

The Preservation
and restoration of
photographic materials
in archives and libraries:
A RAMP
study with guidelines

General Information Programme and UNISIST

United Nations Educational,
Scientific and Cultural Organization

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THE PRESERVATION AND RESTORATION OF
PHOTOGRAPHIC MATERIALS IN ARCHIVES
AND LIBRARIES :
A RAMP STUDY WITH GUIDELINES

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PREFACE

The Division of the General Information Programme of Unesco in order to better meet the needs of Member States, particularly developing countries, in the specialized areas of records management and archives administration, has developed a long-term Records and Archives Management Programme - RAMP.

The basic elements of the RAMP programme reflect the overall themes of the General Information Programme. RAMP thus includes projects, studies, and other activities intended to:

1. Promote the formulation of information policies and plans (national, regional and international).
2. Promote and disseminate methods, norms and standards for information handling.
3. Contribute to the development of information infrastructures.
4. Contribute to the development of specialized information systems in the fields of education, culture and communication, and the natural and social sciences.
5. Promote the training and education of specialists in and users of information.

The present study, prepared under contract with the International Council on Archives - ICA - is intended to inform archivists, curators, and other responsible for the acquisition and preservation of documentary materials in photographic form of the nature and problems associated with this relatively fragile media, and of the measures recommended to help ensure its preservation. The study presents the results of the most recent research and experience in the preservation and restoration of photographic materials.

Comments and suggestions regarding the study are welcomed and should be addressed to the Division of the General Information Programme, UNESCO, 7 place de Fontenoy, 75700 Paris. Other studies prepared under the RAMP programme may also be obtained at the same address.

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FOREWORD

The purpose of the present study is to summarize the currently available knowledge on the preservation and restoration of photographic materials that may serve as a reference guide to maintaining, preserving and restoring photographic collections.

The existence of large quantities of photographic records in archives and libraries has created problems of preserving these records that are, to some degree, comparable to conventional paper objects, but also have special requirements due to their particular nature. The present study aims at outlining the principal photographic processes and describing the characterization and identification of photographic images. It will discuss the factors that affect the stability of photographic materials, the examination of photographic records and the analysis of their deterioration. The duplication of black-and-white negatives and the copying of positive reflection prints will be explained as an important means of preserving photographic images. Such copy photographs must be processed in such a way as to obtain records of maximum possible permanence, and procedures will be outlined to achieve this. A second principal requirement is the prevention of damage and deterioration of photographic materials by keeping them in carefully controlled storage conditions which are conducive to their longevity. Once deterioration has occurred, however, it is sometimes possible to correct the errors of the past through restoration procedures which will also be outlined. Finally, some procedures for testing both the stability of contemporary photographic materials and the suitability of materials used in the conservation of photographs will be discussed.

The emphasis will be on black-and-white photographic materials based on the light sensitivity of silver halides whose image-forming substance, therefore, consists of elementary silver. Monochrome reflection prints made by

non-silver processes, such as platinum and carbon prints, or pictures containing certain metal salts and other pigments will also be mentioned. The scope of this study includes the preservation of contemporary colour photographic materials made by processes such as chromogenic development, silver dye bleach, dye imbibition and dye diffusion transfer (such as instant colour photographs).

The observations and recommendations offered in this study represent the experience which has been developed during the past eight years in the Photograph Conservation Laboratory at the Public Archives of Canada. It may or may not coincide in every aspect with experience developed elsewhere. Our goal has always been to support recommendations by either data from our own experimental work or by those taken from the scientific and technical literature. The author wishes to express his thanks to the numerous colleagues who, in one way or another, have contributed over the past years to our increased understanding of the nature of photographic materials. Among them are D. R. Madeley and D. Hopkins who also assisted in the preparation of this study. Special thanks are also expressed to L. Latka for excellent word processing services.

Ottawa, Ontario, Canada
February 1983.

1. INTRODUCTION

1.1. The Role of Photographic Materials

Still photographic images form an integral part of a country's visual heritage. Their role and importance is reflected by the increasing number of exhibitions and publications containing photographs and the use made of them by authors and researchers. While paper has been the predominant document material throughout centuries, it is steadily supplemented - and sometimes replaced - by photographic materials such as microfilm. A third use of photographic records is made in motion picture film which may be used in documentary form in order to record historical events or as a medium of artistic expression. Any or all of these major applications of photographic records can be found in archives and libraries.

1.2. The Importance of Photographic Records

Photographic procedures and the images made by them have found application and use in nearly every type of human endeavour. Whether they are used in science and technology, the exploration of space and in aerial photography, in radiography or as motion picture film, as a means of preserving the information content of paper documents through microfilm or as a recording medium for historical events, as a medium for artistic expression or as a record of social and family life by millions of amateur picture takers throughout the world - photographic images are produced in very large numbers every year. While not all of them need to be preserved, many are now or will become - records of outstanding importance that will attest to historically or technically important events and achievements. As such they form a principal part of the holdings in archives and libraries.

1.3. The Physical Nature of Photographic Materials

Photographic materials consist essentially of a support onto which is coated a binding agent that contains finely divided elementary silver grains. The most common support materials encountered throughout the history of photography are

paper, glass, metal and plastic film. For the past one hundred years the binding agent used has been almost exclusively gelatin, often referred to in the technical literature as the gelatin matrix. Other binding agents which can be found in historical photographs are collodion and albumen. In addition to silver particles, other image-forming materials have been used in photographic processes: pigments, such as lampblack, and other metals or metal salts, such as platinum or iron salts. The vast majority of black-and-white photographs on paper contain silver particles in a gelatin matrix and are therefore often called silver gelatin prints. The major components of historical photographic materials are summarized in TABLE 1.

TABLE 1: MAJOR COMPONENTS OF PHOTOGRAPHIC MATERIALS

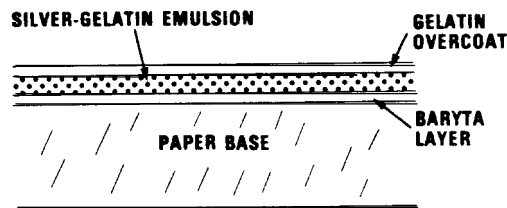
Supports	Binding Agents	Image Forming Substances
Paper	None	Silver
Glass	Collodion	Other metals
Metal (eg. copper, iron)	Albumen	Metal salts
Plastic Film (e. g. cellulose nitrate, cellulose acetate)	Gelatin	Dyes Pigments

With respect to contemporary photographic records, additional materials must be considered. During the past ten years or so, there has been an increase in the use of so-called resin-coated papers, which should be regarded separately from conventional fiber-base papers, and new image-forming systems. TABLE 2 presents the principal support and image-forming materials in use today.

TABLE 2: MAJOR COMPONENTS OF CONTEMPORARY PHOTOGRAPHIC MATERIALS

Supports	Images
Plastic film (e.g. cellulose acetate, polyester) Paper Resin-coated paper	Silver (normally in gelatin layer) Dyes (in colour photographs, normally in gelatin layer) Diazo (monochrome dyes) Vesicular (nitrogen bubbles)

Between support and binding agent there is usually - but not always - an interlayer which may serve various purposes, from an adhesive between the two layers, to improving picture quality. FIGURE 1 is a schematic cross-section of a black-and-white photographic print, showing its major components. There may be present, however, additional layers, for example one to provide anti-curl properties or increased resistance to surface scratching.



CONVENTIONAL SILVER GELATIN PRINT

FIGURE 1: Schematic Cross-Section of a Black-and-White Photographic Print

The se various elements give photographic materials a unique layer structure that is largely responsible for their long-term stability characteristics. It is one of two outstanding properties of photographic records. Generally, the two layers - support and binding medium - react markedly different towards changes in environmental conditions. For example, gelatin contracts at a higher rate than paper at low relative humidity, causing a photographic print to curl up. However, when exposed to a high level of relative humidity (for example, above 80%), the print will flatten itself without external force. The second principal factor determining - even limiting - the preservation of photographic materials is the presence of silver as the image-forming substance. It is more reactive towards a number of chemical reagents - particularly towards oxidizing agents - than one would expect from its classification as a noble metal, i.e. one that is chemically inert. While some details about the image silver's properties will be discussed later, it should be noted that generally the support material is the most stable of the major components of a photograph. Notable exceptions to this observation are cellulose nitrate film base, glass plates (because of their brittleness) and, to some degree, contemporary resin-coated papers.

2. A DESCRIPTION OF THE PRINCIPAL PHOTOGRAPHIC PROCESSES

2.1. Black-and-white Photographic Materials

Under this heading are grouped those photographs which are produced by exposure to light of light sensitive silver salts suspended in an organic binding agent, and subsequent processing (i.e. development, fixing, washing and drying). The silver salts may be any combination of silver chloride, silver bromide and silver iodide. At the end of the exposure and processing cycle, the image consists of elementary silver which is distributed throughout the binding medium in the form of microscopically small grains. Places of high concentration of silver are the blackest. Those areas where the quantity of silver decreases, appear to the eye in various shades of grey, while silver-free areas are transparent in films or glass plates, and white in positive reflection prints. The degree of blackness in a black-and-white photograph is technically called density, which is directly proportional to the amount of silver present. High density areas - often called the shadow areas - contain large amounts of silver, while in the so called mid-tones the silver content is gradually decreasing. Essentially silver-free places are called minimum density, or highlight areas. A densitometer is the instrument commonly used to measure density.

The term density is defined according to FIGURE 2. The amount of light, I_i , falling on a piece of film is partially passing through it, partially absorbed. The ratio of transmitted light, I_t , over the incident light, I_i , is called transmission T:

$$T = \frac{I_t}{I_i}$$

The reciprocal value is called opacity (O):

$$O = \frac{I_i}{I_t} = \frac{1}{T}$$

Density (D) is defined as the logarithm of opacity:

$$D = \log O = \log \frac{I}{I_t} = \log \frac{I_i}{I_t}$$

DENSITY

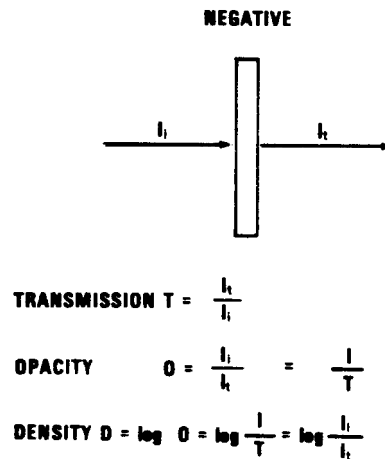


FIGURE 2: Definition of Transmission Density

For reflection prints a similar situation prevails, the transmitted light being replaced by the amount of light reflected by the surface of the photograph. Density values are logarithms of the ratio of incident light over reflected light. These numerical data, when combined with the exposure values required to produce them, are called sensitometric data, where sensitometry is the science that describes 'the measurement of the relation of the exposure and development of a photographic material to the density of silver produced'. (Mees, 1961)

In introducing the concept of density and its measurement - densitometry - it is acknowledged that photographic materials have been for approximately the past one hundred years products of a highly developed and specialized technology. In order to

understand their properties in terms of their stability, as well as concepts of duplicating and copying, it is necessary to understand how they are made and which materials are employed in their manufacture and subsequent processing. Reference will be made in this study to the literature where the reader may find pertinent technical details. Other technical concepts will be introduced throughout this study.

In the following description of the main photographic processes and the pictures made by them, an attempt is made to classify the various types according to their physical properties which, in turn, determine their preservation requirements. Divisions that use format as the distinguishing feature (e.g. carte-de-visite), or physical appearance (e.g. case photograph, such as daguerreotype or ambrotype) are irrelevant, as they do not indicate any generic properties. A carte-de-visite, format 2 1/2 x 4 1/4", could be either an albumen print or a silver gelatin print, the two of which would differ considerably in their properties. Likewise, a daguerreotype, as will be shown later, was made by a process different from the wet collodion process by which an ambrotype was made. Black-and-white photographs are divided in this section into camera originals, i.e. records exposed in a camera which are usually negatives, and reflection print materials, or positive pictures.

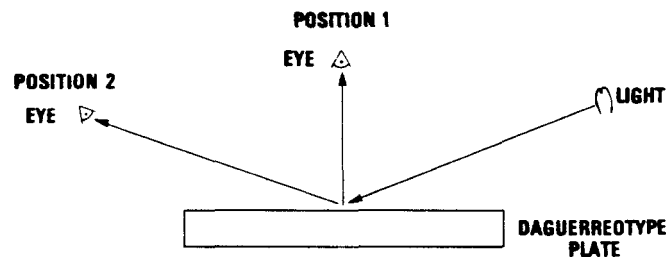
2.2. Camera Originals

2.2.1. Daguerreotypes

Announced by L.J.M. Daguerre in 1839 in Paris, daguerreotypes consist of microscopically small particles of silver amalgam, an alloy of mercury and silver, on a silver-plated copper plate. The daguerreotype process was very popular in North America until approximately 1865. Images made by this process have a jewel-like appearance and are of a delicate nature: they are sensitive to chemicals in their environment and liable to be scratched by the touch of a finger. Consequently, they are usually kept under a glass

Cover in a small case made of leather, wood, or plastic ("Union cases"), and so are often referred to as 'case photographs". Each of these usually requires individual and careful treatment, according to its condition.

Daguerreotypes are negatives, but appear to the viewer alternately either as a positive or negative picture depending on the angles of illumination and observation. In contrast to reflection print materials whose image is caused by adsorption and reflection of incident light, the daguerreotype image is visible because of light scattering phenomena. Pobboravsky (1) has given a good account of the situation, cf. FIGURE 3.



ANGLES OF ILLUMINATION AND VIEWING OF A DAGUERREOTYPE PLATE

L POBBORAVSKY:

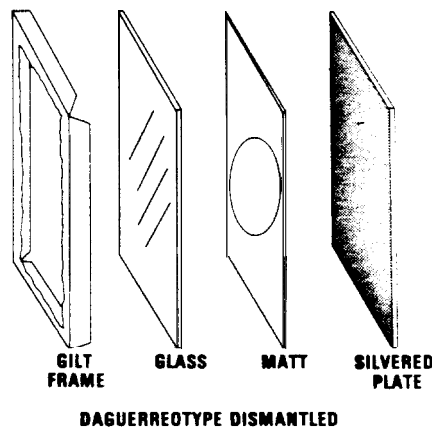
"STUDIES OF IODIZED DAGUERREOTYPE PLATES".

FIGURE 3: Angles of Illumination and Viewing of a Daguerreotype Plate

If a beam of light from a point light source strikes a polished silver surface at a certain angle, an observer in position 1 sees the colour black, since none of the reflected light reaches his eye. The light is reflected at an angle equal to the angle of incidence, and therefore an observer in position 2 sees the polished silver surface. In a second case, when the silver surface also contains more or less fine silver amalgam particles, light is then scattered in all directions,

thus reaching the eye of an observer in position 1. These light scattering phenomena are responsible for the appearance of a daguerreotype as both a positive and a negative image, depending on the angles of illumination and observation.

When found in cases, daguerreotypes are combined with an overmat covered by glass, an assembly which is held together by a gilt frame. FIGURE 4 shows the parts of such a package, according to Gill (2).



A.G. GILL
"THE DAGUERREOTYPE"
1974

FIGURE 4: Daguerreotype Dismantled

The conservation and cleaning of tarnished daguerreotypes has been ably reviewed by Pobboravsky (3). More recently, daguerreotypes have been studied by Swan et al. (4) and Barger, Messier and White (5) using modern analytical techniques.

2.2.2. Calotypes and Historical Paper Negatives

Whereas daguerreotypes are unique camera originals, of which copies could not be made, W. H. Fox Talbot, in Lacock Abbey, England, exposed paper sheets coated with a light sensitive layer in a camera, in order to obtain paper negatives, during the late 1830s. It was the beginning of the negative-positive process as we know it today. A paper negative, in which the bright areas of the original scene

appeared dark and the shadow parts appeared light, could be printed - or exposed to light - in contact with a second sensitized sheet of paper to obtain a laterally and tonally correct positive image of the original scene. These positives were called "salted paper prints" or "calotypes."

Such original paper negatives, in use for about the first twenty years of photography, are rare and of great intrinsic value. Each requires individual treatment as would a water colour or a lithograph.

The light sensitive paper was prepared by brushing a sodium chloride solution onto its surface. After drying, it was floated on a solution of silver nitrate, with subsequent formation of light sensitive silver chloride. Since there was no binding agent, the processed picture consisted of elementary silver particles resting partially on the surface of the paper, partially absorbed into the paper fibers. FIGURE 5 shows a schematic cross-section of a salted paper print.

