



ROGER KOCKAERTS

ARCHIVAL PROCESSING AND CARE
OF FIBER BASE
PHOTOGRAPHIC PAPERS

Editions pH7
Brussels
2005

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Traditional gelatin silver printing on baryta paper still provides the most suitable paper emulsion for the production of fine prints of the highest quality.

The conservation and processing techniques applied to ensure the archival quality of photographic emulsions do not only guarantee their durability; they meet the highest requirements of specialized museums as well as the international art market.

The contemporary photographer has a real interest in taking over these methods.

pH7

PERMADOCUMENT, specialized in photoconservation and historical processes, offers :

- materials, supplies and services for the conservation-restoration of valuable documents
- all sensitizing and processing products for alternative photographic processes
- non-acidic paper and cardboard, neutral matting boards
- prestige platinum-palladium printing
- Heiland digital densitometers, Deville archival washers, the Bergger product line
- atelier pH7, an exhibition and meeting place for photography enthusiasts

(Roger Kockaerts passed away in september 2019, and PH7-Permadocument disappeared with him)



This document contains the notes of the course "Conservation & Restoration in Photography" given by Roger Kockaerts at the Royal Academy of Fine Arts in Antwerp.

Silver printing was crowded out very quickly by digital technology, and can now be considered an historical technique. It has therefore become our task to perpetuate its underlying know-how, and to make this information accessible to the widest public..

We would like to thank Roger Kockaerts for allowing us to circulate the following text through Picto Benelux.

The author :

Roger Kockaerts (1931- 2019) was a photographer, gallery owner, teacher and expert in restoration and preservation- conservation of photographic documents.

He has been practicing photography since 1956, with a predilection for nature and mineral or vegetal textures; he was also interested in structures generated by computer programs and developing in random patterns. He has practiced many historical processes, especially cyanotypy and platinum-palladium printing. Around 1968 he became interested in orotone, a very old and practically forgotten process, to end up with a modernized version of his own which he called orotypy. His recent works are more inspired by photographic intention, and less by the purely aesthetic aspects.

In 1989 he created Permadocument-pH7, a specialized structure for the conservation and restoration of photographic documents. Many institutions (including the Getty Conservation Institute in Los Angeles), museums, galleries, and artists resorted to his expertise. Artists photographers from around the world using alternative photographic processes have exhibited in his gallery "Atelier pH7".

Since 1994 he has lectured at the conservation and restoration section of the Koninklijke Academie voor Schone Kunsten in Antwerp (Royal Academy for Fine Arts in Antwerp) .

Roger Kockaerts has been an active member of Picto Benelux since its inception.

Other publications :

"Archivale behandelingen en conserveringstechnieken voor moderne fotografische zilveremulsies".

"Techniques d'archivage pour les émulsions argentiques N&B modernes"

"Stabiliteit en conservering van fotografische kleuremulsies"

"Techniques d'archivage et stabilité des émulsions couleur"

"Identificatie, technologie en conservatie-restauratietechnieken van historische fotoprocédés.

- Deel 1: procédés gebaseerd op de lichtgevoeligheid van zilverzouten.

- Deel 2: procédés gebaseerd op de lichtgevoeligheid van ijzerzouten.

- Deel 3: procédés gebaseerd op de lichtgevoeligheid van chroomzouten.

"Historiek en praktisch gebruik van historische fotografische apparatuur. (met René Smets)

"Enkele gegevens over de historische en hedendaagse daguerreotypie en zoutdruk" (met René Smets)

"Het platina-palladiumprocédé"

"Procédés nobles en photographie: procédés photographiques basés sur la sensibilité à la lumière des sels de fer: platine-palladium, chrysotype, cyanotype, kallitype, argyrotypie, ziatype", e.a.

"De kunst van het Fotoarchief – 170 jaar fotografie en erfgoed" (avec Johan Swinnen)

Picto Benelux

Picto is an an informal group open to everybody in the Benelux countries having an active interest in photographic processes developed from the very beginning of Photography. The aim is to revisit them, while respecting anyone's creative approach.

<http://www.picto.info/>

Archival Processing and Care of Fiber Base Photographic Papers

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1. Introduction

The falling into decay usually is considered with quite mixed feelings. We are delighted when it allows us to easily get rid of things we are considering ugly or unimportant. But we are sorry when irreplaceable memories are disappearing for good.

Sometimes we try to slow down the decay, but often we do not care and are accepting it as an unescapable law of nature, taking no interest in conservation techniques which could allow us to preserve for our descendants, easily and at little cost, the things we hold dear.

The world of photography therefore only managed rarely to create really permanent images. Silver-based images are fundamentally unstable. The light that created them is also cause of their destruction. The acceptance of their fleeting nature probably is what explains today the lack of concern that endangers the life of our photographic heritage.

Now, as we are confronted with a countless number of photographic emulsions in bad shape, all of a sudden we realize that we do not have all the required information to put things right. The topics related to the decay of photographic images have not been examined seriously and scientifically until recently.

If we really want to salvage our graphic and photographic heritage, we have to develop and to implement without delay extensive preservation programmes.

Preservation includes all the steps to be taken in order to protect objects from potential damages, and to slow down or to stop their decay. The archival processing of photographic emulsions for instance is a first step towards their **conservation**. Photographic emulsions processed this way and stored with care will not need any further **consolidation** treatment in the future.

Since its invention, silver printing has prevailed in popular photography. Most silver-based processes were designed to produce a paper print close to existing printing techniques. The possibility of obtaining images, simply by exposing a sheet of paper to the sunlight, strongly intrigued simple amateurs as well as the intelligentsia and immediately induced their reaction: doctors, chemists, professors or religious, all of them felt called to contribute with more or less success to the development of this new printing technique.

It appeared quickly that many recipes without any scientific basis were used, with the result that very few stable images were produced in the early days of photography. It was soon realized that more research was needed to improve the characteristics and the stability of the image.

The situation remained chaotic until around 1854, and very little serious scientific research was conducted during that period. Many started experimenting, following at first the available instructions and recommendations before trying to design their own improvements. This happened at every level of the photographic process. Image degradation was omnipresent!

The "Société Française de Photographie" (French Society for Photography) undertook a study on image fading in 1855 and organized a commission to investigate this on May 18, 1855.

The Photographic Society of London set up a "Committee on Positive Printing" during the same period.

Its goals:

- to improve the current fixing processes;
- to develop restoration methods for faded prints

Prints made with various methods were collected from prominent photographers. All their technical and production data were recorded. Large-scale conservation experiments were then carried out in the huge space of the Crystal Palace in London. The committee ended up making four suggestions ¹ :

¹ First Report of the Committee Appointed to Take into Consideration the Question of Fading of Positive Photographic Pictures on Paper. In: *The Journal of the Photographic Society*, 36, 21-11-1855, London.

- 1) the print has to be fixed sufficiently and the fixer eliminated very carefully from the emulsion by washing;
- 2) gold should be used in one way or another during the process;
- 3) the print should be stored dry;
- 4) substances should be identified that could protect the print from light and moisture.

Ignorance of the need to fix and to wash the photographic emulsion thoroughly resulted in the loss of countless negatives and prints during the early stages of photography.² A gelatin silver print, fixed or washed insufficiently, will be subject to a weakening of its black tones, and fading of the image will occur when the temperature and humidity conditions are not optimal during its storage.³

Other investigations developed the idea that colouring chemically or toning the print would improve its preservation.

The permanence of photographic images mainly relies on:

- the internal stability of the photographic materials;
- correct processing and its control;
- storage conditions.

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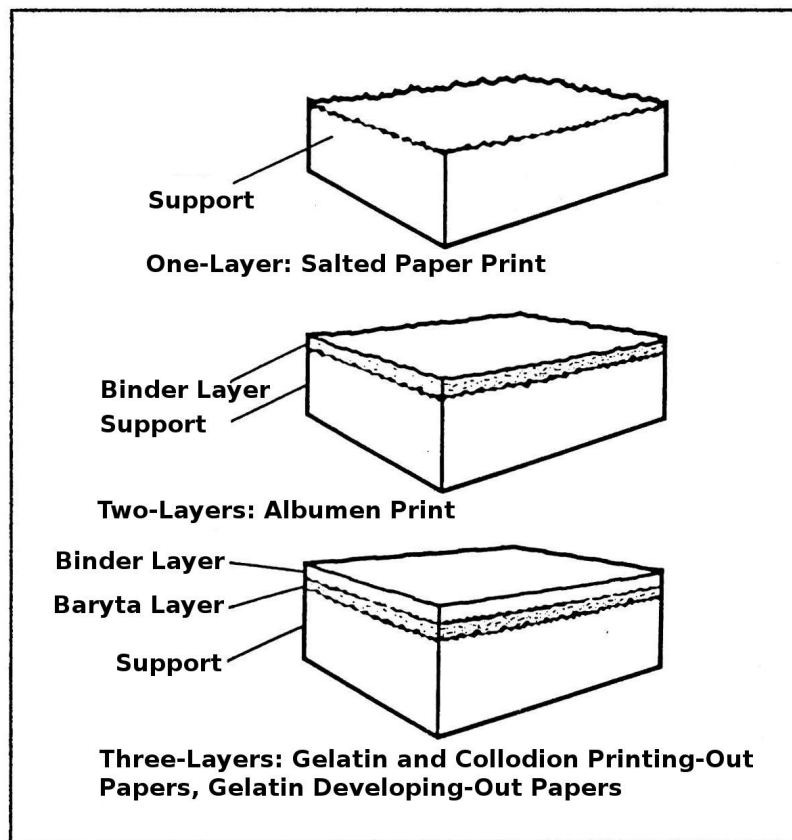
² Is Photographic Permanence Desirable? In: *The Camera*, vol.II, n°3, 1907.

³ What should be the Life of a Silver Print? In: *The Camera*, vol. II, n°7, 1907.

2. Elements composing a photographic emulsion

Structure of the silver print

In principle, a photographic print can have three different structures:



A single layer structure where the print is simply composed of a paper substrate on which the photosensitive solution is applied. The latter penetrates into the fibers of the paper; the image appearing after processing will be totally matte.

A two-layer structure where a binder layer is coated on the paper substrate. This sizing is composed of albumin for albumen prints, and gelatin for Woodbury and carbon prints. These processes are the most common ones for this type of structure.

The modern multi-layer structure has an additional baryta layer between the paper substrate and the photosensitive layer. The latter is composed of a gelatin and barium sulfate mixture. This kind of paper is called baryta paper, and will be studied in the following pages.

In the past, the final image was entirely glued on a mounting board. It was often composed of a main backing sheet, a cardboard of dubious quality, on which was glued a sheet of a better quality paper. The print was stuck to it, either with a starch glue for very thin albumen prints, or with all sorts of more or less adequate glues. We will see later that this cardboard of bad quality has to be removed if we want to store the image in better conditions.

Amongst the baryta papers, a distinction has to be made between **printing-out papers (P.O.P.)**, where the image appears during the exposure and has only be fixed, and the **developing-out papers (D.O.P.)**, where the image remains invisible until after physical development.

Emulsion constituents

Silver

Very pure silver bars are treated with nitric acid to obtain silver nitrate crystals. These crystals are then dissolved in water to make the various types of photographic emulsion.

Silver halides

Salts such as potassium bromide, potassium chloride and potassium iodide are halides. One or more of these salts are combined with the silver nitrate solution to obtain very fine crystals. These silver halides are mixed into a diluted layer of dissolved gelatin. The light-sensitive crystals are evenly distributed in the gelatin.

Gelatin

Photographic gelatin is a highly purified animal protein. A few years ago, inert gelatin was made from bones imported from Pakistan or India. Today, fresh bones as well as cow, veal or pork skin are also used.

Strictly speaking, inert gelatin is not totally free of photoactive elements. But each year, gelatin manufacturers improve the inert characteristics of their product. This progress is mainly made with respect to the natural sulfur content in gelatin. The sulfur content can be evaluated today at 0.1 parts per million, or 0.1 ppm.

From an historical point of view, photographic gelatin has gone through three stages:

- Gelatin was experimentally introduced in photographic technology as a water-permeable binder, replacing the collodion.

- It quickly became the universal photographic binder. For more than half a century, this gelatin was also containing the photoactive elements forming the emulsion.

- Today, gelatin is still the universal binder par excellence. Nowadays however, it is an inert gelatin to which the necessary chemical components have been added.

Gelatin is a very stable material when it is dry. The fact that it swells in water, and in doing so becomes porous enough to allow the diffusion of chemicals into its structure, involves that it will remain sensitive to moisture throughout its lifetime.

Gelatin is resistant for a certain time to dry heat. But heat combined with high humidity quickly turns it into a sticky and soluble substance. As an organic substance, gelatin is also sensitive to the formation of fungi. It is also attacked by strong acids or acid gases from atmospheric pollution or formed by the damage and deterioration of certain materials in the substrates.

But gelatin remains the material of choice, especially due to its remarkable physical and chemical properties. It holds silver halides in a uniform distribution without exerting any negative influence on them. The diffusion of processing products does not influence its resistance, nor its preservation. It is a stable material, which in its dry state can be handled in an easily replicable way.

These characteristics allow the production of photographic products that remain stable, both before and after their processing. Under optimal storage conditions, the gelatin layer is at least as durable as the support on which it was cast.

Support materials

Glass

Because of its transparency, glass was used as a photographic emulsion support immediately after Talbot's invention, to replace the oiled calotype negatives. Its use was widespread throughout the second half of the 19th century, especially for the manufacture of negatives.

A photographic quality glass is chosen according to various parameters:

- perfect transparency;
- the absence of defects (air bubbles, scratches, inequalities, etc ...);
- a uniform thickness;
- a flat surface.

For good adhesion of the emulsion, the glass should be cleaned thoroughly and polished. A new glass must be free of grease, fingerprints and other impurities. This is easily obtained by immersing it in diluted ammonia.

After this cleaning, the glass needs to be polished. For this purpose a chalk paste or a very fine tripoli powder mixed with water and a few drops of nitric acid is used. Tripoli is a siliceous fossil powder mainly used for polishing various kinds of surfaces.

The glass plates should be allowed to rest for several hours before the emulsion is going to be coated : it is necessary to wait for the static electricity caused by the polishing to disappear, as it would attract dust.

Being an inert and transparent material, the glass is in fact an ideal support for photographic emulsions. But its weight, its volume and its fragility make its use impractical for regular photography. Glass emulsions are still used for some technical applications, where dimensional stability is of great importance.

