroom practices should be followed at all times. Label all bottles and containers, keep them closed except when in actual use, and store them in cool, dry areas away from direct sunlight (out of reach of children). Store liquid and processing solutions safely. Breaking a gallon glass bottle of glacial acetic acid is a major disaster. Always add acids and bases slowly and carefully to the surface of the water. Do *not* add water to strong acids and bases. Do not mix chemicals haphazardly, even during final disposal.
>
> Accidents, spills, and mistakes do happen during chemical handling and photographic processing. Clean up promptly all spilled chemicals and solutions. Do not wear sandals, opentoed, or canvas shoes as these provide little protection against spills or dropped containers. Clean gloves, aprons, and clothing or shoes that have become contaminated. Gloves, inside and out, should be clean to avoid chemical contamination of the skin, face, or mouth.
>
> Prompt removal of chemicals from the skin is essential. Wash thoroughly with plenty of water any part of the body that may have contacted chemicals. See a physician if any chemicals reach the eyes, as few substances are not irritating or painful. Chapping of the hands from the drying and cracking effects of alkali on the skin or breaks in the skin from cuts and bruises are major points of entry of poisons into the body. Acid types of hand cleaners are sometimes recommended for the removal of highly alkaline solutions, such as color developing solutions.

Certain photographic chemicals and solutions require greater caution because they may cause allergy or contact dermatitis and skin sensitization of increased reactivity. Color developing agents and color developing solutions containing *para*-phenylenediamines, especially those of low water solubility, are primary causes of dermatitis. Black and white developers containing *para*-methylaminophenol (metol) or tanning developing agents, such as pyrogallol, also require care in handling. Gelatin hardening agents, particularly formaldehyde, glutaraldehyde and chromium compounds, are potential sources of irritation. Certain chemicals that are relatively innocuous by themselves may react dangerously, even explosively, when combined with other chemicals. Other combinations of chemicals may emit poisonous gases, such as cyanide fumes or chlorine. Dangerous mixtures of chemicals are shown in the table.

Dangerous mixtures of chemicals [4]

DO NOT COMBINE	WITH
Acetic acid	chromic acid, nitric acid, peroxides, and permanganates
Ammonia	Halogens, calcium hypochlorite, or household bleach
Ammonium nitrate	Acids, chlorates, nitrates, combustible materials
Cyanides	All acids
Hydrogen peroxide	Most metals (particularly copper, chromium and iron) and their salts
Iodine	Ammonia
Nitric acid	Acetic, chromic or hydrocyanic acids, flammable substances
Oxalic acid	Silver
Potassium permanganate	Ethylene glycol, glycerol, benzaldehyde, and sulfuric acid
Sulfuric acid	Chlorates, perchlorates, and permanganates

Additional precautions

Keep all chemicals away from children and pets. If necessary, lock them up. Label and date all containers. Be sure storage bottles have a secure cap. Store chemicals in a cool, dry area away from direct sunlight.

Become familiar with all the inherent dangers associated with any chemicals being used. When acquiring chemicals, ask about proper handling and safety procedures.

Near the telephone, prominently display the telephone numbers for poison control, health information hot-lines (see **Other Sources** at the end of this chapter) and emergency treatment centers in your area.

Read and follow all instructions and safety recommendations provided by the manufacturer before using any chemical or chemical product. This includes mixing, handling, disposal, and storage. Request a Material Safety Data Sheet (MSDS) from the manufacturers of photo chemicals. Collect these in a loose leaf binder and keep it where someone can find it in an emergency. MSDS's and product label can be valuable sources of safety information.

Some chemicals, such as alcohol, are flammable. Keep them away from any source of heat or open flame to avoid a possible explosion or fire. Keep a fire extinguisher that can be used for both chemical and electrical fires in the work area.

If you are pregnant or have any pre-existing health problem, read all safety information carefully to determine if there are any additional precautions you should be aware of.

People have varying sensitivities to chemicals. If you have had allergic reactions to any chemicals, you should pay close attention to the effects that darkroom chemicals have on you, and you should be extra careful about following safety procedures.