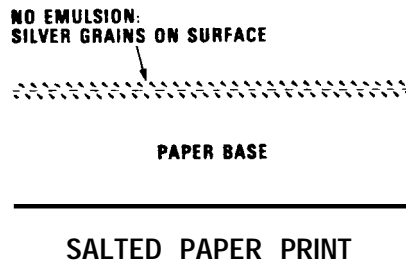


FIGURE 5: Schematic Cross-Section of a Salted Paper Print

An original account of their production is given by Talbot (6). Coe (7) described the printing of salted paper prints from original calotypes for exhibition purposes. During the 1850s, the paper negative was often waxed in order to make the support more transparent and so facilitate printing (8).

2.2.3. Wet Collodion Negatives on Glass and Direct Positives Made by the Wet Collodion Process

Introduced by F. S. Archer in 1851 in England, probably the majority of photographic negatives made during the second part of the last century were exposed on wet collodion glass plates. Collodion, a solution of cellulose nitrate compound in a mixture of alcohol and ether, was mixed with a halide source, poured onto a glass plate with a clean surface, and finally sensitized by bathing it in a solution of silver nitrate. In this way, a light sensitive silver halide was formed. The glass plate so prepared had to be exposed in the camera while it was still wet, hence the name of the process. If the collodion were allowed to dry, the plate would lose its sensitivity.

As the exposed negative was physically developed, the resultant silver image is composed of extremely fine silver grains. Wet collodion glass plate negatives, therefore, have a high resolving power and are capable of rendering fine detail. Because of this property, wet collodion negatives were used until World War 11 in the preparation of photolithographic printing plates. Wet collodion glass plate negatives have usually been varnished - a fact that has contributed much to the preservation of their image silver. Yellowing of these negatives may well be due to a deterioration of the varnish and not of the collodian or the image silver. Photographic journals of the 19th century abound with technical details on the wet collodion process. The modern reader finds interesting summaries in references 9, 10 and 11.

This process was also used to make direct collodion positives, which are now known as ambrotypes and tintypes. After exposure in the camera, a wet collodion glass plate negative was backed with black paper or a black lacquer, which made the image appear to be a positive. The result was an ambrotype. One could also expose a sensitized collodion layer that was poured on a black lacquered iron plate in order to

obtain the same effect. The resultant image was a tintype. Ambrotypes and tintypes were often kept in cases similar to those described for daguerreotypes. Therefore, they are sometimes also called 'case photographs". It must be remembered, however, that daguerreotypes have entirely different image characteristics than ambrotypes and tintypes. The pictures made by these two processes (daguerreotype process and the wet collodion process) have nothing in common structurally or in terms of their properties and stability.

The materials up to this point are distinguished from the subsequent silver gelatin materials by two criteria: they were individually hand-made, and they were sensitized - i.e. made light sensitive - immediately before use by the photographer. The light sensitive salt - a silver halide - was formed in a direct chemical reaction on the surface of the respective support just prior to exposure. This situation is different from the materials described in the following section.

2.2.4. Silver Gelatin Materials

In the manufacture of the predominant photographic recording material for approximately the past one hundred years, the light sensitive silver halides are mixed with the binder, a particular type of highly purified gelatin, and the resulting emulsion, in a separate step, is then coated onto the desired support material. Empirically acquired skills of manufacture, developed during the first three decades since the 1880s, gave way to more scientifically understood and controlled procedures which allowed the emulsion-maker to obtain the many different kinds of black-and-white photographic films and papers in use today. This can be achieved, generally speaking, by changing such variables as the temperature during the emulsion-making process, the type of halide source, the sequence of adding the various ingredients, the mechanical way of adding ingredients, the type of gelatin chosen, and many others. The precise details of such procedures are closely kept trade secrets, as the manufacture of contemporary

multi-layer films is as demanding and elaborate as the manufacture in other high technology fields. The end result of this knowledge is the precise control over the size and shape of the silver halide grains and their distribution in the coated gelatin layer, factors which largely determine the sensitometric properties. Since the size and form of the silver grains in processed photographic records is determined by that of the silver halide crystals in unexposed and unprocessed stock, (c. f. FIGURE 6) such knowledge may be useful to keepers of photograph collections.

DEVELOPED-OUT SILVER GELATIN IMAGES

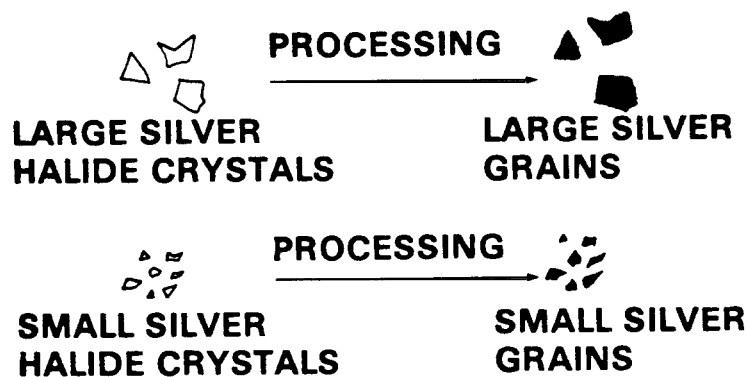


FIGURE 6: Morphology of Silver Grains Depends Upon That of silver Halide Crystals

The properties of processed silver grains have, in turn, a strong bearing on the stability of the photograph in question.

2.2.4.1. Silver Gelatin Dry Plates

These camera materials, in which the collodion was replaced by gelatin as the binding agent necessary to hold the silver halide crystals in place, could, as was pointed out earlier, be manufactured and coated by machines. After 1880 dry plates became rather common. One major drawback was the weight of the glass and its brittleness, a property they shared with wet collodion glass plate negatives. However, they were more sensitive to light (they had "a faster speed" in today's photographer's lingo), and they kept their sensitivity for several months after manufacture. An excellent technical account of their manufacture was given by Jahr (12). The majority of still camera negatives taken during the last two decades of the nineteenth century and about the first twenty years of this century are gelatin dry plates. However, not all images on these plates are necessarily negatives, as they could be processed by reversal development to give positive transparencies, sometimes called lantern slides.

2.2.4.2. Silver Gelatin Negatives on Plastic Films

During the latter part of the nineteenth century many attempts were made to coat plastic materials with light sensitive emulsions in order to overcome the disadvantages of glass plate negatives. Around 1890 the first photographic films on a plastic base appeared on the market, made of cellulose nitrate. The development of this film base laid the foundation for a tremendous growth of the burgeoning motion picture industry. Several years after the commercial introduction of cellulose nitrate film base it became apparent that this material tended to slowly disintegrate with age and was also highly inflammable. New materials were developed of which the three most important ones are cellulose diacetate and triacetate, introduced in the late 1920s, and polyester film base, which was developed during the 1950s. These materials are often referred to as safety film.

In sheer numbers alone, these negative materials (including a small percentage of reversal developed positive transparencies on plastic film base) form the bulk of still photographic negatives in most historical collections, along with black-and-white prints made on developing-out papers, which will be discussed in the following section. Conservation efforts are certain to be directed towards developing high-volume treatment procedures to preserve these materials for future generations.

It is relevant to note here that microfilms and black-and-white motion picture films fall into this category. The study of the properties, in terms of stability, and behaviour of these materials towards various storage conditions is therefore of utmost importance. Heyne (13) has reviewed, in a technical paper, the manufacture of photographic films.

2.2.4.3. Negatives Made by Instant Photography Processes

These sheet film negatives, (e.g. from Polaroid Corporation's Type 665, or Type 55, Positive/Negative Land Film) are made of cellulose triacetate or polyester. If they are processed correctly, i.e. according to the instructions of the manufacturer, they may be treated as any other black-and-white sheet film.

2.2.4.4. Contemporary Negatives on Paper: Photostat Processes

The photostat process (a registered trade name of the Itek Corporation) is one of many available in archives and libraries for the reproduction of original documents. It is used to copy large-format originals, such as maps and newspapers. It produces a negative on paper, where a copy of a newspaper page shows white letters on a black background.

2.2.5. Negatives Made by Chromogenic Development Processes

In these camera materials organic dyes are present which form the negative image. They became commercially available only recently, examples being Ilford XP-1 and Agfa-Gevaert Vario-XL. Since they do not contain silver as the image-forming substance, their properties will be discussed in the context of colour photographic records.

TABLE 3 summarizes the principal groups of black-and-white photographic negatives.

TABLE 3: PRINCIPAL GROUPS OF BLACK-AND-WHITE PHOTOGRAPHIC NEGATIVES

Daguerreotypes
Calotypes and negatives on paper
Wet collodion glass plates
(including ambrotypes and tintypes)

Silver gelatin materials
(i) dry plates (on glass)
(ii) on Cellulose nitrate film base
(iii) on safety film base
(cellulose triacetate and polyester)

Negatives made by instant photography processes
Contemporary negatives on paper (e.g. Photostat)
Negatives made by chromogenic development processes

2.3. Reflection Print Materials

Of the many processes that were used to make positive reflection prints, the emphasis in this study is on silver print materials. They are grouped according to the nature of the image-forming substance first, then according to the binding agent and lastly according to the support. The image-forming material - silver, carbon, metal salts - largely determines the important characteristics, including stability of a photograph. The support is generally the least influential factor, as it is the most stable of the three components and rarely causes problems. Exceptions are cellulose nitrate film base, the brittleness of glass and contemporary resin-coated papers (RC papers). Accordingly, photographic silver prints are divided into printed-out papers (P.O.P.); developed-out papers (D.O.P.) on a conventional fiber-base paper support; developed-out papers on a resin-coated paper support; miscellaneous historical print materials not classifiable according to the properties

Of the silver grain; and contemporary rapid processing materials. As with negative materials, the properties of silver gelatin photographs have been studied extensively by the photographic industry using a wide variety of analytical techniques and testing procedures. Much of that experience has been published, thus providing the keeper of photographic collections with better knowledge on the preservation of these materials.

2.3.1. Printed-Out Photographic Paper Prints

Printing-out papers which contain, in addition to the usual silver halide, an organic silver salt, are exposed by contact under a negative until a positive picture appears, i.e., is printed-out. This process may take from a few minutes to forty-five minutes or more, depending on the type of paper and the light source used. There is no subsequent development. The picture is then toned and fixed. The silver grains obtained in the printing-out process are considerably smaller and of a different shape than those present in developed-out papers. Formstecher, in the 1920s and 1930s, published the results of numerous studies on the properties of printing-out papers, of which (14) and (15) are particularly useful. The more common types of these photographic prints are subdivided into the following four groups.

2.3.2. Salt Papers, or Salted Paper Prints

They are among the earliest positive prints, and have been mentioned earlier as rare and historically important documents (cf. page 9). Since there is no binding agent in these pictures, they often have a somewhat flat appearance, lacking brilliance and depth. However, the paper used was sometimes sized with gelatin first, which caused a change in the properties of the resulting pictures.

Starch was also used as a sizing agent (and probably as a binding medium), but photographs of this kind are rare, and not much knowledge has been published about them.

2.3.3. Albumen Prints

They are probably the most common - and therefore most important - photographic print material of the nineteenth century. Consequently, there is an abundance of literature on their manufacture, use and properties. Some contemporary references are by Aleo (16), Kellner (17), and Schnauss (18). Two important monographs are by Davanne and Girard (19) and by Just (20). A recent introduction into the manufacture and use of albumen papers has been provided by Reilly (21). The tonal range and almost complete lack of graininess of albumen papers perfectly matched the high-contrast fine-grain, wet collodion negatives, from which they were generally printed. These are the first machine-made papers produced specifically for photographic purposes. Albumen prints have a significant place in most historical photographic collections.

2.3.4. Collodio-Chloride Prints

An important print material, in which the albumen was replaced by a collodion layer, they seem to have been used more commonly in Europe than in North America. While albumen papers, coated only with egg-white containing a halide salt, were usually sensitized before use by the photographer, collodio-chloride papers were completely machine manufactured. In contrast to the former, collodio-chloride prints have a baryta layer between the paper support and the collodion layer. A baryta layer, introduced well over one hundred years ago (22), consists of finely ground, white barium sulfate in gelatin. It has a number of important functions. In earlier years, one purpose was to protect the emulsion against harmful chemicals that might be present in the paper base and react with the image silver (23). The baryta layer also provides a smooth, even surface onto which the emulsion can be coated. Lastly, it gives increased whiteness and brilliance to the paper base because of the high reflectance power of barium sulfate.

2.3.5. Silver Gelatin Printing-Out Papers

These materials, which were also machine coated, have been in use since the 1880s, beginning with Eastman Kodak's Solio Paper to the same company's Studio Proof paper, which remains on the market today.

2.3.6. Developed-Out Photographic Paper Prints

This was, and still is, the most common photographic printing medium since the end of the last century. Developing-out papers are exposed in a darkroom under a negative for a few seconds only and are then developed. The gain of speed in processing is their major advantage over printing-out photographic papers.

Sachse (24) gives a fairly early account on the development of photographic papers, while Zimmerman (25) discussed the whole range of photographic printing papers. A most interesting account of the manufacture and properties of emulsion papers was published by Cobenzl (26).

According to their sensitivity, and therefore to the size and shape of the resultant silver grain, developing-out papers have traditionally been divided into chloride papers, bromide, and chloro-bromide papers. This division is also useful in terms of the conservation of these prints. Trumm (27) gives an excellent account of the manufacture of both printing-out and developing-out papers, while Falta (28) discusses the properties of photographic papers and their evaluation.

2.3.7. Bromide Papers

They were the first developing-out papers to appear on the market in the 1880s. Their stability was once considered to be so high in comparison with printed-out photographs that one manufacturer sold his product under the name of 'Permanent Bromide'. Bromide papers were of medium speed and had neutral image tones. As the manufacture of these materials became more complex, the simple term "bromide" probably indicated nothing more than that the predominant light sensitive compound in the

raw material was silver bromide. A glimpse behind the veil of trade secrecy, which demonstrated the complexity of making such a paper, was provided through the publication of the F.I.A.T. reports by the allied forces at the end of World War II. Among the manufacturing procedures revealed is one for a bromide paper made by Agfa forty years ago. It is reprinted by Glafkides (29).

2.3.8. Chloride Papers

These print materials probably contained silver chloride as the prevalent light sensitive compound. Being of relatively low speed, they were mainly used for contact printing. The finished print has a cold-black image tone, a higher maximum density than the other developed-out papers, fine grain and good contrast. As early versions could be used in a moderately illuminated workroom, they were also referred to as 'gaslight papers" (30).

2.3.9. Chlorobromide Papers

Chlorobromide papers are projection-speed enlarging papers, used in many commercial applications. A distinction between such prints and the two preceding prints by visual inspection alone is almost impossible. The general earlier remarks about developing-out printing papers apply here also.

2.3.10. Resin-coated Papers

These photographic papers (in French called "papiers PE", for polyethylene) which were developed during the past 15 years or so, are grouped separately here because they have been shown to exhibit stability characteristics that are different from conventional materials. They are, of course, developing-out papers, and their sensitometric properties are likely to be the same as those of comparable materials on a non-RC paper base. Yet, the presence of a very thin polyethylene layer on either side of the paper sheet has made them suspect of being less stable than conventional black-and-white papers. FIGURE 7 shows a schematic cross-section of a resin-coated paper.

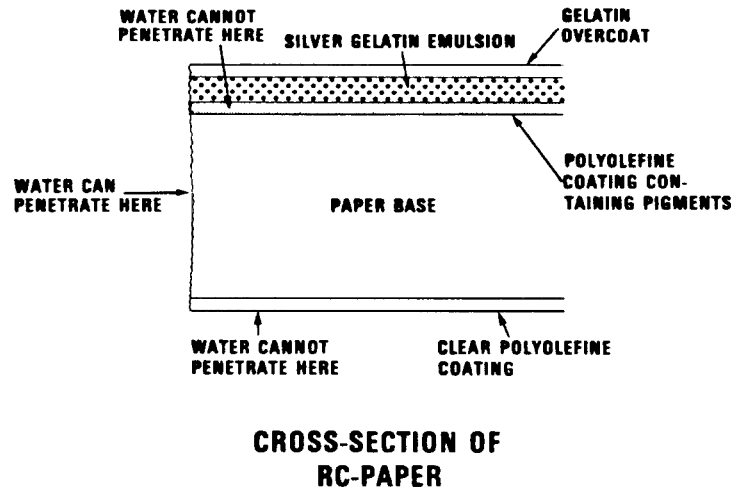


FIGURE 7: Schematic Cross-Section of RC Paper

2.3.11. Miscellaneous Historical Print Materials

The pictures in this group include print materials which are not classifiable according to properties of the silver grain, since too little is known about them. Examples are individually sensitized prints that were physically developed in gallic acid (1840s and 50s); printing-out papers that were developed (cf. 31, 32, 33); and solar prints, or sketch photographs, which consist of a weak silver photographic image (often a portrait) over which pen or ink were used to reinforce the picture (34,35).

