

**Neblette's  
Handbook of  
Photography  
and  
Reprography  
Materials, Processes  
and Systems**

SEVENTH EDITION

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Handbook of  
Photography  
and  
Reprography  
Materials, Processes  
and Systems**

**Seventh Edition**

**Edited by  
John M. Sturge**



**VAN NOSTRAND REINHOLD COMPANY**  
NEW YORK CINCINNATI ATLANTA DALLAS SAN FRANCISCO  
LONDON TORONTO MELBOURNE

Van Nostrand Reinhold Company Regional Offices:  
New York Cincinnati Chicago Millbrae Dallas

Van Nostrand Reinhold Company International Offices:  
London Toronto Melbourne

Copyright © 1977 by Litton Educational Publishing, Inc.

Library of Congress Catalog Card Number: 76-43356  
ISBN: 0-442-25948-4

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Manufactured in the United States of America

Published by Van Nostrand Reinhold Company  
450 West 33rd Street, New York, N.Y. 10001

Published simultaneously in Canada by Van Nostrand Reinhold Ltd.

15 14 13 12 11 10 9 8 7 6 5 4 3 2 1

#### Library of Congress Cataloging in Publication Data

Neblette, Carroll Bernard.

Neblette's Handbook of photography and reprography.

First published in 1927 under title: Photography,  
its principles and practice.

Includes bibliographical references and index.

I. Photography. 2. Copying processes.

I. Sturge, John M. II. Title. III. Title: Hand-  
book of photography and reprography.

TRJ45.N4 1976 770 76-43356  
ISBN 0-442-25948-4

# PREFACE

For more than fifty years this has been the outstanding reference work on photographic technology. Now the expanded seventh edition, completely rewritten, provides today's most comprehensive and up-to-date single source of information on photography and reprography. Accordingly, much of the subject matter covered in the present edition involves materials, techniques, and scientific principles not known, or even anticipated, in 1927, when the first edition was published; or, for that matter, at the time of publication of the sixth edition, in 1961. The new title recognizes the growing importance of *reprography*: the reproduction of flat originals.

The aim of the seventh edition, as it was in the earlier editions, is to provide the reader with an accurate and comprehensive survey of contemporary photographic and reprographic sciences and applications. Unlike earlier editions, a systems emphasis has been added, expanding the treatment of material and processes. Chapters on optics, cameras, and exposure meters, included in the sixth edition, have been omitted; equipment is discussed only in conjunction with specific systems. The historical chapter has been enlarged and updated to provide a measure of perspective. The remaining sixth edition chapters have been extensively rewritten; in many cases, by new contributors. Completely new chapters have been added to cover recent developments in both fields.

This book is as authoritative as it is broad in coverage. Each of its twenty-four chapters is written by one or more leading specialists in photography and reprography. All in all, the book represents the efforts of twenty-four such specialists, most of them new to this edition.

A work of the scope of the present volume is only possible through the combined efforts of a number of specialists, and the group selected by Professor Neblette has indeed proved itself.

John M. Sturge assumed the editorship following the untimely death of Professor C. B. Neblette. Mr. Sturge has been employed at Xerox since 1965, and at present is a Product Marketing Manager in Microsystems.

Prior to Xerox, Mr. Sturge was employed at Cornell Aeronautical Laboratories as an Optical Systems Engineer, with principal involvement in coherent and incoherent information storage and retrieval. At Rochester Institute, he achieved a BS in Photographic Science in 1961 and received an M.S. in Management Science from Rensselaer Polytechnic Institute in 1965.

CAP 1/67

# ACKNOWLEDGMENTS

Completion of this edition has only been possible through the efforts of many individuals. My total gratitude is extended to all contributors for their painstaking excellence.

My family, my wife Judi for her encouragement and support, my daughter Melissa, and especially my son Scott whose untimely death in April 1975 was a source of inspiration to me for the completion of my editorial responsibilities.

Vivian Walworth for her invaluable support and assistance. C. B. Neblette for his confidence and trust. Alberta Gordon for her professional excellence.

This book represents my personal dedication to all who participated in its completion, with special remembrances to:

C. B. NEBLETTE AND SCOTT A. STURGE

JOHN M. STURGE

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# HISTORY OF PHOTOGRAPHIC PROCESSES

C. B. Neblette\*

## EARLY RECORDS OF THE PHOTOCHEMICAL ACTION OF LIGHT

The earliest record of the action of light that has come down to us is found in the works of Aristotle.<sup>1</sup> In his book *On Colors*, Chapter 5, he writes: "Those parts of plants, however, in which the moisture is not mixed with the rays of the sun, remain white . . . . Therefore all parts of plants which stand above ground are at first green, while stalk, root, and shoots are white. Just as soon as they are bared of earth, everything turns green . . . Those parts of fruit, however, which are exposed to sun and heat become strongly colored."

Aristotle refers also to the advantageous effect of light in the formation of a purple dye. This is the famous dye of antiquity which was so highly esteemed that it was reserved by the rulers of Tyre for royal use only. A writer of the third century, Philostratos, wrote, "The purple of Tyre looks dark and derives its beauty from the sun, which gives it the shade of a pomegranate blossom." Another, at about the same time, wrote, "The purple color becomes first class only if the material is exposed to the sun, because the rays of the sun add great fire which darkens the color, and the brilliancy is brought to its greatest perfection by the fire from above."<sup>2</sup>

Many have professed to see in the writings of the alchemist references to the darkening of both silver nitrate and silver chloride by *light*, but the alchemist did not eliminate heat or the atmosphere as darkening agents. The first to definitely prove that silver nitrate darkens

upon exposure to light was Johann Heinrich Schulze, professor at the University of Altdorf, in 1727. Schulze heated silver nitrate in an oven and found that it did not darken, thus eliminating heat as the darkening agent. He applied paper stencils to a bottle containing a solution of silver nitrate mixed with chalk and on exposure to light found the letters of the stencil reproduced in the heavy precipitate. Schulze's account of his investigations, published at Nuremberg<sup>3a</sup> in 1727, did not have a wide circulation, but his *Chemische Versuche*, published after his death in 1745, went through several editions.<sup>3b</sup>

Beccarius, at the University of Turin, followed Schulze in proving that the darkening of horn silver, an imperfect form of silver chloride, darkens on exposure to light (1757).<sup>4</sup> Dr. William Lewis repeated Schulze's experiments in England and published his findings in his *Philosophical Commerce of Arts* (1763).<sup>5</sup>

In 1772, Joseph Priestley, in his *History and Present State of Discoveries Relating to Vision, Light and Colours*, referred to the work of Schulze, Beccarius, and others.<sup>6</sup> It was from Priestley and also from Lewis, whose notebooks were acquired by Josiah Wedgwood, that his son, Thomas Wedgwood, learned of the light sensitivity of silver nitrate.