Protecting your eyes

The most important factors in preventing accidental damage to the eyes are: wearing safety glasses with side shields or goggles or, at the very least, eyeglasses, and having in the darkroom a source of water that you can flush your eyes with that can be found even in the dark. If a chemical is accidentally splashed in the eyes, it must immediately be rinsed for at least 15 minutes in continuously running water, followed by immediate medical attention.[5]

Among other things Henry notes:

> *"Proper ventilation is the first, and possibly the most important, expense, even before an enlarger and lens."*
>
> —STEVE ANCHELL

> Speed is paramount and every laboratory sink should (must) have at least one cold water outlet with an attached soft rubber hose with an easily findable valve so that, groping in the dark, you can easily find it and flush your eyes or whatever with cold water. I cannot overemphasize that, of all the major body organs prone to occupational injury, the eye is the most vulnerable.

Henry notes the hazards connected with wearing contact lenses in the darkroom. Other safety experts now believe that contact lenses may exert a protective effect by preventing the chemical from touching the eyeball. Immediately flushing will take out the contact as well as the chemical.

All of the material we have been able to find on eye safety makes clear that the major hazards are from accidental splashing of strong

acids, such as hydrochloric acid, or caustic alkalis, such as sodium and potassium hydroxide. To avoid these risks, simply do not use these chemicals in your photographic processing. See the section below entitled "Avoiding strong acids and alkalis in photographic processing."

Protecting your hands

We strongly suggest the use of neoprene gloves when mixing and using photographic chemistry of any kind. Wear neoprene or nitrile gloves such as Bluettes or Bench Mark, both made by MAPA, and a plastic apron. Most latex gloves are not suitable. Just as important as wearing gloves is cleaning them after use. Wash thoroughly in mild soap and water, and hang up to dry until the next use.

> *If you find wearing gloves uncomfortable or unnatural, we suggest trying Bluettes in a size larger than you need. Although it is counterintuitive, we have found (a) the glove will still stay on, (b), the glove won't feel as if it's constricting you're fingers, and (c), the gloves will be easier to slip on and off.*

Protecting your lungs

Safety authorities often recommend the use of dust masks, or respirators, when mixing photographic chemicals. Some of the chemicals used by photographers are fine powders which may be hazardous if inhaled. Henry states: "Proper handling, however, can minimize the risk. Many chemicals, on the other hand, are crystalline, not fine powders.... Common sense tells you how to minimize dust problems. For example, in preparation of 1 quart of D-76 developer I fill up a container slightly larger than 1 quart with the prescribed 125F water, but short of the 1 quart mark placed on the container, cut off a corner of the D-76 packet and place the corner *below the water surface* and let the packet's contents fall into the water. Result—no dust. Remove empty packet and carefully fold the top down to close the empty packet. Result—minimal or no dust. After the D-76 is brought into solution, water is added to a final volume of 1 quart and the solution mixed. Small amounts of powders can be weighed out or dissolved with a minimal or no dust problem if care is taken. For example, do not let the material on a spatula or plastic spoon empty on a weighing paper from any height greater than is absolutely necessary. This would definitely produce much more dust."

One recommended way of minimizing exposure to potentially hazardous dust or vapor is to have adequate ventilation in the darkroom. But in the real world, not every photographer has an adequately ventilated darkroom. In such a case, it is especially important to avoid using chemicals that emit gases or vapors. Avoiding acid fixers and stop baths is an excellent precaution. Keeping containers closed when not in use is another. In film development, avoiding the use of open trays by developing only in closed containers, will prevent the buildup of gases and vapors. If there is one thing more than another photographers should consider investing in, it is a well-

engineered ventilation system for their darkrooms. The *Darkroom Cookbook* contains additional information on this subject.