2.3.12. Non-Silver Printing Materials

During the second half of the nineteenth century, when the potential instability of silver prints became apparent, many attempts were made to replace the silver with a more stable material, such as printer's ink or suspensions of carbon particles (lampblack) in gelatin. Numerous processes were in use at one time or another, but only a few have gained high rank and recognition for their perfect rendering of tones and their permanence. These are the Woodburytypes, carbon prints,

collotypes, and photogravures, as well as modifications of these processes. Other processes that must be mentioned here are handmade, non-silver pigment printing processes such as platinum prints, cyanotypes (blue prints), gum bichromate prints, and bromoil prints. All of the latter should be conserved as works of art on paper according to conventional prints and drawings conservation techniques. However, they will not be discussed any further in this study.

2.3.13. Miscellaneous Contemporary Print Materials

For reasons of completeness and of their wide-spread occurrence, some print materials are mentioned which have been developed during the past 35 years. Their principal purpose is to obtain a black-and-white print quickly. The more common of these are instant black-and-white print materials, made by the Polaroid Corporation since the late 1940s (36, 37); prints made, within a few minutes, by the stabilization process (38, 39), in which residual light sensitive silver salts are not removed by the fixing process, but are converted into another silver compound whose stability is limited; and dry silver prints by the 3M Company (40, 41), in which silver compounds other than silver halides are used. Prints produced by the latter two processes are not easily distinguished from conventional developed-out silver gelatin prints.

The principal groups of monochrome positive prints are summarized in TABLE 4. The logical basis of dividing silver prints, as shown in TABLE 4, is provided by the relationship between the size, shape and distribution of the silver grains in the binding medium and their resultant stability. Thus, the larger silver grains are more resistant to chemical and physical changes than the smaller ones, and those grains with a relatively large surface area in relation to their mass are more susceptible to react with chemical reagents than grains with a smaller surface. Photographic pictures made by

TABLE 4: PRINCIPAL GROUPS OF MONOCHROME REFLECTION PRINT MATERIALS

I. SILVER PRINTS

1. Printed-out Papers (P.O.P.)
 - (i) Salted paper prints
 - (ii) Collodio-chloride prints
 - (iii) Albumen prints
 - (iv) Silver gelatin P.O.P.
2. Developed-out Papers (D.O.P.)
 - (i) Chloride papers (contact speed)
 - (ii) Chloro-bromide papers (enlarging speed)
 - (iii) Bromide papers (fast enlarging papers)
3. Resin-coated Papers (all D.O.P.)
4. Papers not classifiable according to properties of the silver grain
 - (i) Individually sensitized prints physically developed with gallic acid
 - (ii) Developed printing-out papers
 - (iii) Solar prints and sketch photographs
5. Contemporary Rapid Processing Materials
 - (i) Stabilization prints (several manufacturers)
 - (ii) Dry silver prints (3M Company)
 - (iii) Instant black-and-white prints (Polaroid Corporation)

II. PAPERS USING NON-SILVER METALS, OR METAL SALTS

1. Platinum prints
2. Palladium prints
3. Cyanotypes

III. PAPERS USING NON-SILVER PIGMENTS

Examples: Gum bichromate prints, carbon prints, woodburytypes, carbro prints, bromoil prints, ozobrome Prints, oil prints, photogravure.

printing-out processes have silver grains of distinct properties which are quite different from the silver grains produced in developed-out prints. Within each of these two principal groups, the properties of silver grains differ again according to either the binding agent or to the respective amounts of silver halides that were built into the emulsion during manufacture. Resin-coated papers deserve a separate placement as a principal group, not only because of the polyolefin coating of the paper stock, but because that coating has a weakening effect on the stability of the silver grains in a processed print, when compared to the stability of the same type of silver gelatin layer coated on a fibre-base (non RC) paper.

2.3.14. Black-and-White Positive Transparencies

These materials were mentioned earlier as a product of reversal development of black-and-white negatives. A picture so obtained would be a camera original. Positive transparencies can, however, also be made by printing a negative onto a suitable black-and-white film. If the binding agent is gelatin, previous observations made about silver gelatin materials apply here also. Usually, positive transparent pictures are fine grain materials with a gelatin layer that is thinner than usual.

2.4. Colour Photographic Materials

Colour photography, as we know it today, came into being in 1935 with the commercial introduction of Eastman Kodak Kodachrome film, a subtractive colour process. The earliest commercial colour photographic process before that date was the Autochrome Transparency Plate made by Lumière in 1904. It used the screen plate process, which is based on the additive system of colour formation. Other manufacturers followed suit, of which the best-known products are the Finlay Colour Plate, the Dufay Colour Plate, the Agfa Colour Screen Plate, and the

Duplex Colour Plate. All of these products were rapidly superseded in the marketplace by the appearance of the subtractive systems of colour formation. The latter may be grouped into four major categories.

2.4.1. Chromogenic Development Processes

In these processes the dyes that form the final image are chemically synthesized during development. The first of these films was Eastman Kodak's Kodachrome (1935), followed closely by Agfa's Agfacolor films in 1936 and Eastman Kodak's Ektachrome films in 1940. Today, all camera films, with the exception of instant colour films, are based on chromogenic development: colour negatives and transparencies, and the majority of reflection colour prints. They are made by a handful of companies including Eastman Kodak, Agfa-Gevaert, 3M, and Fuji Photo Film. As about 85 percent of all photographs today are taken on colour films, these materials will play a tremendous role in future considerations for the conservation of contemporary photographic records.

2.4.1.1. Using External Dye Couplers (Kodachrome principle)

While in black-and-white processing the oxidized developer is discarded, it is utilized in colour photography to react, in a secondary step, with compounds known as dye couplers to form the dyes present in the finished product. According to the provenance of the dye couplers, three different groups of materials can be distinguished. In the Kodachrome process (42,43), the dye couplers are introduced from an external source, for example along with the developer. Consequently, no residual couplers remain in the finished picture. The processing, however, was - and remains to this day - a lengthy and complex procedure which can be carried out only by a few specialized laboratories.

2.4.1.2. Using Non-Diffusing Incorporated Dye Couplers

(Agfacolor principle)

In the Agfacolor transparency films, which were introduced commercially in 1936 (44, 45, 46), the three different dye couplers - one each for the formation of yellow,

cyan and magenta dye - were for the first time incorporated into three gelatin layers coated on top of each other. This was achieved by attaching long-chain molecules to the couplers, thus making them immobile, or non-diffusing, without affecting their photographic properties (47). In a single development, which could be performed by the user, all three dyes were formed simultaneously. Some drawbacks of this system gradually rendered it less and less effective, so that today it is used in only a few products.

2.4.1.3. Using Protected Incorporated Dye Couplers (Kodacolor principle, or Ektachrome principle)

In addition to its Kodachrome process, Eastman Kodak also developed in the 1940s a subtractive colour photography system with incorporated dye couplers (48, 49). In films and papers using the Ektachrome principle, the dye couplers are suspended in microscopically small droplets of an oily substance, hence the term oil-protected coupler process. To this day it remains the prevalent chromogenic development system.

2.4.2. Dye Imbibition Processes

Preformed dyes can be successively built up in a gelatin mordant layer from a printing matrix film to produce dye imbibition prints. The only procedure available in North America is Eastman Kodak's Dye Transfer Process (50, 51). In Japan, Fuji photo Film provides a similar process known as Fuji Dyecolor. Dye imbibition prints, whose production is painstakingly time-consuming, are used mainly by artistic photographers. Their role in an archives collection appears to be small.

2.4.3. Silver Dye Bleach Processes

In this process, preformed dyes, incorporated into the emulsion during manufacture, are catalytically destroyed imagewise during processing. The only material of this kind manufactured now is the Cibachrome Color Print Material by Ciba-Geigy in Switzerland (52, 53, 54, 55). It is distributed

in North America by Ilford. This material is not sensitive enough to be used for camera exposures, but it is suitable for the preparation of colour reflection prints and colour positive transparencies.

2.4.4. Dye Diffusion Transfer Processes

In 1965 the Polaroid Corporation of Cambridge, Massachusetts, U.S.A., surprised the world of photography with the introduction of the first instant colour photographic print process, now known as Polacolor 1 (56). In 1972, the non-peel-apart system SX-70 was introduced (57), followed by Polacolor 2 in 1975. In 1976, the Eastman Kodak Company marketed its instant colour print process under the name of PR-10 (58). In 1981 Fuji Photo Film of Japan announced the availability of its Fuji Instant Colour Film. Billions of pictures are taken annually on these materials, of which a sizable portion may be expected to find their way into museums and archives throughout the world.

Besides these four principal groups of colour photographic print materials, there are printing processes using pigments (for example, tricolour carbonyl) and modern electrophotographic methods. While the number of colour pictures made by the former appears to be small, many developments are in progress with respect to the latter and products are undergoing rapid changes. Not enough is known about their stability characteristics at this time. Neither will be discussed further in this study.

The foregoing is but a brief and simplified summary of the more important colour photographic processes. The classical histories of colour photography are by Wall (59) and Friedman (60). A purely technical account on colour photography is given by Evans, Hanson and Brewer (61). The volume by Mutter (62) summarizes technical developments in colour photography from its inception to 1967. A recent work in three volumes by Koshofer (63) contains an incredible amount of detail on the many different colour film and paper products made by the world's leading manufacturers. This work will soon be available in English also.

3. CHARACTERIZATION AND IDENTIFICATION OF PHOTOGRAPHIC IMAGES

There is no sure and quick way to identify photographic pictures. The exceptions are, of course, materials that have the manufacturer's logo and the brand name embossed or printed on them. There are a few simple laboratory tests, yet they are not always conclusive. Beyond that, complex analytical techniques have to be applied which require expensive instrumentation and - more important - the necessary expertise.

The best help in this respect is to gain experience in looking at photographs and working with them. Through experience it is possible to develop a degree of certainty about which type of film or photograph one is dealing with. Knowledge of the exact date of a photograph can eliminate some materials and narrow the alternatives down to a few. Several pamphlets have been published which are designed to guide the keeper of still photographic pictures through the amazing number of different types towards a recognition of the principal processes. Of these, the papers by Gill (64) and Bovis (65), the latter in French, are recommended.

3.1. The Support

Five predominant support materials have been mentioned earlier: metal, glass, plastic film, paper and resin-coated paper. In general, it should not be too difficult to identify each of these. The following remarks add some specific details.

There are only two important silver photographic images on a metal support: daguerreotypes and tintypes. The former, besides having a mirror-like appearance, are recognized, when disassembled, by their copper plate support. Tintypes, being on an iron sheet, can be identified, while remaining in their case, by holding a magnet to the cover glass: a tintype will be attracted to it.

While glass and paper are easily recognized, it requires some experience to identify resin-coated papers. Their back has a slippery feel to the touch, and when over-washed during processing the four corners curl upwards. The best laboratory technique for the identification of films and papers is the

microscopic examination of their cross-sections (Cf. FIGURE 7). It allows one to clearly distinguish between fiber-base papers and resin-coated papers and between developed-out and printed-out photographic pictures.

A glance at a cross-section of a photographic print through an ordinary light microscope allows the viewer to study the size of the particles and their vertical distribution throughout the gelatin. A developed-out print has distinct silver grains with an even concentration in the gelatin. By contrast, the particles in an albumen print - a printing-out paper which did not undergo development - are so small in size that they remain indistinguishable at a magnification of 400X. More silver can be seen to be accumulated towards the surface of the picture than on the side towards the paper base, indicating a concentration gradient for the silver particles. Light microscopy also reveals the presence or absence of a baryta layer, an important interlayer between the paper support and the gelatin layer. It does not, however, resolve the fine structure of the developed or printed-out silver particles, which can be studied only with the help of an electron microscope.

It may be useful to be able to distinguish between the three major film materials. Of these, cellulose nitrate, which was never used in the manufacture of microfilm, but was last manufactured as sheet film in 1939 and as motion picture film in 1951, is highly inflammable, and this property can be used for its identification. In fact, the American National Standards Institute (ANSI) specification for safety photographic film, ANSI PH1.25-1976 (66), defines details for the burning test conditions, such as sample size and burning time.

Another simple experiment consists of dropping a small punched-out film sample into trichloroethylene, an organic solvent. If it sinks to the bottom, it is likely to consist of cellulose nitrate. Often the word 'nitrate' is printed along

the edge of a film sheet. If a piece of film has the word "safety" printed on it, it is made either of cellulose acetate or of polyester. Of these two, cellulose acetate tears relatively easily, whereas it is virtually impossible to tear polyester materials. All the types of films can, of course, be analyzed chemically and thus unambiguously identified (67).

Other support materials, besides those described here, have been used throughout the history of photography, but their occurrence is rare. Examples are wood, linen, leather, ivory, and porcelain, none of which should be difficult to recognize.

3.2. The Binding Medium

Some early types of silver prints, as well as some non-silver prints, have no binding medium at all. Examples are salted paper prints, or platinum prints and cyanotypes (blue prints). Their surface, when viewed by reflected light, does not show any gloss. The picture has a somewhat flat look caused by the image-forming particles being partially absorbed by the paper fibers. Formstecher (68) has described some simple tests which help to determine the type of a photographic paper. If the binding agent dissolves in a bath consisting of equal parts of alcohol and ether, it is indicative of a collodio-chloride printing-out paper. If the image layer is insoluble in alcohol/ether, it can be tested in a waterbath of about 50°C. If the layer dissolves completely, it consists of gelatin. If it becomes only slippery and sticky, it could consist either of hardened gelatin, or of starch and starch-like materials. The testing is continued in glacial acetic acid, in which gelatin layers are completely dissolved, while starch materials remain unaffected. If the layer has neither dissolved nor swollen in hot water, it consists of albumen. Formstecher's article also contains valuable hints for identifying photographic prints based on their sensitometric properties such as scale index and rendering of shadow detail.

3.3. The Image-Forming Substance

A silver print can, with some practice, be recognized by its visual appearance (see preceding paragraph), image tone and, in older materials, often by a metallic blue sheen in the maximum density, or shadow, areas. Chemically, it is bleached by a potassium bichromate solution. With modern analytical techniques using X-rays, the presence of silver can be unequivocally determined in a non-destructive way. The importance of the fine structure of the silver and its distribution for purposes of identifying photographic materials has already been pointed out.

The examination of processed photographic materials with a transmission electron microscope (TEM) at magnifications of about 40,000 times shows a surprising variety of particles of different sizes and shapes, from very small spherical particles to compact silver grains and fine silver filaments resembling steel wool. The correlation between the size and shape of processed silver particles and important image properties has been studied for many years. Most picture-takers are familiar with the relationship between graininess and speed - or light sensitivity - of a film: the faster - or more light sensitive - it is, the grainier the image will be. In processed materials, other properties result directly from the size and shape of the silver grains. Examples' are contrast, covering power and image tone. Of importance to the preservation of photographic records is the observation that silver particles have a tendency to undergo chemical reactions, and therefore their stability depends to a large degree on their morphology. Large, compact particles are less prone to react with oxidizing agents than small, spherical grains of silver with a fine filamentary structure. The nature of these particles varies with the type of photograph and can thus be used to accurately identify a given black-and-white material. Moreover, the silver particles undergo characteristic changes upon fading or discoloration of a picture. The changes might

involve many small particles lumping together to form fewer, but larger, units or individual grains altering their structure. In this way, the nature of the deterioration can be determined precisely from electron microscope studies. Such information, in turn, may help us to decide with certainty whether a given restoration procedure will be successful.

In fact, preserving black-and-white photographic records amounts to understanding the chemical and physical changes in the nature of the elementary silver grains which, embedded in gelatin, form the image.

3.4. Organic Dyes

Dyes are the components present in the colour photographic materials listed earlier. Dyes, as opposed to pigments, may be described as being soluble and as undergoing some kind of chemical or physical link with the material to which they give colour. In modern colour photographs, that material is gelatin. They are commonly of an organic nature or origin. Except for monochrome photographs (for example, a cyanotype), all of the above-mentioned pictures contain dyes. Recognition is thus done visually. Since many thousands of dyes have been synthesized to be used for photographic purposes during the past 50 years in hundreds of processes by many manufacturers, only a complex chemical analysis can identify the precise nature of the dyes in any given photograph. Fortunately, such knowledge is usually not necessary in order to preserve them.

Colour photographs using pigments, which are mostly of a mineral, or inorganic nature, can be identified by microscopic study of cross-sections: the thickness of the gelatin layer varies with the density. Variations in density are achieved by changes in the thickness of the pigment containing gelatin layer. This is also true for monochrome pictures made by pigment printing processes, such as carbon prints, or Woodburytypes.