The film

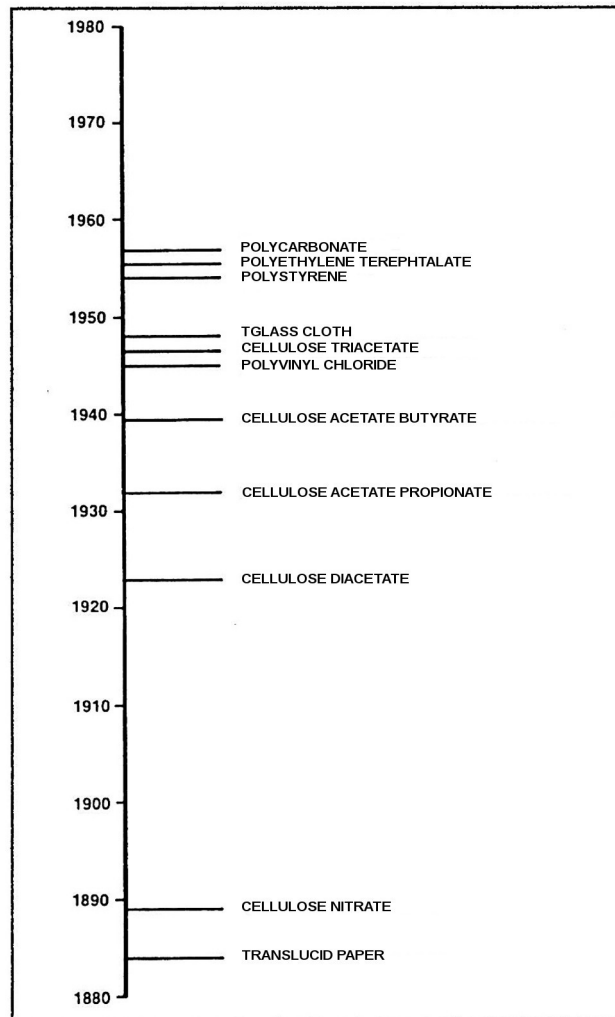
The photographic industry always used materials from other industries for its backing. The first inventors of photography had few materials to choose from: Daguerre used copper. Later on, albumin and collodion were used as binders for the manufacture of photographic glass plates. Metal plates were used for the ferrotypes. All these materials presented advantages and disadvantages. Apart from glass, none was transparent or flexible – two essential features for films as we know them today.

Georges Eastman first attempted to make a paper backing translucent, treating it with oil and wax before applying a photo-sensitive emulsion. This was the birth of the rollfilm, a revolution in the film industry. Paper being rather weak, other flexible materials were soon sought after.

Cellulose nitrate was one of the few plastic materials existing at that time, and was mainly used for the manufacture of billiard balls and hard collars in the shirt industry. Cellulose nitrate has been used for nearly 60 years as a film carrier. Its main disadvantages, chemical instability and high flammability, were known for a long time, but the photographic world still suffers from them. Chemical instability has caused all major film archives to duplicate their nitrate films on more stable media. It will take many years before this gigantic task will be completed.

Cellulose acetate appeared as a safer substitute for the production of films. However, it was not until the 50's that a "safety" support in tri-acetate appeared, and that the dangerous nitrate film was abandoned. But acetate film was not of optimal stability either, as we will see later.

Nowadays **polyethylene terephthalate**, better known as polyester or Mylar, is preferred to tri-acetate for the production of films.



Historically, photographic prints were first made on cotton fiber paper, sized to prevent the emulsion from penetrating. The texture of the paper influences the way light is reflected.

Baryta Paper

Around 1865, the idea was launched to create a smooth backing for the emulsion by applying a mixture of barium sulfate and gelatin to the paper. Barite was not used for all papers, and highly textured photographic papers could be found until World War II.

In photography, the paper support has to be as strong and permanent as possible. There should not be any chemical interaction with the silver halide emulsion. The support has also to be physically and chemically resistant to the various chemical treatments necessary to produce the silver image. A photographic record obtained under these conditions, when stored in ideal conditions, can then be kept almost indefinitely.

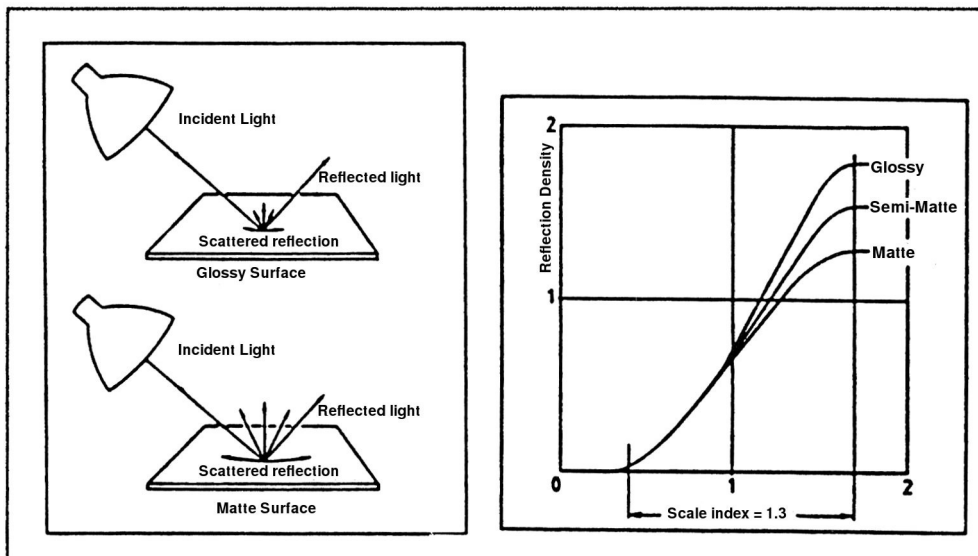
Due to the varying quality and relative scarcity of cotton rag available at that time, finding a standard basic material was a necessity. Wood pulp was a potential source. The impurities were removed in order to obtain cellulose of similar purity to that from freshly picked cotton.⁴ However, the purity of this wood pulp had to be maintained through the whole process until the final product, paper. In-depth research eventually led to a wood pulp paper whose quality was in no way inferior to that of paper made from quality rag. A photographic emulsion on wood pulp paper, according to extensive studies⁵, has conservation properties equivalent to those of an identical emulsion cast on a glass plate. Fine wood pulp paper also meets the highest permanence requirements.⁶ Traditional rag paper thus disappeared from the photography market and was replaced by the stabilized cellulose blends mentioned above.

For traditional photographic paper, a first layer of gelatin containing barium sulfate, or barite, is poured onto the paper substrate. Sometimes hardeners, optical brighteners or dyes are added to obtain an opaque and smooth base on which a uniformly thick emulsion layer is poured. The photosensitive emulsion contains silver halides with specific dimensions, shapes and sensitivities, mixed with gelatin to allow for chemical development. A protective layer of gelatin and hardeners is applied over the emulsion layer. Matte paper, for example, is obtained by adding a matting agent, usually starch or a colloidal silicate to this layer. It is this layer that determines the texture of the photo paper and thus also its reflectivity as shown in the following figure.

⁴ RASCH, R.H. et al - Highly Purified Wood Fibers as Paper Making Materials. In: Journal of Research of the National Bureau of Standards, nov. 1931.

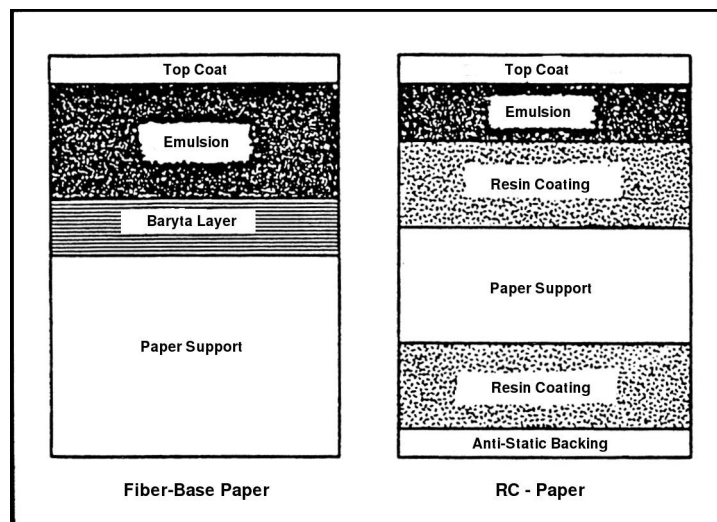
⁵ JANE, G.T. - Permanence of Paper, Eastman Kodak, 1935.

⁶ SCRIBNER, B.W. - Comparison of Accelerated Aging of Record Papers. In: Journal of Research of the National Bureau of Standards, sept. 1939.



Plasticised paper, RC or PE

In the past, there were many variants of the traditional baryta emulsion. In some papers the barite layer was omitted and in others there was, or was no, protective layer on top of the emulsion layer.

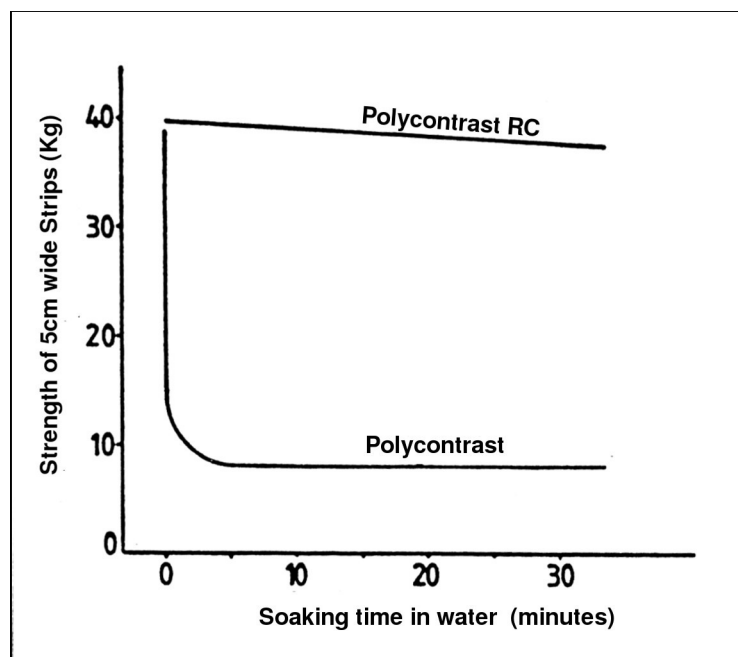


A modern variant is Resin Coated (RC) paper. Here, the paper support is covered on both sides with a layer of polyethylene (PE paper). The advantages of resin coated paper are as follows:⁷

⁷ PARSONS, T.F. et al - To RC or not to RC. In: *Journal of Applied Photographic Engineering*, vol.5, n°2, 1979.

- accelerated processing thanks to reduced washing and drying times;

- since the paper fibers are no longer saturated with liquid during processing, the normal strength of the dry paper is practically maintained during and after processing in the various baths, as shown in the following diagram. It shows that the resistance of the RC paper is almost entirely preserved, while that of the baryta paper decreases immediately with the saturation of the paper fibers.



- Because of its special structure, the paper stays flat and buckling is avoided almost completely.

- The texture of the emulsion can be imprinted in the RC layer, so that glazing for example becomes superfluous.

- The thinner emulsion layer is cheaper to manufacture. While this is advantageous from an economic point of view, it becomes a drawback when it is crucial to get quality prints with rich shades of gray, intense blacks and pure whites. High quality baryta papers are then the more obvious choice.

All the above mentioned benefits, as well as a strong promotional action, resulted in RC paper sales quickly superseding baryta papers during the years 1976 to 1978.

In response, a large-scale protest campaign was launched by the fine-art photography community when, in 1976, it was decided in the United States to stop the manufacture of baryta paper. This action, which got countless supporters throughout both Europe and the United States, finally led to the major paper manufacturers deciding to continue the manufacture of conventional baryta paper as long as demand existed.⁸

In the fine-art photography press, grievances against the use of RC paper for the creation of artwork and archival documents were also appearing⁹, mainly because of the reduced permanence of RC silver emulsions.

In its relatively short existence, RC paper has proved to be subject to oxidation problems in the emulsion and, like most plastic products, to be very sensitive to aging resulting in embrittlement of the emulsion when exposed to strong sunlight.

Here is what happens: during the day, the light and the increase in temperature evaporate some of the water naturally contained in the emulsion. At night, the drop in temperature and the reduction of energy causes a new absorption of the lost moisture.

This results in a series of contractions and swellings of the emulsion while the plasticized paper support is virtually insensitive to these repeated deformations. This can in turn lead to separation of the emulsion and its plasticized backing.

It is not recommended to soak the RC paper for more than four minutes in water, as this may reduce the adhesion between different layers and cause buckling around the edges. It has also been noted that chemical residues can be concentrated along the edges. A suitable means is to cut the edges by at least three mm after drying.

⁸ MESSER, William. - Ilford à Arles. In: *Galerie: de la photographie et de ses applications*, Ilford, 1979.

⁹ ANON. - In: *Camera*, Lucerne, Suisse, janvier 1978.

Other typical problems with RC emulsions (colour or black and white) include fading and yellowing of the image as well as the formation of cracks due to atmospheric contamination.¹⁰

Paper manufacturers and photographic research laboratories are working to solve the problems of plasticised emulsions.

Baryta emulsions and RC papers both have a place in photography. The choice between the two, depending on the destination of the final print, has ultimately to be left to the photographer. When conservation is especially sought after, baryta paper and its archival processing should always be preferred.¹¹

Types of baryta paper

Bromide paper

The main characteristics of bromide papers are: high sensitivity to light, relatively limited exposure latitude and a tonal value that generally is neutral black, and can quite easily be toned chemically.¹²

Ifobrom has these characteristics and, with its six gradations and pure white substrate, is often considered as the basic silver bromide paper of reference

Agfa Brovira, traditionally known for its cold tonal value, is no longer manufactured as a baryta paper.

Forte Bromofort now seems to have taken over.

Chloride paper

Chloride papers are containing a high percentage of silver chloride; they are therefore very slow and have warm tones. These are usually papers for contact printing, and they are quite rare now.

In the past (1885-1940) these paper also were called "gaslight papers". The gas lighting in the living room provided enough light for contact exposures of this paper, which could also be developed safely, once the light source was put at safe distance.

¹⁰ SCHWALBERG, Bob. - Color Preservation Update. In: Popular Photography, January 1982.

¹¹ SWAN, Alice. - Conservation of Photographic Print Collections, In: Library Trends, fall 1981.

¹² RADISIC, Pierre - Les papiers bromure. In: Clichés, n°24, 1986.

Chlorobromide paper

(40% silver bromide + 60% silver chloride)

Chlorobromide paper has low sensitivity to light, a fairly large exposure latitude, gives a lot of detail in shadows without maximum blacks and a specific tonal value that can be changed from brown to olive green by varying the composition of the developer.¹³

One of the most used papers in this group is the Agfa-Gevaert Record Rapid.

Other papers include: Kentmere Kentona & Art Classic, Sterling Tapestry, Oriental Portrait, Kodak Ektalure and Forte Fortezzo Museum.