Electricity in the darkroom

Avoid touching any electrical equipment with wet hands. Install shockproof outlets (ground fault interrupters) in your darkroom. Henry states: "*All* electrical equipment used in a darkroom should be properly grounded. If the wire cord has a 3-prong male connector, or has a UL (Underwriter's Laboratory) label on the equipment, you can assume proper grounding as long as the outlet receptacle will accept the 3-prong male plug. Similarly, if there is a 2-prong male connector with 1 prong larger than the other so that it can be placed in the female wall outlet only one way, you can assume proper grounding. If, however, there are only 2 prongs which are the same size, this signifies you have a problem and need to ground the equipment. Unless you are trained in such electrical problems, I can only advise you to have a qualified electrician do so for you."

Specific cautions for strong acids and alkalis

In addition to all other safety precautions, there are specific guidelines for handling strong acids and alkalis, particularly any hydroxide, and hydrochloric acid. Fortunately, it is possible to avoid completely the presence of strong, undiluted acids in the darkroom. It is harder, but not impossible, to avoid the hydroxides, which are useful alkalis. Hydroxides are used in Agfa Rodinal, photography's oldest continuously manufactured product, in the Windisch pyrocatechin developer, in many Edwal formulas, and in most monobath formulas.

Sodium hydroxide is a caustic alkali and possesses extremely corrosive properties. It can burn the skin, can cause blindness, and can be fatal if swallowed. The fact that sodium hydroxide is available in every American supermarket as Drano is not an indication that this is a harmless chemical. The warning label on Drano makes clear that safe handling of hydroxide requires care and caution. Wear some kind of protective eyewear, such as goggles, and gloves. Goggles are particularly important: you may not be able to feel a splash of sodium hydroxide on your eyes, and damage to the tissues may be done before you are aware of it. Products similar to Drano are used throughout the world.

Mixing sodium hydroxide solutions

Begin with cold water and have ice handy in case the solution starts to boil. If it does, drop in the ice and leave the room until it cools! If any of the material falls or splashes on you or the counter top, wash it off immediately

with water. If you detect a soapy feeling on your skin, sodium hydroxide is present.

The cardinal rule when mixing sodium hydroxide is to add the chemical to the water. **Never add water to the hydroxide**.

To begin, add a few pellets of sodium hydroxide to the cold water. Stir until dissolved. Monitor heat by touching the outside of the container. Keep on adding hydroxide slowly, a little at a time, allowing it to dissolve before adding any more.

Always wear safety goggles when handling sodium hydroxide. In the event of a splash, rinse with cold water for 15 minutes and seek medical help immediately.[5]

Mixing strong acids

The same precautions must be taken when mixing strong acids such as hydrochloric or sulfuric. The acid must be slowly poured into water, **never the other way around**. Always wear protective eye goggles.

In the event of a splash, rinse with cold water for 15 minutes and seek medical help immediately.[5]

Avoiding strong acids and alkalis in photographic processing

There is no need to be in contact with strong acids when developing films and prints. The only developer in this book that contains sulfuric acid is Edwal Super 20. Simply avoid it, if you do not want to be in contact with strong acids. As we do not recommend the use of acid stop baths and fixers, it is easy to avoid their use. The only acid commonly recommended in this book is boric acid, which, at a pH of about 5, is one of the mildest of all acids, and is not commonly regarded as hazardous.[6] Sodium hydroxide is used in only a few developers in this book: Rodinal, the Windisch Pyrocatechin formula, Acuspeed (FX 20), Muir Pyrocatechin, and the two monobath formulas in Appendix I. It is also used in the Kodak patent formula for a rapid fixer, where it is reacted with acetic acid to create sodium acetate. If you didn't want to handle sodium hydroxide, you could use the equivalent amount of sodium acetate instead, but it would be more expensive. These are easy chemicals to avoid. If you wish to use Rodinal, but would rather avoid the care necessary in mixing it, simply buy it prepackaged from Adox. Even in this form, Rodinal requires careful handling, but the prepared solution should have a pH considerably lower than a sodium hydroxide solution. Even so, if you have decided not, in ordinary darkroom use, to use protective eyewear, then, at the very least, you should use protective eyewear when you develop with any developer containing a hydroxide.