4. EXAMINATION OF PHOTOGRAPHIC MATERIALS AND THE STABILITY OF THEIR COMPONENTS

4.1. Techniques for the Examination of Photographic Materials

4.1.1. Visual Inspection

Visual inspection is the simplest, but nevertheless potentially one of the most effective means of examining photographic materials. Archivists and librarians, charged with the preservation of photographic collections, may gain experience in assessing the preservation conditions of materials under their control by looking for cracks, breaks, tears, missing parts as well as for discoloration, such as fading or yellowing. There are many types of surfaces (for example, mat, glossy, velvet, textured) as well as image tones occurring in various reflection print materials. Both are distinguishing characteristics of photographs. The better one's familiarity with them, the better one's ability to examine and evaluate the condition of the record under investigation.

4.1.2. Microscopy

The light microscope extends the ability of the human eye to see and identify details at various magnifications up to about 1000X. It is probably the single most important instrument in the conservation laboratory. The usefulness in examining cross-sections of films and papers has been pointed out earlier.

4.1.3. Densitometry

A densitometer, next to a light microscope, is the second most important instrument in a conservation laboratory for photographs. For transparent materials (negatives, slides) a transmission densitometer is used; for positive reflection prints, a reflection densitometer. However, modern instruments combine the ability to measure densities in both materials, whether black-and-white or colour. While in conventional fine art conservation (watercolors, oil paintings) colour and brightness changes are judged visually, densitometry permits us

to measure - and monitor - changes in the tonal scale of photographs quantitatively. Therefore it is indispensable in accelerated aging tests, the monitoring of photographic prints while on display, copying and duplicating work (where an original photograph has to be reproduced tone for tone) and in chemical restoration work. By measuring through the three colour filters, blue, green and red - in addition to the black-and-white, or neutral, density - changes in image tone can be determined. A densitometer is also necessary in controlling the processing (i.e., development, fixing, washing and drying) of photographic materials, in particular in monitoring the developer activity.

4.1.4. Chemical Laboratory Tests

These range from easily performed test tube experiments, such as the behaviour of the photographic layer towards water, acetic acid and alcohol, or the solvent test for the identification of cellulose nitrate film base, to the use of specialized techniques requiring complex instrumentation. Nearly all analytical methods common to a modern chemical laboratory can be applied to the examination of photographic materials, including chromatography, amino acid analysis, energy-dispersive X-ray spectroscopy and electron microscopy. While the photographic manufacturing industry routinely uses this type of equipment, conservation laboratories rarely have access to such facilities. In addition, there are many test instruments which have been developed by the manufacturers for quality control purposes and stability testing. They are usually not commercially available, but must be custom built from precise specifications. Examples are devices to measure the brittleness and curl of films and papers, the scratch resistance of the gelatin layer and its swelling in chemical solutions, its melting point and its adhesion to the support. Light sources of known intensity and spectral distribution in a climatically controlled environment, and incubation chambers using high temperature and relative humidity for accelerated aging tests are also part of this specialized equipment.

4.2. The Stability of the Support

This section and the following one summarize the Current knowledge of the stability of the major components of photographic materials.

4.2.1. Metal

Few observations have been published with respect to the stability of the metal support in either daguerreotypes or tintypes. Both appear to be rather stable, however, formation of rust has been observed at times on tintypes. Antonacci (69) has described this deterioration and proposed a method for rust removal.

4.2.2. Glass

Glass plates were the first transparent support material to be used for negatives, from which positive prints could be drawn with shorter exposure times than was possible with translucent materials. The major disadvantage of glass, as pointed out earlier, is its brittleness. Its outstanding dimensional stability is the reason why the glass plate negatives are still used in astronomical photography. Altman and Ball (70) as well as Burnnam and Josephson (71) have reviewed the spatial stability of photographic plates.

4.2.3. Paper

During the first two decades or so of photography, the paper used for negatives and for the subsequent printing of positive salt prints was often described as a 'fine quality writing paper'. It should be of even texture and free of chemicals that might interact with the image silver. During the 1850s, manufacture of paper for exclusively photographic purposes began, especially for the then prevailing albumen papers. Two companies, Blanchet Frères and Kléber in Rives, and Steinbach and Co. in Malmedy, had a virtual monopoly on the manufacture of the thin-base albumen papers throughout most of the 19th century. The location of the paper mills and the quality of their products was closely related to the purity and suitability of the water supply. Reilly's (21) recent review

Of the manufacture and use of albumen papers has been mentioned earlier. In addition to the references quoted in the second chapter, a most interesting historical treatment of the development of photographic papers, ranging from salted paper prints and non-silver pigment papers to the then most advanced, graded developing-out papers, was published by the Leonar Works in 1955 (72). More recent accounts of the manufacture of photographic papers have been given by Kasper and Wanka (73) and by Woodward (74).

Photographic papers have often been characterized in the technical literature by their sensitometric properties, i.e., their sensitivity to light, contrast, maximum density and scale index. Although this may seem too technical a subject for curators of photograph collections, an understanding of these properties will contribute greatly to the ability to identify photographic prints and to assess their state of preservation. One of the earliest investigations of the sensitometry of black-and-white photographic papers was carried out by Jones, Nutting and Mees (75). Jones, in 1926, published an important contribution on the contrast of photographic printing papers (76). More recent summaries on this subject were given by Centa (77) and in an anonymous discussion of the systematic identification of photographic papers (78). An important observation by Kieser (79) about the ability of the three major types of developed-out papers to be toned visually by selenium salt solutions led to a procedure for their identification: chloride papers undergo a marked change in image tone to purplish red or chalk red, whereas pure bromide papers become purple-black. Chloro-bromide papers assume tones that are between these extremes, depending on their original silver chloride content. Lastly, it should be mentioned that information has been published periodically about the properties of specific printing papers which were in the marketplace at a given time. Examples include a list of papers available in Germany in 1954 (80), a discussion of papers in

North America in 1960 (81), a report on darkroom tests of numerous papers in 1965 (82), and another survey of printing papers in 1967 (83).

None of the quoted articles can answer alone all questions about the stability of photographic paper prints. Together, however, they convey to the reader an excellent idea of the manufacture of these papers, the materials used to make them and their structure. Positive reflection prints are the final product of the photographic process and the more knowledge and understanding about their properties that becomes available, the more successful will be the efforts to preserve them. The older references are useful, as they apply to the kinds of photographic papers that were made at that time. While precise details of the manufacture remain trade secrets - and are moreover liable to be changed regularly - experience has shown that photographic paper is a product of outstanding quality that rarely poses severe conservation problems. It seems to be superior than any other type of record paper to be found in archives and libraries. A high alpha-cellulose content, freedom from aggressive chemicals, and special sizing agents that give photographic papers excellent wet strength, are but a few of the known properties. The type of mechanical treatment which the pulp undergoes in the paper making process and which determines the length of the paper fibers and their inter-connection is also of importance, but the exact know-how remains privy to the respective manufacturer. Lane (84) published some information on the properties of one manufacturer's photographic paper.

4.2.4. Resin-Coated Paper

Photographic paper, like many other types, consists of a sized tissue of fibers capable of swelling in water and interspersed with cavities. These are sponge-like properties, enabling the paper to absorb and retain both gases and liquids, unless they are washed out carefully. In order to lend to photographic paper water-impermeable properties - as possessed

by glass plates and plastic film - the paper base is coated on either surface with a thin film of plastic material (see FIGURE 7). Many different types of coatings were tried, before the industry settled on polyethylene about fifteen years ago. Right from the beginning, resin-coated papers (RC papers) were received with skepticism by fine art photographers and some segments of the photographic press. Dieuzaide's article (85) is a good example of a passionate and well-meant, but technically inaccurate plea against the use of RC papers. More detailed discussions about the stability of RC papers have been published by Parsons, Gray and Crawford (86) and Kolf (87). RC papers have much shorter processing times than fiber-base Papers (approximately four minutes as compared to about one hour), because processing solutions cannot penetrate into the paper. Therefore, there is no need for either extensive washing or long drying. Manufacturers generally provide users of RC papers with new processing guidelines. The above mentioned articles by parsons and Kolf point out the potential instability of RC papers caused by cracking of the RC layer. Such cracking has been observed on early colour prints and some types of black-and-white prints on RC papers. It has been determined to be the result of a photo-chemical oxidation of the polyethylene film. More recent types of RC papers have anti-oxidants built into the paper base which are expected to migrate into the polyethylene layer and there to counteract any oxidizing agents. One major manufacturer has recommended that conventional fiber-base papers should be used preferentially if maximum permanence of the print is the ultimate goal. However, many photographs are made for short term use in teaching or publishing and for similar purposes, and RC papers have a definite use in all such applications. The processing of RC papers requires only small amounts of wash water, thus contributing to the conservation of this valuable resource.

4.2.5. Plastic Film

The first plastic film materials which appeared on the market towards the end of the 19th century were made of cellulose nitrate. It is an inherently unstable material which becomes weak and brittle during natural aging. The major drawback, however, is its high inflammability. Several large fires have occurred in motion picture film exchanges and hospitals as a consequence of cellulose nitrate materials becoming ignited. Some of these fires may have been caused by spontaneous self-combustion of cellulose nitrate, while others may have been sparked by an external source of heat. Cummings et al. (88) have reviewed exhaustively the causes of spontaneous ignition of decomposing cellulose nitrate film. The hazardous properties of cellulose nitrate based motion picture film were described by Nuckolls and Matson (89) as early as 1936. Calhoun (90) pointed out that large amounts of densely packed cellulose nitrate material are required in order to create a possibility of spontaneous ignition. Still camera sheet film negatives, especially when kept in individual envelopes, do not pose a fire hazard, unless there is an external heat source, such as an electric light bulb, a burning cigarette, etc. One reason for the high inflammability is that the ignition temperature is significantly lower in aged cellose nitrate film than it is in freshly produced material. It may be as low as 120°F in old film materials. To make matters worse, decomposing cellulose nitrate film releases gaseous compounds which catalyze further degradation and have a damaging effect on the silver gelatin photographic records that may be stored nearby. This was demonstrated impressively by Carroll and Calhoun (91), leading to the important recommendation that cellulose nitrate films should be stored separately from other materials.

The last cellulose nitrate film for motion pictures was manufactured in 1951. Since the 1930s it had been gradually replaced by cellulose acetate film materials. The earlier products, so-called cellulose diacetate, may suffer from shrinking of the film base caused by the evaporation of plasticizer. The improved cellulose triacetate plastic films have been shown to have good long-term stability as demonstrated by accelerated aging tests and the behaviour of naturally aged films (92, 93, 94, 95, 96). The prevalent material in use today is polyethylene terephthalate, generally known as polyester. It appears under several trade names, such as Mylar, Estar or Cronar. Developed during the 1950s by Imperial Chemical Industries (I.C.I.) in England, it has been shown to be of outstanding dimensional stability and chemical inertia (97, 98, 99). One recent paper by Adelstein (100) not only presents new data derived from accelerated aging tests, but compares the properties of microfilm samples on cellulose triacetate and on polyester after 26 years of natural storage.

The American National Standards Institute has published specifications for silver gelatin film which are to be used for archival record on either cellulose triacetate or polyester film base (96, 99). Both film types, if they meet the ANSI requirements, were declared in 1977 to be permanent record materials. by J. B. Rhoads, then Head of the U. S. National Archives. (101, 102, 103) .

The knowledge of the precise nature of a film material is, of course, a big asset in its preservation. In this regard, it is reassuring to know that cellulose nitrate was never used in the manufacture of microfilm. With respect to motion picture films, Mees (104) published an excellent account of the various types of professional motion picture films manufactured by the Eastman Kodak Company, while Mathews and Tarkington (105) recorded a similar account for early types of amateur cinematography film materials.

4.3. The Stability Of The Binding Medium

Much less is known about the stability of the albumen and collodion layers prevalent in 19th century photographic materials than about the supports. Both materials tend to harden upon aging and become more impermeable to water or aqueous solutions as a result, cf. FIGURE 8.

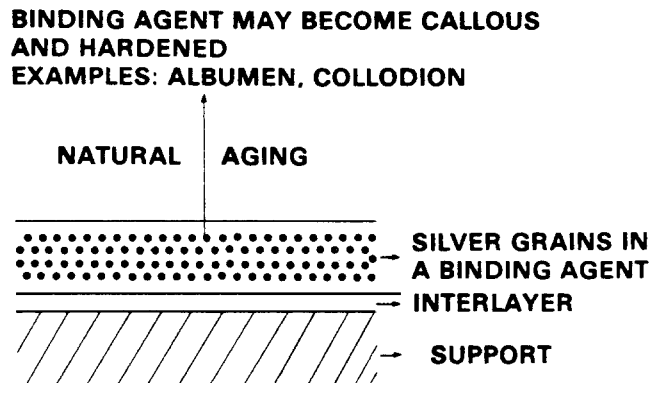


FIGURE 8: Schematic Representation of Changes in the Binding Medium

Wentzel (106) pointed out that the binding medium in collodio-chloride prints can form cracks in aged photographs. Often, they form clean curved lines on the print surface which are indicative of this material. In general, both types of coatings appear to be surprisingly stable, thus causing no problems for their preservation.

The properties of gelatin, an important material in photographic films and papers for about one hundred years now, have no doubt been studied extensively by the photographic industry, but not much data have been published about them. The outstanding property is its affinity for water, which it absorbs effectively, causing it to swell to such a degree that it may reach several times its original thickness) in the dry state, and continuing to do so until it literally dissolves into the water (107). In dry heat, however, it has been shown to be rather stable, comparable to the stability of cellulose

triacetate film base (108). Gelatin, when exposed to aggressive chemicals in filing enclosures or in the atmosphere, may become water soluble in time, as opposed to the hardening observed in albumen layers. It is a rare occurrence which, however, has happened at times. The two possible changes in various binding media are schematically shown in FIGURE 9.

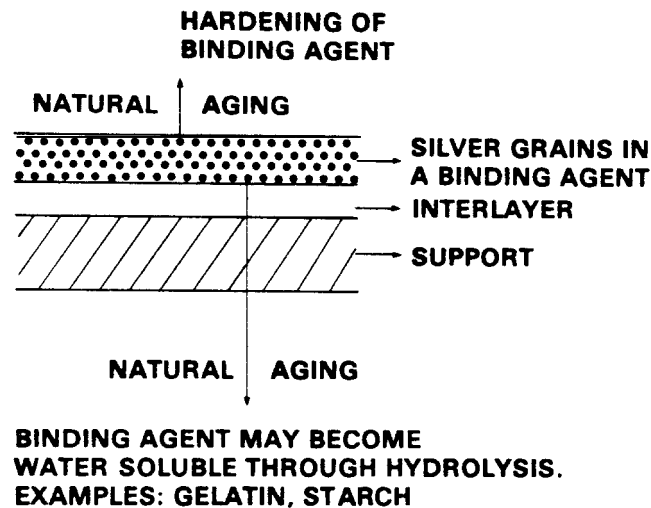


FIGURE 9: Schematic Representation of Changes in Various Binding Media

For many years, the photographic industry has counteracted gelatin's tendency to absorb water by treating it with chemical compounds known as hardeners. The effect of hardeners can be monitored by measuring the melting point of gelatin (109). Hardening is applied during manufacture as well as during processing, where hardeners may be incorporated in one of the processing solutions, usually in the fixing bath. Treatment of silver gelatin materials in a hardener also appears to be a useful step before proceeding with attempts to restore faded photographs in chemical solutions. In a study on emergency procedures for photographs, Hendriks and Lesser (110) have

found that hardened prints withstand soaking in water for extended periods of time better than the same types of prints which had not been pre-hardened. In the same study it was found that no significant changes in the properties of gelatin could be observed after it had undergone various soaking and drying cycles. It was concluded from these observations that gelatin, within a certain range of circumstances appears to undergo changes reversibly, until it reaches a breaking point, or point of destruction. There seems to be no gradual deterioration. However, when conditions are driven beyond a limit, destruction of the gelatin is irreversible.

4.4. The Adhesion Between the Support and the Binding Medium

This particular property - the strength of the bond between the support, such as glass, plastic film and paper on the one hand, and the binding agent, such as gelatin, collodion or albumen on the other - is sometimes considered to be a problem of importance in photograph conservation. In fact, it usually is not. From the days of the wet collodion glass plate negative on, support materials were usually specially treated or coated with an interlayer in order to provide or improve good adhesion. In the technology of film manufacture, it is known as a substance, which is sometimes called the subbing layer. The peeling off of the emulsion layer from its Support is, under normal circumstances, observed only rarely. In some cases, the albumen or gelatin layer can be found to loosen along the edges of a print or glass plate, a condition that has been called frilling. It is not a major problem. The situation changes when historical photographs are subjected to treatments in aqueous solutions. Tests must be carried out first in order to establish whether the binding agent, or its adhesion to the support, has become weakened. This is particularly necessary if a treatment requires the use of successive solutions having different pH values, where the pH value - most important characteristic of an aqueous solution - gives a measure of a particular solution's degree of acidity (or alkalinity).