The Swedish chemist, Carl Wilhelm Scheele, in 1777 studied the darkening of silver chloride in the prismatic spectrum and discovered that it darkened more rapidly in the blue and violet. From his studies of the decomposition of silver chloride, he concluded that the darkened deposit consisted of silver.<sup>7</sup>

Hagemann (1782) and Senebier (1782) each studied the effect of light on various resins.<sup>8</sup> Hagemann reported that guaiacum turned blue upon exposure, and Senebier

\*Deceased.

found that some, like mastic and sandarac, faded and that others, including gamboge, gum ammoniac and guaiacum, darkened. It is not known, however, if any of this work was known to Niépce, whose first attempts in photolithography (1817) were with guaiacum.<sup>9</sup>

### THOMAS WEDGWOOD

The history of photography begins with Thomas Wedgwood.<sup>10</sup> In 1802 he and Humphrey Davy published a paper entitled "An Account of a Method of Copying Paintings Upon Glass, and of Making Profiles by the Agency of Light on Nitrate of Silver," in the *Journal of the Royal Institution*.<sup>10c</sup> In this paper, Wedgwood described how he was able to make copies of tracings, leaves, and similar objects on paper sensitized with silver nitrate. It darkened when exposed to light to produce a reversed (negative) image. Attempts to use a camera obscura failed, as did all attempts to fix the image. Wedgwood concluded, "Nothing but a method of preventing the unshaded parts of the delineation from

being colored by exposure to the day is wanting, to render the process as useful as it is elegant."

Wedgwood died in 1805 without having found a fixing agent. The *Journal of the Royal Institution* had a limited circulation, and Wedgwood's paper passed unnoticed. Those who followed—Niépce, Talbot and Daguerre—were unaware of it. But it would not have been of much value to them, for all three soon surpassed Wedgwood, and two of the three found a fixing agent.

### DISCOVERY OF A FIXING AGENT

What neither Wedgwood nor Davy could find in 1802 was discovered in 1819 by Sir John Herschel.<sup>11</sup> In a paper, "On the Hyposulphurous Acid and its Compounds," published in the *Edinburgh Philosophical Journal*, he wrote, "Muriate of silver (silver chloride), newly precipitated, dissolves in this salt (hyposulphite), when in somewhat concentrated solution, in large quantity and almost as readily as sugar in water."

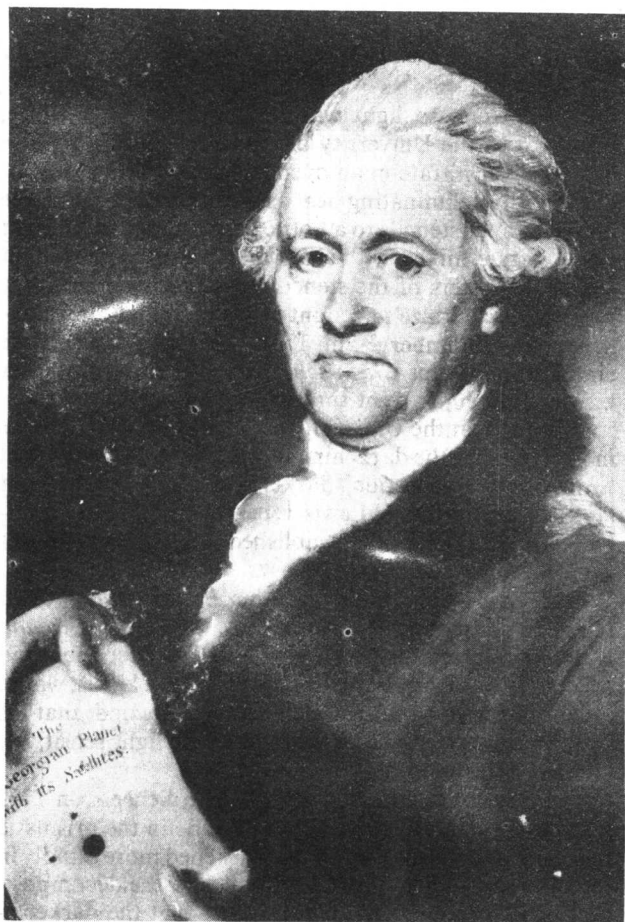
Herschel's paper was unknown to Niépce, Daguerre or Talbot, despite the fact that Brande's *Manual of Chemistry*, a leading work of reference at the time, contained in the edition of 1821 a reference to Herschel's paper and in later editions the statement "Hyposulfite of soda . . . Its aqueous solution readily dissolves chloride of silver."

Herschel showed Talbot the fixing properties of hypo on February 1, 1839. Talbot wrote in his notebook for February 18 that it "Answers very well." Talbot wrote Biot, of the French Academy, on February 20 about the new fixing agent given him by Herschel, but did not disclose that it was hypo until March 1.

### NICÉPHORE NIÉPCE

Joseph Nicéphore Niépce experimented with a number of processes over a period which extended from 1816 to his death in 1831.<sup>12</sup> His first experiments were with silver nitrate. With this he was able to produce a negative image in a camera obscura, but the exposure was several hours and he could find no way of removing the unexposed silver nitrate to render the image permanent. In the search for a substance which would be bleached by light and produce a positive rather than a negative image, he experimented with manganese dioxide and with phosphorus, both without success.

Niépce's experiments in lithography suggested asphaltum, whose light sensitivity had been observed by Hagemann in 1782. In 1822 Niépce used asphaltum on glass to copy an engraved picture of Pope Pius VII. In 1824 he used it on stone, etched the stone and made proofs from the inked surface, as in lithography. To adapt his process to the camera obscura he used pewter plates, and when Lemaitre, who was printing his plates, complained that pewter was too soft, he changed to copper. The Museum of the Royal Photographic Society, London, has three plates produced by Niépce before



Sir John Frederick William Herschel, who studied the interaction of light and silver salts, introduced hypo as a fixing agent, devised the first blueprint process, and first proposed the use of the word "photography."