Acetic acid is the weak acid in common vinegar, usually at a level of 4–5%. It is used in some of the acid fixers formulas given in this book, though we generally prefer to recommend alkaline fixers. It is also listed in the formulas for acid stop baths, only one of which we recommend. It is thus possible to avoid acetic acid in common photographic processing. If you

choose to use acetic acid, do not use glacial acetic acid (99%). Instead, use the far more common 28% solution sold by photographic chemical suppliers. The moment acetic acid is diluted to the strength used in photographic products, it is no more harmful than the 4–5% vinegar used to mix salad dressing. Some countries produce specialty vinegars for pickling and cleaning whose acetic acid content may reach up to around 15%.

Special cautions for pyrogallol and pyrocatechin

According to Gordon Hutchings, “Pyro may be the most toxic chemical used in the darkroom. The combination of toxicity and the ease of bodily absorption demands careful handling of the chemical. It is not a matter of individual sensitivity. I know of a few longtime pyro users who have not exercised normal precautions and are experiencing the debilitating effects of kidney dysfunction or other illness. It may take a lifetime for the damage to occur, but the effects are inevitable. Despite the danger, however, it is not difficult to avoid the harmful effects of pyro.” Hutchings also notes that pyrocatechin should be used with the same precautions as pyrogallol.[7]

Hutchings then presents several pages of material on safety precautions which pyro and pyrocatechin users should read. It appears that the greatest danger with pyrogallol is in developing films in a tray with bare hands. Using gloves while tray developing is thus an essential precaution. Hutchings notes that “for most non-tray film processing, there is no need for gloves. A drop or two of the developer on the hands is relatively harmless. All tank, reel and nitrogen burst systems may be operated without gloves. Each photographer will have to decide what level of exposure is acceptable.”

The additional level of risk that using staining developers entails can be avoided by simply not using them.

Disposal and safety

When working with any chemical, you assume the responsibility for its safe use and disposal. Follow any special instructions included with each chemical or process being used. Laws concerning disposal of chemicals vary widely. Contact the Hazardous Material (HazMat) Unit of your local fire department. They will explain in detail exactly what you can and cannot do in terms of disposal in your area.

Read MSDS sheets for disposal information. Do not mix any chemical with any other chemical unless you know it is safe to do so. Do not mix liquid and solid wastes together, as dangerous reactions might occur. Be sure to read and follow all safety recommendations that come with the chemicals.

Follow instructions for proper disposal of all chemicals. Wash yourself and any equipment that has come into contact with any chemicals. Launder darkroom towels after each session. Dispose of gloves and disposable masks to avoid future contamination. Keep your work space clean and uncontaminated.

Additional Information

On the World Wide Web

A highly detailed resource is http://www.ehs.msu.edu. This is the web page of the Office of Environmental Health & Safety (EHS) of Michigan State University (telephone 517-355-0153).

Books

The presence of a book on the list below does not necessarily convey an endorsement by us.

Michael McCann, *Artist Beware*, New York: Watson-Guptill, 1979.

Susan Shaw, *Overexposure: Health Hazards in Photography*, San Francisco: The Friends of Photography, 1983.

Siegfried and Wolfgang Rempel, *Health Hazards for Photographers*, Lyons & Burford Publishers, 1992.

Judy Tell, *Making Darkrooms Saferooms* (1989). Available from National Press Photographers Association, 3200 Croqsdaile Drive, Suite 306, Durham, North Carolina 27705.

Richard Henry, *Controls in Black and White Photography*, Focal Press, Boston & London, 1986, 2nd edition. See Chapter 4, "Safety in the Darkroom".

Gordon Hutchings, *The Book of Pyro*, 3rd (revised) printing. Granite Bay, CA: Bitter Dog Press, 1992. Excellent guidelines on darkroom safety, especially with regard to pyrogallol.

Other Sources

AAOC (American Ass'n of Poison Control Centers), 24 hour hotline (800) 222–1222 which will connect you with local poison centers in the US; www.aapcc.org; www.poison.org

Chemtrec 24-hour hotline (800) 424–9300; www.chemtrec.com

Tox Info Suisse, Zurich, 24-hour hot line, +41 44 261 51 51; inside Switzerland dial 145; https://toxi.ch.