4.5. The Stability of the Image-Forming Substance

4.5.1. Silver

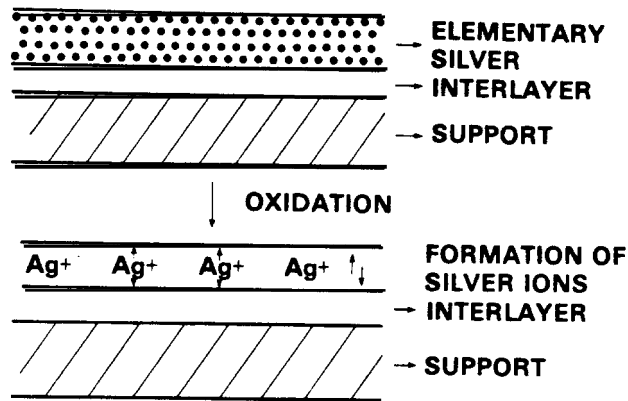
In all photographic processes that are based on the sensitivity to light of silver halides, the image-forming substance in the final picture - negative or positive - is finely divided silver, as has been pointed out earlier. It has also been mentioned already that silver, in the particular form in which it is present in photographic materials, is capable of reacting chemically with oxidizing agents. A visual discoloration of the photographic picture is a first indication that the image silver has been affected. The principal exception here is the staining of the gelatin layer which was, for example, caused by early tanning developers, such as pyro developer. It can be recognized in negatives in the clear margin along the edges, which should be colorless. If the picture-free margin in silver gelatin prints, particularly in photofinishing prints, is discolored to a yellow or light brown tint, it is most likely caused by the presence of residual silver salts, that is by incomplete fixing. Unless the paper base has been tinted, the margin of the silver gelatin print should be white. Incomplete fixing and inadequate subsequent removal of fixing compounds have long been considered one of the principal causes of discoloration, especially yellowing, of photographs. Correct processing procedures to prevent such discoloration will be discussed later. In recent years, however, other sources of chemicals have been identified as contributing to the discoloration of photographs. Weyde (111) observed that certain phenol-formaldehyde resins can produce gases harmful to photographic materials. Electrostatic office copiers can produce ozone, a reactive form of oxygen, which may react with image silver in photographs. Similar effects on photographs can be caused by exhaust gases emitted from automobiles, and other industrial gases. Feldman (112), in an elegant study, examined the effect of different types of house paints on the

discoloratio_n of photographic prints and found that alkyd based paints produce peroxides during drying which may react with image silver. Whereas latex-based paints were shown to be harmless, photographs should not be placed for display or storage in rooms that have been painted with alkyd-based paints for at least six weeks. Another example of the susceptibility of image silver in photographs towards oxidizing agents was discovered on processed microfilm camera original film rolls. Such reproductions of line copy documents (dark ink printing on white background) are negative pictures with a high silver content, where the letters appear as white, essentially silver-free, images, but the background as black area with a high silver density. Such film rolls are sensitive to a type of deterioration which is now known as the appearance of redox blemishes. The name was chosen because of the formation of these blemishes - microscopically small, usually circular, orange or reddish coloured spots - by a chemical oxidation-reduction mechanism. First reported about twenty years ago by Henn and Wiest (113), they have been shown to be caused by an attack on the image silver by oxidizing agents, particularly peroxides which are formed during the slow degradation of paper and cardboard materials. McCamy summarized the formation and characterization of redox blemishes in processed microfilm in a handbook published by the Us. National Bureau of Standards (114). Results of further research on redox blemishes were given by Pope (115), and survey studies of their occurrence were published by McCamy (116) et al. and Hendriks (117).

The foregoing observation indicates clearly that the permanence of black-and-white photographic materials is threatened largely by the presence of aggressive oxidizing chemicals. These may be present in the image layer or the support as a result of careless processing, in which case certain sulfur containing compounds provide the reactants, or from external sources by the presence of gases such as sulfur

dioxide, hydrogen sulfide, oxides of nitrogen, peroxides and ozone. Another potential source of reactive chemicals are materials with which photographic records are in close contact during storage, such as unsuitable filing enclosures or newsprint. The first step in the described image degradation is, chemically speaking, always an oxidation of elementary silver to silver ions, i.e., electrically charged particles. Silver ions can migrate through the gelatin layer and form silver compounds, usually silver salts. FIGURE 10 shows a schematic representation of this observation.

FORMATION OF SILVER MIRROR



SILVER IONS CAN MIGRATE
AND BE REDUCED TO
ELEMENTARY SILVER ON THE
SURFACE OR AT THE INTER LAYER

FIGURE 10: Schematic Representation of Image Silver Degradation

The blue metallic sheen which can often be observed on the surface of high density areas in historical silver gelatin negatives and prints, consists essentially of a very thin layer of elementary silver centered around silver sulfide nuclei. The presence of transfer images in the baryta layer of

deteriorated silver gelatin prints - visible after the image bearing gelatin layer has been stripped off - is further evidence for the ability of oxidized silver to migrate. Chemical reactions of this kind are made possible, and are accelerated, by the presence of moisture or high relative humidity. Silver ions, besides forming silver compounds, can under certain circumstances be reduced again to elementary silver which then may have a morphology different from that of the original image silver. Such changes are apparent in a different image tone. They can be measured with a densitometer. One particular form of elementary silver, the so-called colloidal form, is orange-yellow in colour and is produced in the redox blemishes observed in processed microfilm.

Silver gelatin photographic materials, if correctly processed, are essentially stable to dry heat and light. The often raised argument that light should have a deteriorating effect on the paper base of a photographic print does not take into account the presence of the baryta layer which, because of its specific purpose of providing a high reflectance of light, provides the underlying support with adequate protection. Long term exposure to light cannot, however, be recommended for salted paper prints and similar individually sensitized and processed, albumen prints, all so-called pigment prints and non-silver metal prints and modern resin-coated papers. The early prints, made during the first two or three decades since the beginning of photography on paper of unknown quality, were individually processed in a way essentially unknown to us today. Albumen prints have recently been observed to undergo changes upon prolonged exposure to light (personal Communication by J. Reilly and D. Munson). Prints with non-silver metal, metal salts and pigments as the image forming substance have likely been made on paper of inferior quality, as opposed to silver prints on paper which was produced specifically for photographic purposes (118). The caution against long term exposure to light of paper may be justified here. Finally, the possibility of photo-chemical oxidation of the polyethylene layer in RC papers has been pointed out earlier.

TABLE 5: PRINCIPAL FACTORS AFFECTING PERMANENCE

Temperature
Relative Humidity
Chemicals
 built into the product;
 from processing residues;
 from external sources, e.g. the atmosphere
Irradiation

TABLE 5 summarizes the principal factors which affect the stability of photographic materials. They are not listed in any order of priority, nor does each of the factors have an equal impact on all materials. Usually the combined action of two of the listed factors is required to produce a damaging effect on a photograph. As an example, certain chemicals used in the processing of photographic records, such as microfilm, may cause yellowing and discoloration of these materials when allowed to remain on them. A well-known example is residual fixing salt, commonly called hypo, a chemical that falls into the third group in TABLE 5. These residual chemicals will not cause staining at very low relative humidity of about eight percent (119). The presence of moisture is necessary to bring about a reaction between the hypo and the image silver. Another example is provided by the fading of colour photographs under the influence of light rays, in particular those at the violet end of the spectrum. However, such fading occurs at a much slower rate in the absence of moisture and oxygen, two other elements in TABLE 5. The presence - or absence - of moisture will eventually turn out to be the single most important factor controlling the longevity of photographic materials.

4.5.2. Organic Dyes

It was noted that in the majority of colour photographic materials organic dyes form the image, the exception being pictures made by pigment printing processes. Apart from varnish layers on oil paintings which display different behaviour in the dark than under exposure to light, dyes in colour photographs appear to be the first materials in a visual art medium that fade appreciably in the dark. 'In addition, like many other dyes in textiles, watercolors and printing inks, they fade when exposed to light. Consequently, the photographic industry monitors the stability of its products under so-called dark storage conditions as well as under light fading conditions. Dark storage stability is assessed under the influence of heat and high relative humidity alone, whereas light fading is monitored during constant temperature and relative humidity (20°C and 60%) while under exposure to light sources of known intensity and spectral distribution. The longevity of a colour photograph is defined as the time until the limiting dye - i.e., the weakest - has lost 10 percent of its dye density.

One of the earliest articles to describe methods for the measurement of dye fading in photographs was by Hubbell, McKinney and West (120). It laid the groundwork for the current specification of the American National Standards Institute (ANSI) for establishing methods for testing the image stability of processed colour photographic materials (121). Hubbell's paper described the methods for measuring the fading of dyes under various accelerated radiant energy and heat and humidity test conditions, which were referred to earlier as light fading and dark storage conditions. A most valuable paper on the preservation of motion-picture colour films having permanent value was published in 1970 by Adelstein, Graham and West (122). Notwithstanding the term 'motion-picture film', in the title of their paper, the authors provide a lucid description of the factors which affect the permanence of

processed colour films and present several options for long-term storage of these materials. The article also contains one of the earliest recommendations for the use of low temperature storage. Colour films can either be moisture conditioned to a relative humidity between 15 and 30% and stored at 0°F (-18°C) or below in hermetically sealed containers, or stored in a vault at 35°F (2°C) - just above the freezing point of water - at 15 to 30% relative humidity. In 1979, Tuite (123) published an article on image stability in colour photography, in which the value of the so-called Arrhenius equation, which describes the rate of a chemical reaction as a function of temperature, is emphasized for predicting the dark keeping characteristics of processed colour pictures. The article also presents data that clearly show the tremendous increase in the longevity of image dyes as the storage temperature decreases, provided the relative humidity is also controlled, for example at 40% for the data quoted by Tuite. That the Arrhenius equation can serve to make accurate long term stability predictions, when applied to data obtained from accelerated aging test conditions, was demonstrated convincingly by Bard, Larson, Hammond and Packard (124). Dye fading rates at room temperature and constant relative humidity which were extrapolated from data obtained at six different elevated temperature levels, were in close agreement with the actual dye fading observed on colour film samples kept at 24°C and 40% relative humidity.

Much less data are available on the light fading stability of processed colour photographic materials because of the many possible test conditions, such as spectral distribution of the fading source, its intensity, intermittence effects, etc. Recently, one major North American manufacturer has published data on both the dark-keeping stability and light-keeping characteristics of a number of their commercially available films and papers (125). These Current Information Summary pamphlets are illustrated by accurate colour reproductions

which demonstrate the visual effect on a colour photograph of incubation tests or of prolonged exposure to a high-intensity light source. Similarly, another manufacturer published data on the effect of ultraviolet radiation on colour prints made by two different companies which had been given a proprietary protective coating (126). The only other source of information on light fading characteristics of processed colour photographic materials comes from the results of independently performed comparative testing. Such data have been presented and reviewed by Schwalberg (127) and also by Wilhelm (128).

While the deterioration of the image silver in black-and-white photographs is, at least in theory, reversible, the destruction of dyes in colour photographs, due to changes in their molecular structure and caused by chemical agents as well as by exposure to light in the presence of oxygen and moisture, is considered to be irreversible. This thought is summarized in the following scheme, where Ag is the chemical symbol used by chemists for silver (from Latin argentum) and X is any combination of halides, i.e. chlorine (symbol: Cl), bromine (symbol: Br) or iodine (symbol: I):

In black-and-white photographs,



In colour photographs:

- (i) $\text{AgX} + \text{dye couplers} \xrightarrow[\text{oxidized developer}]{\text{exposure, processing}} \text{dye image}$
- (ii) $\text{dye image} \xrightarrow[\text{irreversible}]{\text{light}} \text{oxidized or decomposed dyes}$

This means in practice that, as far as is known, chemical restoration of faded colour photographs by converting oxidized or hydrolyzed dye fragments back into the original dyes, is not possible.

5. FACTORS AFFECTING THE PERMANENCE OF PHOTOGRAPHIC MATERIALS

5.1. Relative Humidity

Relative humidity (R.H.) is defined as the ratio of the absolute humidity of the measured air to that of air saturated with water at the same temperature (129).

$$\text{relative humidity} = \frac{\text{absolute humidity of measured air}}{\text{absolute humidity of saturated air}} \times 100$$

Since the absolute humidity of saturated air depends upon the temperature, relative humidity is also temperature dependent. Macleod (129) gives an excellent review of relative humidity and its effect on the behaviour of various materials. It is now well established that photographic materials based on the light sensitivity of silver halides (that is, the majority of still photographic records, all motion picture films and microfilms) are more sensitive to environmental conditions than most other materials to be found in libraries and archives. The destructive effect of high relative humidity on the stability of photographic images has been amply demonstrated throughout the history of photography: Gladstone (130) reported in 1892 on the effect of the humid climate in India on the permanence of bromide prints. In 1923, Deck (131) observed the stability of various types of photographic prints in tropical climates. Pouradier (132) determined that control of relative humidity is the overriding factor in the long term stability of photographs. More recently, Reilly (133) has found that relative humidity is the rate-controlling step in the yellowing reaction of albumen prints. It seems appropriate from the available evidence that relative humidity is the one environmental factor that must be controlled tightly because of its effect on the physical properties of materials and because the presence of moisture is a powerful catalyst of most chemical reactions: it promotes the foxing of album pages; the blocking, or sticking together, of gelatin layers;

the yellowing of albumen prints; the growth of mould; the formation of rust on metal cases, and other phenomena. Not only must the relative humidity in storage environments for photographs be kept at reasonable levels (for example, at 40%, Cf. chapter 9), but a chosen level must be maintained consistently. Cycling relative humidity conditions are used by the photographic manufacturing industry to artificially age films and prints for testing purposes. Such conditions (for example, low relative humidity during daytime, high R.H. at night) are particularly destructive in their effect on photographic materials.

5.2. Temperature

Temperature is, qualitatively speaking, the cause of our physical sensation of hot or cold. It is the cause for many other physical changes in matter. The majority of physical and chemical phenomena shows a dependence upon temperature. To the physicist the absolute temperature of an ideal gas is a measure of the mean kinetic energy of its molecules.

The effect of high storage temperatures (i.e. above 30°C) on photographic records has been well established. As a rule of thumb, the rate of chemical reactions doubles if the reaction temperature is raised by about 10°C. Conversely, low storage temperatures will cause a considerable decrease in the rate of deterioration reactions and are therefore beneficial for the long term preservation of archive materials. Cycling temperature levels are as detrimental to the longevity of photographic materials as cycling relative humidity conditions. They cause the expansion and contraction of materials, but such movements occur differentially in the structure of photographs: film support vs. gelatin emulsion, or paper base vs. albumen layer, etc., giving rise to various types of physical damage.

There are a number of instruments available that measure and monitor either relative humidity or temperature, or both simultaneously. Lafontaine (134) has written an excellent discussion of the various types of equipment which are commercially available.

5.3. Chemical Reagents

Chemical components which are capable of oxidizing image silver in photographs and which can be encountered in the environment have been mentioned earlier. They include peroxides, ozone, sulfur oxides, and nitrogen oxide. Elementary silver has a strong affinity for certain types of sulfur containing materials, forming a very stable compound called silver sulfide. Hydrogen sulfide, a colorless gas of unpleasant odour, which is a by-product of industrial activity and as such present in the atmosphere, can react readily with photographic image silver to form silver sulfide. Another source of sulfur-containing chemicals are certain residual processing compounds. The so-called fixing bath contains sodium, or ammonium thiosulfate dissolved in water, which serves to remove unexposed - and therefore undeveloped - silver halide salts. The thiosulfate portion of the fixing compound contains sulfur in a form liable to react with image silver if it is allowed to remain on films or papers. Special care must be taken to remove such residual compounds carefully from processed photographic materials intended for long term preservation (cf. chapter 7).

Chemical reagents which have been shown to have a detrimental effect on the permanence of photographic materials may originate from the degradation process of inherently unstable photographic films. The example of cellulose nitrate film base has been mentioned earlier (91). Finally, it is well established that certain filing enclosures (folders, sleeves, envelopes) are made of chemically unstable materials which may affect adversely the films or papers stored in them because of the close contact between photograph and envelope.

5.4. Irradiation

A good discussion of the nature of light and an explanation of concepts and units for the measurement of light is given by Macleod (135). It was mentioned earlier that correctly processed silver gelatin prints are essentially

stable to light, but that caution should be exercised with respect to the long term display of salt prints, albumen prints and the various non-silver pigment prints. Colour photographs are particularly susceptible to light fading. A general account of the effect of light on museum objects was given by Feller (136).