Joseph Nicéphore Niépce, first to produce an image in the camera and first to produce a lasting photographic image.

1827. All are copies of engravings. The University of Texas has a pewter plate which, according to Helmut and Alison Gernsheim, was made directly in the camera obscura with an exposure of 10 to 12 hours in 1826.

In France, Niépce is generally recognized as the inventor of photography, although his process was not practical. His "heliographic process," in which metal plates were coated with asphaltum, exposed and etched, then printed like an etching on copper, can justly claim to be the beginning of photogravure.

### THE DAGUERRETYPE PROCESS

The first practical process of photography was the *daguerreotype* of Louis Jacques Mandé Daguerre (1839).<sup>13</sup> The process, details of which were made public at a joint meeting of the Academie des Sciences and the Academie of Beaux-Arts in Paris, August 19, 1839, was based upon the light sensitivity of silver iodide. The process produced a positive image directly and used a silver-coated plate of copper. There were five operations:

1. Cleaning and polishing the silver surface of the plate to a mirrorlike finish.
2. Sensitizing in a wooden cabinet, in which the polished silvered surface of the plate is exposed to iodine to form silver iodide.

3. Making the exposure. Originally, with the lenses used by Daguerre, the exposure for a subject in bright sunshine was 6–10 min.
4. Developing the latent image. Daguerre had discovered both the latent image and a method of development. To bring out or develop the latent image, the exposed plate is placed in a cabinet over a tray of heated mercury. The mercury attaches itself to the exposed silver iodide to produce an amalgam of silver and mercury, which forms a positive image.
5. Fixing. The unexposed silver iodide is removed by fixing in hypo. Daguerre had first used a solution of common salt (NaCl), but prior to the publication of the details of the process had learned of the use of hypo from Biot.

Improvements followed rapidly. The first of importance was a toning process which greatly increased the contrast of the image. The process consisted in treating the fixed image in a solution of sodium hyposulfite and gold chloride (Fizeau, 1840).<sup>14</sup>

Herschel, studying the sensitivity of silver nitrate, silver chloride, and silver bromide in the solar spectrum, found that the response with wavelength increased in that order, and in 1840 he concluded, "We must create a new photography of which silver bromide will form the basis."<sup>15</sup> Within a year Goddard in London and Kratochwila and the Natterer brothers in Vienna independently described methods of obtaining greatly



Louis Jacques Mandé Daguerre, inventor of the daguerreotype.

**DESCRIPTION**  
OF THE  
**DAGUERREOTYPE PROCESS,**  
OR  
**A SUMMARY**  
OF  
**M. GOURAUD'S PUBLIC LECTURES,**  
ACCORDING TO THE PRINCIPLES OF  
**M. DAGUERRE.**  


---

WITH A  
**DESCRIPTION OF A PROVISORY METHOD FOR TAKING**  
**HUMAN PORTRAITS.**  


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**BOSTON:**  
**DUTTON AND WENTWORTH'S PRINT.**  
.....  
**1840.**

Fig. 1. Title page of an American manual of the Daguerreotype process.

increased sensitivity through the use of mixtures of iodide and bromide, or bromide, chloride and iodide combined, in the sensitizing of the daguerreotype plate.<sup>16</sup> With this development and the 1840 introduction by Voigtlander of Petzval's  $f/3.6$  portrait lens, which reduced the exposure to about a minute, portrait photography spread rapidly throughout the civilized world.<sup>17</sup> (Fig. 1)

### Herschel Uses the Word Photography

The word *photography*, from the Greek *phos* (light) and *graph* (to draw), was suggested by Herschel in a paper "On the Art of Photography, or The Application of the Chemical Rays of Light to the Purpose of Pictorial Representation," presented before the Royal Society (London) on March 14, 1839. The term was adopted im-

mediately by the French physicist Arago and used by him when the details of the daguerreotype process were made public at a meeting of the Académie des Sciences later in 1839.<sup>18</sup> Many professional portrait photographers, however, used the term *daguerreotypist* for many years.

### PHOTOGENIC DRAWING—A NEGATIVE-POSITIVE PROCESS

*Photogenic Drawing*, the first negative-positive process, was described by William Henry Fox Talbot in a paper presented to the Royal Society (London) on January 31, 1839—seven months before the daguerreotype.<sup>19a,b</sup> For the negative, Talbot bathed paper in a solution of common salt and silver nitrate. Camera exposures required several hours, but copies of drawings could be made by contact printing in a few minutes. After the exposure the negative was fixed in a solution of common salt, washed and dried. From the negative a positive print was made by contact printing onto sensitized paper. Talbot had made four advances over Wedgwood, whose prior work he acknowledged. He had found (1) that silver chloride darkens more rapidly than silver nitrate and (2) that it darkens more rapidly with an excess of the halide, (3) that the image can be "fixed" in a solution of common salt, and (4) that a positive image can be obtained by printing from the negative onto sensitized paper. Sodium chloride



William Henry Fox Talbot, inventor of the first negative-positive process of photography.

was replaced by hypo as a fixing agent within a few weeks after Talbot had been informed by Herschel of its properties.

In 1841 Talbot obtained a British patent for a process which he termed *calotype* (Greek *kalos*, meaning beautiful—i.e., beautiful picture). In this process the paper for the negative was first sensitized with a solution of silver nitrate and then with a solution of potassium iodide to form silver iodide. When dry, the paper was brushed with a solution containing acetic acid, silver nitrate and gallic acid, rinsed briefly in water and dried. The exposure in full sunshine was from 5–10 minutes with a lens aperture about  $f/30$ . Brushing the paper after exposure with the solution of acetic acid, silver nitrate and gallic acid brought out the latent image. Talbot had found a developing agent in gallic acid. After fixing in hypo, washing and drying, contact prints were made from the negative on paper sensitized with silver chloride.<sup>19c,d</sup>

The portrait lens of Petzval reduced the exposure of Talbot's negative to one or two minutes, making portraits possible. The daguerreotype process was much preferred, however, for professional portraiture because of the sharpness of the image.



