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The Preservation, Storage, and Handling of Black-and-White Photographic Records

INTRODUCTION

The English physician Richard Leach Maddox is generally credited with the invention of the silver gelatin glass plate negative. In 1871, he reported some experiments in which he used silver bromide salt, a light-sensitive compound, suspended in a gelatin layer to produce a negative picture after exposure in a camera (Maddox, 1871). The purpose of his experiments was to find a replacement for the liquid collodion which was used at the time as a binding agent for making glass plate negatives. This wet collodion process had the much-lamented disadvantage that the glass plates had to be exposed right after coating lest they lose their sensitivity to light. While the experiments performed by Maddox did not lead to any marketable product, let alone to a photographic material resembling anything on the market today, they did incite other experimentally minded photographers to continue using gelatin as a binding agent, until the Liverpool Dry Plate Company in 1878 placed the first silver gelatin dry plate negatives on the market under the name Bennett Dry Plates. The term *dry plates* was used to distinguish the gelatin materials from the collodion wet plates with their limitations, as noted above. The experiments performed by Maddox ushered in *the era of silver gelatin photographic technology.* The new materials had a number of advantages over all previous methods of producing photographs. For example, the glass plates could be manufactured by machines and so obtained a consistent quality. A second advantage was that the finished plate was light sensitive, i.e., it did not have to be sensitized immediately before exposure in a camera. Third, the coated, light-sensitive plates, i.e., the raw stock, kept their sensitivity for weeks and months, which allowed them to be shipped and stored before being sold. Most important, manufacturers learned how to control precisely the properties of the final product and to adjust these properties to an intended purpose.

Consequently, numerous types of negative materials have now appeared on the market, all tailored to specific applications. Silver gelatin photographic technology has dominated photography for approximately the past one hundred years. It has produced diverse products such as negative films for studio work, duplication and copying work, motion pictures, microfilming, x-ray films, astronomical photography, aerial photography, and others.

Processed silver gelatin films and papers contain finely divided particles of silver distributed throughout a gelatin layer which has a thickness of about 0.01 mm. According to strict physical terminology, the silver particles form a suspension in the gelatin, but traditionally the term *emulsion* has been used to describe the image layer.

FACTORS AFFECTING STABILITY OF PHOTOGRAPHIC IMAGES

The subject of this article is the preservation of processed black-and-white photographic records in libraries. Since silver gelatin photographic films and papers have been around for about a century, and since by far the largest number of black-and-white photographic images are silver gelatin images, knowledge of the properties of these records is extensive. Factors that may affect their stability are, for the most part, well known. They are listed in general form in Table 1 in order of decreasing importance.

TABLE 1
FACTORS AFFECTING THE PERMANENCE OF BLACK-AND-WHITE PHOTOGRAPHIC MATERIALS

Relative humidity
Oxidizing chemicals
Temperature
Light
Handling and use

Relative Humidity

Relative humidity constitutes the overriding influence in the permanence of photographs. Moisture catalyzes or accelerates many chemical reactions, and some mechanisms of image degradation in black-and-white photographs simply would not occur in a dry environment. One example is the reaction of residual processing chemicals with silver particles in a photographic image to produce discoloration; this deterioration does not occur in a completely dry environment. Another relates to acidity. It has been observed that the presence of moisture is necessary to produce acidic conditions in paper that contains certain chemical compounds. Since the concept of acidity applies only to (generally aqueous) solutions, water—in whatever form—must be present to produce an acidic reaction. Known examples of compounds that can produce acidity in the presence of moisture are alum rosin size, as an internal source, and sulfur dioxide, which may be absorbed into the paper from the surrounding atmosphere. A third example of the effect of relative humidity relates to the physical changes that can occur to objects when relative humidity changes. Some materials expand in an environment of high humidity and contract if that condition is reversed. This is demonstrated impressively by archival records that have a layer structure of two components which react differently to changing relative humidity.

Photographic records are a case in point. The gelatin layer that carries the image has a high affinity for water, which it absorbs quickly when available. Conversely, in dry conditions, the gelatin layer dries out faster than the support—either plastic film or paper—and contracts at a rate that forces the photograph to curl up. A change to high humidity will quickly relax and flatten such a photograph. Thus, relative humidity is well established to be the overriding single factor controlling the longevity of photographs.