Bromochloride paper

(40% silver chloride + 60% silver bromide)

Color variations are less marked with this type of paper than with chlorobromides. For example, selenium toning usually produces a rather purplish color.

In this category: Ilford Gallery and Oriental Seagull.

Variable Contrast Paper (VC)

Variable contrast baryta papers form a separate category. The big advantage of this type of paper is the ability to locally change the contrast of the image by using a combination of yellow and magenta filters.

The paper has two photosensitive layers, each of which is sensitive to a different part of the light spectrum; hence the need to use a series of different color filters. All major paper brands now have their own VC paper.

The light source of the enlarger also changes the print contrast: condensor enlarger = more contrast; cold light enlarger = softer contrast.

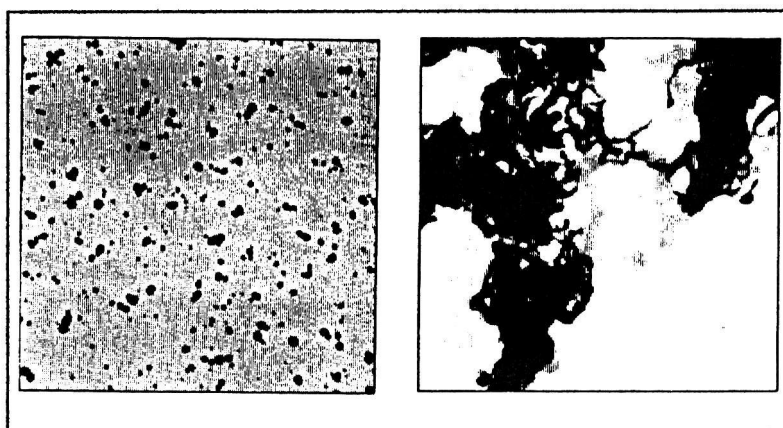
Forte Polywarmtone VC and Polygrade, Agfa Classic, Ilford Multigrade FB, Kodak Polymax Fine Art and Kentmere Fineprint are well-known examples of VC baryta papers.

¹³ RADISIC, Pierre. - Les papiers chlorobromure. In: Clichés, n°26, 1986

Image-forming silver

A two-dimensional image consists of particles that absorb, reflect or scatter light. In the case of a silver print, finely dispersed silver particles are selectively absorbing the light that would otherwise be reflected by the paper substrate.

The difference in aspect and the variations of the relative silver emulsion stability depend on the physical form of the metallic silver in the silver image.



Small silver particles give warm tones (leaning towards yellow, red and brown), while relatively large silver particles produce more neutral black tones. The shape of the silver particles is also important. The stretched or irregularly shaped silver particles make the image more neutral than the same amount of spherical particles.

A third element influencing the color of the image is the distance between the silver particles. A compact group reacts to light in the same way as one single larger particle.

The color shades of silver prints are caused by the interaction of these microscopic structural properties. The microstructure of the silver images is put in place during the initial formation of the image.

For all P.O.P. (Printing-Out-Paper), the image consists of **photolytic silver**. "Photolytic" literally means "degraded by light".

The photolytic silver particles are more or less spherical. The silver particles in the resulting images are smaller and fewer in the highlights than in the shadows, since the size of the individual particles is directly proportional to the amount of light absorbed during the exposure.

During processing, **filamentous silver** is created in the form of fine intertwined filaments. A filamentary particle typically consists of a bundle of intertwined filaments that appear to be huge compared to the small spheres of photolytic silver.

Conservation problems specific to the baryta structure

All silver prints are formed of finely divided silver in an organic colloidal layer coated on a paper backing. They are all subject to the chemical instability problems of this silver, that oxidizes and tarnishes.

The problems inherent in the delicate laminar structure of the assembled materials are less well known, although they can cause as much damage as the well-known fading of the image.

First, there is the expansion and contraction of different layers during atmospheric humidity changes. The emulsion layer expands more than the paper backing. As a result, the print is wrinkling and / or curling.

The amount of buckling depends on the surrounding humidity and the thickness of the different layers. If the buckling is recent, this kind of deformation can be eliminated from an unassembled print by using a hot press and moistening the print or, when the buckling is important, by re-soaking and re-drying the print.

The use of so-called "Print Flattening Solutions" in order to avoid buckling should be strictly discouraged. These solutions contain hygroscopic (moisture absorbing) substances, generate abnormal moisture in the print, and cause the emulsion to swell. High humidity levels also favor the formation of fungi.

Traditionally, wrinkling and buckling problems have been solved by so-called hot-press mounting; that is, by bonding the print to a support in a heated mounting press. As we will see later, this kind of mounting is not recommended for archival quality prints.

A second problem related to the print structure is its extreme vulnerability due to the deformation of the paper. Even a slight curvature subjects the outer layer to significant pressure and tensile stresses. As a result, the emulsion may crack and bend and the paper support may eventually tear.

Storage boxes for unmounted baryta prints should provide a rigid support to prevent bending. In most cases, conservation tasks involve correcting or minimizing existing damage, and/or improving storage conditions.

As well-defined and well-described conservation treatments exist today, it is possible to require guarantees, as far as conservation techniques for newly acquired photographic works are concerned.

The life of a silver print depends on a number of factors. The most common among them certainly is the presence of residual chemicals in the emulsion and the paper backing. The photographer is not always aware of the reliable treatments that should be used in order to ensure a good permanence to his work.

The photographer, and especially the fine-art photographer, has an important moral responsibility towards the person who buys his work and wishes to preserve it for future generations in a private or museum collection.

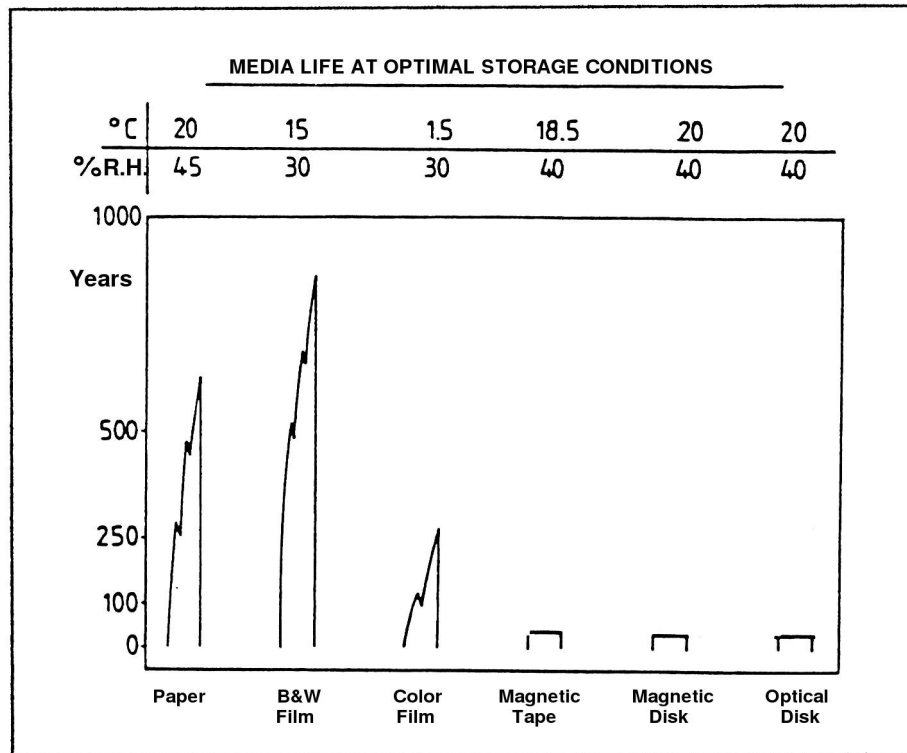
Conservation techniques that attracted a lot of attention in recent years in international art circles offer the necessary guarantees. It is therefore important that all trained photographers, and certainly those who received an artistic training, develop their skills in these techniques and apply them methodically in their own work.

In the popular press, not much has been published on this subject, while most museums and galleries have only recently developed an interest in photographic permanence. However, most photographers are aware of the possible effects of improper processing and storage on photographic materials.

Old photo albums usually offer excellent examples of deterioration, fading, discoloration, staining and other damage.

The main studies about photographic permanence were mostly made in the United States in the 1940s.¹⁴⁻¹⁵⁻¹⁶ But only a small part of this information did reach the average photographer.

The following illustration gives an idea of the relative lifespan of various visual media according to a study conducted in the United States.¹⁷



Compared to the most modern substrates, black and white emulsions processed and stored under optimal conditions remain the most stable.

¹⁴ CRABTREE et al. - The Elimination of Hypo from Photographic Images. In: Journal of the Photographic Society of America, October 1940.

¹⁵ CRABTREE et al. - The Removal of Hypo and Silver Salts from Photographic Materials. In: Journal of the Society of Motion Picture Engineers, July 1943.

¹⁶ CRABTREE et al. - The Quantitative Determination of Hypo in Photographic Prints with Silver Nitrate. In: The Journal of the Franklin Institute, vol.235, April 1943.

¹⁷ CALMES, Alan. Relative Longevity of Archival Information on Paper, Film, Magnetic and Optical Recording Media. In: Proceedings of the International Preservation Symposium, Bangkok, 1986.

Conservation processing consists, among other things, of processes that remove most traces of residual products such as: silver salts, fixing salts and silver-fixer composites from silver prints and negatives.

All operations described should be done carefully, using fresh solutions. Careful attention should therefore be paid to avoid exceeding the chemical capacity of the various baths. It must also be ensured that the solutions are not contaminated by splashing. Last but not least, the tanks and trays used must be clean and the most impeccable working conditions must be guaranteed.

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3. Comparison between traditional and conservation processing

Traditional processing of baryta emulsions

- 1- Exposure
- 2- Developer: minimum 3 minutes
- 3- Stop bath or water rinse: minimum 30 seconds
- 4- Fixing: from 3 to 10 minutes
- 5- Wash: in running water for minimum 30 minutes
- 6- Drying: natural or in the glazing press
- 7- Storage

Preservation processing of baryta emulsions according to pH7

- 1- Exposure: leave unexposed margins of 2 to 2.5 cm.
- 2- Develop the print thoroughly.
- 3- Stop bath: 30 sec. under constant agitation
- 4- Allow to drain for 5 sec.
- 5- Fixing: 30 sec. under constant agitation in a rapid fixer, at film concentration.
- 6- Allow to drain for 5 sec.
- 7- Wash: in running water for 30 seconds. Then put the print in a water bath, until having a full series of prints available for toning at once. If there will be no toning, go to 10).
- 8- Selenium toning: in a warm bath (24 to 26 ° C), with rotation of stack for 6 min, or until a barely perceptible color shift appears.
- 9- Rinse: in cold running water (<20 ° C) for 5 min.
- 10- Washing aid: with rotation of stack for 6 min. in 1+10 diluted pH7 wash-aid.
- 11- Final wash: in a vertical washer, for 15 min. under running water (4 l/min.), then soak for 30 min. in still, clean water.
- 12- Remove excess water by squeezing between two sheets of polyester.
- 13- Drying: slow air-dry, on fiberglass screen (mosquito net).
- 14- Mounting: two-element mount, with acid-free bottom board and mounting materials.
- 15- Framing: a possible frame should be made according to archival standards.
- 16- Storage of prints, mounted or not, in acid-free storage boxes.

4. Exposure and development

Exposure of a baryta emulsion

Exposure as such is not part of the conservation processing process. The paper is exposed as usual, but it is best to keep an unexposed margin of 2 to 3 cm around the image. This will protect it from mechanical damage to the edges and also reduce the risk, after a certain time, of possible deterioration – fading or metallisation from the edges inwards – a phenomenon that is frequently observed in historic photographic images.

This will also leave an unexposed margin allowing to check the presence of residual products by means of a visual test.

Development

After exposure, the emulsion is developed in an alkaline solution. The development is simply a conversion of exposed silver salts or silver halides into metallic silver. The latter will only have a very short life if it does not receive any additional treatment. The emulsion is still sensitive to light and the gelatin is saturated with alkaline developer which may turn yellow on contact with air (oxidation).

Developers

The developers contain a development or reduction agent, or a mixture of several of them which, together with other chemical components, contribute to the formation of the image.

When the photographic emulsion is exposed, some of the photosensitive silver salt crystals are struck by light. This allows for the formation of a latent image. The image forming process will transform this latent image into a metal image by the action of a reducing agent.

The most common developer formulas combine hydroquinone, metol and phenidone. Other development agents are used for special purposes. They include, among others: amidol, catechol, chlorohydroquinone, para-aminophenol, para-phenylenediamine, and pyrogallol.

The addition of a preservative substance prevents the developer from oxidizing before having been able to react with the latent image. Routinely used preservatives include: sodium sulfite, sodium metabisulfite, potassium metabisulfite, sodium bisulfite or potassium bisulfite.

Other chemicals are added, including accelerating alkalis, to create an appropriate oxidizing environment for the reducing substances. Following accelerators are used: sodium carbonate, potassium carbonate, ammonium carbonate, sodium hydroxide, potassium hydroxide, ammonia, sodium phosphate, acetone, methyl alcohol and borax.

Small amounts of potassium bromide in the developer act as a restrainer or as antifogging, to prevent the developer from depositing small amounts of silver in the unexposed emulsion parts, which would generate a haze.

The main risk associated with the use of developer solutions is that they might cause skin and/or respiratory allergies. These products can also cause skin inflammations resulting in small red spots, and/or itchy, rough and flaky pimples.

The danger of inhalation exists especially during the preparation of powdered developers. The use of a dust mask is therefore desirable.

It is important to avoid swallowing these products. Ingestion of small amounts of certain developer products such as catechol may be fatal for an adult. To reduce the risk of accidentally drinking liquid solutions, it is recommended that you never ever eat or drink in the darkroom. Children and pets should not have access to it, even under supervision.

Recommendations for the use of developers

The use of liquid developers reduces the risk of physical injury or irritation. This danger is also reduced by replacing toxic developers with less toxic ones. Catechin, paraphenylenediamine or pyrogallol developers should be replaced, for example by phenidone.

Preparation

If possible, mix the ingredients under a fume hood, protect hands with plastic or rubber gloves, and your breathing system with a dust mask.

Processing

Never put your bare hands in the developer: use plastic tweezers or plastic gloves. The developer on the skin should immediately be rinsed with plenty of water.

If developer gets in contact with your eye, flush for at least 15 minutes and consult a physician.

Return developers to their containers after use and close the latter, or cover the developer tray to prevent evaporation. This will also increase the life of the developer. Store corrosive products as low as possible to avoid eye and face injury in case of breakage.

Example of a developer formula

- Water, 50°C	750	ml
- Sodium sulfite, anh.	85,0	g
- Hydroquinone.....	5,0	g
- Borax	7,0	g
- Boric acid	2,0	g
- Potassium bromide	1,0	g
- Phenidone	0,13	g
- Water, to make	1000	ml

Reference sheets of the chemicals used

HYDROQUINONE

Discovered: in 1880.