Frederick Scott Archer, inventor of the wet collodion negative process.

must be completed without allowing the collodion to dry. Once dry, it can no longer be processed.<sup>22</sup> (Fig. 2)

## NEGATIVE PROCESSES ON GLASS—WET COLLODION

It was obvious to all that a negative on a transparent medium such as glass would produce sharper images than a paper negative, but the problem was to find a substance that would hold the silver halide to the glass plate. The first workable process was described by Niépce de Saint-Victor, a cousin of Joseph Nicéphore Niépce, in 1847.<sup>20</sup> He coated his plates with the whites of eggs (albumen) containing potassium iodide. When dry, the plates were sensitized by immersion in a solution of silver nitrate. After exposure, the plate was developed in a solution of gallic acid and fixed in hypo. The exposure, however, was much longer than for the daguerreotype.

In 1851, a more practical process, using collodion, was published by Frederick Scott Archer of London.<sup>21</sup> It was not a simple process, nor was it convenient, but it produced sharp negatives from which any number of positive prints could be made on silver chloride printing-out paper. It soon replaced all other processes, including the daguerreotype.

In the collodion process potassium or ammonium bromide and iodide are added to collodion, which is then poured onto a clean glass plate to obtain an even coating. As the solvents in the collodion evaporate, the collodion "sets" sufficiently to adhere to the glass. The coated plate is then sensitized by immersion in a solution of silver nitrate, placed in a plate holder which is inserted in the camera, and the exposure made. After the exposure the plate is developed immediately in a solution of pyrogallol and silver nitrate, fixed in a solution of hypo, washed and dried. The collodion process is often termed *wet collodion* because the entire operation of coating the plate, making the exposure, and processing

## SILVER PRINTING-OUT PROCESSES

The silver chloride impregnated paper used by Talbot to make prints from calotype negatives was replaced soon after 1850 by albumen paper. Paper coated with egg whites containing salt was sensitized in a solution of silver nitrate. After exposure the image was toned with gold (a technique adopted probably from the daguerreotype), fixed in hypo and washed. The use of albumen to coat paper appears to have been suggested by Blanquart-Évrard.<sup>23</sup> Albumen paper produced a sharper image because the image formed in the albumen layer rather than in the fibers of the paper. At first the paper was coated by the photographer, but around 1870 it was found that the albumen layer could be preserved with citrates, and albumen-coated paper ready for sensitizing in a solution of silver nitrate became available.

An almost identical process, except for the use of collodion (*collodio-chloride* paper), was described by Simpson in 1865, but papers of this type were not widely used until placed on the market about 1886.

A formula for a printing-out paper using gelatin was published by Abney in 1882,<sup>24</sup> and gelatino-chloride

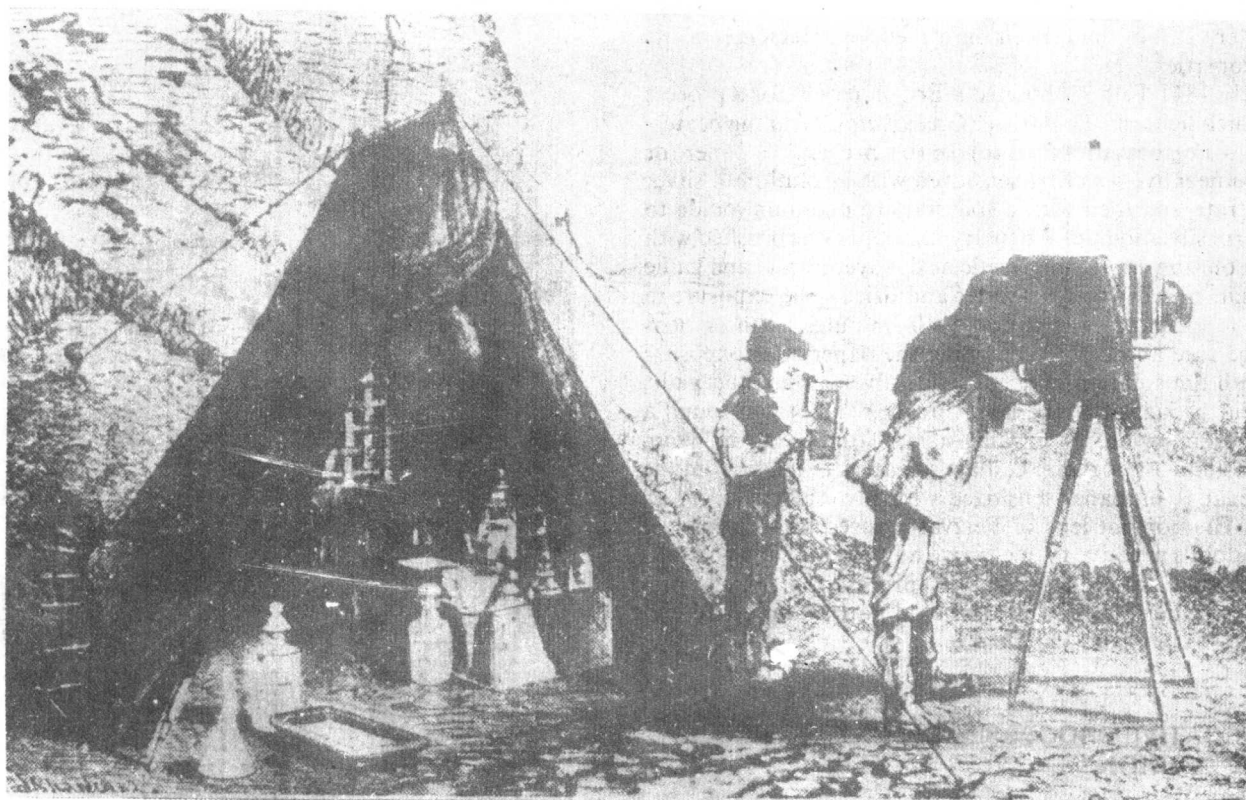


Fig. 2. Portable field laboratory for the wet collodion process (from Thompson, *History and Handbook of Photography*, 1874).

paper was introduced in England by Ilford, Ltd., in 1885 and in other countries soon after.

