The Preservation of Photographic Records

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The photographic record, whether a century-old plate or modern microfilm, is indispensable to archival institutions and researchers. Photography has preserved a unique view of the past in a form particularly suited to an increasingly visually oriented society. Like traditional manuscript material, such records can be "read" for information and fully exploited by researchers. Furthermore, the medium itself has already become a fundamental and relatively inexpensive means of compactly preserving information conveyed by the "paper explosion," as well as saving at least the image of older, deteriorating manuscripts. Photography has also become a basic technique for disseminating data for many purposes, including, for example, the use of interlibrary loan to overcome in some measure the constraints imposed on research by distance. The multitude of photographic products defy exhaustive enumeration here but there are, in addition to the traditional historical still photographic negative, print and transparency, the mountains of motion picture films and the growing number of microfiches and reels of microfilm which reproduce maps, pictures, books and manuscripts.

The preservation of these materials on film, including photographic records in colour, is of prime interest to their keepers who must be deeply concerned with suitable storage conditions, and with the stability of such support materials as plastic film, metal, glass and paper, and with photographic processing, especially the steps of fixing and washing. Some of these factors have been explored very thoroughly during the past several decades, and the results lead to definite conclusions concerning the handling and keeping of photographic materials. The influence of various other elements, however, remains largely unknown in the archival context, and much work remains in order to clarify the possible role they play in the deterioration of these records. This paper examines the influence of residual processing chemicals, support materials and storage conditions on the image stability of black-and-white photographic records.

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1 This paper addresses itself primarily to the curator, archivist and historian, and therefore does not contain chemical formulae or schemes of chemical reactions. The interested reader will find more detailed accounts of most of the topics discussed here, written from the point of view of the photographic research scientist, in J.M. Sturge, ed., *Neblette's Handbook of Photography and Reprography*, 7th ed. (New York, 1977), and in T.H. James, ed., *The Theory of the Photographic Process*, 4th ed. (New York, 1977).

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THE FORMATION OF THE PHOTOGRAPHIC IMAGE

Photography may be defined as any method of producing a visible image by the action of light on a light-sensitive material, including blue print methods, diazo systems, Kalvar or vesicular photography, such electro-photographic methods as Xerography, and thermographic imaging systems. Conventional black-and-white photography is based on the sensitivity to light of certain silver salts, known as silver halides. In the unexposed film, these salts are embedded in a gelatin layer which rests on a solid support. Silver halides (chloride, bromide, iodide, or a mixture of these) are reduced to elementary black silver when exposed long enough to visible light, or more exactly, to the short wave portion of the visible spectrum and ultraviolet light.[2] Early in the history of photography it was discovered that the use of a certain chemical solution (a developer) dramatically reduced the exposure time that a support material coated with silver halides required to produce black silver. A brief exposure creates a so-called "latent image," which may be considered to be a catalyst which accelerates the rate of development. The latent image actually consists of exposed silver-halide molecules characterized by their susceptibility to being developed, a process which forms a silver image having a range of gray tones. A finished photographic record is composed of elementary black silver finely divided in a gelatin coating on a support. This silver image is potentially very stable, but certain conditions are known to destroy it rapidly.[3]

THE PROCESS OF FIXING AND WASHING

The unexposed silver halides which remain in the gelatin layer after development are still light sensitive and must be removed to make a lasting image. This is usually accomplished by immersing the film in a photographic fixing solution ("fixer," "fixing bath," "hypo" or "hypo solution") to dissolve the residual silver halides, followed by a thorough wash. The most common fixing materials are solutions of sodium thiosulfate or ammonium thiosulfate in water. Many other compounds are known which dissolve silver halides; however, factors including cost, toxicity and stability have established these thiosulfates as the most suitable fixing agents.[4] The importance of proper fixing and washing to the longevity of the photographic image cannot be overestimated.

The rate of the photographic fixing process is determined by three steps: the diffusion of the fixing solution into the gelatin layer, the conversion of the remaining light-sensitive silver-halide salts into one or several silver-thiosulfate complex compounds, and the removal by washing of these complex compounds from the emulsion layer. It is the third step which is crucial to the stability of the photographic record.

2 The non-specific term, "light sensitive," does not indicate how silver halides react to light. Other light-sensitive materials react quite differently upon exposure to light. For instance, a mixture known as bichromated gelatin hardens when exposed to light; exposed areas cannot be washed away with water, since they have been hardened, whereas unexposed areas remain soft and can be removed by washing with water.