Oxidizing Chemicals, Temperature, and Light

A truly devastating effect might be expected by the action of a combination of any two conditions listed in Table 1. This is true in particular if one of these conditions is the presence of oxidizing chemicals. While well-processed contemporary black-and-white photographic records are essentially stable with regard to heat and light, the image-forming substance—elemental silver, as noted—is sensitive to chemical oxidation reactions triggered by aggressive chemical compounds capable of reacting with the image silver.

Examples of materials that have been observed to cause discoloration to black-and-white photographs include adhesives from the seam used in filing enclosures; deposits from fingerprints; inscriptions in ink on silver gelatin glass plate negatives; and chemicals emanating from newsprint, which cause a noticeable effect after photographic negatives are kept for some time in close contact with newspaper clippings. The exact nature of the compounds causing these discolorations is not known. However, several cases of deterioration of image silver have been well documented in the technical literature, with corresponding identification of the nature of the aggressive compounds. Table 2 gives some examples of degradation reactions which have been confirmed by laboratory experiments, along with the corresponding references.

The technique of attempting to recreate a deterioration reaction in the laboratory is worth explaining. To begin with an analogy, in the chemistry of natural products it has been customary for decades to isolate in pure form a specific compound whose existence is somehow suspected—for example, an antibiotic—and to determine its often complex molecular structure. After all physical and chemical properties of the new compound, including its geometrical structure, have been determined, chemists attempt the crowning achievement, which is to synthesize the natural product in the laboratory. If all the properties of

TABLE 2
KNOWN SOURCES OF CHEMICALS THAT CONTRIBUTE TO THE DEGRADATION OF SILVER IMAGES

Source	*Active Chemical Compound*	*Reference*
Cellulose nitrate (decomposing)	Nitrogen oxides	Carroll and Calhoun, 1955
Aging cardboard containers	Peroxides	Henn and Wiest, 1963
Electrostatic copy machines	Ozone	Weyde, 1969
Car exhaust gases	Nitrogen oxides; sulfur oxides	Weyde, 1972
Oil based paints	Peroxides	Feldman, 1981
Residual processing chemicals	Thiosulfate and its complexes	Numerous; cf. Eaton, 1970; Kopperl and Huttemann, 1986
Adhesives used in mounting print	Thiourea	Hendirks, 1989
Laboratory tests	Neutral and acid peroxides; sulfides; cumene peroxide; zinc dust; peroxide plus sulfide	Henn and Mack, 1965

the synthetic product are identical with the compound isolated from nature, then, and only then, can the structure of the new compound be said to be confirmed. Similarly, if a characteristic type of deterioration has occurred to a photograph in its natural environment, it is possible to speculate on a possible cause in order to confirm that cause in laboratory experiments.

A specific example may illustrate this. Some photographic prints made during the first decade of photography and mounted on album pages show pronounced fading along the four edges of the picture. A likely cause for that discoloration is the adhesive that was used to attach the photograph to the mountboard. These early photographic prints are of a type known as salted paper prints. Sample photographs can be prepared by that process in the laboratory today in order to study the effect of various kinds of adhesives, applied to the back of photographs, on the stability of the image silver. Adhesives used in the nineteenth-century were largely either of animal origin, generally called glues, or derived from plants, when they are referred to as pastes. After application of numerous commercially available glues and pastes to sample prints made for the purpose, it was established in the author's laboratory that pastes show no harmful effects on salted paper prints. By contrast, animal glue did cause discoloration of the image silver under accelerated aging conditions, as well as in normal room conditions, where the reaction takes a little more time to occur. Glue—a coarse and unrefined material related to gelatin—was chemically analyzed by a complicated process known as amino acid analysis which revealed the presence of at least one compound that is capable of reacting with image silver even in high dilution. The compound is called *thiourea*. When applied in various concentrations to the back of photographic prints, it is capable of migrating through the paper base and reacting with the image silver to cause discoloration (Hendriks, 1989).