Collodion and gelatin printing-out papers which could be sold ready for use, requiring no sensitizing, replaced albumen paper after 1890 and remained in use until they were superseded by developing-out papers.<sup>25</sup>

### COLLODION POSITIVE PROCESSES

Archer, in his paper on the wet collodion process,<sup>21</sup> pointed out that the negative appears as a positive when placed against black velvet, the grayish-white of the silver image forming the highlights and the black velvet visible through the transparent areas of the collodion image forming the shadows. The first to apply this phenomenon practically were Adolph Martin in Paris (1852–1853)<sup>26</sup> and James Ambrose Cutting in Boston (1854), who patented a process for making what came to be called *ambrotypes*.<sup>27a</sup> The positives on glass were mounted in plush cases, similar to those used for daguerreotypes, and were produced in large quantities for about two decades. Many family “daguerreotypes,” particularly in the post-Civil War period, are actually wet collodion positives on glass.

Martin also described the use of blackened metal plates in place of glass. This system was patented in the United States by Hannibal Smith in 1856, and

japanned metal plates were placed on the market by Griswold of Peekskill, New York. The process was known as the *melainotype* or, more frequently, as the *ferrotype* or *tintype*.<sup>27a,b</sup> These processes were used by photographers in parks, at fairs and at scenic vacation spots for many years. I remember one at Charlotte Beach Park in Rochester, New York, as late as 1932. Black metal plates coated with gelatin emulsion replaced wet collodion for this purpose towards the end of the nineteenth century.

### COLLODION EMULSION

Sayce and Bolton, in 1864, described a process of working with collodion in which the silver nitrate was added to the collodion before coating, thus eliminating the separate silver bath. Plates prepared in this manner were slower than wet collodion, and the process was not widely adopted except for photo-mechanical processes, where a green-sensitive “orthochromatic” collodion emulsion, developed by Albert of Munich, was used for color reproduction for many years.<sup>28</sup>

### DRY COLLODION PROCESSES

The inconvenience of the wet collodion process (Fig. 3), particularly out of doors, prompted a search for a dry



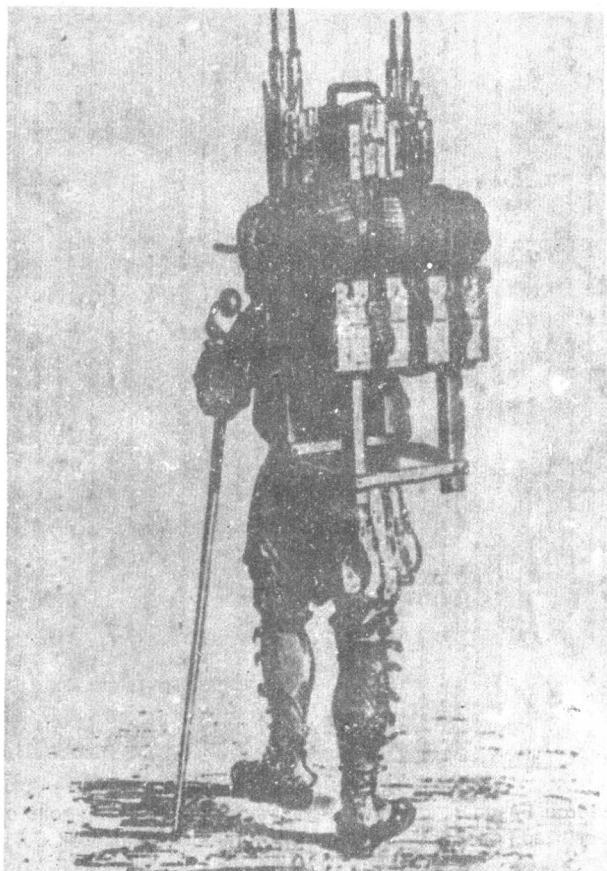


Fig. 3. A wet collodion process photographer in the field (from an early manual).

plate process, which would permit the glass plate to be coated, dried and exposed at a later time.

Taupenot, in 1855, described a process in which the glass plate, after having been coated in the usual way and immersed in the silver bath, was washed briefly, coated with albumen and dried.<sup>29</sup> The plates would keep for several weeks but were much slower than wet collodion.

A similar process using gelatin was patented in England by Norris (1856).<sup>30</sup> "The Norris Dry Plates, ready for use, are sold in all the larger towns of England and are said to give good results", according to a report published in 1862.

In the *tannin* process of Russell (1861) the sensitized collodion plate was washed, then placed in a solution of tannin and dried.<sup>31</sup> The process was simpler and more reliable, and it produced better negatives than the other methods. At first the plates were developed with a developer containing silver nitrate, as was the practice with wet collodion, but the following year Russell found that the plates could be developed in pyrogallol and ammonia without silver nitrate.<sup>32</sup> This was the beginning of alkaline development, which was to become of major importance with the introduction of gelatin emulsions.

All of these processes required more exposure than wet collodion and found only limited use.

## GELATIN EMULSION<sup>33</sup>

Robert Bingham, in his book *Photogenic Manipulation*, published in 1850, described a workable process with gelatin,<sup>34</sup> but this was overshadowed by the wet collodion process which appeared the following year. In 1868 W. H. Harrison, another English experimenter, attempted to make a gelatin emulsion but could not obtain a uniform coating on the glass plate.<sup>35</sup> Dr. R. L. Maddox described a gelatin process in the *British Journal of Photography* in 1871 which was workable but too slow to compete with wet collodion.<sup>36</sup>

Two years later Burgess advertised gelatin emulsion in the same journal.<sup>37</sup> Burgess was the first to show that good negatives could be made on gelatin emulsion. It met with a mixed reception; some had good results, but many complained of uneven coating, the long times required for the coated plates to dry, fog, and the difficulty of estimating the proper exposure. Burgess claimed that most of these difficulties were experienced by those who had not followed his directions; whatever the cause, the venture was unsuccessful. Richard Kennett of London, who placed coated dry plates on the market in 1873, was equally unsuccessful.<sup>38</sup>

In 1873, J. King recommended the shredding and



Richard Leach Maddox, who pioneered in the preparation of gelatin emulsions.

washing of the chilled emulsion to remove the by-products of the emulsification process,<sup>39</sup> and in the very same issue of the *British Journal of Photography* J. Johnston proposed the use of an excess of soluble bromide in the formation of silver halide,<sup>40</sup> both steps of great importance. In 1877, Johnston recommended the use of ammonia in emulsification as a method of increasing the sensitivity of the emulsion.<sup>41</sup> The next year Charles Bennett reported that a gelatin emulsion far more sensitive than wet collodion could be produced by heating the emulsion.<sup>42</sup>