3 The method of development and type of developer do not appear to have any bearing on the permanence of photographic images.

4 The principal difference between the sodium and the ammonium salt is the rate at which they fix photographic film. Ammonium thiosulfate solutions, sold usually as a concentrate under the name of "rapid fixer," generally fix films twice as fast as the sodium thiosulfate.

The compounds formed in the initial reaction between the fixing agent and the unexposed silver halides tend to associate closely with the fibres of the paper in the case of a print, as well as be absorbed by the gelatin of the emulsion. The plastic support material of photographic films absorbs only very small amounts of fixing salts and, therefore, films are washed more easily and more quickly than papers. Detailed investigations have shown that the migration of these complex salts from the paper and the gelatin is retarded as the concentration of silver salts in the fixing bath builds up. The use of a second fixing bath helps: formation and removal of most of the complex silver-thiosulfate compounds from the film or print will occur in the first bath and immersion in a second, fresh, fixing solution will nearly complete the process.

Any salts still remaining in the gelatin layer of the film or attached to the fibres of photographic paper are conventionally removed by washing in running water. However, no amount of washing completely removes all fixing salts from paper prints. This problem is solved by using "hypo clearing agents" and "hypo eliminators," two different washing aids (the terms are sometimes incorrectly used interchangeably.) Their actions on the thiosulfate ions in the support material and in the gelatin binder are quite different. Hypo clearing agents remove the hypo complexes from the photographic support by increasing the polarity of the wash water. They do not react chemically with the residual thiosulfate, but the rate at which it migrates from the support into the wash water is increased. Hypo clearing agents usually contain sodium sulfite at an optimal concentration, and are the washing aids most often used in both machine and manual processing.[5] By contrast, hypo eliminators contain compounds which convert thiosulfate ions to less harmful and more soluble materials which are easily washed from the gelatin and paper. Hypo eliminators contain hydrogen peroxide and ammonia, a combination which is not very stable. Therefore, the hypo eliminators have to be prepared shortly before use, an inconvenience rendering them less popular than hypo clearing agents, which can be purchased ready to use.

Should any complex silver-thiosulfate salts remain, they may convert the elementary silver, which forms the image, into a *compound* which no longer contributes to image formation, resulting in fading and stains. The compound most often generated is silver sulfide. The adverse effect of residual fixing salts and their decomposition products on the stability of the image silver is so well demonstrated that the use of either of the washing aids is mandatory for a photographic record to have any degree of permanence. Results of experimental work published during the past thirty-five years have also established that fine-grain photographic materials such as chloride papers, fine-grain films and ordinary microfilm are more susceptible to chemical attack by residual thiosulfate than medium- or coarse-grain materials.

Tests for Residual Thiosulfate

The possible image instability caused by the presence of residual thiosulfate in photographic records makes the testing of processed film mandatory to deter-

5 Hypo clearing agents were developed as a consequence of the observation that films are washed faster and more efficiently in sea water than in fresh water. This discovery led to tests using a variety of salt solutions in a 2 percent concentration as washing aids.

mine the fading potential. A number of fairly simple qualitative tests are described in readily available current literature. The best known of these tests employs a drop of silver nitrate solution, placed on the surface of the film or paper. Silver nitrate reacts with residual hypo to produce a stain, the density of which may be compared visually with that of a scale of calibrated densities. The method can also be adapted for quantitative determination of hypo by comparing the density of the stain to that of an unstained area. The instrument used to perform such measurement, a densitometer, must be equipped with a special filter in order to detect the differences in density. This variation of the test is called the "silver densitometric method." Another and better known quantitative test is the "methylene blue method" in which the residual thiosulfate is extracted from a piece of film base of known surface into a solution, then converted chemically into another compound (sulfide), which in turn reacts with an organic reagent forming a blue dye, commonly known as "methylene blue." The dye's absorbance in the visible spectrum at a given wavelength is measured by a spectrophotometer and the thiosulfate content is determined through a comparison with the measured absorbance of a series of solutions of known hypo concentration.