Turning back to Table 2, it may be seen that the effect of residual processing chemicals, in particular fixing salts, is among the most thoroughly studied reasons for image silver degradation (Eaton, 1970). Discovered within the first two decades of photography, it remains an important subject of studies and experimental work today (Kopperl & Huttemann, 1986). Of special interest to librarians is the occurrence of redox blemishes on processed microfilms. The term *redox* is an abbreviation for reduction-oxidation and indicates the chemical mechanism by which the blemishes are formed. Another term often used to describe them is *microspots*. Redox blemishes are generally too small to be seen with the naked eye, but a glance through an ordinary light microscope at a magnification of 50X or higher will easily reveal their presence. They usually occur on negative films, i.e., camera original microfilm, that have been stored in cardboard boxes. Such boxes, if they contain groundwood, can emit peroxide. *Peroxides* are gaseous compounds which can be envisaged as reactive forms of oxygen and are capable of chemically attacking image silver in processed microfilm. The result is the formation of redox blemishes: microscopically small, circular spots of an orange-red color (Henn & Wiest, 1963). The blemishes are not contagious. If the source of the oxidizing chemicals is removed, formation of redox blemishes ceases. In practice, it is recommended that processed microfilm rolls be removed from cardboard boxes and be stored in either metal cases or in boxes of rigid polypropylene which are supplied by photographic manufacturers.

The danger posed by the presence of peroxides and similar, chemically active compounds has been confirmed by studies on other materials that were observed to have detrimental effects on black-and-white photographs. For example, it was reported in 1981 that freshly applied oil-based paints produce peroxides during drying, which can affect photographs kept in recently painted rooms (Feldman, 1981). While J. F. Carroll and John M. Calhoun (1955) described in detail the effect of gaseous nitrogen oxides emanating from aging cellulose nitrate films, R. W. Henn and B. D. Mack (1965) published experimental conditions for the artificial aging of silver gelatin microfilms through exposure to various oxidizing atmospheres under laboratory conditions. Other examples of potential danger include the presence of ozone produced in the vicinity of electrostatic copy machines (Weyde, 1969), certain compounds present in automobile exhaust gases (Weyde, 1972), and as described earlier, sulfur-containing substances that are part of animal glues. All these conditions which have been observed in actual conditions of storage and use have been replicated in laboratory experiments.

Handling and Use

Along with the potentially harmful effects of a combination of oxidizing chemicals with either high relative humidity or temperature, ranks the influence of handling and use on the well-being of photographs. Photographic materials are in high demand in their numerous applications: for study and research, publications, and exhibitions. Widespread handling can present a danger to rare historical photographs. Microfilm, so widely used as a preservation medium, suffers mechanical damage from frequent consultation by microfilm readers. Fortunately, the clients' copies are positive images which can be reprinted from the original camera negative. The purpose of these negative originals, in some institutions referred to as master copies of valuable historical documents, is to make positive user copies. The camera originals can be placed into inactive storage for many years without concern for their stability. They are taken out only for the purpose of making additional positive prints when the previous set has been worn out. The historical document itself need never be used in its original form.

Correct handling of still photographic images is, for the most part, a matter of common sense. Since negatives and prints are liable to be damaged physically through fingerprints or scratches, unsleeved negatives and prints should be handled only by people wearing protective gloves made of lintless cotton or nylon. This is general practice in major photographic collections. Ideally, photographs are handled in a clean, dust-free environment. No food or drinks should be tolerated in their vicinity. Photographs should not be left lying around unattended or unprotected. Exposure to direct sunlight will result in lasting damage to any photographic image. Large-format negatives or prints must neither be rolled nor folded. Care must be taken not to damage the corners and edges of a photographic print while examining it. This can largely be prevented if prints are mounted before handling them. Paper prints should not be stapled or attached to other documents with paper clips. Inscriptions in common ink are liable to fade when photographs are on display and will invariably bleed or become illegible if accidentally immersed in water. This is not likely to happen if special inks are used which are manufactured for the purpose of marking prints permanently. Examples of pens with permanent inks are Lumocolor 313 by Staedtler and Film/Printing Marking Pen available from Light Impressions in Rochester, New York. If something must be written on the back of photographic prints to identify them, a soft lead pencil is the preferred medium. Inscriptions in pencil will neither smear nor bleed or transfer when immersed in water, but remain erasable should it become necessary to change the inscription (Hendriks & Dobrusskin, 1990). For optimum protection, negatives and prints should be placed first into sleeves of uncoated polyester or cellulose triacetate (both commercially available), and then in paper envelopes on which is written all necessary documentation. Prints can be viewed without removing them from the transparent sleeve.