In 1878 Bennett Dry Plates were placed on the market by the Liverpool Dry Plate Company. That same year Wratten and Wainwright began the manufacture of dry plates in London and soon established an international reputation for excellence. These two were followed by Mawson and Swan at Newcastle-on-Tyne, by Monckhoven in Ghent, Schleussner in Frankfurt and John Carbutt of Philadelphia. George Eastman began the manufacture of dry plates in Rochester in 1880, as did Cramer and Norden in St. Louis. Other manufacturers of note established in these early years were Otto Perutz (1882), Lumière in Lyons (1882), M. A. Seed in St. Louis (1883), Hauff in Fuerbach (1890) and the company Allgemeine Gesellschaft für Anilin Fabrikation, later called Agfa, in Berlin (1893).

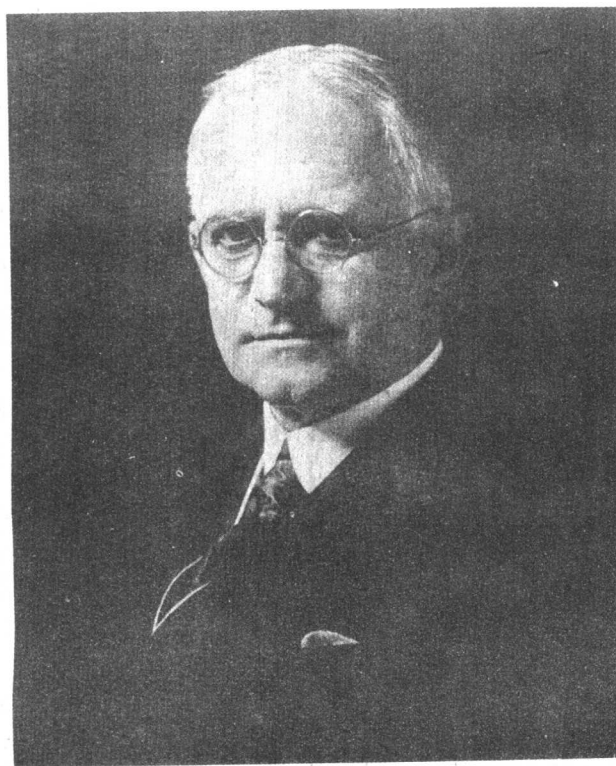
The beneficial effect of ammonia observed first by Johnston was greatly advanced by Monckhoven and by Eder in Vienna.<sup>43</sup> A further important addition to the technology of gelatin emulsion was the study by Abney, in 1880, of the effect of the addition of a small quantity of potassium iodide to the bromide in precipitation.<sup>44</sup> Today the use of iodide is almost universal.

## FILM BASE

The first satisfactory photographic film was produced by John Carbutt of Philadelphia in 1888 by coating sheets of celluloid produced by John W. Hyatt of Newark, New Jersey. The next year roll films on a base prepared by dissolving nitrocellulose in methanol with camphor and amyl acetate were placed on the market by George Eastman in Rochester, New York.<sup>45,46</sup> A patent covering the transparent film base was granted in December of that year.<sup>47</sup>

The film was designed for use in a new camera, the Kodak, ® making 100 circular pictures 2½ in. (6.5 cm) in diameter. It sold for \$25 loaded with one roll of film. When the roll had been exposed, the camera was returned to the company for processing. The prints, made at first on a gelatin printing-out paper, were sent to the customer along with the camera and a new roll of film. Extensively promoted by advertising featuring the slogan "You press the button, we do the rest," the Kodak was a huge success and the beginning of a new era in photography.

In 1898 a patent for a photographic film, which had been originally applied for in May, 1887, by Reverend Hannibal Goodwin, of Newark, was finally granted by the U.S. Patent Office.<sup>48</sup> The rights to the Goodwin patent were acquired by the Ansco Company of Bing-



George Eastman, inventor of amateur camera using rolls of sensitized paper and film; founder of the Eastman Kodak Co.

hamton, New York, which promptly charged the Eastman Kodak Company with infringement of the Goodwin patent. A long legal battle which ensued was finally settled in 1914, when the courts upheld the validity of the Goodwin patent.

Daylight loading film was patented by S. N. Turner, a camera maker of Boston. His company was purchased by the Eastman Kodak Company, and daylight loading roll films were placed on the market in 1894. Rights to the film pack, invented by Parker B. Cady in 1894, were also acquired by the Eastman Kodak Company. Noncurling film with a gelatin coating on the side opposite the emulsion was introduced in 1903.

Nitrocellulose film base is highly flammable, and from 1910 on it was gradually replaced with cellulose acetate except where the physical properties of the cellulose nitrate base were important, as in the motion picture industry. Later, bases having the required tensile strength and stability were made from cellulose esters, including cellulose acetate propionate, cellulose acetate butyrate and cellulose triacetate. Since World War II, polyethylene terephthalate has been widely used under such trade names as *Cronar* (Dupont) and *Estar* (Kodak). It is stronger and tougher than the acetate bases and less subject to dimensional change.

## SPECTRAL SENSITIZATION<sup>49</sup>

The spectral sensitivity of the silver halides is limited essentially to the blue and violet regions of the spectrum, so

# A Transparent Film

for Roll Holders.

The announcement is hereby made that the undersigned have perfected a process for making transparent flexible films for use in roll holders and Kodak Cameras.

The new film is as thin, light and flexible as paper and as transparent as glass. It requires *no stripping*, and it is wound on spools for roll holders.

It will be known as *Eastman's Transparent Film*, and will be ready for market on or about July 1st. Circulars and samples ready, and will be sent to any address on receipt of 4 cents in stamps.