A Definition of Permanence

"Archival processing," "permanent records," and "archival records" have become key words among custodians of historical records, although they have not been accurately defined. Late in 1975, P.Z. Adelstein of the Eastman Kodak Company, in his role as chairman of an American National Standard Institute (ANSI) Task Group on Vesicular and Diazo Film, wrote to the Archivist of the United States, J.B. Rhoads, asking for clarification on the exact meaning of "archival." The reply, which was published in 1976 in at least three different journals reads in part as follows: "Essentially the term 'archival' is synonymous with 'permanent' and the two are frequently used interchangeably. To us they have the same meaning: that is forever."[6] In more technical terms, Rhoads continued: "Permanent or archival record film can be defined as any film that is equal to or better than silver film, as specified in ANSI specifications PH 1.28 and PH 1.41." The Dominion Archivist of Canada, W.I. Smith, while pointing out that the minimum requirement for archival record film has always been that the film support material used for copying historical records should have the same life expectancy as the original paper record, recently endorsed this definition. It is noteworthy that the Canadian Standards Association (CSA) has adopted the majority of the ANSI specifications "as being completely applicable to Canadian requirements."

Practical Considerations

The American National Standards Institute has prepared a number of specifications of desirable properties for archival record film, its processing and storage which provide excellent guidelines for archivists wishing to establish and maintain microfiche and microfilm collections. Specifications are available for films on cellulose ester base (usually various types of cellulose acetate) and on polyester base (polyethylene terephthalate), and on the property of

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6 *Journal of Applied Photographic Engineering, Journal of Micrographics*, and *Microform Review*.

"safety photographic film" including silver, diazo and vesicular films.[7] These standards require film support materials to possess certain physical properties, including their degree of flammability, burning time, nitrogen content and acidity, and outline suitable test methods for each of these requirements. Although few archival institutions have the laboratory facilities to conduct such testing, there are numerous other means of determining the conformity of actual film properties with those specified by the ANSI standards. Photographic film support materials meeting the requirements of ANSI PH 1.25-1976 are usually marked with the word "SAFETY" or the letter "S" on the edgeprint beside the name of the manufacturer. The archivist preparing to microfilm large quantities of historical documents has the choice, if not the obligation, to determine from the film manufacturer whether or not the products to be used meet the ANSI specifications. In the United States, film manufacturers can have their materials tested by an independent commercial laboratory approved by the General Services Administration (GSA). If, on the basis of the test results submitted by the independent laboratory, the GSA judges that the film material in question is capable of meeting archival permanence requirements as outlined in the various standards, then a small triangle may be included on the edgeprint. While the triangle indicates certain properties of the film material, it conveys nothing about what may happen to the film as a result of poor processing or inadequate storage conditions.

These standards also specify maximum permissible levels of residual thiosulfate concentrations on film, expressed in micrograms per square centimetre ($\mu g/cm^2$). Films are divided into class 1 or 2 films according to the graininess of the developed image. Class 1 films include ordinary microfilm and other fine-grain copying, duplicating and printing films. The maximum permissible thiosulfate ion concentration for these materials is 0.7 $\mu g/cm^2$. Class 2 films are medium-grain, continuous-tone camera films and coarse-grain X-ray films, with a maximum allowable hypo level of 2 $\mu g/cm^2$. These values are of extraordinary significance to the survival capacity of record films, and are based on published results of experimental work correlating thiosulfate concentrations with the corresponding fading potential.

The methylene blue method provides the means of determining whether a processed film meets the established standards specified in ANSI PH 4.8-1971 (now under revision). The standard also details the procedures for the silver densitometric method. The methylene blue method must be applied to a film sample within two weeks of the time of processing. Under conditions of high relative humidity, residual thiosulfate reacts quickly with the image silver as described above, causing a decrease in its original concentration. For example, if tests for residual thiosulfate on old film rolls show negative results, it cannot be concluded necessarily that the film has been processed perfectly. Rather, it would be more reasonable to assume that the material was kept under adverse storage conditions, most probably at high relative humidity levels. Curators setting up microfilm collections should demand evidence from the processor that the residual hypo levels do not exceed the limits specified by ANSI and that the testing was carried out according to the applicable standard.