Trade names: Hydroquinon, Hydrokinone, Hydroquinol, Quinol, Tecquinol.

Chemical name: hydroquinone or para-dihydroxybenzene.

Skin contact: moderately toxic - causes allergic reactions and irritation. In solid form, it can cause burns and in liquid form, dermatitis.

Eye contact: moderately toxic

Inhalation: moderately toxic

Ingestion: toxic

In case of decomposition due to heating, corrosive vapors containing quinone may be released.

Protection:

- when mixing: extraction ventilation, dust mask, eye protection, plastic apron and rubber gloves
- during processing: extraction ventilation, plastic apron and rubber gloves

PHENIDONE

Discovered: in 1890.

Trade names: Phenidone and Graphidone.

Chemical name: phenidone or 1-phenyl-3-pyrazolidone.

Skin contact: not very toxic

Eye contact: moderately toxic

Inhalation: moderately toxic

Ingestion: toxic

In case of decomposition due to heat: possible nitrogen oxide fumes

Protection:

- when mixing: extract ventilation, dust mask, eye protection, plastic apron and rubber gloves.
- during processing: extraction ventilation, plastic apron and rubber gloves.

SODIUM SULFITE

Also called sulfurous acid or disodium salt

Skin contact: not very toxic - may cause irritation.

Eye contact: not toxic - may cause irritation.

Inhalation: moderately toxic - may cause irritation.

Ingestion: Toxic - may be fatal at high doses.

In case of decomposition due to heat or contact with acid: may cause toxic sulfur dioxide fumes.

Protection:

- extract ventilation, dust mask, eye protection, plastic apron and rubber or plastic gloves when mixing.
- during processing: requires ventilation and plastic gloves

BORAX

Also known as sodium borate, sodium tetraborate, or disodium tetraborate.

Skin contact: not very toxic - may cause irritation.

Eye contact: Moderately toxic, possible irritation or allergic reactions.

Inhalation: moderately toxic - dusts may cause irritation.

Ingestion: Moderately toxic - may be toxic at high doses.

In case of decomposition due to heat: may cause toxic fumes of sodium oxide.

Protection:

- when mixing: extract ventilation, dust mask, eye protection, plastic apron, rubber gloves.
- during processing: extract ventilation, eye protection, rubber or plastic gloves.

BORIC ACID

Also known as hydrogen borate, boracic acid, orthoboric acid.

Skin contact: moderately toxic - may cause irritation.

Eye contact: moderately toxic - may cause irritation.

Inhalation: moderately toxic

Ingestion: toxic

Protection:

- when mixing: extract ventilation, dust mask, eye protection, plastic apron and rubber gloves.
- during processing: extraction ventilation, eye protection, plastic apron and rubber or plastic gloves.

POTASSIUM BROMIDE

Skin contact: not very toxic - prolonged exposure may cause irritation.

Eye contact: temporary irritation.

Inhalation: moderately toxic.

Ingestion: Moderately toxic - dangerous if in large quantities.

Decomposition due to heat: possible bromide gas fumes

Protection:

- when mixing: extract ventilation, dust mask, eye protection, plastic apron and plastic gloves.
- during processing: extraction ventilation and plastic gloves.

Regarding the actual long-term stability of the baryta emulsion, there is little to say about development, except that it is important to develop thoroughly if subsequent toning is considered. For most baryta papers, the development time may be extended a little more than recommended by the manufacturer. It is preferable to develop each print individually, with sufficient agitation to ensure that the emulsion is in permanent contact with fresh developer.

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5. Stop bath

A stop bath, which is a solution that is less alkaline than the developer, is used to interrupt the action of the developer. The stop bath significantly prolongs the life of the fixer and prevents the staining of the print resulting from the oxidation of the alkaline developer. Rinsing with an acidic solution also reduces the swelling of the emulsion.

The most commonly used stop bath is a very dilute solution of acetic acid with an acidity of about pH = 3.5 for a fresh solution, and a pH = 5.5 for the exhausted bath.

Kodak SB-118 Formula¹⁸

- Acetic acid 28% 48 ml
- Water, to make 1000 ml

For a 28% acetic acid solution, dilute three parts of undiluted acetic acid with eight parts of water.

Undiluted acetic acid is dangerous for the skin and the breathing system. Acetic acid must be mixed in a well ventilated room to prevent inhalation of the acid. To avoid splashing and contact with acid, **pour the acid into the water, and never the other way around.**

The capacity of the stop bath mentioned above is about 1 m² of emulsion per liter of stop bath, which is about 10 sheets of 30x40 cm. It is impossible to determine visually the degree of exhaustion of such a bath. A special test formula has to be used for this.

A safer but more expensive alternative is the use of stop baths containing a coloured indicator. A stop bath that has been exposed to air can be kept for about three days. In case of exhaustion, the bath must be completely replaced. Do not try to regenerate it by adding acetic acid, as the reactive products formed during the use of the bath might cause stains in a toning bath.

¹⁸ EASTMAN - KODAK - Preservation of Photographs, Publication n° F-30, Rochester, 1979.

Usually, the stop bath is allowed to act for about thirty seconds on the emulsion, whether film or paper. The length of this action has to be sufficient to cause an effective transition from an alkaline to an acid state in the emulsion.

Human skin is very sensitive to a pH change: the paper emulsion appears slightly sticky when soaked with alkaline developer. In a properly functioning stop bath, the emulsion quickly loses that slightly soapy feeling and is no longer sticky as soon as the acid status is reached.

Stop bath test

A stop bath without coloured indicator can be tested as follows: about 25 ml of stop bath are poured into a test tube. Two drops of the SBT-1 solution are added. A usable stop bath, still acidic, remains yellowish. Once the acidity neutralized, the solution becomes purple and the stop bath must be replaced.

Kodak SBT-1 Formula¹⁹

- Distilled water at 27°C750 ml
- Sodium hydroxide6 g

To this solution is added, while stirring:

- Eastman Bromocresol Purple4 g

Mix this solution for 15 to 20 minutes. before adding the following products:

- Sulfuric acid3 ml
- Water, to make1000 ml

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¹⁹ EATON, George, M. - Conservation of Photographs, Kodak Publication n° F-40, Rochester, 1985.

6. Fixing

To stabilize as much as possible a negative or a print, two conditions have to be met:

- all the undeveloped silver halides in the emulsion must be reduced by the fixer into a water-soluble state so that they can be removed by a water rinse;

- the fixing chemicals must in turn be removed from the emulsion and the paper by a water rinse.

An insufficiently fixed and/or rinsed silver emulsion will cause bleaching if the storage conditions are not optimal. The reason for this fading usually is the partial/total conversion of silver attacked by sulfur into silver sulfide.

This sulfur may be contained in the residual thiosulfate or be formed by the decomposition of silver thiosulfate complexes which have not been removed by rinsing. Sulfurous gases from the atmosphere also accelerate the formation of sulfides.

A first sulfide formation can be observed as a metallic gloss on the surface of the silver image. In addition, the formation of sulfides causes a gradual color change of the negatives from deep black to a purplish black, then to a brownish black, to brown and finally to a yellowish brown. The faded prints are generally yellowish brown to yellow.

Yellowish or yellowish brown spots may stain the clear parts of the negatives and prints. Sulfurization may be accompanied by an apparent loss in the dark tones.

The fading caused by sulfurization is more visible in fine-grained emulsions than in larger-grain emulsions. Their finer silver grains and more difficult rinsing make baryta emulsions more susceptible to deterioration than film emulsions. Silver chloride emulsions are more sensitive than silver bromide emulsions.

The fixing bath

A fixing bath, formed by 250 g of sodium thiosulfate in 1 liter of water, can fix both film and paper emulsions but would be active for a limited time. A fixing bath usually contains other ingredients such as:

- sodium sulfite as a preservative to prevent the breakdown of the thiosulfate in the acid;

- acetic acid, providing the acidity required for a fixing bath to be effective (pH=5) and to eliminate the alkaline state in the emulsion;

- boric acid, a buffer, to maintain the correct acidity during the operating time.

- alum, to harden the emulsion.

Non-tanning fixer formula

- Water800 ml
- Sodium thiosulfate240 g
- Metabisulfite (K or Na) 67,5 g
- Water, to make1000 ml

This fixer should not be used with bath or wash temperatures higher than 21°C or when a "hypo eliminator" is to be used.

Kodak F-5 Standard Tanning Fixer

- Water600 ml
- Sodium thiosulfate240 g
- Sodium sulfite – anh. 15 g
- Acetic acid 28% 48 ml
- Boric acid - crystals 7,5 g
- Alum 15 g
- Water, to make1000 ml

The ingredients are to be dissolved in the order indicated.

Effect of the fixer's pH

A protein such as gelatin has both acid (-COO-) and basic (NH₃⁺) groups. The acidic groups form protein salts and the basic groups can form proteinate.

Gelatin can be found in the form of a positive or negative molecule, except in one specific case where the molecule is neutral: this is called the "isoelectric point".

In that case, all basic groups have a positive charge, and an equal number of acidic groups are negatively charged.

The isoelectric point for photographic gelatin usually is around pH=4.9

Below the isoelectric point (pH<4.9), the gelatin is positively charged and this charge attracts the negative ions, such as e.g. thiosulfate or silver thiosulfates. They are then very difficult to remove by washing.

Above the isoelectric point (pH>4.9), the gelatin is negatively charged. The thiosulfate ions are no longer retained. Positive ions, such as sodium or potassium, are then attracted.

In the case of a film emulsion, where the substrate absorbs virtually no residual processing product and where the gelatin layer therefore prevails, it might be interesting, to foster a good wash, to use a fixer with a pH value nearing the isoelectric point.

When washing baryta emulsions, however, other factors intervene which will be examined later.

The effects of fixer exhaustion

The increase of silver thiosulfate complexes in the fixer during its use plays an important role in the composition of the latter.

The depletion of the fixer is also fostered by the transfer of an uncontrollable amount of developer, which increases the pH of the solution. However, when an acidic stop bath is used after the developer, this pH increase is small.

Fixing film emulsions

Sodium thiosulfate is by far the most commonly used fixer. Ammonium thiosulfate is mainly used in rapid fixers; it reduces the fixing time by about 50%.

Usually, the fixing time for films is considered to be equal to twice the time necessary for the film to become transparent in the fixing bath. This rule of thumb is valid when the fixing solution stays in contact with the entire surface of the film emulsion for the entire immersion time. This is practically the case when the film is correctly wound on a reel, or when a sheet film is processed alone in a tray.

When several sheet films are processed simultaneously, things are very different. The films tend to stick together and then prevent the fresh fixer from being in contact with the entire surface of the emulsion. When multiple films are fixed at the same time, they must be constantly in motion during the whole fixing time.

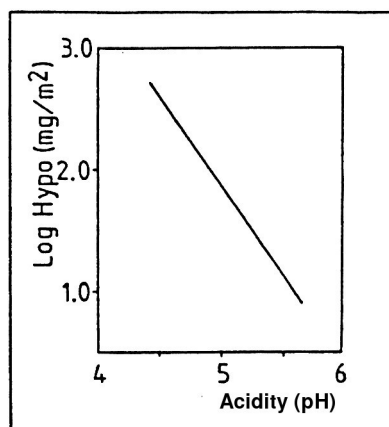
The presence of a more or less large spot in the middle of a processed sheet is a sign of incorrect agitation and indicates that the fixing solution was active only on the sides.

It is very important not to exceed the exhaustion limit of the fixer because the silver concentration increases gradually as more and more silver halides are being dissolved. The silver thiosulfate salts then become more and more complex and are therefore more difficult to remove in the wash.

The influence of the fixing bath's pH on the residual thiosulfate in a film emulsion should not be underestimated. The figure below shows the effect of a tanning fixer's pH on the residual thiosulfate in a Kodak Verichrome Pan film.

The residual thiosulfate is presented on a logarithmic scale so that:

1,0 = 10 mg/m² and
2,0 = 100 mg/m².



The fixing of baryta emulsions

The amount of thiosulfate absorbed by a paper emulsion is proportionally greater than that absorbed by film. Finely divided silver from a silver print, and especially from warm-toned paper, is quite prone to be attacked by the residual thiosulfate in the baryta layer and the paper. Such damage is usually quickly noticeable because the white of the paper backing brings out the stain.

Many photographers use to fix a number of prints simultaneously in the same bath. We have seen above that this increases the risk of stains. We have therefore to make sure that the prints are fully fixed if we want to get a stable image.

It is often asked whether it is better to introduce the prints into the fixer with the emulsion side down or up. In any case, as the paper tends to float on the bath, it should never just be left to its fate.

If the sheet is not completely submerged, and if air bubbles form under the sheet, this may cause stains on both sides. The print must therefore be kept in constant motion. In general, it is recommended to use the same agitation scheme as for development.

Single bath fixing

As successive prints pass through the fixer, the silver content increases continuously. It goes without saying that a very clear ("high key") print leaves more silver to be dissolved than a very dark ("low key") one. The rules of thumb specifying a paper surface per liter of fixer should therefore not be followed blindly. The safest method is to test regularly the fixer. Knowing that the concentration of silver generates silver components that are almost impossible to eliminate once they have reached a certain level in the support, it is of utmost importance to be very attentive to this.

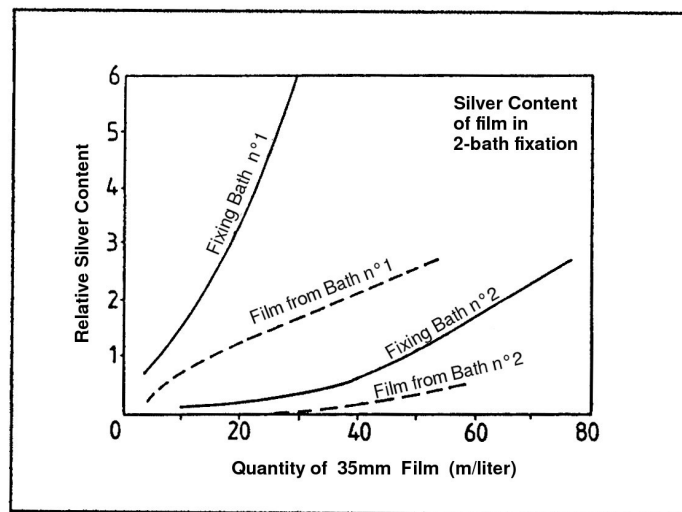
It has been experimentally determined that one should not exceed 1.5 g to 2.0 g of silver per liter of paper fixer. When fixing in a single bath, it is therefore necessary to test the latter very regularly, as the silver content can easily be exceeded without the operator noticing.

Two-bath fixing

Nowadays, many photographers use the two-bath method, and are processing their prints for respectively half the total fixing time in two separate baths. It goes without saying that these baths, after use, can not be mixed.