The National Poisons Information Service in the UK (www.npis.org) advises calling the NHS on 111 for specific information on poisons; it advises health care professionals seeking poisons information to consult www.toxbase.org.

NOTES

1. *The New York Times*, April 9, 1998, p. A 19.

2. *Encyclopedia of Occupational Health and Safety*, 3rd (revised) edition, Geneva: International Labour Office, 1983, p. 85.10

3. Focal Encyclopedia 3.

4. Haist.

5. Henry.

6. Grant Haist, Chemical section in *Photo Lab Index*, 1990 edition, Morgan & Morgan, NY.

7. Hutchings.

Appendix 4
HENN'S FORGOTTEN SUGGESTIONS FOR USING MICRODOL AND D-25

Popular Photography, September and October 1945, features two articles on fine grain developers signed by Richard Henn and his boss J.I. Crabtree. These articles appear to have been forgotten since the day they were published. Yet they contain unique observations and suggestions that may interest super-fine grain fans today. They are available via Google Books and are referred to here as 'Henn Pop Phot 1' and 'Henn Pop Phot 2.' Their respective titles are "The Present Status of Finegrain Developers" p. 40 and "A New Finegrain Developer" p. 32.

Henn Pop Phot 1 traces the history of fine grain development starting with the 1904 Lumiere & Seyewitz developer (L&S 1904 PPD), and its most important 1930s successors by Sease, Lowe, and Champlain, noting incidentally that the notorious Champlin No. 15—in spite of its crazed agglomeration of exotic ingredients—does give good results. He notes the desirability of getting away from the toxicity problems of PPD. 20 diameter comparative prints from Super-XX show D-25 on the left and L&S 1904 PPD on the right. As near as one can tell from the reproductions, D-25 is very slightly grainier but has visibly higher micro-contrast and, accordingly, greater sharpness, than the PPD developer. Significantly, Henn does not mention whether the PPD developer had been ripened. Henn had a way of leaving out details that could get in the way of his argument. Henn states that D-25 nearly matches the graininess of L&S 1904 PPD.

Also interesting is a set of photos which shows results in a metolsulfite developer with bisulfite to pH 7 (i.e., D-25), which Henn states is comparable in graininess to the 1904 PPD developer. Going to an even greater extreme, Henn mentions a developer where "a considerable excess of sodium bisulfite was used, and 3 hours were required for development. The extreme reduction in graininess was accompanied by severe loss of emulsion speed." The excess bisulfite print is very interesting. It has grain lower than the 1904 PPD developer, and though detail is softened, it is still there. The softening of detail is pleasing. For anyone interested in trying this out, we would recommend D-25 with an additional 15 g/L of bisulfite as a starting point.

Henn states that though D-76 and D-23 are comparable, D-23 has better highlight separation. (Both points are arguable.)

D-25 required 25–50 minutes developing time with the films of the day at 65°F; the time could be halved by developing at 75–80°F.

Henn invented a new class for D-25, what he called 'true finegrain developers', that is, they give low graininess at equal contrast, as opposed to those developers which only produce fine grain at lower than normal contrast.

Henn states that the speed loss with D-25 is one half to one stop, but given that ASA film ratings at this time still contained a full stop extra safety factor, we would be inclined to say one to two stops speed loss.

Most significantly, in the processing sequences for D-23 and D-25, Henn explicitly directs they should be rinsed in *water* after development, and then fixed in a normal acid hardening fixer. Only if temperatures exceed 80°F should a chrome alum stop bath be used.

Henn is careful to note that if the long developing times of D-25 are found inconvenient, then the new product Microdol can be used. He states that Microdol has about twice the activity of D-25 "and yet produces satisfactorily low graininess." Which brings us to Henn Pop Phot 2, which discusses the newly introduced Microdol.