7 The most recent issues are ANSI PH 1.28-1976, *Specifications for Photographic Film for Archival Records, Silver-Gelatin Type, on Cellulose Ester Base;* ANSI PH 1.41-1976 *Specifications for Photographic Film for Archival Records, Silver-Gelatin Type, on Polyester Base;* and ANSI PH 1.25-1976, *Specifications for Safety Photographic Film.*

The importance of processing techniques using two fixing baths, hypo clearing agents and proper wash times has already been pointed out. These procedures to free photographic materials completely of any potentially harmful chemicals are sometimes referred to as "archival processing" or "processing to archival permanence." Obviously this concept has little significance for collections of historical still photographs since in most cases the curator cannot determine how these materials were processed. It is difficult to analyze accurately old materials, because residual processing chemicals, particularly the salts containing thiosulfate, do not remain indefinitely in their original state, but start to react chemically and to degrade. The value of the concept of "archival processing" lies in its application to the planning and establishment of new collections likely to house large numbers of images produced from original documents. A case in point is the microfilm project of the National Map Collection in the Public Archives of Canada. During the next ten years or so, about one-half million maps and architectural plans will be copied twice onto 105mm silver-gelatin microfilm. One copy will be placed in inactive storage, the second will be used for the production of positive prints. The curators engaged in this project have the responsibility and authority for choosing appropriate materials, processing methods and storage conditions. Their choices will determine whether or not this collection will still be in pristine condition decades from now. P.Z. Adelstein observed recently that three groups of people are usually responsible for the property of the material, the processing and the storage: the manufacturer, the processing laboratory and the curator. While the curator at least has a choice of which material he will use, he may also exercise some control over the processing by collaborating with the laboratory. The curator may specify, for example, that fixing solutions contain a certain concentration of potassium iodide (about 0.2g/litre), or that thiosulfate levels be checked and reported regularly to the curator (such levels should not exceed 0.7 $\mu g/cm^2$). Entirely the curator's responsibility is the provision of safe containers and proper environmental storage conditions.

Suitable storage conditions are the third major factor in the preservation of photographic film, paper and plates. ANSI PH 1.43-1976 also makes recommendations that "pertain to enclosure materials, containers, atmospheric conditions, fire protection, and inspection of stored film as considered necessary for the preservation of film" for both short-term and archival storage.[8] The specific recommendations for environmental conditions are particularly instructive, being based on both wide experience and experimental evidence regarding the effect of extreme temperature and relative humidity levels on the stability of processed photographic films. For instance, it is well known that at a very low relative humidity of around 15 percent, the gelatin emulsion tends to become brittle, whereas at levels above 60 percent fungal growth may occur. Also, high relative humidity reduces the stability of residual chemicals, particularly thiosulfate, which will quickly decompose causing stains and fading. Consequently, the recommended relative humidity lies generally between 15 and 40 percent. More specific values are given for various silver-gelatin film records on two different support materials, and for colour, diazo and vesicular

8 ANSI PH 1.43-1976, *Practice for Storage of Processed Safety Photographic Film.*

films. Temperatures for archival storage should never exceed 21°C (70°F), and low temperature storage affords added protection for all films. This follows from the useful rule of thumb that the rate of a chemical reaction is cut approximately in half with each 10°C decrease in temperature.

A notorious and increasingly serious type of deterioration in processed microfilm records is the formation of so-called redox blemishes. Described for the first time in 1963 by scientists at the research laboratories of the Eastman Kodak Company and subsequently studied in great detail by that company's researchers and at the United States National Bureau of Standards, the cause, formation and means of preventing such blemishes is now well known. These microscopically small blemishes are formed by a conversion of the image silver into silver oxide under the influence of oxidizing agents. The agents can be aerial oxygen, ozone produced by electrostatic copy machines, sulfur dioxide and other similar compounds, as well as the peroxides produced by the decomposition of the aging cardboard boxes used for film storage. Since there is no published evidence that acidity in the cardboard catalyzes or accelerates the formation of peroxides, there is no reason to assume that acid-free cardboard would be safe to use for storage boxes. The use of containers made of either plastic or metal, as specified in ANSI PH 1.43-1976, is therefore mandatory. Research on the nature of the redox blemishes has also revealed that the addition of a small amount of potassium iodide, a fairly common salt, to the fixing bath will largely inhibit the occurrence of this oxidation process. The recommended concentration is about 0.2 g/litre of fixing solution. This procedure is now applied in all major processing laboratories. The principal advantage of this technique is low cost. Other more expensive methods are known to increase the stability of the image silver. For example, the process of gold toning, in addition to changing the hue of the photograph, protects quite effectively the image silver against oxidizing, gaseous pollutants. The toning aspect has been known almost since the beginning of photography and was once widely used in pictorial photography. In the 1960s, scientists of the Eastman Kodak Company published the results of extensive research on the stability of microfilm treated with a gold-protective solution. Microfilm images, the silver grains of which were coated with a gold-protective layer, were shown to be highly resistant to oxidizing atmospheres and to accelerated aging.