Although the four principal factors that affect the permanence of photographic materials have been discussed separately, it must be remembered that it is usually the combination of at least two of these which is particularly destructive, such as a chemical plus moisture, or light in the presence of moisture and oxygen.

6. DUPLICATING AND COPYING

The foregoing considerations have emphasized the structure of photographic materials and the factors which may effect their permanence. The objective has been to provide an understanding for the subsequent recommendations for the storage, preservation and restoration of these records. The dilemma that keepers of photograph collections face constantly is between the requirement that the images be used and at the same time be preserved. Brown (136) has stated that the value of any collection can be measured in terms of the amount of use that is made of it. Photographic pictures are used for historical research, for publications of all kinds and in exhibitions. This demand necessitates a number of abilities and technical facilities which allow photographs to be made accessible to users.

Negatives are 'used to make positive reflection prints, either by contact exposure or, if a print larger than the original negative is needed, by enlargement. If the deterioration of negatives is advanced, duplicate negatives are made. If positive prints are in such a condition that they cannot be handled safely anymore, a copy negative is made in a camera.

This chapter intends to review the principal methods of duplicating and copying photographic images. In the English language the term "copying" is used rather loosely by laymen to indicate various ways of reproducing photographically an original picture. In professional circles, a negative made from an original negative is a duplicate negative (same tonality, similar materials for both pictures) and similarly, a transparency (either in black-and-white or colour) from an original transparency is a duplicate transparency. If a positive picture is made from a negative - or vice versa - copy pictures are made. Thus a negative made in a camera from a positive print is a copy negative, likewise for a transparency from an original print (change of tonality).

6.1. Duplicating Black-and-White Negatives

The reasons for the duplication of historical black-and-white negatives are well known: the possibility of making prints from the duplicate negative available to users while saving the original from being handled; procuring a faithful record of the original if the latter requires restoration treatment; and the inherent instability of some plastic film bases. There are several potential ways to make a duplicate negative (144):

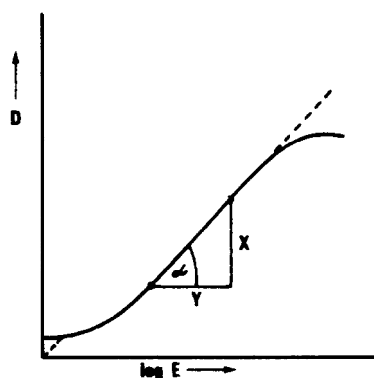
1. By using a suitable duplicating film to obtain an interpositive which may be exposed by contact to another sheet of film (either of the same type or a different type).
2. By using a direct duplicating film, sometimes referred to as autopositive film.
3. By using a suitable fine-grain copy film which may be reversal developed.
4. By making a positive print on paper from the original negative which may then be copied in a camera to produce a copy negative.
5. By using an instant black-and-white material, such as Polaroid Type 665 Positive/Negative Land Film.

of these, reversal development is difficult to control, and making a copy negative from a print which was made from the original negative leads inherently to inferior results for sensitometric reasons (difference between paper exposure scale and negative density range). Using an instant black-and-white material, as suggested in option no. 5, is an economical way which has been used in at least one major photograph collection in England, even if the results may be expected to be slightly inferior.

A review of the photographic literature reveals that only a few authors have dealt with the topic using sensitometric concepts. While many writers have treated the subject somewhat superficially, Crabtree (137) has given a concise procedure for

making a duplicate via an interpositive. Many procedures were published which described the use of direct duplicating films, which were first introduced by Agfa in 1933 (138, 139), followed by Eastman Kodak's Safety Autopositive Commercial Film in 1938 (140). These films can be placed in contact with a negative, exposed to a point light source, and developed directly to a negative. The principles of motion picture duplication have been well reviewed by Capstaff and Seymour (141), Ives and Huse (142) and by Crabtree and Schwingel (143). Their observations are pertinent for the duplication of negatives in general. Hendriks, Madeley and Toll (144) have recently presented the results of a study on duplicating historical black-and-white sheet film negative by contact exposure, using a variety of film materials for the interpositive as well as a direct duplicating film. In this study, the use of an optical system (camera, enlarger) was avoided. The original negatives were exposed by contact, thus maintaining their original format. In order to obtain a faithful duplicate from a historical negative, the density range of the original negative must be placed on the straight-line portion of the characteristic curve of the duplicating film. FIGURE 11 shows a generalized characteristic curve of a light sensitive film.

CHARACTERISTIC CURVE
(H&D CURVE)



$$f = \text{tang } \alpha$$
$$\text{tang } \alpha = \frac{\Delta X}{\Delta Y}$$

FIGURE 11: Characteristic Curve (or H&D Curve) of a Photographic Material

It is sometimes called the H & D curve after F. Hurter and v. C. Driffield (145), who first studied the reaction to light of silver halide photographic materials in a systematic way. It shows how a film - or paper - responds, after development, to receiving increasing amounts of light exposure. Ideally, the response, i.e. the formation of density, would be a linear one. If the characteristic curve of a film, which shows the build-up of density (a logarithmic number) against the log exposure, were a straight line rising at an angle of 45° to the abscissa, that film would produce an ideal tone reproduction. Such is never the case. Instead, the characteristic curve of photographic films and papers have a region of underexposure, the so-called toe region, where an increase in exposure causes little or no increase in density.

When a nearly proportional response is reached, the curve turns into its straight-line portion, i.e. the region of correct tone reproduction. The curve finally reaches a point where it flattens out again: an increase in exposure causes no further increase in density. The maximum density (D_{\max}) is reached. This part of the characteristic curve is called its shoulder. An essential requirement in quality duplicating work is to make use of the straight-line portion of the characteristic curve of the duplicating film. A second requirement is that the duplicating film must have a high density range so as to be able to accommodate the density range of the original negative. Density range is defined as the difference between the maximum, or highlight density with recognizable detail and the minimum, or shadow density (D_{\min}) with details. Therefore, at the beginning of any duplication work, the characteristic curves of the film, or films, to be tested are determined in order to establish density range, straight-line portion and the slope of the curve. The extent of the curve, i.e. the maximum density, and its slope, i.e. the rate at which it reaches D_{\max} , are indicative of the contrast

of a film or paper. Contrast depends on the film itself, the exposure, the choice of developer and the development time, and thus can be controlled by changing these variables. In practice, the film material, if it is at all suitable for the chosen purpose, and the exposure can be kept constant. The required properties of copy films in order to be considered suitable for duplication work are summarized as follows:

1. They should have a high density range in order to accommodate the density range of the original negative.
2. Their resultant characteristic curve of the tone reproduction system must have a long straight line portion, which will accommodate the density range of the original negative.
3. They must be capable of being developed to gamma unity, where gamma is the tangent of the angle alpha (see FIGURE 11) , and an indicator of contrast.
4. They must have fine grain and high resolution.

It is useful here to recall the orientation of the image when it is duplicated. FIGURE 12 demonstrates that a negative image formed in a camera is upside down and laterally reversed.

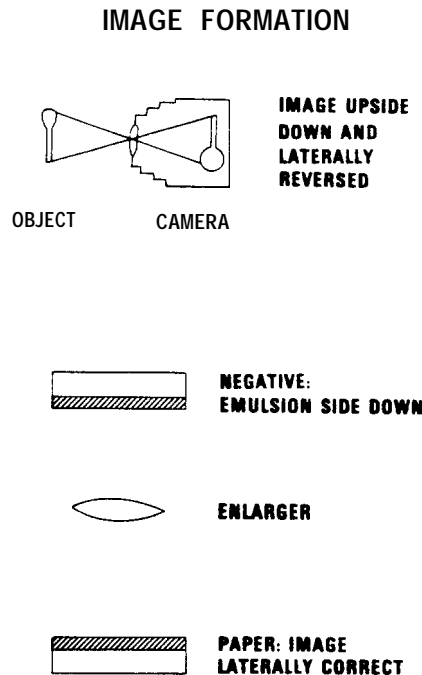


FIGURE 12: Image Formation in Camera and Enlarger

This situation is corrected if the negative is placed in an enlarger with the emulsion side down. In contact printing it is placed emulsion to emulsion with the printing paper. The emulsion layer is the shaded layer in the schematic FIGURES 12 to 14. When duplicating an original negative by the two-step method, i.e. via an interpositive, it is clear from FIGURE 13 that the interpositive (as would be a positive reflection print) is laterally correct (being printed from a laterally reversed negative) and that the final duplicate negative is laterally reversed, as is the original - and as it should be.

DUPLICATING

I. TWO-STEP METHOD

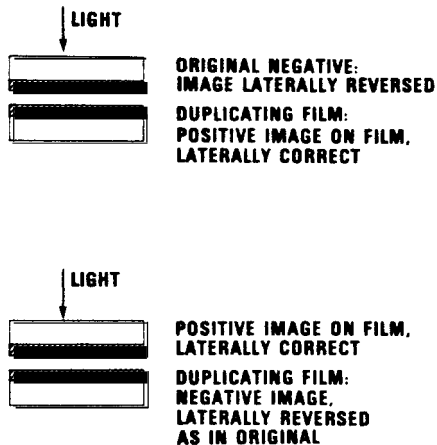


FIGURE 13: Maintenance of Image Orientation in Negative Duplication

However, when using a direct duplicating film, it would be preferable, for maximum sharpness to be achieved, to expose it to the original negative emulsion to emulsion, as shown in FIGURE 14(a). Such a duplicate negative is laterally correct and must be printed emulsion side up in the enlarger. In order to obtain a laterally reversed duplicate negative, as in the original, the arrangements shown in FIGURE 14(b) and 14 (c) can be used. Exposure is taking place either through the base of the duplicating film, or through the base of the original negative.

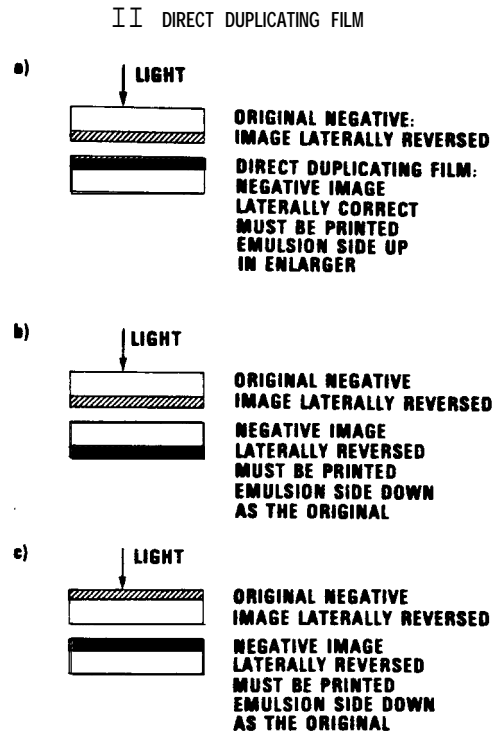


FIGURE 14: Negative Duplication Using Direct Duplicating Film

Both procedures are objectionable, but the latter one is more likely to yield an unsharp duplicate negative, because of possible physical (abrasion!) and chemical (staining!) deterioration of the old film base. A duplicate negative obtained by the procedure shown in FIGURE 14(a) must be marked somehow to indicate that it is laterally correct and therefore needs to be placed in an enlarger with its emulsion side up.

6.2. Copying the Black-and-White Print

When compared to the duplication of negatives, the difference in the exposure scale of papers as compared to the density range of negative films constitutes the main problem of this activity. Rudd (146) has published an authoritative account on copying black-and-white reflection prints using a camera. The principal requirement is the same as described for negative duplication, that is to make use of the straight-line portion of the characteristic curve of the copy film in order to obtain good tone reproduction. However, experimental details cannot be discussed here within the scope of this study.

6.3. Copying of Other Materials

The duplication and printing of black-and-white films in long rolls, such as microfilms or motion picture films, is done in machines specifically designed for that purpose. It is usually contracted out to special processing laboratories. The same is true for the duplication and printing of colour photographic materials: it is rarely done in-house by archives and libraries, but is performed by specialized laboratories.

6.4. Autoradiography

A particular type of copying has been developed during the past twenty years, which has been erroneously referred to as 'restoration.' It is a contact copying procedure for the copying of faded photographs. It was discussed earlier that the silver in discolored and faded photographs has been converted into silver salts which may be yellow or brown. In autoradiography the silver (whether present as salt or in elementary form) is made radioactive, and the so prepared print is placed in contact with a sheet of radiographic film, which is exposed imagewise by the radiation. Such experiments were carried out by Sayre using neutrons from an atomic reactor as the source to make the silver radioactive, and reported by Ostroff (147). Good copies could be obtained from completely faded photographic prints. Since atomic reactors are usually not available to conservation laboratories, attempts were made to simplify the procedure. Houtman (1967) used radioactive toners (gold and selenium salts) to obtain radioactive silver in the photograph. Askins reported first in 1976 (148) the use of radioactive thiourea which would react with image silver to produce radioactive silver sulfide. The method has reportedly been used to intensify underexposed medical X-ray pictures and for copying of faded historical photographs.

7. THE PROCESSING OF CONTEMPORARY BLACK-AND-WHITE
PHOTOGRAPHIC MATERIALS FOR MAXIMUM POSSIBLE PERMANENCE

It has been mentioned earlier that among the chemical reagents, capable of reacting with the image silver in photographs, certain residual processing chemicals play an important role. Attempts to eliminate these compounds have led to procedures which are often referred to as 'archival processing". They are more elaborate for photographic prints than for films, since the paper base can absorb and retain processing chemicals which may prove to be detrimental to the permanence of the picture. These chemicals must be removed by special washing procedures. Since plastic film base does not absorb aqueous solutions, the processing of films is somewhat less complicated. While residual developer compounds have not been shown to have a detrimental effect on the stability of photographs, the choice of the developer can have a marked influence on the morphology (size, shape) of the processed silver grain and therefore on its stability. The removal of residual fixing salts (sodium or ammonium thiosulfate; trivial name: hype) has been recognized in the early days of photography, as is shown by some articles published in 1866 (147). Since then much literature has been published on the subject which cannot be reviewed here entirely. An excellent recent summary of the problem with emphasis on the effect of the pH of processing solutions was given by Eaton (150). Special salt solutions designed to aid in the removal of residual fixing compounds were proposed as early as the end of the 19th century. Weyde (151) pointed out in 1933 that a final treatment of photographs in a dilute solution of sodium carbonate in water could be used to improve the permanence of photographic prints. Much experimental work on the subject was carried out and its results published in the 1940s and 1950s by Eaton and Crabtree (152), Crabtree, Eaton and Muehler (153), Crabtree, Henn and Edgerton (154), Henn, King and Crabtree (155), and Crabtree, Eaton and Muehler (156). As a consequence washing aids were introduced commercially in North America.

There are two main groups according to the mechanism of their action: the hypo clearing agents and hypo eliminators. The former consist primarily of a simple salt solution which has been found to accelerate the washing rate for films and papers, following the discovery that sea water was effective in washing films and prints, provided they were rinsed afterwards in fresh water (152). The effectiveness of hypo clearing agents appears to be based on a simple ion effect caused by an increase in the polarity of the wash water. Hypo eliminators, on the other hand, are oxidizing agents which chemically convert unwanted fixing salts into compounds (sulfates) which are washed out faster than thiosulfate and are not likely to react with image silver even if traces of it would be allowed to remain in the film or paper. Elaborate procedures for archival processing have mostly been suggested for paper prints, since for films a short treatment in an approximately 2% sodium sulfite solution, the most commonly used hypo clearing agent, was considered to be effective in removing harmful fixing compounds. Thus, a traditional procedure for the processing of fibre-base prints employs (after treatment in a developer followed by a stop bath to arrest the developing action) two successive hardening fixing baths, of which the second must be a freshly prepared solution. The presence of a hardening compound in the fixing baths has the undesirable side effect of rendering the fixing salts more difficult to remove from the material. Consequently, the print is, after a short rinse in water, treated in a hypo clearing bath for a few minutes. After a twenty-minute wash, the print is treated in a hypo eliminator bath consisting of a solution of hydrogen peroxide in ammonia. This procedure indicates that fixing prints in a hardening fixing bath for several minutes requires special measures, i.e. the use of both a hypo clearing bath and a hypo eliminator. An even more stringent procedure has been published by the American

National Standards Institute (157). It also makes use of two fixing baths, but they do not contain a hardening agent. In spite of this, both a hypo eliminator solution and a hypo clearing agent are prescribed to ensure complete removal of residual fixing compounds. Recently, a European manufacturer published recommendations for the processing of a new fibre-base enlarging paper. After development and stop bath, the print is fixed in a non-hardening rapid fixer for 30 seconds. That the fixing time for a bromide paper, using a non-hardening fixer, is less than 30 seconds was established by Lumière et al. about 60 years ago (158). A so-called rapid fixer, which contains ammonium thiosulfate instead of the sodium salt, requires even shorter fixing times. The advantage of a 30 second fixing time is that the paper base cannot absorb large quantities of fixing salts. As a result, there simply remain very small amounts of residual fixing compounds which have to be washed out. A proprietary washing aid solution is then used to complete the processing. In all procedures, prints are air dried to prevent possible contamination from a drying belt or drum.