A further consideration regarding the preservation of documentary or artistic still photographic prints is the effect of display upon their stability. The use of photographic pictures in exhibitions is becoming increasingly common. Such use requires that photographs be matted and mounted, framed, packed into boxes or crates, shipped by various means, unpacked, hung onto walls, exposed to changing environmental conditions, etc. Photographs must also be taken down after the exhibition and shipped back to their home base. Keepers of photograph collections are well-advised to consider the implications of photographs on display and to prepare thoroughly and well the arrangements for an exhibition in order to avoid disappointment later.

Table 3 summarizes some principal strategies for preventing photographic materials from being damaged.

ENVIRONMENTAL STORAGE CONDITIONS

It is ironic that the recommendations for the storage of processed photographic materials written by the American National Standards Institute (ANSI) do not contain maximum permissible threshold values for concentrations of oxidizing gases in storage areas. An excellent example to follow would be the clean-room conditions set by photographic manufacturers. These spaces must be dark for obvious reasons and completely free of dust, particulate matter, and gases such as hydrogen sulfide, sulfur dioxide, and hydrogen peroxide. Some manufacturers have not instituted specific numerical values for clean-room conditions. The purification of the atmosphere in the manufacturing areas is so effective that the concentrations of any of the above irritants are beyond the ability of analytical techniques to detect them. That is, any present air pollution is below the detection limit of modern analytical instruments!

Temperature and Relative Humidity Levels

Current ANSI standards regarding the storage of processed photographic materials address mainly temperature and relative humidity levels. Table 4 summarizes recommendations for the storage of photographic plates (ANSI, 1981).

Recommendations are set at realistic levels. The wide temperature range within which photographic plates can be kept indicates the slight effect that temperature alone is expected to have on their stability. While a relative humidity of below 40 percent is preferable, any level

TABLE 3
PRESERVATION: PREVENTIVE MEASURES

1. Provision of correct storage conditions
2. Use of correct storage enclosures [sleeves; envelopes; boxes; cans]
3. Instructions for handling and use
4. Instructions concerning display conditions
5. Provision of emergency plans
6. Application of copying and duplication techniques

TABLE 4
ANSI PH1.45-1981
PRACTICE FOR STORAGE OF PROCESSED PHOTOGRAPHIC PLATES

	Storage Temperature	*Relative Humidity*
Recommended:	15-25°C. (59-77°F.)	20-50%
Preferably:	20°C. (68°F.)	40%

between 20 and 50 percent is acceptable. Table 5 shows similar recommendations for the storage of photographic paper prints (ANSI, 1987).

Recommended environmental conditions are similar to those for photographic plates. The maximum permissible threshold value of 60 percent relative humidity is significant. A high moisture content of the air is conducive to mold growth, which can completely destroy the image in time. Daily cycling of more than 4°C should also be avoided. Specifications for the storage of processed photographic film are divided into one set for medium-term and another for archival. *Medium-term film* is a photographic film that is suitable for the preservation of records for a minimum of ten years. *Archival film* is a photographic film suitable for the preservation of records having permanent historical value. Table 6 summarizes the recommended relative humidity and temperature conditions for the storage of processed photographic film for *medium-term* storage (ANSI, 1985). Film includes all the variations mentioned earlier.

Table 7 shows the recommended relative humidity and temperature conditions for the storage of processed photographic film for *archival* storage.

Table 7 features a confusing range of recommended relative humidity levels. Upon closer examination, it becomes clearer that the materials listed in the extreme left column of Table 7 can be rearranged so as to group together films of similar composition with respect to the support and the nature of the image-bearing layer. There are three such support groups: conventionally processed silver or dye (color) gelatin images on a cellulose ester base; silver or dye (color) gelatin images on a polyester base; and nonsilver, nongelatin images on either base.