Most of the silver halides are dissolved in the first bath; the remainder is then dissolved or solubilized in the second. Kodak recommends the following method:

- mix two fresh baths placed next to each other;
- fix for half of the total time in each of the two baths;
- replace the first bath after having processed about 2.7 m² of paper per liter (?) of fixer;
- the second bath then becomes the first;
- a fresh bath is prepared for the second;
- this cycle is repeated four times;
- After the 5th cycle, a fresh solution is prepared for both baths.



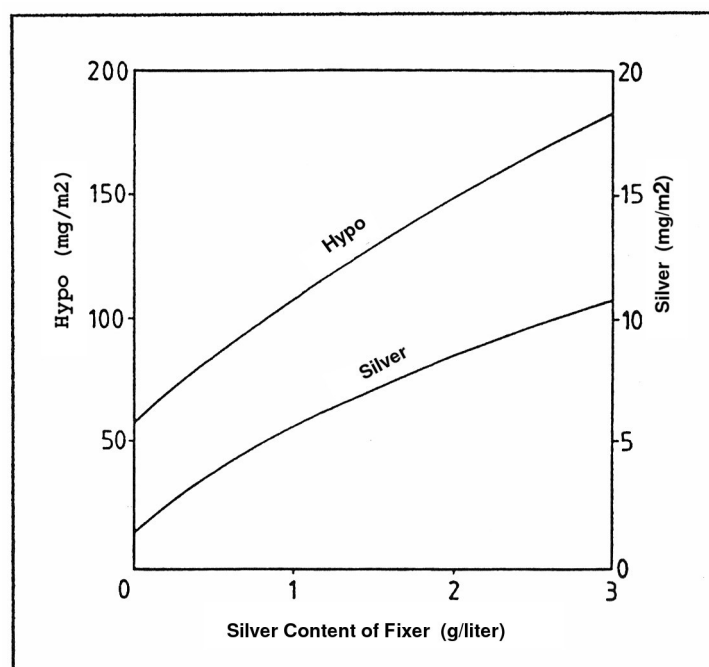
G. Eaton²⁰ shows in the graph above that most of the silver is dissolved in the first bath, and that the fixing is then completed in a second fresh bath where the silver concentration remains very low. The dashed lines show the silver retention in the processed film. A similar phenomenon also occurs with paper emulsions.

²⁰ EATON, George, T. - Preservation, Deterioration, Restoration of Photographic Images. In: The Librarian Quarterly, Jan. 1970.

Fixer tests

In order to avoid an undesirable increase of the silver content, the fixer must be tested regularly. A convenient way to do this is to use a test paper specially designed for this.

The paper developed by Agfa-Gevaert to test the silver content has the form of a yellow 10 mm wide paper strip. The test strip is immersed for a few mm in the fixer, then shaken. After 10 seconds, it is compared to an associated color scale, graduated for a silver content from zero to 10 g./liter. The test paper turns brown when the silver content increases.



Above, a graph showing the silver and thiosulfate content of a silver print as a function of the fixer's silver content. A stop bath was used to keep the acidity of the fixer constant. Here, a single weight Kodak Velox paper was fixed in the Kodak F-5 fixer for 10 minutes, then rinsed for 30 minutes.

Kodak FT-1 Test Solution for fixers

- Water (26 - 27°C)750 ml
- Potassium iodide190 g
- Water, to make1000 ml

The solution can be stored in an air-tight bottle for one year.

For single bath fixing:

Five drops of the fixer to be tested are added to 5 drops of a FT-1 solution and 5 drops of water. The fixer should be replaced if a yellow-white precipitate forms immediately. A slightly milky appearance is negligible.

For two-bath fixing:

First bath: test as above.

Second bath: five drops of fixer and 15 drops of water are added to 5 drops of FT-1 solution. Test as above.

The following table shows the currently prescribed maximum values for the permissible thiosulfate content in modern black and white emulsions:

	<u>commercial</u> <u>use</u>	<u>Long-term conservation</u>	
		>100 year	archival
<u>Baryta paper</u>			
double weight	0,4 g/m ²	0,2	0,1
single weight	0,2	0,1	0,05
<u>film emulsion</u>			
X-ray film	0,1	0,05	0,025
microfilm	0,06	0,03	0,014

It appears that the values for films are quite different from those for paper emulsions. This is due to the fact that the acetate or polyester substrates absorb little or no liquid, whereas the paper support is made of cellulose fibers that are almost immediately saturated with liquid when immersed.

The study of the ratio between the residual thiosulfate content and the image stability in silver emulsions is based on the use of artificially accelerated aging tests.²¹

²¹ KOPPERL, D.F. - Use of Arrhenius Testing to Determine Thiosulfate Tolerance in Silver Halide B/W Materials. International Symposium: Storage of Recorded Images. Royal Photographic Society of Great Britain, Oxford, 1987.

Fixing time

The ideal fixing of baryta papers is a very controversial problem, misunderstood by many photographers. We know that prolonged fixing can lead to the presence of thiosulfate-silver components that are difficult to remove. This can cause yellowing throughout the thickness of the paper. The fixation time therefore plays an important role in the archival processing for baryta emulsions.

Kodak recommends a total fixing time of 6 to 10 minutes. This includes a margin to compensate for the risk of fixing flaws when several prints are fixed simultaneously, and for the increase of silver content in the fixing bath. This overestimated fixing time was taken over by other photographic paper manufacturers.

For his Gallery paper, Ilford recommends a total fixing time of 1 minute in a **non-tanning** fixer (Hypam) at **film strength**.

In this regard, D. Vestal²² emphasizes the lack of protection due to the use of a non-tanning fixer, resulting in soft and fragile prints. He recommends the use of a rapid tanning fixer at film strength, for 30 seconds and with continuous agitation.

Since the permissible and sufficient fixing time for film can be estimated at twice the clearing time of this emulsion in the fixer, the same tends to be applied for baryta papers.

Experimentally, the photosensitivity of paper emulsions can be compared to that of a known low sensitivity film, such as e.g. a microfilm emulsion.

T. Hill²³ compared the Kodabromide double weight baryta paper with the Agfa-Gevaert Copex microfilm. This emulsion becomes transparent in the fixer after 20 seconds. After fixing the Kodabromide for 30 sec. in a Kodak rapid fixer, the Kodak ST-1 test did not show any presence of residual silver in the emulsion.

This test uses a weak solution of sodium sulfide applied in an unexposed part of the print. Staining caused by the ST-1 solution indicates the presence of silver and therefore insufficient fixation.

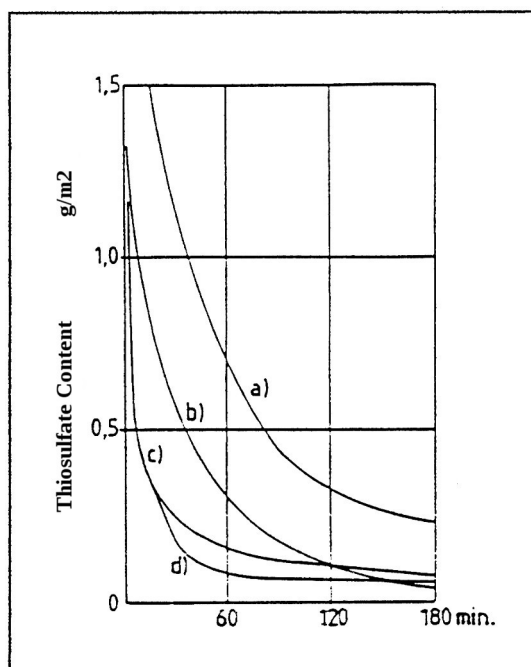
²² VESTAL, David. - Letter tot the Editor. In: *Photographic Conservation*, vol 1, n°1, 1979.

²³ HILL, Thomas, T. - In-Forum. In: *Photographic Conservation*, vol. 1, n°1, 1979.

R. Steiner²⁴ compared Kodak's standard 2-bath fixing time with a fast 30-second fix in Kodak Rapid Fixer (tanning) at film strength. Immediately after fixing, he used the Kodak Hypo Clearing wash-aid for 3 min. The residual thiosulfate content was determined by the silver nitrate ASA method.

For the print fixed the standard way, he extended the wash for two days; the residual thiosulfate content then corresponded to that found for a 12-minute wash after the rapid fixing method !!

The following graph shows the results of a study²⁵ concerning, among other, the fixing time of the Agfa Brovira 111 baryta paper.



Curve a corresponds to the fixing salts elimination by a running water wash after a 2-bath fix in Agefix 1+9, without wash-aid after fixing.

Curve b = 2-bath fix as above, but with wash-aid after fixing

Curve c corresponds to a rapid fix in Agefix 1 + 5 followed by a wash-aid bath.

²⁴ STEINER, Ralph. - Comparing Fixing Methods. In: *Photographic Conservation*, vol.2, n°1, 1980.

²⁵ KOCKAERTS, Roger- *De Deville archivale spoelbak en de spoeling in 2-tijden*, Deville publicatie, Photokina Köln, 1992.

The residual thiosulfate values were measured by spectrophotometric analysis according to the international standard ISO-417²⁶

Various conclusions can be drawn:

- both fixing techniques make it possible to reach the archival 0.1g/m² value for thiosulfate content and are therefore both recommendable;

- rapid fixing reduces the accumulation of fixing salts between the cellulose fibers, which allows to develop an economical archival washing technique as described below;

- in order to respect the archival authorized limit for thiosulfate content, a wash-aid bath after fixing is absolutely essential.

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²⁶ ISO - 417 -1979. - Methylene Blue Method for Measuring Thiosulfate, and Silver Densitometric Method for Measuring Residual Chemicals in Films, Plates and Papers.

7. The wash-aid bath

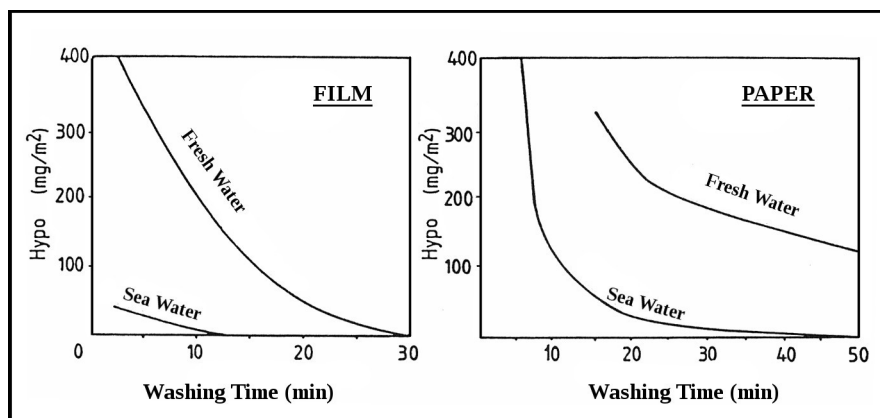
Since the end of the last century (Dr. Bannow in 1889 and Dr. Bayselance in 1903), experiments have shown that seawater removes thiosulfate from photographic emulsions faster than fresh water.

During the second world war, this phenomenon was also observed by American press photographers and filmmakers on mission in the South Pacific.

Eastman-Kodak used these findings for further experiments, to design and market a washing aid bath, the Kodak Hypo Clearing solution.

Seawater contains about 3.5% of different salts, 25% of which is sodium chloride and more than 3% magnesium chloride.

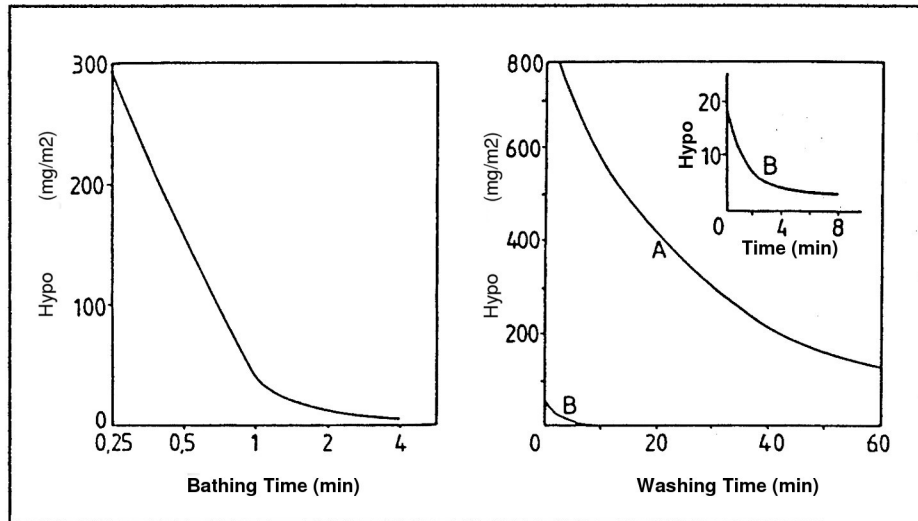
A certain number of carbonates, nitrates, sulfates, bromides, etc. are also present in small quantities. The graph below clearly shows the effect of salt water on film and paper emulsions.



Among other things, it can be seen that with paper emulsions the residual thiosulfates are very difficult to remove with fresh water.

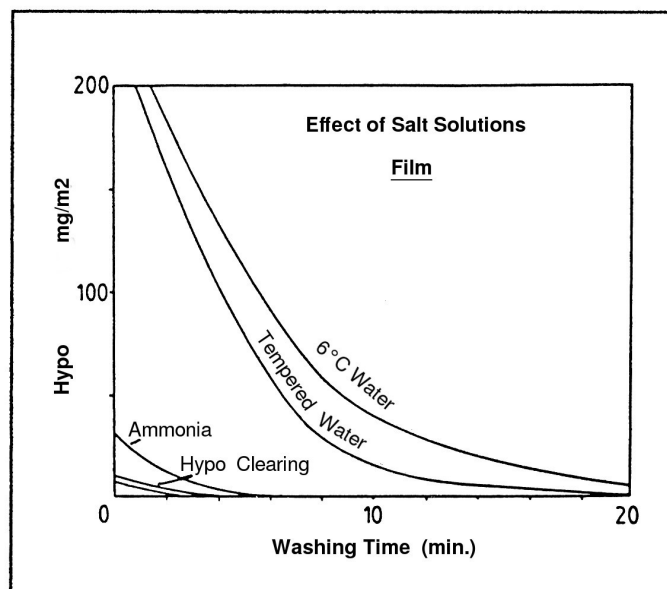
Research on this phenomenon has shown that some inorganic salts behave in the same way as seawater salts.²⁷

²⁷ HENN, R.W. et al. - The Effect of Salt Baths on Hypo and Silver Elimination. In: *Photographic Engineering*, 7, 1956.



The figure above shows the effect of softening a sheet film in a sodium sulfite solution after fixing (left). After two minutes of soaking, the film was washed (curve B right) and the result compared to a prolonged water wash (curve A right) without wash-aid.