Mention must be made here of methods to determine the presence of residual silver salts in a processed record (indicating incomplete fixing), and of residual fixing salts which would point to insufficient washing. Qualitative tests for residual silver compounds are outlined in a publication by the Eastman Kodak Company (159), One using a 1.6% aqueous solution of sodium sulfide which, in the presence of silver salts, would form a yellow or brown stain. The other employs a rapid selenium toner solution. A qualitative test for residual fixing compounds ("hypo test") uses a dilute acidic solution of silver nitrate which also forms a yellow stain of silver sulfide in the presence of residual fixing salts. This test can be modified to serve as a quantitative method for the determination of residual fixing compounds. It is then called the silver densitometric test, which has become a method of

the American National Standards Institute (160). The same standard, ANSI PH4.8-1978, also describes the so-called Methylene Blue Method for measuring thiosulfate in processed films which is used particularly in the microfilm industry.

In summary, the objective of such procedures is to obtain photographic materials that are essentially free of residual fixing salts, as these compounds have been shown in the past to contribute to the discoloration of these materials. For over one hundred years, a procedure known as toning has been used either as an integral part of processing or as post-processing treatment of developed and fixed photographs. The word toning indicates that the process causes a change in the image tone of a processed photograph. For example, untoned printed-out pictures are either brown, reddish-brown or even chalk-red. Toning with a solution of a gold salt shifts the image colour to colder tones, i.e. to purple, blue-black or, at times, to neutral black. A second effect of toning procedures is an increase in the stability of the, image silver. When photographic prints are treated with solutions of certain metal salts, the image silver may be converted either into a more stable compound, possibly even an alloy, or covered with a protective coating of a noble metal (161). While the exact mechanism of the toning reaction does not appear to be well understood (162), the protective effect of such treatments has been well established. When toned prints are exposed to oxidizing or sulfiding atmospheres, discoloration occurs at a much slower rate than that observed in untoned prints. The oldest method of toning appears to have been the use of gold salts. The majority of printed-out photographic pictures, in particular albumen prints, were gold toned. A second procedure involves the conversion of image silver into stable silver sulfide. It is interesting to note here that silver sulfide formation in negatives and prints is a major reason of discoloration if it occurs unchecked and irregularly. In the process of toning all image silver is, of course, converted

into silver sulfide in a controlled and consistent fashion. Nitze (163) has written an excellent study of the sulfide toning process with emphasis on procedural details that must be observed in order to obtain permanent pictures. The use of selenium salts as toning agents was introduced at the beginning of the 20th century in Germany (164). Selenium salts are widely used for the toning of prints, however their application to negatives is also possible (165). The use of a selenium toner to distinguish between bromide and chloride prints has been pointed out earlier. Many other solutions of metal salts have been proposed for toning purposes in the literature, including those of other noble metals such as platinum and palladium, but solutions of gold, selenium and sulfide are to this day the most widely used and most intensely studied.

The use of toning procedures has recently gained renewed significance. Early silver gelatin photographic materials, for example those made around the turn of the century, had a higher silver content than contemporary products. Manufacturers have learned how to decrease the amount of expensive silver salts without sacrificing important photographic properties, such as sensitivity, sharpness, contrast and maximum density. In order to do so with less silver salts, it is likely that more filamentary silver with a large surface area is present in contemporary processed black-and-white materials. This form appears to be more susceptible to chemical attack than earlier materials. It was acknowledged by at least one manufacturer through the recommendation that one particular film be treated in a selenium toner in order to maximize the permanence of the final image (166). A new fixer has also been developed for use in processing that particular film, although its formula has not been made public. About twenty years ago, a recommendation was made to add 0.2 g potassium iodide per litre to the fixing bath in order to increase the resistance of the image silver to the formation of redox blemishes in microfilm (167). It is

recalled here that microfilm is a high contrast material, of slow speed and fine grain, which is likely more readily attacked chemically than more coarse grained materials. The recently observed tendency of prints on resin-coated paper to develop discoloration of orange-yellow spots after years of display might also be prevented by toning these prints after processing. It is believed that the presence of a pigmented polyethylene layer below the silver gelatin layer prevents the migration of oxidized silver (silver ions) into the paper base, which would effectively remove them from catalyzing further oxidation of image silver. In fibre-base prints the baryta layer and the paper base could act as a reservoir into which silver ions could migrate, thus keeping them away from participating in further reactions. Therefore toning procedures will likely play - once again - an important part in the processing of contemporary photographic materials. Because of the very high price of gold and its compounds, and because of the marked shift in image tone to brown colours obtained in sulfide toning, selenium salts will likely find wide-spread application as the toner of choice.

8. TESTING OF PROCESSED PHOTOGRAPHS AND) OF MATERIALS USED IN THEIR CONSERVATION

The testing of photographic materials during and after manufacture and after processing has been performed by photographic manufacturers for many decades, mainly as part of quality control procedures, but also in order to investigate and understand customer complaints (168,169). While the nature of many of these tests either remain proprietary knowledge of the manufacturer or are too complex to be carried out by conservation laboratories, others are part of standard specifications of ANSI. In these tests, processed photographic pictures are exposed to exaggerated environmental conditions in order to enable the user to observe changes in them within a reasonable time, usually 30 days. The pictures have the form of test strips on which is printed a so-called grey scale. It consists of a series of zones (either eleven or up to 21) of equal density representing the highlights, midtones and shadows of a photograph. When accelerated aging studies are performed (sometimes called incubation studies) the test samples are exposed to a combination of high temperature and high relative humidity in the dark. An example is the test of the effect of accelerating aging to determine the quality of processing in black-and-white photographic prints as specified in ANSI PH4.32-1980 (157). The test sample is exposed to a temperature of $30^{\circ}\text{C} \pm 1^{\circ}\text{C}$ ($100^{\circ}\text{F} + 2^{\circ}\text{F}$) at $94\% \pm 4\%$ relative humidity for 30 days to test for optimum processing. Another example is the humidity cycling adhesion test (96, 99), during which a sample is kept at $50^{\circ}\text{C} \pm 2^{\circ}\text{C}$ ($122^{\circ}\text{F} \pm 4^{\circ}\text{F}$) and $96\% \pm 2\%$ relative humidity for eight hours, then for 16 hours at the same temperature, but at $11\% \pm 2\%$ relative humidity. Such a cycle is repeated twelve times before the sample is evaluated. In another test, the photographic sample is exposed in a desiccator to an oxidizing or sulfiding atmosphere ("gas fading") (167). Conditions for light fading of processed colour photographic materials have been described by Hubbel, McKinney and West (120).

As in the conservation of works of fine art, where traditional materials have been questioned as a result of tests in order to be replaced by more suitable ones, the question which mount boards, filing enclosures, and storage cabinets can be used with photographs, without running the risk of damaging them, has received much attention in recent years. Another specification of ANSI deals specifically with that question by proposing a photographic activity test which serves to distinguish between high quality and poor performance filing enclosures (170). The envelope sample to be tested, which may be of either paper or a plastic material, is placed in close contact with a representative sample of the type of photograph that is to be stored in the envelope in question. If albumen prints are to be kept in that envelope the test photograph must be an albumen print, or if a Dye Transfer print is to be stored, the test must be carried out using a Dye Transfer print, etc. The combined test photograph and filing enclosure sample are kept at a temperature of $50^{\circ}\text{C} \pm 1^{\circ}\text{C}$ ($122^{\circ}\text{F} \pm 2^{\circ}\text{F}$) and $86\% \pm 2\%$ relative humidity for 30 days. After that period there must be no sticking together of the two materials, no transfer of fibers from the paper to the gelatin layer of the photograph, no discoloration of the photographic image. etc. The test allows to distinguish between various filing enclosures and to determine those which are suitable.

Most of these tests can be carried out with relatively simple equipment. The quoted references describe the requirements and how the specified conditions can be achieved. Performing these tests leads to an experience and understanding of the behaviour of photographs under aggravated conditions and of the effects which may cause - or prevent - their degradation.

9. PRESERVATION AND STORAGE

The factors which affect the permanence of processed photographic materials have been discussed in detail in chapter 5. The objective of preservation efforts is to set up storage conditions which are conducive to the longevity of these records. Such conditions should obviously include controlled and constant temperature and relative humidity conditions, an environment free from aggressive chemicals and, for display purposes, moderate light levels. The influence of light appears to be minimal in normal storage, as photographic materials are usually kept in boxes and cans (microfilm, motion picture film) or sleeves, envelopes and albums (still photographic negatives and prints). The American National Standards Institute has published four specifications with respect to the storage of processed photographic records which are summarized in TABLE 6.

TABLE 6: CURRENT ANSI STANDARDS REGARDING THE STORAGE OF PHOTOGRAPHIC RECORDS

Subject	Standard
Film	ANSI PH1.43-1981 "Practice for Storage of Processed Safety Photographic Film"
Plates	ANSI PH1.45-1981 "Practice for Storage of Processed Photographic Plates"
Papers	ANSI PH1.48-1974 "Practice for Storage of Black-and-White Photographic Paper Prints"
Filing Enclosures	ANSI PH1.53-1978 "Requirements for Photographic Filing Enclosures for Storing Processed photographic Films, Plates and Papers"

ANSI PH1.45-1981 ("Practice for Storage of Processed Photographic Plates") recommends a storage temperature of between 15°C and 25°C (59°F-77°F), but preferably it should be below 20°C (68°F). The relative humidity can vary between 20% and 50% but should preferably be below 40% and must, as has been emphasized earlier, of course be constant, whatever level is chosen between the two limiting values. Similar values have been given in ANSI PH1.48-1974 ("Practice for Storage of Black-and-White Photographic Paper Prints"): acceptable storage temperatures are between 15°C and 25°C (59°F-77°F), but should never exceed 30°C (86°F). Daily cycling of more than 4°C (7°F) should be avoided at any level. Relative humidity should be kept between 30% and 50%, but must never exceed 60%. Specification ANSI PH1.43-1981 ("Practice for Storage of Processed Safety Photographic Film") is the most specific of the three documents. While it does not cover the storage of films with a cellulose nitrate base, it provides recommendations for both short term storage (of up to ten years) and archival storage (of up to 100 years) of microfilms, motion picture films, historical still photographic negatives and other images on a safety film base. They are summarized in TABLE 7.

The distinction of short term storage from archival storage is significant, as many photographic materials need not to be retained beyond a limited time period and therefore can be kept under less stringent conditions. The requirement that the relative humidity must not exceed 60% is recurring for a good reason: bacteria and mould growth are encouraged to develop in photographic gelatin layers if kept at 65% relative humidity or higher. An optimum average value of the various levels from PH1.43 is 35%. If relative humidity can be maintained at that level in a storage area for photographic materials, the most powerful factor determining the permanence of these records is well under control.

TABLE 7: PRACTICE FOR STORAGE OF PROCESSED SAFETY PHOTOGRAPHIC FILM: KEY RECOMMENDATIONS FROM ANSI PH1.43-1981

A. SHORT TERM STORAGE

Storage Temperature

- (i) Preferably below 21°C (70°F)
- (ii) If possible not above 24° (75°F)
- (iii) Peak temperature not above 32° C (90°F)

Relative Humidity

- (i) Below 60%
- (ii) For polyester film base: not below 30%

B. ARCHIVAL STORAGE

STORAGE TEMPERATURE

Preferably not above 21°C (70°F)
Low-temperature storage may provide added protection.
For colour film: preferably 2°C (35°F)

Relative Humidity

The optimum storage relative humidity varies with the product type.

Sensitive Layer	Base Type	Recommended Relative Humidity
Microfilm:		
Silver gelatin	Cellulose ester	15-40%
Silver gelatin	Polyester	30-40%
General:		
Silver gelatin	Cellulose ester	15-50%
Silver gelatin	Polyester	30-50%
Colour	Cellulose ester	15-30%
Colour	Polyester	25-30%
Diazo	Cellulose ester and polyester	15-30%
Vesicular	Polyester	15-50%

Notable is the lack of specifications for maximum permissible levels of air pollution, such as caused by sulfur dioxide, peroxides, hydrogen sulfide etc. Simple and inexpensive instruments which could determine the concentration of each pollutant present in the environment do not exist. Furthermore, no data have been published that indicate what the threshold values for each of these oxidizing gases are, above which chemical attack on a photograph will occur.

The most important factors governing the longevity of photographs should be controlled by the building in which the collections are stored: it must be air-conditioned with independent temperature and relative humidity control, and the incoming air must be washed of soluble components and freed of solid and dust particles. Ideally it should have cold storage vaults with complete relative humidity control. Storage areas, which should never be located in a basement (flooding!), must be equipped with thermohygrographs, instruments that measure and record continuously the surrounding temperature and relative humidity. The storage building should be equipped with fire warning and extinguishing systems and with flood warning devices. These are requirements of primary importance.

The second major requirement is the choice of filing enclosure. TABLE 6 shows the pertinent specification published by ANSI. It distinguishes between folders, sleeves and envelopes and sets guidelines for their geometry and for the location of seams with adhesives. Filing enclosures made of paper should have a high alpha-cellulose content (above 87%), be free of metal particles, harmful sizing agents, acids, peroxides and highly lignified fibers. Suitable plastic enclosure materials are uncoated polyethylene, cellulose triacetate and uncoated polyester. Cellulose nitrate is specifically disrecommended, and so is chlorinated sheeting. The standard not only makes specific recommendations, but quotes for most of the requirements the test method which should be used to verify them.

Plastic sleeves made of either uncoated cellulose triacetate or uncoated polyester - both recommended because their properties are well known from their use as film bases - are commercially available. However, it is difficult to write on them. If resources allow, valuable negatives and prints should ideally be placed in a polyester or cellulose triacetate sleeve and the sleeve kept in a suitable paper envelope, which can also contain all necessary written information. Not much data have been published on the properties of filing enclosures. A notable exception is a paper by Henn and Olivares on the storage of negatives in tropical climates (171). It presents results of experiments designed to protect negatives from fungus growth by impregnating their paper filing enclosures with a suitable fungicide. Specific recommendations for storage envelopes were made. Laminated foil envelopes - now commercially available in heat-sealable form - were found to be very satisfactory.

While the suitability of uncoated cellulose triacetate and polyester for storing photographs seems to be uncontested, the criteria for paper used for the same purpose are not undisputed. For example, the ANSI specification PH1.53-1978 (170) recommends that the pH of the paper should be between 7.0 and 9.5, whereas the Eastman Kodak Company suggests it should be between 6.5 and 7.5 (172). While ANSI PH1.53-1978 advises against the use of glassine papers, Henn and Olivares found it to be of good quality. Results of further tests and observations may be expected to become known in the future.

ENCAPSULATION WITH MYLAR

A. WITH DOUBLE-SIDED ADHESIVE TAPE

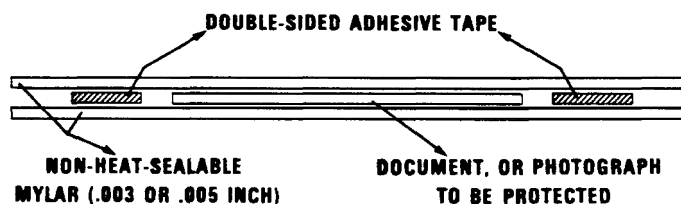


FIGURE 15: Encapsulation with Mylar Using Double-Sided Adhesive Tape

In order to protect photographic prints that are frequently used from mechanical damage, a technique known as encapsulation may be used. As can be seen from FIGURE 15, the photograph to be protected is placed between two sheets of mylar (polyester) which are cut at least one inch larger on each side than the photograph. The two mylar sheets are then held together by four strips of double-sided tape, one along each edge, with about 1/2" distance between the margin of the photograph and the tape. It is also possible to use heat-sealable mylar as shown in FIGURE 16.