Regrouped together in this fashion, the recommendations for relative humidity are shown in Table 8. In the new arrangement, materials of similar properties with regard to their reactivity towards

TABLE 5
ANSI PH1.48-1982 (R1987)
AMERICAN NATIONAL STANDARD FOR PHOTOGRAPHS (FILMS AND SLIDES)—BLACK-AND-WHITE PHOTOGRAPHIC PAPER PRINTS—PRACTICE FOR STORAGE

	Storage Temperature	*Relative Humidity*
Acceptable:	15-25°C. (59-77°F.)	30-50%
Never:	30°C. (86°F.) Avoid daily cycling of 4°C. (7°F.)	60%

changing relative humidity levels are combined because they require similar RH levels for long-term permanence. For example, gelatin layers and cellulose acetate bases behave similarly with regard to their shrinking properties; by contrast, gelatin contracts at a faster rate than polyester at low RH; consequently, 30 percent is the minimum recommendation for that system. In addition, polyester may become too brittle below that value. Since materials in the third group do not contain gelatin layers, interactions do not occur between support and binding mediums due to their different shrinkage characteristics. Finally, color photographic films have the narrowest recommended RH range, of which the higher threshold value (30 percent) is in the interest of the permanence of the dyes, whereas the lower level (25 percent) is designated for the benefit of the polyester support.

Since few photographic collections could afford several storage areas with different RH levels for various materials, the new arrangement, most importantly, facilitates the selection of a single optimum RH level beneficial to a variety of photographic films. That level should be 30 percent, plus or minus three percent, in line with the most recent recommendations for the storage of paper records in archives and libraries, and significantly lower than the 50 percent RH recommended a decade ago for the storage of such materials.

Natural Disaster Contingency Plans

Stored photographic materials are threatened by floods, fire, and the aftereffects of attempts to extinguish a fire. Contingency plans for dealing with natural disasters are therefore necessary in archives and libraries, and should include provisions for photograph collections. A recent publication from the author's laboratory summarized the results

TABLE 6
ANSI PH1.43-1985
AMERICAN NATIONAL STANDARD FOR PHOTOGRAPHY (FILM)
PROCESSED SAFETY FILM—STORAGE
RECOMMENDED RELATIVE HUMIDITY AND TEMPERATURE
CONDITIONS FOR MEDIUM-TERM STORAGE

Sensitive Layer	*Base Type*	*Relative Humidity Range (%)*	*Maximum Temperature (°C.)*
Microfilm:			
Silver-gelatin	Cellulose ester	15-60	25
Silver-gelatin	Polyester	30-60	25
Heat-processed silver	Polyester	15-60	25
General:			
Silver-gelatin	Cellulose ester	15-60	25
Silver-gelatin	Polyester	30-60	25
Color	Cellulose ester	15-30	10
Color	Polyester	25-30	10
Diazo	Cellulose ester	15-50	25
Diazo	Polyester	15-50	25
Vesicular	Polyester	15-60	25
Electrophotographic	Polyester	15-60	25
Photoplastic	Polyester	15-60	25

of an extensive study on the recovery of water-soaked photographic materials (Hendriks & Lesser, 1983). Ideally, water-soaked photographs are air-dried. This should be done if enough space is available to spread out the water-soaked photographic records. Time is also required for air drying. However, the significant result of the study was the observation that most photographic materials, including all contemporary silver gelatin and dye gelatin photographs, can be frozen after they have been soaked in water and can be left in the frozen state for some time to await later treatment. Freezing slows down dramatically any further degradation and so provides time for gradual recovery. Frozen photographs should be thawed and air-dried which is the preferred second option after air drying without freezing. A third possibility is freeze-drying photographs in a vacuum chamber, which leaves photographs virtually unharmed. Freeze-drying means that the photographs are kept during this process below 0°C, i.e., in the frozen state. By contrast, freezing followed by thawing and vacuum-drying at 4°C, i.e., above the freezing point of water—as is done with books—is not recommended because of blocking or sticking of gelatin layers. When wet, gelatin has adhesive properties which cause photographic negatives or prints packed in a bundle to stick together. It must be emphasized