*The Eastman Dry Plate and Film Co.*

Rochester, N. Y.,

June 15, 1889

Fig. 4. An early advertisement for Eastman's roll film.

that such brilliant colors as yellow, orange and red were not recorded on collodion plates and the early dry plates. In 1873 Vogel discovered that an emulsion to which the dye coralline had been added to prevent halation had sensitivity to yellow and green light.<sup>50</sup> Further work by Vogel resulted in the discovery of a more powerful sensitizer for the green, isoquinoline red, in 1882. Its mixture with quinoline blue (cyanine), which sensitized to the orange and red, was used in Vogel's "azaline" plates, the first which might be called panchromatic.<sup>51</sup> The sensitivity was very low, however, and the sensitized plates did not keep well. Meanwhile, Waterhouse, in 1875, had discovered in eosin a good sensitizer for green,<sup>52</sup> and in 1883 Tailfer and Clayton placed dry plates sensitized with eosin on the market.<sup>53</sup> In 1884 Eder discovered that another dye of the eosin group, erythrosin, was a much better sensitizer for the green and yellow.<sup>54</sup> Orthochromatic and isochromatic plates sensitized with erythrosin remained on the market through the first quarter of the twentieth century.

By this time it was clear that the best sensitizing dyes were derivatives of cyanine, and Miethe and Traube in

Berlin and E. König at Höchst a/M began to make and test new cyanine dyes as photographic sensitizers. In 1902 Miethe and Traube introduced a new class of green and yellow orthochromatic sensitizers, which became known as the *isocyanines*.<sup>55</sup> These were followed by König's isocyanine dyes of extended range, which were used extensively in orthochromatic films,<sup>56</sup> and by *carbocyanine* dyes, which were excellent sensitizers for the orange and red. Of this series *pinacyanol*, discovered by Homolka in 1905, was outstanding, and it remained in general use as a panchromatic sensitizer for about 20 years.

The work of Hamer in the laboratories of Ilford, Ltd., and of Brooker in the Kodak Research Laboratories produced new dyes which could be used together to complement or enhance one another. These combinations led to new supersensitive panchromatic films and plates with a more uniform and higher sensitivity than the older films. In 1933 an important new class of cyanine dyes, known as the *merocyanines*, was discovered independently by Brooker and by Kendall at Ilford, Ltd.<sup>57</sup> The carbocyanines and merocyanines are of continuing importance in current sensitization technology.



your old friend  
H. Vogel

Hermann Wilhelm Vogel, who discovered spectral sensitization of silver halides by the addition of dyes.

## HYPERSENSITIZATION

In the early days of aerial photography there was a need for panchromatic materials of higher sensitivity than were then available. Jacobsohn<sup>58</sup> recommended hypersensitization with ammonia and ammoniacal silver chloride (1929). Dersch and Dürr<sup>59</sup> found that exposure to mercury for several hours increased the speed of a panchromatic material by two times, but not all emulsions responded. Wightman and Quirk<sup>60</sup> found that a dilute solution of hydrogen peroxide increased the effective speed, but the process was not sufficiently reliable for practical employment. Mueller and Bates<sup>61</sup> found that a number of acids (acetic, oxalic, and sulfurous) used after exposure and directly before development increased the effective speed with Metol-hydroquinone-borax developers. Simmons found that exposure to sulfur dioxide before development increased the speed by two to four times.<sup>62</sup> Interest in hypersensitizing declined rapidly after the introduction of supersensitive panchromatic emulsions in 1931.

## METHODS OF DETERMINING EMULSION SPEEDS

When commercial dry plates began to appear on the market, the plates of the different manufacturers differed in speed, and a method of measuring and expressing speed became necessary. To meet this need, Warnerke devised a sensitometer consisting of a scale of graded density steps with numbers (1880).<sup>63</sup> The plate was exposed behind this to a phosphorescent plate which was activated by burning a fixed quantity of magnesium. English dry plate makers adopted the Warnerke sensitometer and marked their plates with numbers indicating the sensitivity. In Germany, Scheiner (1894) devised a sensitometer with 21 steps in a rotating sector, using a lamp burning amyl acetate for the exposure.<sup>64</sup> With both of these sensitometers, speed was based upon the exposure required for the first visible density (the so-called *threshold speed*).

The first method to relate speed to the exposure required for good tone reproduction was outlined in a paper published by Hurter and Driffield in 1890.<sup>65</sup> In this paper they described a sensitometer producing nine exposures from a standard candle, the development of the plate under standardized conditions, the measurement of the densities of the developed image in a densitometer, the graphic representation of the relation between exposure and density in the  $D \log E$  curve, and the use of inertia as the measure of speed.

The work of Hurter and Driffield has had a profound effect on the development of photographic science. Their procedures, greatly refined over the years, are still followed, and the  $D \log E$  curve is as useful today as when it first appeared in 1890. Their method of measuring speed was adopted throughout the English-speaking world, and the speeds of plates for years were expressed in *H and D numbers*. In time, however, lack of standard-

ization in the equipment and methods made the *H and D* speeds published by different manufacturers meaningless as a basis of comparing the actual speeds of their plates.

In 1931 the German photographic industry discarded Scheiner speeds, which also had become meaningless, and adopted an industry-wide system (DIN), in which speed was based on the exposure required for a density of 0.1 above the fog density.

Jones and his co-workers in the Kodak Research laboratories, operating on the principle that speed should be based on the exposure required to produce a negative which will make a satisfactory print, reached the conclusion that speed must be based on density differences rather than any single density.<sup>66</sup> In 1939, as a result of these studies, the Eastman Kodak Company adopted a method of measuring speed based on the minimum useful gradient, and in 1947 the American Standards Association adopted this method as an American standard. Difficulties arose with this system, however, and in the interests of international agreement the American Standards Association adopted a new system of ASA speeds in 1960 which, like the DIN method, based speed on the exposure required for a density of 0.1 above fog with a specified degree of development.<sup>67</sup> This method was adopted also by the British Institute for Standards (BSI speeds) and by the German photographic industry for new DIN speeds.

## DEVELOPING PAPERS

Bromide paper was advertised in 1874 by the Liverpool Dry Plate Company, but it apparently was of poor quality. In 1881 formulas for silver chloride paper emulsions were published by Eder and Pizzighelli of Vienna.<sup>68</sup> They pointed out the superiority of silver chloride papers over those of silver bromide, the deep blacks of the image on a silver chloride paper being much more pleasing than the grayish black of bromide papers. They also pointed out that warm tones could be obtained with different developers. For their work Eder and Pizzighelli were awarded the Progress Medal of the Royal Photographic Society of Great Britain in 1884. Soon afterward bromide paper was being produced by several manufacturers, including the Eastman Dry Plate and Film Co. at Rochester. The Eastman Company was the first to coat paper by machinery (1884) and to produce it on a large scale.