ENCAPSULATION WITH MYLAR

B. WITH HEAT-SEALABLE MYLAR

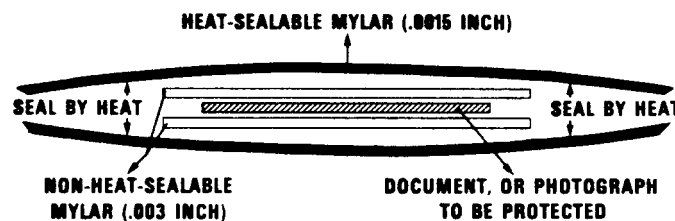


FIGURE 16: Encapsulation with Mylar Using Heat-Sealable Mylar

In order to prevent the heat-sealable mylar - drawn in solid black in FIGURE 16 - from sticking to the original photograph to be protected, the photograph is first placed between two sheets of non-heat-sealable mylar. This assembly is then held together by two outer sheets of heat-sealable polyester which is passed through a pair of heated rollers. The mechanical protection provided to documents kept in this manner is excellent. The procedure is completely reversible, as no material is permanently attached to the original document. Finally, it is also good practice to prepare detailed instructions for users which outline how photographs are handled properly.

Contingency plans for dealing with natural disasters are often prepared in major archives and libraries for their respective holdings. They should include provisions for photograph collections. Hendriks and Lesser (110) have found recently that most photographic materials - including silver gelatin photographs - can be frozen after they have been soaked in water. However, soaked photographs are ideally air-dried without prior freezing. Freezing slows down temporarily further degradation and provides time for the preparation of the next step in the salvage operation. If the situation permits, frozen photographs should be thawed and air-dried. Freeze-drying in a vacuum chamber is also possible, but freezing-thawing and vacuum-drying at 4°C, as done with books, is not recommended due to blocking or sticking of gelatin layers. Glass plate negatives made by the wet collodion process are the materials most susceptible to water damage. They should never be freeze-dried once they have been immersed in water.

General accounts of the requirements for the preservation and storage of photographic materials have been published by the Eastman Kodak Company (172), Eaton (150) and recently by Hendriks (173). The influence of environmental factors, such as temperature, relative humidity and light, on the preservation of contemporary photographic materials has been studied by Gillet, Gamier and Flieder (174).

10. RESTORATION OF PHOTOGRAPHIC MATERIALS

Besides the preservation of photographs - that is implementing measures to prevent damage or deterioration - there are three areas of activities designed to conserve photographs:

1. duplicating and copying;
2. the application of conventional prints and drawings conservation techniques to photographs;
3. the restoration of discolored or faded photographs in chemical solutions.

The importance of competent copying techniques has been emphasized earlier. It is a discipline which requires familiarity with photographic technology, such as sensitometry and photographic processing control. Yet it is an integral part of the conservation of photographs. Methods of restoration - i.e. work on the original photograph to repair damage and enhance its permanence - are not well developed at this time, but just begin to emerge. A first logical step has been to apply traditional techniques of conserving paper documents and works of art on paper to photographic prints. While they cannot be described in detail in the present study - being largely based on manual skills and judgement acquired by experience - they may include techniques of dry cleaning, washing, dismounting photographs from aged and brittle cardboards containing lignified fibers, flattening curled-up pictures, repairing tears and losses by laying down the print on a new support, and matting and mounting photographs for long term storage and display. Preceding any such activity is a thorough examination of the item to be conserved, an assessment of its condition and the preparation of a proposed treatment report. Much useful and beneficial work can be done this way on photographs.

A procedure inherently suitable for application to photographic negatives if referred to as emulsion transfer. Mentioned as early as 1851 by F. S. Archer, it is a technique widely used for various photographic purposes. Some sensitized materials known as "stripping plates" and "stripping films" were made for the specific purpose of removing the image-bearing layer from its support (175, 176). The technique of emulsion stripping can be applied to restore negatives whose film base has shrunk or deteriorated due, for example, to a loss of plasticizer (177, 178, 179). Principally, there are two possibilities to accomplish this: either the film base can, in some cases, be dissolved, leaving the emulsion layer behind; or the adhesion between the support and the emulsion layer is destroyed so that the image layer can be removed and placed on a new and stable support.

Prospects of more exciting work are provided by the possibility of restoring faded and stained photographs in chemical solutions. Such techniques, when applied to black-and-white negatives, are known as "reduction" and "intensification" (the terms being used with reference to the density of the image), but are traditionally referred to as "bleach and redevelopment" when applied to photographic prints. FIGURE 17 gives a schematic overview of various changes that the image silver in photographs can undergo.

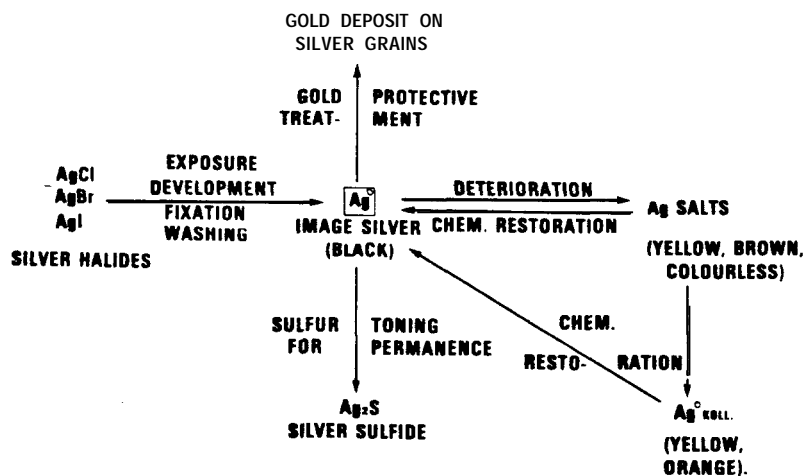


FIGURE 17: Schematic Presentation of Changes of Image Silver

Black image silver, produced by exposure to light and subsequent processing of silver halide salts, can undergo numerous changes. In a deliberate and controlled reaction, it can be completely converted into silver sulfide, or coated with a layer of gold under possible formation of an alloy. These are toning reactions which alter the image tone and usually increase its stability. The first step of any deterioration reaction is the oxidation of some image silver to silver ions, followed by the formation of silver salts. It is the conversion of these silver salts back to elementary silver which, if successful, constitutes chemical restoration. However, silver ions can also migrate within the gelatin layer and be reduced on or near its surface as colloidal silver, marked as Ag^0 KOLL in FIGURE 17.

Attempts to convert silver salts or colloidal silver in photographs to black elementary silver are not without pitfalls which require certain precautions in order to be avoided. In the majority of these reactions, all silver and its compounds are uniformly and completely converted into a silver halide which is then reduced to elementary silver. The first requirement is that the gelatin layer is stable enough to survive treatment in several chemical solutions of different pH values. With respect to the reduction to elementary silver, it is obvious that the resultant image must have the same density range, contrast, graininess and image tone as were present in the original, undeteriorated photograph. Any of the above properties may change during a restoration reaction. Finally, the stability of the restored image must be a consideration in the selection of a restoration treatment. Some procedures, for example, have been described as effective in intensifying a negative image, but the permanence of the so intensified image was observed to be inferior than that of the original.

There is no shortage of formulae for chemical restoration procedures. There is, however, a lack of knowledge of which formula works for which type of material and for which kind of

deterioration. Wall (180) has compiled several hundred procedures for the reduction and intensification of negatives, but in only a few cases it is indicated to which type of negative a given procedure can be applied. Stenger (181), in what could be described as a first textbook on the keeping and restoration of photographs, places the emphasis on correct copying techniques and on chemical restoration procedures without, however, presenting data on their performance. Another classical text is by Crabtree (182) which deals with the removal of stains on negatives and prints. Of the more recently published procedures, two stand out as effective in removing the blue metallic sheen on the surface of silver gelatin photographs: Crabtree (183) used an acidic ammonium thiosulfate reducer, whereas Weyde (111) proposed the use of a dilute solution of iodine in dry alcohol. The iodine can react only with the surface silver forming silver iodide, because the alcohol does not penetrate into the gelatin. Subsequent treatment in a fixing bath removes the silver iodide in this elegant method. Eastman Kodak's publication F-30 (172) also proposes some formulae for restoration treatments in chemical solutions. None of the above treatments should be attempted on valuable photographs without the conservator having performed extensive tests and trials of these formulae on different photographic materials. Much more experimentation needs to be done before firmly established procedures can be recommended.

11. SUMMARY GUIDELINES

11.1. General

The present study has emphasized the structure of photographic materials and their properties in terms of stability in order to create an understanding of the subsequent recommendations for preservation and storage. After accessioning and cataloging, the overriding factors determining the longevity of these records are control of relative humidity, air pollution, temperature and exposure to light. The choice of a suitable filing enclosure is of crucial importance to the preservation of negatives and prints, as they are in direct contact with it. Original photographs, when used, should be handled in a sensible way as carelessness can cause irreversible damage. Ink must never be used to write on the back of photographic prints. If unique and valuable photographs are in high demand by users, duplicate or copy negatives should be made for use, while the originals are retired to inactive storage. Several conservation techniques developed for works of art on paper can be applied successfully to photographs. The restoration of discolored or faded black-and-white negatives and prints remains of an experimental nature, but its further development will surely lead to firm procedures. The destruction of organic dyes in colour photographs through oxidation or hydrolysis is thought to be irreversible, and such pictures can be saved only by placing them into cold storage and by making duplicate copies.

The conservation of photographs is still a young field which does not have the body of knowledge available in older, more established fields, such as fine art conservation. While the testing of materials and experimental work have increased our knowledge of the stability of photographic materials during the past decade, many problems remain unsolved, but which will eventually become understood. Progress in the field is signalled by a number of recent events and developments, such as: the involvement of the American National Standards Institute (ANSI) as well as the International Organization for

Standardization (ISO) in formulating specifications for the storage of processed photographic records; the investigation of the occurrence of redox blemishes in processed microfilms; the emergence of cold storage conditions as an immediate solution to the dark storage instability of chromogenic colour materials; the thorough investigations into the stability of resin-coated papers; the mechanism of image silver deterioration; the development of emergency procedures for photographs following a natural disaster; and the occurrence of seminars, workshops and conferences on the subject, such as the International Symposium on "The Stability and Preservation of Photographic Images", which was held in the fall 1982 in Ottawa, Canada, and sponsored by the Society of Photographic Scientists and Engineers (SPSE). The majority of problems in the preservation of photographic collections is under control. The quest for solutions to the remaining ones promises to be both exciting and rewarding.

11.2. Specific Recommendations

11.2.1. Identification

Only complex scientific examination can replace extensive experience in visually recognizing types of photographs. Simple and inexpensive experimental techniques include testing the surface in non-image areas of photographs with alcohol and water, and looking at the surface of photographs through a light microscope. While gelatin swells under a water droplet, neither collodion nor albumen react to it. Alcohol dissolves collodion, but leaves a gelatin layer unaffected. Albumen layers react with neither water nor alcohol.

11.2.2. Storage Conditions: Relative Humidity

Relative humidity is the single most important factor affecting the permanence of photographic records. It must never exceed 60% in storage areas. The optimum storage relative humidity varies with the product type. A level of 35 to 40% is recommended as the value which best accommodates different kinds of photographic materials. Such level should be kept constant, i.e. daily or weekly cycling is to be avoided.

11.2.3. Storage Conditions: Temperature

Photographic records must be stored at a temperature preferably not above 21°C (70°F). Daily or weekly cycling of more than 4°C must be avoided.

11.2.4. Storage Conditions: Low-Temperature Storage

Low-temperature will provide added protection. For color film, a storage temperature of 2°C (35°F) is recommended. However, processed photographic materials can be kept at temperatures well below the freezing point of water (0°C; 32°F), provided the relative humidity is kept at recommended levels.

11.2.5. Storage Conditions: Air Purity

Chemically reactive materials pose the greatest threat to the stability of black-and-white photographic collections, especially in the presence of moisture. The source of such chemicals can be the surrounding atmosphere, the photograph itself, residual processing chemicals and materials in direct contact with the photographs. They should be stored in a pollution-free area, i.e. in the absence of sulfur oxides, nitrogen oxides, peroxides and other oxidizing agents.

11.2.6. Storage Conditions: Dust

Photographs of all kinds should be stored in dust-free areas, as fine sand and dust may become embedded into gelatin layers and cause damage by abrasion.

11.2.7. Storage Conditions: Light Levels

Well processed contemporary black-and-white photographs are essentially stable to light. By comparison, color photographic materials are rather sensitive to long-term light exposure in the presence of oxygen and moisture. This should, however, not prevent a problem in storage, as photographs are usually kept in sleeves, boxes or albums and thus are protected from light exposure.

11.2.8. Storage Conditions: Filing Enclosures

The correct choice of filing enclosures - sleeves or envelopes - can be made of paper or plastic materials. Paper enclosures are more difficult to evaluate. They should have a

high alpha-cellulose content (preferably above 90%), contain no mobile adhesives or sizes and have an extraction pH of between 6.5 and 7.5. Plastic enclosures should be made of uncoated polyethylene, uncoated cellulose acetate or polyester. For cold storage purposes a heat-sealable envelope can be used that consists of a laminate of polyethylene, aluminium foil and paper. As it is not easily possible to write on most plastic materials, photographic negative and prints are placed ideally first into a plastic sleeve, which is then put into a paper envelope. The photograph can be looked at while remaining in its transparent enclosure, while all necessary information can be written on the envelope.

11.2.9. Storage Conditions: Inherently Unstable Materials

Cellulose nitrate film base is the most prominent example of a material which can itself be the source of contaminating chemicals. As these materials can also be a fire hazard, they are to be stored separately from other photographic records. Apart from using the time consuming and labour intensive technique of emulsion transfer, cellulose nitrate film materials are best duplicated onto safety stock. They can be sealed in appropriate envelopes described earlier and kept in cold storage in order to provide temporary protection.

11.2.10. Storage Conditions: Boxes and Shelves

Photographs in filing enclosures are normally kept in boxes on shelves. Boxes should be made of stable cardboard materials having properties similar to those described for paper envelopes. Stable boxes are available in North America which are made of stainless steel which is covered with an electrostatically applied polyester coating.

11.2.11. Processing of Contemporary Photographs

Best results, in terms of permanence of the resultant image, are obtained by following meticulously the recommendations of the respective manufacturer. Certain residual chemicals must not be allowed to remain on the film or photograph. Recent materials may require toning as a post-processing treatment to achieve permanence.

11.2.12. Handling of Photographs

When handling valuable photographs, white lintless cotton gloves should be worn in order to avoid producing finger-prints. These impressions, unless removed immediately, may cause irreversible damage to a gelatin-coated photograph.

11.2.13. Housekeeping

When working with photographs, no food or drinks should be tolerated in their vicinity. For reasons of keeping a clean, dust-free environment, smoking is not allowed in areas where photographic materials are handled.

11.2.14. Marking of Photographic Prints

Information about a photographic print must never be written on it in ink, neither front nor back. In the occurrence of a flood, the ink may transfer onto the image side of the next photograph in a stacked pile, and become itself illegible in the process. If any information has to be written at all on a print, a soft pencil can be used. Applying too much pressure, however, may cause the writing to become visibly imprinted on the image side.

11.2.15. Display

The two important choices which have to be made in the display of photographic prints are the selection of mount board and appropriate light levels. The former should have a high alpha-cellulose content, free of lignin and volatile chemicals. Smith (184) has published specifications for materials to be used in matting and hinging of works of art on paper, as well as techniques for these activities. Light levels for color photographs on display should be kept around 100 lUX. Normal display times, however, ranging from a few weeks to perhaps several months, are not expected to cause excessive damage to most types of color photographs. Such damage usually occurs when chromogenically developed prints are exposed to light for many years, as often occurs in typical home and office situations.

11.2.16. Emergency Procedures

If photographic materials become water-soaked following a natural disaster, they can be frozen in order to slow down dramatically further deterioration. Materials can then be freeze dried, or thawed and dried in a vacuum, or thawed and air dried. Glass plate negatives made by the wet collodion process should not be frozen and under no circumstances be freeze dried.

11.2.17. Fumigation

Recent experiments have shown (185) that most photographic materials can be exposed to common fumigants without suffering changes to image density or gelatin stability. The fumigants include ethylene oxide, methyl bromide, thymol and p-dichlorobenzene.

11.2.18. Printing, Duplication and Copying

Photographs are collected and preserved in order to be used for many purposes. Negatives are printed to provide positive reflection images. Valuable historical negatives which are in high demand may suffer from continued use and handling. They can be duplicated to produce faithful duplicate negatives for further use. Unique photographic prints can be copied camera with a camera to give copy negative from which correct copy prints can be obtained. To perform these activities well, an understanding of photographic technology and sensitometry is required.

11.2.19. Restoration

Many kinds of deterioration can be corrected through the application of restoration techniques. It is useful to remember, however, that such work should be attempted only by trained conservators. In any experimental work, where the outcome is unknown, only expendable photographic materials must be used.

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