TABLE 7
ANSI PH1.43-1985
AMERICAN NATIONAL STANDARD FOR PHOTOGRAPHY (FILM)
PROCESSED SAFETY FILM—STORAGE
RECOMMENDED RELATIVE HUMIDITY AND TEMPERATURE
CONDITIONS FOR ARCHIVAL STORAGE

Sensitive Layer	*Base Type*	*Relative Humidity Range (%)*	*Maximum Temperature (°C.)*
Microfilm:			
Silver-gelatin	Cellulose ester	15-40	21
Silver-gelatin	Polyester	30-40	21
Heat-processed silver	Polyester	15-50	21
General:			
Silver-gelatin	Cellulose ester	15-50	21
Silver-gelatin	Polyester	30-50	21
Color	Cellulose ester	15-30	2
Color	Polyester	25-30	2
Diazo	Cellulose ester	15-30	21
Diazo	Polyester	15-30	21
Vesicular	Polyester	15-50	21
Electrophotographic	Polyester	15-50	21
Photoplastic	Polyester	15-50	21

that glass plates made by the wet collodion process, including the collodion positives known as ambrotypes and tintypes, are the materials which are most susceptible to water damage. They should neither be frozen nor freeze-dried once they have been immersed in water. Other exceptions to the recommendations given above are daguerreotypes and color lantern slides made by the pre-1935 additive color processes (such as Lumiere Autochrome Transparency Plates, Agfacolor Plates, and others). Samples of these photographs were not included in the experiments on disaster recovery.

CONCLUSION

Conventional silver halide photography is being replaced in many applications by electronic imaging technologies, particularly by video imaging. Cost effectiveness and the instant availability of the image on a viewing screen are but two reasons for this change. Traditional photographic materials have one particular requirement that seems to be dreaded by anyone involved in photography: they are the only materials collected in archives and libraries that require processing in

TABLE 8
ANSI PH1.43-1985
AMERICAN NATIONAL STANDARD FOR PHOTOGRAPHY (FILM)
PROCESSED SAFETY FILM—STORAGE
OPTIMUM STORAGE RELATIVE HUMIDITY FOR ARCHIVAL STORAGE

Sensitive Layer	*Base Type*	*Relative Humidity Range (%)*
1. Cellulose Acetate/Gelatin/Silver or Dye:		
Silver-gelatin (Microfilm)	Cellulose ester	15-40
Silver-gelatin	Cellulose ester	15-60
Color	Cellulose ester	15-50
2. Polyester/Gelatin/Silver or Dye		
Silver-gelatin	Polyester	30-40
Silver-gelatin	Polyester	30-50
Color	Polyester	25-30
3. Polyester or Cellulose Ester/Nongelatin/ Nonsilver		
Diazo	Cellulose ester	15-30
Diazo	Polyester	15-30
Vesicular	Polyester	15-50
Electrophotographic	Polyester	15-50
Photoplastic	Polyester	15-50
Heat-Processed Silver	Polyester	15-50

a series of chemical solutions in order to produce a visible record. From a technical point of view, processing can actually be used as an important tool to control or determine the properties of the final image, such as contrast, resolution, and graininess; but it is often not well-understood and is done preferably by machines which require little human intervention. Processing is also one of three factors that may have a profound effect on the permanence of the record, the other two being the inherent properties built in during the manufacture of the material and the conditions under which it is kept. The requirement for chemical processing of photographic records and its perceived uncertainties have contributed much to the declining popularity of chemical processing when compared with electronic imaging. It is worthwhile to remember, however, that modern black-and-white film bases used in the manufacture of microfilm, motion-picture film, aerial film, and still photographic negatives are made to such rigid specifications and have been tested so extensively that they merit their official recognition as permanent records materials. They remain the only nonpaper records in libraries and archives having that status. They are human-readable, and their permanence under a given set of conditions is well-established. Modern safety film is clearly superior to any other nonpaper, nonparchment record materials in common use or under consideration for use in libraries and archives.

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