Using Microdol full strength

At this period, the technique of using Microdol 1:3 had not yet been devised. It was used full strength. Henn recommends using the replenisher with the full strength developer until 30 rolls of 80 square inch film or equivalent have been developed (per quart/liter), at which point the solution should be replaced with fresh. He states that activity is about the same as D-76 and twice the activity of D-25, with an average tank development time for films of the day of 16 minutes at 68F. As with all developers providing this level of graininess reduction, there is some loss in speed, 1/2 to 1 stop according to Henn. As with D-25, and given that the ASA standard still had a 2.5x safety factor (halved to 1.25x around 1960), we would say, as conventional wisdom has it today, that full strength Microdol loses one stop of emulsion speed.

Henn illustrates his remarkable fine grain claims with four 25x enlargements from Super XX film, using D-76, L&S 1904 PPD, Micro-dol, and Microdol modified with BZT for still lower graininess. Henn states that Microdol produces graininess equivalent to the Lumiere developer. He states that modified Microdol with BZT produces even lower graininess than the Lumiere developer. One has to wonder, if these claims are true, why anyone would use PPD after this. But they did.

Modifying Microdol for extremely fine grain

Microdol produces low grain with only moderate speed loss, but where finer still grain is desired, and further speed loss can be tolerated [1–2 stops, or, realistically, 2 stops below the film's EI], the developer can be modified with an antifoggant. According to Henn (and we think this is challengeable), inorganic antifoggants such as potassium bromide not only reduce emulsion speed but also reduce graininess. Henn states that the newer organic antifoggants are much more effective than bromide, and that Kodak Antifog No. 1 "has been selected as giving an especially desirable effect when added to Microdol." No. 1 is simply benzotriazole, and each tablet contained 0.03 grams of the chemical. Instructions are to add BZT at the rate of 0.06 g/L or two tablets per quart of Microdol. Developing times are lengthened by about half. Henn states, somewhat confusingly, that graininess with this modification is extremely low, "much less than that produced by Microdol, by PPD, or any other reasonably active developer, and compares with that produced by the extreme low activity developers mentioned in the previous article.... Also image sharpness is retained to a remarkable extent." As I read it, the low activity developer he refers to is D-25 with additional excess of bisulfite. As near as I can judge, Henn achieved, with metol alone, in the D-25 with excess bisulfite, and with Microdol plus BZT, finer grain than had ever been realized before.

Could these techniques be useful today? What would their effect be on tabular films? We don't have the answers yet. One thing we would suggest, though, if you are making your own Microdol-X equivalent, is not to omit the suggested addition of 0.1 to 1.0 g/L of benzophenone.

Modifying Microdol for higher activity

Graininess reduction is “not quite as great”, but users who need a faster developer, for example for press work, may add a mild alkali such as sodium metaborate (Kodalk), “but better results are obtained by using Microdol Replenisher, than the Microdol developer, and restraining its action somewhat with Kodak Antifog No. 1 [BZT].” This advice is a little sly, since the only primary difference between Microdol and Microdol Replenisher is that the replenisher uses sodium carbonate. So why not recommend carbonate in the first place? Well, more sales for Kodak this way, and perhaps the replenisher was more expensive—and it was yet one more way of keeping a trade secret. In any case, Henn advises adding 0.1 gram BZT to a liter of Microdol Replenisher. Speed loss is about a stop.

Some perspective

These articles add new tricks to our toolbox when it comes to finding creative ways of working with Microdol and D-25 type developers. The future would bring dilution techniques that Henn did not foresee in 1945.

One problem with D-25 and Microdol undiluted is that they don't exhaust because of the ample quantities of metol and sulfite. There is no mechanism to achieve the adjacency effects and "internal contrast" effects that Crawley mentions as possibilities with ripened PPD developers. The advantage of the D-25/Microdol type is their simplicity, better speed, and lack of toxicity compared to the PPD types.

Henn's work makes it clear that the Microdol and D-25 type developers have better definition than PPD developers when those developers are fresh. But he does not address what takes place when, as commonly advised, PPD developers are ripened. By the mid-1960s, the preferred way of working with Microdol had become the 1:3 dilution, which provides better sharpness because it is less solvent, and because some adjacency effects can form (chapter 7).