Although slower than bromide paper, the first chloride papers were too fast for contact printing. Baekeland, using an unwashed emulsion, produced a slower paper for contact printing, which was placed on the market in 1893 under the trade name *Velox*.<sup>®</sup> Used chiefly by amateurs and photofinishers, it was followed by papers for professional portraiture, and within a decade the developing papers had largely replaced collodion and gelatin printing-out papers.

The use of a substratum of barium sulfate (*baryta*) to produce a white glossy paper, according to Eder,<sup>69</sup> was introduced by the Neue Photographische Gesellschaft of



Berlin in 1894. The Eastman Kodak Company introduced a matte bromide paper the same year, produced by adding starch to the emulsion. Methods of controlling the exposure scale of emulsions for developing papers by the addition of iodide to increase contrast or bromide to lower contrast had been indicated by Eder and Pizzighelli.<sup>68</sup> The commercial introduction of developing papers in varying degrees of contrast (Grades 1, 2, 3, etc.) was an important step forward. It made the development of the negative by controlled time practical and prepared the way for the general acceptance of panchromatic negative materials, which, because of their sensitivity, could not be developed by inspection.

The first multicontrast paper, *Multigrade*,<sup>®</sup> was produced by Ilford, Ltd., in 1940. This paper, based on the work of Renwick,<sup>70</sup> was coated with two emulsions of different contrast, one spectrally sensitized and the other blue-sensitive only. The contrast of the print was controlled by the use of filters which determined the participation of each emulsion in formation of the image. Additional papers employing the same basic principle have since been placed on the market by other manufacturers.

## DEVELOPERS FOR GELATINO-BROMIDE EMULSIONS

The developers used in the wet collodion process were of the type known in the literature of photography as "physical" developers, the developing solution containing silver nitrate, a reducing agent and an acid. The silver image was formed by reduction and deposition of silver from the solution onto the exposed silver halide. The reducing agent was either ferrous sulfate (Robert Hunt, 1844) or pyrogallol (1,2,3-trihydroxybenzene) (Regnault and Liebig independently, 1851).<sup>71</sup> An alkaline developer of pyrogallol and ammonia, recommended by Burgess for gelatin emulsion in 1873, was generally adopted as dry plates replaced wet collodion. The use of sodium sulfite as a preservative of pyrogallol (Berkeley, 1882),<sup>72</sup> was an important step forward, not only in the use of pyrogallol but with other organic developing agents that followed. Pyro-ammonia with sodium sulfite as a preservative came into general use after 1882. Gradually the volatile ammonia was replaced by the alkaline carbonates, and pyro-soda became the favorite negative developer.

The developing properties of hydroquinone (1,4-dihydroxybenzene) were discovered by Abney in 1880, and pyrocatechin (1,2-dihydroxybenzene) was found to be a developing agent by Eder and Toth the same year. Following these discoveries, there was great activity in the search for new developing agents.<sup>73</sup>

Some of the more important early developing agents were:

COMPOUND	INTRODUCED BY	TRADE NAME
2,4-Diaminophenol dihydrochloride	Andresen and Bogisch (1891)	Amidol
<i>p</i> -Aminophenol	Andresen (1888)	Rodinal, Azol

COMPOUND	INTRODUCED BY	TRADE NAME
4-Amino-2-hydroxymethyl-phenol	Hauff (1901)	Edinol
<i>N</i> -Methyl- <i>p</i> -aminophenol sulfate	Bogisch (1891)	Metol
<i>N</i> ( <i>p</i> -hydroxyphenyl) aminoacetic acid	Bogisch (1891)	Glycin
<i>p</i> -Phenylenediamine	Andresen (1888)	
Chlorohydroquinone	Lüppo-Cramer (1899)	Adurol
1-amino-2-naphthol-6-sulfonic acid sodium salt	Andresen (1889)	Eikonogen
<i>N</i> -methyl- <i>o</i> -aminophenol + hydroquinone	Bogisch (1896)	Ortol

Of these, only hydroquinone, *n*-methyl-*p*-aminophenol sulfate (Metol, Elon) and *p*-phenylenediamine are used extensively today.

The familiar combination of Metol and hydroquinone originated around the beginning of the century as a developer for papers. At first the advantages of the combination were thought to be due simply to the complementary characteristics of the two as developers. Later it was learned that the two form a superadditive combination; i.e., their activity together is greater than the sum of their activities separately. The phenomenon of superadditivity had been observed earlier by Lüppo-Cramer in combinations of gallic acid and Metol.<sup>74</sup> Combinations of Metol and hydroquinone were studied intensively by Reinders and Beukers<sup>75</sup> and later by Levenson<sup>76</sup> and by James.<sup>77</sup> The combination of Phenidone and hydroquinone shows the effect to an even greater degree than Metol and hydroquinone.

With the introduction of the precision 35 mm camera came the search for a developer which would produce finer grain negatives than did developers then in use. The first to achieve wide popularity was a Metol-hydroquinone developer using an excess of sodium sulfite as a silver halide solvent and borax as the alkali. This was the famous D-76 formula, introduced by Capstaff in 1927 and still in widespread use. In 1929 Crabtree and Henn published a Metol-hydroquinone formula using potassium thiocyanate as a silver halide solvent. Formulas employing Metol alone and with sodium bisulfite were later described by Henn and Crabtree (1944).<sup>78</sup> None of these equaled the original D-76 formula in popularity.

The use of *p*-phenylenediamine as a fine grain developer was recommended by A. and L. Lumière and Seyewetz in 1904, and *o*-phenylenediamine was recommended by Seyewetz in 1936.<sup>79</sup> Developing solutions employing *p*- or *o*-phenylenediamine in conjunction with Metol or glycin for greater energy with less loss of emulsion speed were published by Sease (1933), Lowe (1936), Champlin (1937), and others.<sup>80</sup> As fine grain emulsions improved, interest in this type of developer diminished.

The formation of an image of tanned gelatin in developing with pyrogallol was observed and patented by Swan (1879)<sup>81</sup> and again by Warnerke in 1881.<sup>82</sup> Haddon and Grundy, in 1896, pointed out that the tanning of the gelatin was associated with the oxidization products of