In the following illustration, Eaton²⁸ demonstrates the efficient operation of the Kodak Hypo Clearing Solution (KHCS). It is observed that KHCS allows for a fairly quick thiosulfate elimination, regardless of the temperature of the wash water.



²⁸ EATON, George, T. & CRABTREE, J.I. - Washing Photographic Films and Prints in Sea Water. In: *Journal of the Society of Motion Picture Engineers*, n°40, June 1943.

The effect of KHCS on baryta emulsions is similar to that on film emulsions, but the last traces of residual chemicals are more difficult to remove, especially with "double weight" baryta paper.

Here is a table with the uses of KHCS²⁹

	Rinse after fixing	KHCS	Final wash	Number of 8x10" prints per liter
Film	W/O	1 to 2 min.	5 min.	12 to 15
Film	30 sec.	1 to 2 min.	5 min.	35 to 50
Baryta, double weight	sans	2 min.	10 min.	20
Baryta, double weight	1 min.	2 min.	10 min.	50
Baryta, double weight	sans	3 min.	20 min.	20
Baryta, double weight	1 min.	3 min.	20 min.	50

A proven way of handling the fixed prints in the washing aid is by manual rotation through a stack of 6 to 10 prints.

We start with a stack of prints, image side up. The prints are pulled one by one from bottom to top, and turned over as well. Once through the whole stack, the latter is flipped so that the prints are face up again. This cycle is repeated. Total processing time: usually 6 to 10 minutes.

After the wash-aid and before carrying out the final washing, it is generally recommended to rinse the baryta paper with pure water, or even to rub it with a cotton swab moistened with pure water. In doing so, any undesirable sediment will be removed from the surface of the emulsion.

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²⁹ EASTMAN-KODAK - Kodak B/W Darkroom Data Guide, Rochester, n.d.

8. Toning

Photographic emulsions toned by a process converting the silver image into silver sulfide or selenide are more stable than emulsions that were not.

On one hand, silver sulfide or selenide is less affected by the oxidizing gases of the atmosphere and on the other, the success of the toning requires correct fixing and removal of the thiosulfate by washing. A properly toned emulsion therefore is also free of residual chemicals. The success of the toning is thus also a sign of archival quality.

For sepia toning, either the hypo/alum or the bleach/redevelopment technique can be used.

If a color change of the image is not desired, other methods are used. For example, the partial selenium or gold chloride toning, where the image undergoes only a slight change of color.

These are not toning processes in the normal sense of the term: the silver grains are coated with a layer of selenium or gold, which protects them from atmospheric oxidizing gases.

For a more in-depth study of toning techniques, we refer to a recent research report "KASKA"³⁰. (Koninklijke Academie voor Schone Kunsten van Antwerpen – Royal Academy of Fine Arts Antwerp)

Kodak T-1a Sepia Toning

This toning bath gives very stable images, more resistant to fungi formation than any other treatment. This treatment is especially recommended for use in tropical regions.

- Cold water2800 ml
- Sodium thiosulfate 480 g

Dissolve completely before adding the next solution.

- Hot water 70°C 640 ml
- Alum, powder 120 g

³⁰ Sylke HEYLEN - Studie van de chemische omkleuring van fotografische emulsies. Unpublished research report. c&r fotografie, Hogeschool Antwerpen, 1997-1998.

Next, slowly add the following solution to the alum/thiosulfate solution while stirring continuously and rapidly :

- Cold water 64 ml
- Silver nitrate 4 g
- Sodium chloride 4 g

When the above mentioned solutions are mixed, add :

- Water, to make : 4000 ml

Note: Silver nitrate must be completely dissolved before adding sodium chloride. The milky white precipitate is then mixed with the hypo/alum solution as prescribed. The formation of a black precipitate does not affect the toning potential of the bath.

Procedure

The toning bath is heated to 50°C in a water bath. At this temperature, the prints are toned in 12 to 15 minutes, depending on the emulsion used.

This toning causes a loss of density and contrast. The prints to be toned must be fully fixed and rinsed for 5 to 15 minutes before being placed in the toning bath. Dry prints have first to be saturated with water.

After toning, the prints are wiped with a soft sponge or cotton wool and warm water to remove any sediment. Then they are treated in a wash-aid bath and finally rinsed with running water.

Bleach/redevelopment process

From the point of view of preservation, this method is to be preferred: the solutions are used at normal temperature and do not contain thiosulfate. In addition, all the processing defects are highlighted, as the bleaching of the image is accompanied by a formation of silver halides, which are very sensitive to the presence of residual thiosulfate.

If thiosulfate remains in the emulsion, either pale yellow or yellow spots or a yellow haze are formed over the entire area of the print. If residual silver is present, it will discolour in the same way as the image forming silver and cause spots in the highlights and unexposed edges.

Kodak T-7a Sepia Toning

Bleaching bath A

- Water 2000 ml
- Potassium ferricyanide 75 g
- Potassium oxalate 195 g
- Acetic acid 28% 40 ml

For a ready-to-use bath, mix 1 part of solution A with 1 part of water. Preferably use a plastic container.

Toning bath B

- Water 500 ml
- Sodium sulfide 45 g

For a ready-to-use toning bath, mix 1 part of solution B with 8 parts of water.

Kodak F-5a tanning bath

- Water 50°C 600 ml
- Sodium sulfite 75 g
- Acetic acid 28% 235 ml
- Boric acid, crystals 37,5 g
- Alum, powder 75 g
- cold water, to make : 1000 ml

Procedure

The prints to be toned have first to be fully washed. Dry prints are first saturated with water.

The prints are placed in the bleach until only a weak yellow-brown image subsists. Next, the print is carefully rinsed in cold running water for at least 2 minutes.

The print is then processed in the toning bath until every detail is visible again. This takes about 30 seconds. The print is rinsed with pure cold water for at least 2 minutes.

Next, the emulsion is tanned in the F-5a solution diluted 1 + 8. Neither the color nor the contrast are affected by this bath.

The final wash is carried out at a temperature of 18 to 21°C for at least 30 minutes.

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9. Combined toning & wash-aid

Conservation toning baths

Selenium toning

- Water, 24-26°C 3000 ml
- Kodak Rapid Selenium Toner..... 200 ml
- Wash-aid, working sol. 800 ml

With this method, the image undergoes only a slight, easily controllable color change.

After fixing, the prints are rinsed for five minutes and toned for 5 to 6 minutes, with agitation.

A practical method is to manipulate all the prints to be toned at the same time, after having reserved the prints of an entire session in a tray filled with pure water. Before placing the prints one after the other in the selenium bath, emulsion upwards, they are allowed to drain for five seconds. The prints are then kept in constant motion for the entire processing time, placing the bottom print on top of the stack at a steady rate, one at a time. This way, each print can be checked visually.

The image changes color slightly after 5 to 6 minutes. This results in richer black tones and a slight shift to purple. But there is no radical change. The change in intensity is noticeable by a sudden deepening of black and dark gray tonal values. After that, the prints are rinsed with cold water for 5 minutes. A water temperature $> 20^{\circ}\text{C}$ removes almost all the selenium color cast. After this short rinse, the prints are treated in a wash-aid bath as prescribed, followed by the final wash.

Warning!

It has long been known that the use of a selenium solution can be hazardous to health. It is therefore recommended to wear rubber or plastic gloves when using this bath.

Gold chloride toning

Gold can also be used to protect the silver emulsion of black and white baryta papers. The gold chloride bath is of course more expensive than the selenium bath, but its costs can be minimized by keeping the fully processed and dried prints until having a sufficient number of them. They can then be toned together, and the bath used as efficiently as possible.

The best results are obtained when the last traces of residual thiosulfate are removed by means of a hyposulfite eliminator solution, completely reducing the thiosulfate to harmless sodium sulfate which can be removed easily from the emulsion.

Kodak Hypo-Eliminator HE-1

- Water	500 ml
- Hydrogen peroxide, 3%	125 ml
- Ammonia 28%, 1+9 sol.	100 ml
- Water, to make	1000 ml

The solution must be mixed immediately before use.

Do **not** place this preparation in a stoppered (cap or screw cap) bottle, as the generated gas may burst the bottle.

The capacity of the HE-1 solution is about 0.7 m² of baryta papers per liter of solution. The storage time is about 1 hour!

The HE-1 solution should **not** be used for film emulsions because the gas formation can crack their support.

After the wash-aid step, or after washing with water for about 30 minutes at a temperature of 18 to 21°C, each print is immersed in the HE-1 solution at 20°C for 6 minutes. This is followed by a water rinse for 10 min. The rinsing time should be extended if the temperature is lower.

Kodak Gold Protective Solution GP-1

- Water 750 ml
- Gold chloride, 1% sol. 10 ml
- Sodium thiocyanate 15 g
- Water, to make 1000 ml

A 1% gold chloride solution is obtained by dissolving 1 g of gold chloride in 100 ml of water.

The gold chloride solution is added to the indicated volume of water. Sodium thiocyanate is mixed **separately** in 125 ml of water and this solution is **slowly** mixed into the gold chloride solution with constant and rapid stirring.

The GP-1 toning capacity is about 0.4 m² of emulsion per liter of solution. The GP-1 solution has to be prepared just before use.

After treatment with the hyposulfite eliminator, the print to be toned is placed in a GP-1 solution at 20°C for about 10 minutes, or until a slight color change occurs. The color becomes slightly bluish in the black tonal values.

Finally the print is rinsed under running water for 10 minutes, and dried as usual.

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10. Washing

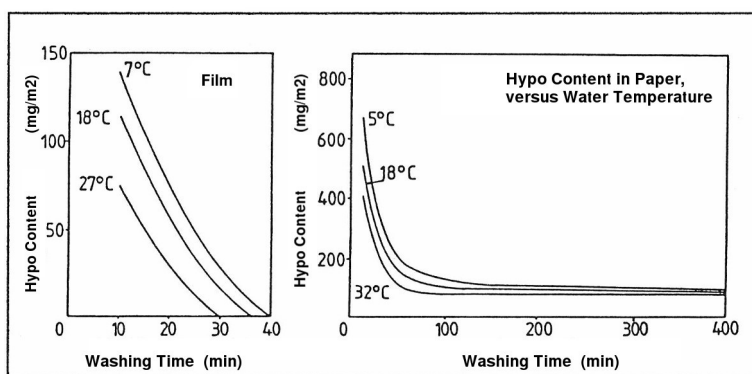
Wash water

In principle, the archival processing of baryta emulsions requires significant amounts of pure water to remove the residual chemicals from the emulsion and the paper support. Tap water is generally satisfactory for the final washing of film and paper emulsions.

The water is hard or soft, depending on the amount of dissolved calcium and magnesium salts. Hardness of water has little influence on the stability of photographic emulsions, except that lime can be deposited on the gelatin layer. Very soft or alkaline water causes the gelatin to swell. This is particularly the case with the low-salt water coming from a water softener.

Spring water may contain sulfides or dissolve plant materials. The presence of sulfides can be detected by a characteristic smell of rotten eggs when heated. A greenish color indicates the presence of dissolved vegetable substances. These impurities can be removed by filtration or by chemical means. In general, it is assumed that water is satisfactory for photographic washing when it is colourless and odorless and does not have a sulfurous smell when heated.

The temperature of the wash water has a significant influence on the rate of removal of the thiosulfate and silver components.



Eaton²⁸ mentions that it is desirable to maintain the temperature of the wash water between 14 and 17°C. The effect of temperature on the washing time for film and baryta emulsions is presented above. Once again, this chart makes clear that it is easy to achieve complete elimination for films, but impossible for paper.

A water temperature increase thus accelerates the washing. However, the washing temperature must not exceed 25°C in order to avoid putting at risk the adherence of the gelatin layer.

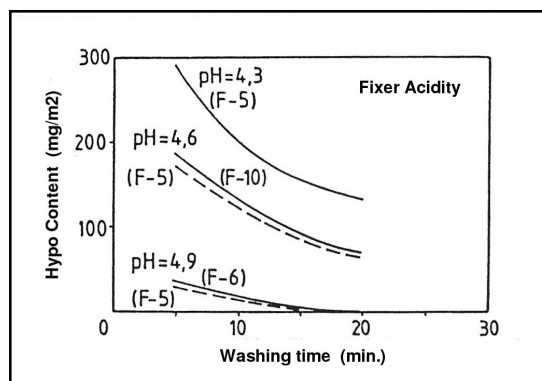
Washing equipment

It is regularly stated in the specialized literature that the water must have a flow sufficient to fill the tank or the wash tray in 5 minutes. However, this flow must not generate excessive turbulence, which could damage photographic emulsions.

This requirement is easy to deal with when using a small volume washing equipment. But in the case of a medium size tray, a vertical washer with a volume of 50 liters for example, how to ensure a flow of 10 l/min. without causing excessive turbulence? It therefore seems preferable to stick with a fixed water flow, for example 4 l/min.

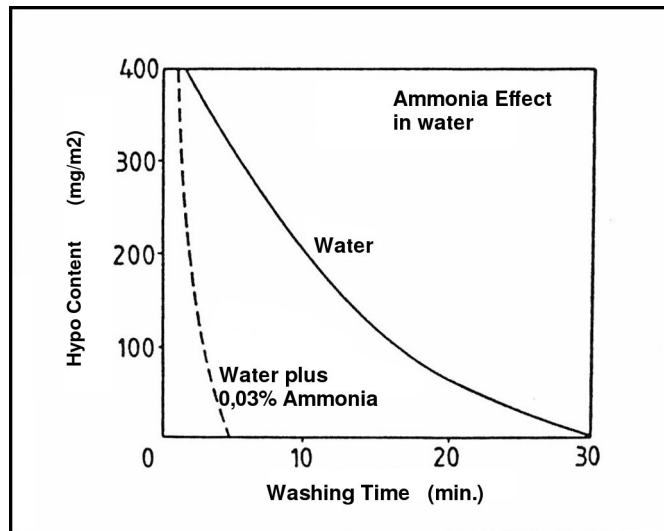
Washing films

Washing film emulsions is relatively easy since the film substrate absorbs little or no chemicals. It is admitted that under good conditions, a film emulsion is sufficiently washed in 15 to 20 minutes.



We know that photographic gelatin has a pH = 4.90. The graph above shows the effect of fixer acidity on thiosulfate removal. Solid curves show how increasing pH accelerate its elimination. The dotted curves show what happens when the pH of the same fixer solution is increased. The effect of pH is even greater as soon as the pH of the water exceeds 5.0.

The following figure shows how a 0.03% ammoniacal solution increasing the pH of gelatin to 9.0 allows an extremely rapid elimination of thiosulfate.



This pH effect is only observed with film emulsions. According to Eaton²⁸, this is not true for paper emulsions where the effect seems insignificant.

Washing baryta papers

Recent research determined that the acceptable thiosulfate content for long-term storage of a baryta emulsion is currently not exceeding 0.1 g/m². The removal of residual fixing salts has posed major problems for many generations of photographers for the good reason that no source of harmful substances can be detected visually, either during or after treatment.