At the time of writing, Microdol-X had been discontinued, but Adox Atomal 49 is still available, as is Perceptol. For the time being, then, the PPD approach to ultra-fine-grain and the Henn approach both have sufficient adherents to keep such developers in commerce. As we have suggested in chapters 5 and 7, there is room for research and innovation when working with sodium chloride and DTOD as fine grain enhancers, and with PPD derivatives as fine grain developers.

BIBLIOGRAPHY

Out of print photographic books are now easy to find using the Internet.

Books

Adams, Ansel. *The Negative*. New York:New York Graphic Society, 1981.

Anchell, Steve. *The Darkroom Cookbook*. Newton, MA: Focal Press, 1994 See expanded 4th edition 2016, Routledge.

Arentz, Dick. *Platinum and Palladium Printing*, 3rd ed. Woburn, MA: Focal Press, 1999.

Clerc, L. *Photographic Theory in Practice*. London:Focal Press, 1971.

Crabtree, J. I. and G. E. Matthews. *Photographic Chemicals and Solutions*. Boston:American Photographic Publishing Co., 1939.

Dignan, Patrick D. *150 Do-It-Yourself Black and White Popular Photographic Formulas*. North Hollywood, CA:Dignan Photographic Inc., 1977.

Glafkides, Pierre, Photographic Chemistry, Vol. 1, Fountain Press, 1958.

Haist, Grant. *Monobath Manual*. New York:Morgan & Morgan, 1966.

Haist, Grant. *Modern Photographic Processing*. Volumes 1 and 2. New York: John Wiley & Sons, 1979.

Henry, Richard. *Controls in Black-and-White Photography*. 2nd ed. London and Boston: Focal Press, 1986.

Hutchings, Gordon. *The Book of Pyro*, 3rd ed. Granite Bay, CA: Bitter Dog Press, 1998. Can be ordered directly from the author, P.O. Box 2324, Granite Bay, CA 95746.

Jacobson, C.I. and R.E. Jacobson. *Developing*. 18th ed. London: Focal Press, 1976.

James, T.H. *The Theory of the Photographic Process*, 4th ed. New York: The Macmillan Company, 1977.

Mees, C.E.K. and T.H. James, *The Theory of the Photographic Process*, 3rd ed. New York: The Macmillan Company, 1966.

Mees, C.E.K. *The Theory of the Photographic Process*. New York: The Macmillan Company, 1942.

Mason, L.F.A. *Photographic Processing Chemistry*. 2nd ed. London: Focal Press, 1975.

Stroebel, Leslie, and Richard D. Zakia. *Focal Encyclopedia of Photography*. 3rd. ed. Boston: Focal Press, 1993.

Stroebel, Leslie, John Compton, Ira Current, and Richard Zakia. *Photographic Materials and Processes*. Boston: Focal Press, 1986.

Vestal, David. *The Craft of Photography*. New York: Harper and Row, 1975

Vestal, David. *The Art of Black and White Enlarging*. New York: Harper and Row, 1984.

Wakefield, G. *Practical Sensitometry*. London: Fountain Press, 1970.

Wall, E.J., Franklin I. Jordan. *Photographic Facts and Formulas*. Revised and Enlarged by John S. Carroll. Garden City: AMPHOTO, 1975.

Woods, John C. *The Zone System Craft Book*. Dubuque, IA: Brown & Benchmark, 1993.