The records manager of the Bank of Canada is exploring another technique which entails the sealing of microfilm rolls in plastic bags containing nitrogen or argon gas. The bags used for this project consist of a centre metal foil which is coated on either side with polyethylene or polypropylene plastic layers. These containers are impermeable to the gases in question which in turn provide an inert atmosphere by replacing potentially reactive oxygen. As this form of storage does not appear to be in use anywhere in North America, the project is a pioneering effort.

All custodians of photographic collections must keep in mind that the holdings will be used — the principal reason for their existence. Since the handling of any archival collection is an important factor in its longevity, a continuing process of educating users is necessary to create the needed consciousness of the fragility of archival records in any medium.

HISTORICAL STILL PHOTOGRAPHS: A COMPLEX CASE

Historical still photographs not on rolls,[9] while falling within the general bounds of much of the previous discussion on roll film, often present particular problems. Historical photographs are almost always handled and used in their original form. They are characterized by a multitude of support materials (metals, glass, paper, and plastic film), diverse formats (usually 35mm up to fourteen-by-seventeen-inch glass plates and larger) and were produced by now unknown photographers using procedures which often cannot be reconstructed. Historical photograph collections consist of unique images, each different from the other. Copying historical negatives of obscure provenance to produce faithful facsimiles is no easy task. Nevertheless, much of what has been discussed earlier may be applied to the keeping of historical photograph collections. Furthermore, various ANSI specifications exist for such collections: for filing enclosures, for the storage of photographic plates and prints, and for the manual processing and evaluation of the processing of black-and-white photographic materials.[10]

Any form of conservation treatment, such as cleaning, washing, copying, and chemical restoration in solution (redevelopment, reduction and intensification) must be carried out on an individual item basis. Consequently, conservation work on historical photograph collections is labour intensive and is very expensive per image by comparison with material on roll film. Furthermore, there seems to be little prospect of the appearance of suitable archival techniques for mass treatment which would ameliorate the situation.

In addition, the ideal technician for a photo conservation laboratory, combining the abilities of a photographer with those of a chemist and traditional conservator, does not seem to exist. For this reason, the photo conservation laboratory at the Public Archives of Canada, for example, will have to engage three specialists: one for the application of techniques of copying and optical restoration; a second for paper conservation to explore methods of restoration and mending of support materials including broken and cracked glass plates, damaged paper prints, and torn plastic materials; and a third with a chemistry background to analyze and correct changes in the image silver of photographic negatives and prints which may have occurred as a consequence of processing or of prolonged storage under adverse conditions. Much experimental work

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9 Still photographs may also be on rolls. For example, the photographs of the moon and various other space missions were taken on rolls of lengths varying from about fifty to four hundred feet. Often such roll filming, though actually of the nature of still photography, was produced with such archivally beneficial considerations in mind as the choice of film material, its processing for permanence, and the realization of likely subsequent handling and the consequent need for duplication. Furthermore, such photographs carry the same advantages as other types of roll filming, including the use of only one type of support material (plastic), consistency of format for any one collection, uniform processing for large numbers of images, the capacities for being cleaned by machines (tacky roll cleaner, or ultrasonic systems) and high-speed and quality mechanical duplication. Duplicate copies are invariably used when these collections are needed for research or other purposes.

10 ANSI PH 4.20-1958 (R1970) (currently under revision), *Photographic Filing Enclosures for Storing Processed Photographic Films, Plates, and Papers;* ANSI PH 1.45-1972, *Practice for Storage of Processed Photographic Plates;* and ANSI PH 1.48-1974, *Practice for Storage of Black-and-White Photographic Paper Prints.*

needs to be done. The challenge is fundamental to the survival of historical photograph collections. The permanence of a photographic image depends upon the stability of the silver of which it is formed, the gelatin in which it is embedded, and the support material onto which both are coated. The true life-span of silver photographic images in different kinds of emulsions and on various support materials remains conjectural. Accelerated aging and other stability tests cannot replace the true test of time. Yet, from available evidence and from experience with the many historical photographs and old films which now form part of our cultural heritage, it appears safe to conclude that carefully processed films and photographs, made of stable base materials and kept in well-defined atmospheric environments, may last as long as any record material known to mankind.