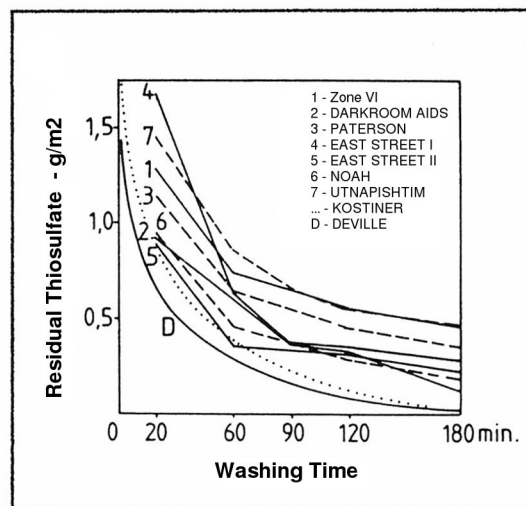
Over the years, various methods for washing baryta emulsions have been recommended and a list of more or less effective washing devices established. These include vertical compartment washers, whose apparent ease of residual processing products' removal is highlighted by the manufacturers' advertising.

Washing in a vertical washer

A comparative study of seven washers on the American market highlighted the essential characteristics of such washing devices:

- compact size;
- emulsions remain separated during washing;
- pure water must reach the surface of each print;
- the prints can soak in clean, still water;
- easy cleaning without accumulation of inaccessible dirt.

The graph below is a visual representation of the study in question, where the residual thiosulfate content (g/m^2) in the paper emulsion was expressed as a function of wash time (in minutes). The water flow was 3.8 l/min .



The washing curve of the recently discontinued Kostiner washer was added in dashed lines, as well as a "D" curve for the French Deville washer. The washing scheme of all these tests is almost identical, so that the results can be compared to each other.

It is striking that in order to obtain a thiosulfate content $<0.1 \text{ g/m}^2$, which is the archival limit value, remarkably large quantities of water are required. Only two washers reached this limit after 120 minutes of washing and 480 liters of water!

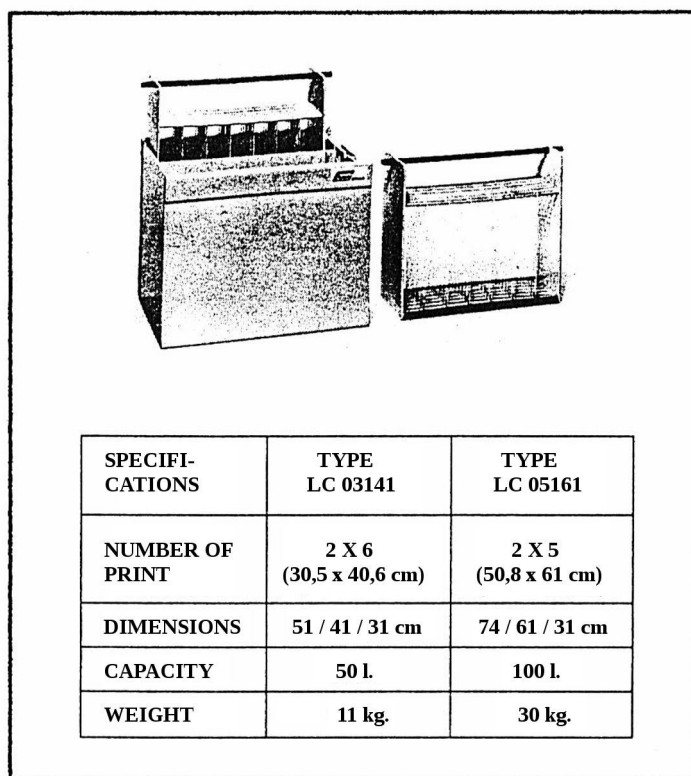
In the study of a representative washing curve, two steps are observed, as far as residual thiosulfate removal is concerned:

- During the first step, most of the thiosulfate is removed fairly quickly by the flow of water on the print, which removes mainly the fixer from the surface;

- Next, the thiosulfates are removed by ion exchange with the wash water: a much slower process. Pure water contains only H⁺ and OH⁻ ions, which are replaced slowly with adsorbed thiosulfate ions. At this stage, running water is not essential; **it is important however for the water to be pure.**

Considering these observations, it seems logical to wash baryta emulsions in two stages according to the following scheme: **a first wash in running water, followed by a soak in still and clean water.**

Of all the archival washers available, only the Deville washer is designed for this purpose. This washer has two separate wash compartments.

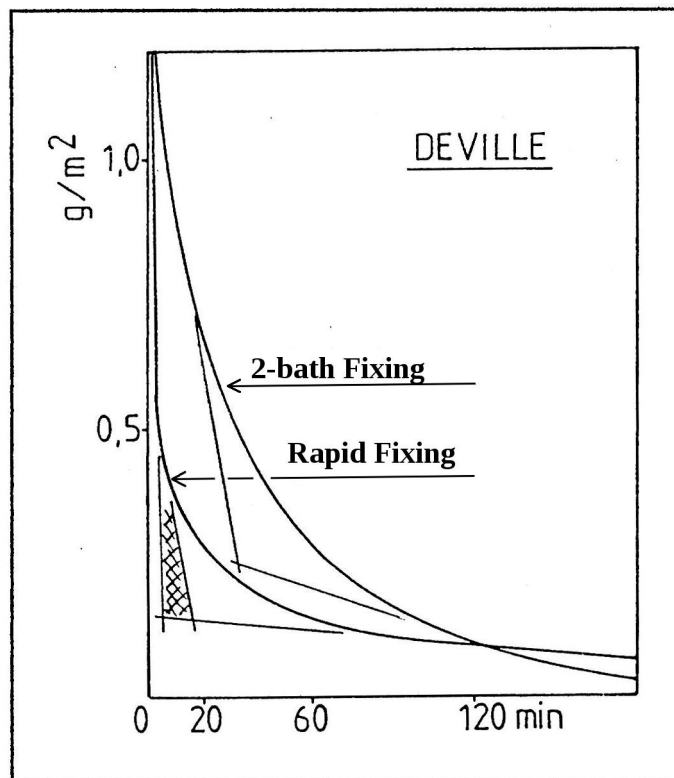


The washing compartment has a removable rack for the prints to be washed. The latter are held by nylon threads and can not stick together. The water supply is through the bottom of the washer and the fixing salts are removed by the water flow under the rack.

A series of tests were carried out with the Deville washer, in order to develop an efficient washing method while saving water. This study was carried out with the following material:

- paper: Agfa Brovira 111 - 30x40cm
- fixer: Asefix diluted 1+9 for fixing in 2 baths and 1+5 for the rapid fixing method;
- wash-aid bath: pH7 wash-aid at 1+10 dilution.

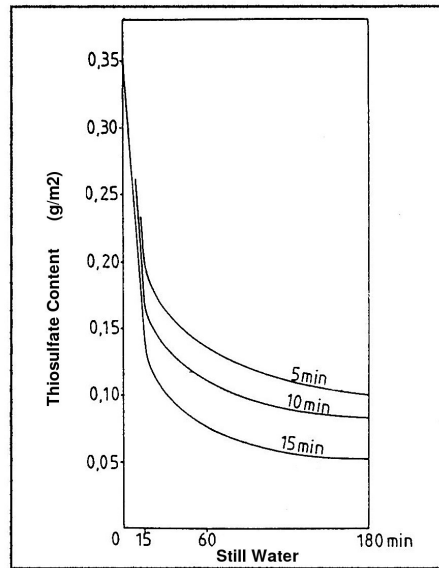
10 cm² samples were taken from the middle of the processed test sheets and dried. These were subjected to a spectrophotometric analysis, as described in the ISO-417 standard.



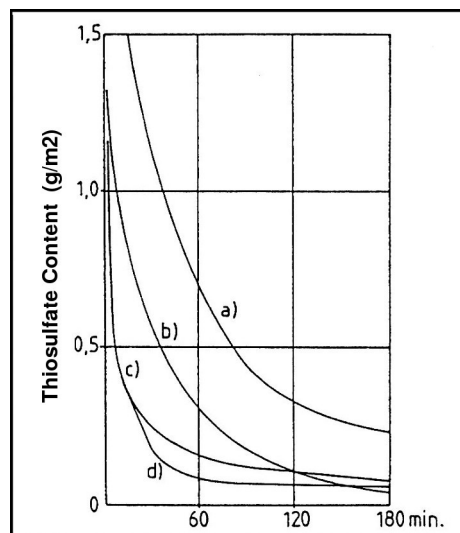
The washing curves obtained made it possible to estimate the duration of washing phase 1, i.e. the required washing in running water. This is:

- about 30 minutes for 2-bath fixing
- between 5 and 15 minutes for the rapid fixing method.

As a starting point for the research, we chose the most efficient method, rapid fixing combined with the pH7 washing aid.



The papers of the test were rinsed respectively in water flowing at 4 l/min for 5, 10 and 15 minutes. This in the first compartment of the Deville vertical washer. After that, the water supply was cut off and the rack with the papers was transferred to the second washing compartment. The papers soaked in pure water for periods of up to 180 minutes. These papers were tested at regular intervals to obtain the wash curves shown above.



Curve d), corresponding to 15 minutes of washing in running water, combined with the rapid fixing curve, shows how the soaking of the second wash phase improves the final wash without additional water consumption.

The following table gives a general overview of the results of the study mentioned above.

	RUNNING WATER WASH			2-BATH WASH	
	2-BATH FIX		RAPID FIX	2-BATH FIX	RAPID FIX
	W/O wash-aid	With wash-aid	With wash-aid	With pH7 WASH-AID	
				Running + Still Water	Running + Still Water
Commercial use salts content > 0,4g/m ²	95 min.	45	15		
Conservation >100 yr salts content > 0,2g/m ²	>180	80	40	30+15	15+15
Archival Conservation salts content > 0,1g/m ²	?	120	120	30+30	15+30

In conclusion, it could be established that fast fixing in a fresh rapid fixer, combined with a passage in the pH7 wash-aid bath, and followed by a 2-step washing in the Deville print washer, makes substantial water savings possible, while residual fixer traces are effectively removed from the baryta print.

Washing with other devices

A good rule of thumb: if the length of the print is greater than the circumference of the wash drum, or the inside size of the washer, it is advisable to wash one print at a time.

For smaller prints, multiple sheets may be processed at the same time. But some testing will be necessary. Most washers work more efficiently if you take care to separate the prints from time to time.

Washing with manual rotation

In the past, this particularly efficient method was the most recommended for a thorough wash. Its drawback is that it requires significant manual work, and extreme care to avoid damaging the prints - which happens easily, given the numerous manipulations they must undergo.

D. Vestal suggests the following method:

- a water flow filling the tray in 5 minutes is used ;
- start with a stack of 6 prints, the image side upwards;
- process all the prints by turning successively each print over, taking it from the bottom and putting it on top of the pile;
- once through the stack, turn it over so that the image side is upwards again;
- empty completely the tray;
- this cycle is repeated every 5 minutes. (regardless of the image on top of the pile at the time)
- the number of rotation cycles must be determined experimentally

This way, there is always another print on top of the pile at the change of water and all the prints receive an identical wash. Otherwise, the bottom and top prints would be washed well before the prints in the middle. The faster the rotation rate, the faster and more efficient the washing.

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11. Checking the residual substances content

The washed print might, due to the operator's negligence, still have some residual silver and / or thiosulfate content. This can endanger the long-term conservation of the print. There is a series of tests allowing a qualitative or quantitative determination of residual harmful substances.

Checking the silver content

An exhausted fixing bath does contain complex compounds of silver thiosulfate which are retained by the baryta emulsion and can not be completely removed by washing.

These salts cause spots that become noticeable after some time. Since only very little of these silver compounds is required to yellow a print, there is no simple quantitative measurement method. However, the coloration that may appear after a while in the presence of such silver compounds can be simulated by the following test.

Kodak Residual Silver Test

Put a drop of ST-1 solution on an unexposed part of a processed print or negative and remove the excess solution with a paper towel.

Any yellowing of the tested spot, other than a barely visible cream shade, indicates the presence of silver.

If the test is positive, the residual silver can be removed by refixing in a fresh fixer. After that, of course, all the other archival processing steps following the fix must also be repeated.

Tests that have been transferred to a sulfidation or selenium bath can not be recovered because the residual silver has been toned with the entire silver image. The existing yellow color is permanent.

Kodak Residual Silver Test Solution, ST-1

- Water 100 ml
- Sodium sulfide (anhydrous) 2 g

This solution can be stored in a small stoppered bottle for 3 months. Before use, dilute 1 part of the ST-1 solution with 9 parts of water. The diluted solution can be stored for 1 week.

Kodak Rapid Selenium Toner Test

A more stable reagent than the ST-1 solution is a diluted Kodak Rapid Selenium Toner solution. One part of KRST is diluted with 9 parts of water; then proceed as above. The diluted solution can be stored for a long time.

Test for the presence of thiosulfate

The content of the residual thiosulfate in film and paper emulsions can only be accurately determined by testing the fully processed photographic material. This is particularly important for paper emulsions, where the support retains the thiosulfate in its structure.

Quantitative determination of thiosulfate content

International Standard ISO 417-1993 defines three procedures for the quantitative determination of thiosulfate and other residual chemicals in photographic plates, films, and paper emulsions: the methylene blue photometric method for the test of baryta papers and films, the iodine-amylose method for the above emulsions as well as for RC papers, and the silver sulfide densitometric method.

These analyses are mainly done to control the quality of film processing – microfilm, radiographic, cinema – and all photographic emulsions where the thiosulfate content must meet the requirements of the international standard ISO 1062-1993, for the purpose of their long term conservation.

Methylene blue method

The residual thiosulfate of a fully processed 10 cm² sample is reduced to sulfide by potassium borohydride. The sulfide is then reacting with the N, N-dimethyl, p-phenylene diamine to form methylene blue.

Using a spectrophotometer, the blue color absorption is measured at the wavelength of 650 nanometers and the thiosulfate concentration is read on a calibration curve.

Iodine amylose method

A reagent is added to the sample in order to extract residual ions of thiosulfate, tetrathionate and pentathionate. Formalin forms a complex with any sulfite ion present. Iodide is added to an amylose indicator to obtain a blue solution. Mixed with the amylose solution, the remaining thiosulfate reacts with iodine and reduces the intensity of the blue color. The loss of color is proportional to the thiosulfate concentration. This method gives a good correlation with the accelerated aging tests of processed microfilm and can be used for color and B/W emulsions.

Silver sulfide method

In this process, acidified silver nitrate is applied to an unexposed portion of the treated emulsion. The excess silver nitrate is removed with a solution of sodium chloride which converts the silver salt into silver chloride ; and finally, the latter is dissolved in thiosulfate.