Temperature Conversion Chart

64˚F	66˚F	68˚F	70˚F	72˚F	75˚F	77˚F	80˚F
5.0	4.5	**4.0**	3.5	3.25	2.5	*	*
5.5	5.0	**4.5**	4.0	3.75	3.0	*	*
6.0	5.5	**5.0**	4.5	4.0	3.25	*	*
6.5	6.0	**5.5**	5.0	4.5	3.5	*	*
7.25	6.5	**6.0**	5.5	5.0	4.0	3.75	*
8.0	7.25	**6.5**	6.0	5.25	4.5	4.0	3.5
8.75	7.75	**7.0**	6.5	5.75	5.0	4.5	3.75
9.25	8.25	**7.5**	6.75	6.0	5.25	4.75	4.0
9.75	8.75	**8.0**	7.25	6.5	5.5	5.0	4.25
10.5	9.5	**8.5**	7.75	7.0	6.0	5.5	4.75
11.25	10.0	**9.0**	8.0	7.25	6.25	5.75	5.0
11.75	10.5	**9.5**	8.5	7.75	6.5	6.0	5.25
12.5	11.25	**10.0**	9.0	8.0	7.0	6.25	5.5
13.0	11.75	**10.5**	9.5	8.5	7.25	6.5	5.75
13.75	12.25	**11.0**	10.0	9.0	7.5	6.75	6.0
14.25	12.75	**11.5**	10.5	9.25	8.0	7.25	6.25
14.75	13.25	**12.0**	10.75	9.75	8.25	7.5	6.5
15.25	13.75	**12.5**	11.25	10.0	8.75	8.0	7.0
16.0	14.5	**13.0**	11.75	10.5	9.0	8.25	7.0
16.75	15.0	**13.5**	12.0	11.0	9.25	8.5	7.25
17.25	15.5	**14.0**	12.5	11.25	9.75	9.0	7.75
17.75	16.0	**14.5**	13.0	11.75	10.0	9.0	7.75
18.5	16.75	**15.0**	13.5	12.25	10.5	9.5	8.0

64°F	66°F	68°F	70°F	72°F	75°F	77°F	80°F
19.25	17.25	**15.5**	14.0	12.75	12.75	9.75	8.25
19.75	17.75	**16.0**	14.5	13.0	11.0	10.0	8.5
20.5	18.5	**16.5**	14.75	13.5	11.5	10.25	8.75
21.0	19.0	**17.0**	15.25	13.75	11.75	10.5	9.0
21.75	19.5	**17.5**	15.75	14.25	12.0	10.75	9.25
22.25	20.0	**18.0**	16.25	14.5	12.5	11.25	9.75
22.75	20.5	**18.5**	16.75	15.0	12.75	11.5	9.75
23.5	21.0	**19.0**	17.25	15.5	13.25	12.0	10.25
24.25	21.75	**19.5**	17.5	16.0	13.5	12.25	10.5
24.75	22.25	**20.0**	18.0	16.25	13.75	12.5	10.75
25.25	22.75	**20.5**	18.5	16.75	14.25	12.75	11.0
26.0	23.5	**21.0**	19.0	17.0	14.5	13.0	11.25
26.5	23.75	**21.5**	19.5	17.5	15.0	13.5	11.5
27.25	24.5	**22.0**	19.75	17.75	15.25	13.75	11.75
27.75	25.0	**22.5**	20.25	18.25	15.5	14.0	12.0
28.25	25.5	**23.0**	20.75	18.75	16.0	14.5	12.5
28.75	26.0	**23.5**	21.0	19.0	16.25	14.75	12.75
29.75	26.75	**24.0**	21.75	19.5	16.75	15.0	13.0
30.25	27.25	**24.5**	22.0	19.75	17.0	15.25	13.0
30.75	27.75	**25.0**	22.5	20.25	17.25	15.5	13.25

INDEX

The Index of Formulas is on page viii. Page numbers in this index may point to material in the main text, the marginalia, and the footnotes.

A

B

C

D

E

F

G

H

J

K

L

M

N

O

P

R

S

T

W

The typeface Miller, in which the text of this book is set, is described as a ‘Scotch Roman’, a style that originated in Scotland in the early 19th century but had its greatest popularity (and was given its name) in the United States. Types from the two Scottish type foundries, Wilson in Glasgow and Miller in Edinburgh, were imported or copied by American foundries and quickly earned a reputation for their good color on the page and the generous proportions of their letterforms. Miller revives the legible style of ‘Scotch Roman’ without being a facsimile of any one of the Scottish foundry’s types. The originals are attributable to the punch cutter Richard Austin. Miller, the digital adaptation, was designed by Matthew Carter.