This step is necessary because exposed silver nitrate residues would blacken and thus bias the analysis.

Using a densitometer, the reflection densities of the emulsion are recorded before and after treatment with the silver nitrate solution. The difference between these density readings indicates the thiosulfate content of the emulsion.

Qualitative determination of the thiosulfate content

Qualitative tests for film emulsions

After final rinsing and drying of the film emulsion, a small strip of the transparent edge is cut off and a portion of it is immersed for three minutes in a small volume of the HT-2 test solution. A well-washed film should show little or no discoloration.

Kodak Hypo Test Solution, HT-22

Water	750 ml
Acetic acid 28%	125 ml
Silver nitrate (crystals)	7,5 g
Water, to make	1000 ml

The solution can be stored in a brown bottle, closed with a glass stopper or screw cap.

The solution leaves black stains on hands and clothes!

Qualitative tests for paper emulsions

To test whether a print has been sufficiently washed, excess water is removed from an unexposed edge of the paper with a paper towel.

A drop of the HT-2 test solution is deposited on the emulsion side. It is allowed to act for 2 minutes and then the excess reagent is removed by rinsing.

The colored spot is then compared with the calibrated grades of the Kodak Hypo Estimator. A light cream color indicates sufficient washing. However, if the discoloration is yellowish-brown or brown, this indicates an excessive level of thiosulfate.

This is a qualitative estimate of the wash of a print ; it can not be used to certify the archival quality of baryta emulsions.

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12. Drying

After the final wash, the baryta emulsion is particularly vulnerable because of the swelling of the water-saturated gelatin. In addition, the paper base is so softened that the slightest crease can leave permanent marks. Once the print is removed from the water, it is preferable to always work on a flat surface.

Air drying

If one can spend the necessary time for it, this is the safest way to perfectly dry a print. It has to be made sure that air can circulate on both sides of the print. This fosters uniform drying and reduces buckling.

The print can be suspended, or put on a screen to dry it: a mosquito net is ideal for this purpose. Drying screens can easily be made with wood or aluminum frames on which fiberglass is stretched. The screens can be stacked on interlocking corner blocks, or can be mounted as sliding frames either in a cabinet or under the workspace.

The print is taken out of the tray and placed immediately between two sheets of polyester on a smooth surface. Excess water is removed by means of a rubber squeegee.

The polyester sheet is then removed from the back of the test and, using a sponge or paper towel, the excess water is removed around the print. The paper sheet is also wiped. The print is then left for a few minutes, back up. This allows some of the water absorbed in between the fibers to evaporate.

After that, the second polyester sheet is removed and the print, image side up, is placed on the drying screen. When the emulsion is no longer sticky when touched, it can be turned over and continue to dry without excessive curl.

The curl of the baryta emulsions is the result of a different water retention in the gelatin and in the paper base. Irregular drying causes stresses that distort the photo paper. Thin paper obviously will be deformed more than a double-weight base.

When the print is completely dry to the touch, it can be pressed for several days between blank archival blotters or acid-free boards. Balancing the natural water content of paper is a particularly slow process.

The print can also be flattened with a dry-mount press after air drying, by heating it between two sheets of acid-free cardboard. The procedures differ widely for this technique. Some photographers place the print in a moderately (? °C) heated press for a few minutes, while others will heat the print at 105°C and leave it in the press for twenty to thirty seconds. You will have to test in order to find out what works best for you.

Blotting

After having drained it briefly, as told above, you can dry the print by pressing it lightly between archival blotters. The two sheets in direct contact with the print should then be removed after about half an hour.

Since air can not circulate freely around the print, drying can take several days. This can be accelerated by periodically replacing the blotting papers in contact with the print.

The danger of this method lies in the possible contaminants accumulation within used blotters, as they risk to migrate to the print.

Drying by heat

Electric glazing presses, which were utilized in the past for getting high-gloss prints, can also be used. Such equipment does not seem to be much in use today. Few photographers still have a preference for a brilliant surface, known to possibly reach the deepest black tones. From the permanence point of view, there is no objection to use this equipment, apart from the fact that the canvas in contact with the back of the print can absorb over time harmful substances and transfer them to the paper. These substances however can be removed by cleaning the cloth regularly with a good detergent, such as Agepon or Kodak Photo'Flo.

To dry a print without gloss, simply turn the image side towards the canvas and heat the press until the print is dry.

Flattening a dry print

Cold press

For this method, several archival-grade blotting papers, a relatively thick metal (or wooden) plate, demineralised water, a clean sponge, and weights (e.g., a pile of books) are required. The work surface is covered with a sheet of blotting paper to collect any drop of spilled water.

The back of the first print is slightly moistened with a sponge and demineralised water. The paper reacts immediately and spreads out. The print is placed between two blotters, under an evenly distributed load. The same is done with all the consecutive prints which are stacked between pressed dry blotters.

Hot press

The essential element of this method is a hot mounting press. In addition, 3 or 4 sheets of acid-free cardboard of the same size as the press, a non-sticky silicone sheet and a flat, metal, heat-diffusing plate are required.

Heat the press to a temperature not exceeding 95°C. Preheat the cardboard sheets in the press; open and close it several times to allow the absorbed moisture to escape.

The print is placed between two sheets of dry cardboard and the emulsion is protected with the silicone sheet. It is essential to remove all particles from the surface of the emulsion before applying pressure.

The press is closed for about ten seconds. The press is then opened and closed several times to allow the moisture of the print to escape. Then, close the press for 30 to 45 seconds, and finally open the press and place the print **immediately** between two sheets of dry cardboard under the metal plate.

The print must cool under press, otherwise it will absorb the atmospheric moisture while still hot, and return to its original shape.

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13. Two recommended processing methods

The most remarkable divergences in the usual archival processes are related to fixing. Fixing is done either in two successive fixing baths at normal dilution, or in a single, concentrated, rapid fixing bath. Here is a brief description of the two most popular procedures in contemporary photography.

Conservation processing of baryta papers according to Kodak³¹

- 1) The development is done in the prescribed way.
- 2) Stop bath: for 30 sec. with agitation, in a fresh bath.
- 3) Fixing: in two successive baths, with continuous agitation for 3 to 5 min.
- 4) Rinsing: for 30 seconds in running water.
- 5) Washing aid: with agitation in a work solution of Kodak Hypo Clearing Agent, for 2 to 3 min.
- 6) Hyposulfite eliminator: 6 minutes with agitation in Kodak Hypo Eliminator, HE-1 formula, to remove the last traces of thiosulfate from the emulsion (replace the exhausted solution after 1 hour).
- 7) Wash: for 10 minutes in running water with a flow sufficient to replace the entire volume of water in 5 minutes.
- 8) Gold toning: for 10 minutes or until a color change becomes barely noticeable. The treatment is carried out with agitation in a Kodak Gold Protective Solution, GP-1 & 2 toning bath.
- 9) Washing: for 10 minutes in running water with a flow sufficient to replace all the water in 5 min.
- 10) Drying: in a clean room without dust.

³¹ EASTMAN - KODAK - Kodak Black & White Darkroom Data Guide, Publication n° R-20, Rochester, USA, n.d.

Archival processing of baryta papers according to pH7 ³²

- 1) Exposure: Leave an unexposed edge of 2 to 2.5 cm.
- 2) Develop the print thoroughly.
- 3) Stop bath: for 30 seconds under constant agitation.
- 4) Allow the print to drain for 5 sec.
- 5) Fixing: for 30 sec. under constant agitation, in a fresh rapid fixer at film strength.
- 6) Allow the print to drain for 5 sec.
- 7) Rinsing: for 30 sec. in running water, then reserve in a tray with water, until having a sufficient number of prints to tone in one go. If no toning is planned, go to 10).
- 8) Selenium toning: Swap the stacked prints for 6 min, or until a color change becomes barely noticeable. Perform this operation in a warm bath (24-26°C).
- 9) Rinsing: in cold running water (<20 ° C) for 5 min.
- 10) Washing aid: constantly swap the stacked prints in 1+10 pH7 Wash-Aid for 6 minutes
- 11) Final wash: in an archival print washer, in running water for 15 minutes (4 liters/min.), Then soak for 30 minutes in pure still water.
- 12) Remove excess water by squeezing between polyester sheets.
- 13) Drying: slowly air-dry on a screen (fiberglass mosquito net).
- 14) Mounting: Two-part conservation mounting with acid-free mounting board and assembly materials.
- 15) Framing: the possible frame has to be made according to archival standards.
- 16) Keep (un)mounted prints in acid-free storage boxes.

³² KOCKAERTS, Roger. - *Techniques d'archivage pour les émulsions argentiques N/B modernes*, Editions pH7, Bruxelles, 1985, 2^e éd. 1989.

14. Mounting

Presentation and protection of baryta prints

In principle, the presentation of a photographic print is a matter of personal taste. For reasons of conservation however, it is necessary to adapt the means and techniques to the degree of protection and permanence desired. The basic materials used for a temporary exhibition are almost identical to those used for long-term conservation.

The installation, protection and archival presentation of baryta prints require special techniques and safe materials for their preservation. Silver is indeed sensitive to mechanical manipulations as well as to the chemical effects of sulfur, of an acid atmosphere or of the materials in contact with the prints.

In anticipation of a possible mounting or framing, flattened baryta prints should preferably be stored in an acid-free storage box. A prerequisite is to keep the prints in a place where they are protected against heat, excessive moisture and mechanical damage.

Markings and notes

After processing and drying, photographic prints are usually completed with information about the photographer's identity, location, date, title of the work, and other information that is important to the photographer.

The only means of marking photographic prints that offer sufficient security are Indian ink dissolved in water, applied with a fountain pen or technical pen, and the traditional pencil. Pencils are usually made of graphite and powdered carbon black, mixed with a clay-based binder.

Pencil markings are very stable and insoluble in water; even after inscription, the print can be processed or washed again without risk of erasure or sagging.

However, care should be taken not to exert excessive pressure on the tip of the pencil when marking the backs of baryta prints. It is best to write on the back of the white margin around the image. For this, the print is placed on a smooth and hard surface. Cardboard is not suitable for this. When writing, only light pressure should be exerted on a pencil of medium hardness.

For inscriptions on the emulsion side, India ink is used, as gelatin hardly accepts pencil.

There are two types of markers: some use water-soluble ink remains soluble after drying and other have fast-drying waterproof ink based on volatile solvents. These writing tools are not suitable for baryta papers. The back of the RC paper can be marked with felts of the second type. It is nevertheless desirable to avoid any contact of the so marked backs with the emulsion sides in a stack. The use of ballpoint pens is also to be avoided.

In the past, many rubber stamps were used with the photographer's name and address, copyright information, and so on.

If they have to be used, care should be taken to ensure that the imprint is light and placed on the back of an unexposed edge, or inside the conservation board. Too bold an imprint can migrate relatively quickly to the emulsion and, when it comes into contact with the emulsion side in a print stack, contaminate it in an irreversible and indelible way.

Spotting and retouching

Most photographic prints have a number of white spots due to dust on the negative. Some photographers are spotting their prints before mounting; others prefer to do it afterwards.

For the permanence of this intervention, only neutral and stable materials are to be used. A product that has already been proven and recommended by Edward Weston³³ is the stick-shaped Indian ink mixed with an equal weight of gum arabic. Dissolve in enough water to immerse and mix the ingredients. Allow the mixture to dry by evaporation, preferably in a flat saucer, moisten the retouching brush with water and rub it on the retouching pad. Apply on a sheet of paper until you get the right gray value. A dry brush is more effective than a soaked brush. It is possible to use 2 to 3 times more gum arabic than ink, depending on the gloss of the spot to be retouched.

During the spotting, only marks caused by dust, fibers, scratches and other damage to the negative are corrected.

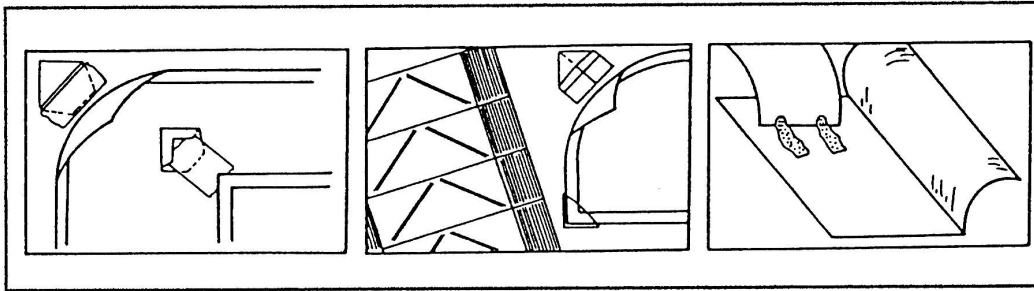
³³ Ansel ADAMS - The Print, Basic Photo 3, New York Graphic Society, Boston.

Retouching usually involves a substantial intervention on the image itself. This can range from eliminating wrinkles in a face, to telephone poles from a landscape, introducing clouds, etc.

Spotone and other liquid retouching products became popular because of their ease of use and the fact that they hardly change the structure of the print, the dye being absorbed by the emulsion and leaving almost no residue on the surface of the print. Spotone # 3 neutral black is often used for neutral or near neutral tones. Exposed to light, the density of the dye can change much faster than the densities of the silver emulsion, especially if the latter has undergone archival processing.

Once it is decided that a photo is worth the effort and the investment of mounting or framing, a protection mount is first realized. The backing board on which the print is attached, the mat, and the binders used must necessarily be free of acid and sulfur.

The mounting of prints – especially large ones – as done in the past, remains the subject of conflicting recommendations. From a conservation point of view, each mounting must be completely reversible, that is to say it must be possible to recover the object in its original state at any time. Most of the applied mounting techniques do not take this into account.

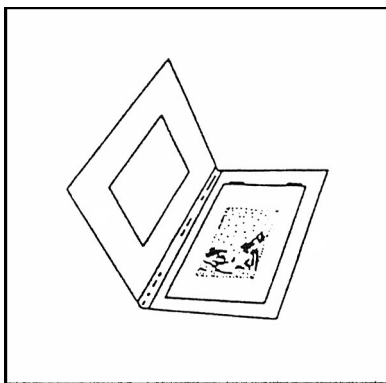


For reversible assemblies, acid-free papers and polyester photo corners or completely reversible fastenings are used.³⁴

³⁴ Anon - Archival Notes: Aids for the Family Archivist. In: *The Light Impressions Review*, n°14, 1984.

Conservation mounting

The conservation mount is the most effective and most used way to preserve, present and conserve a valuable print.



The mounting board described above forms the back of the assembly. The front of the latter is usually composed of a thicker acid-free cardboard with a beveled window cut to the dimensions of the print. The two boards are joined from the inside, along the longest dimension, by a hinge tape.

This configuration allows to see and manipulate the work without touching it. In addition, the assembly being generally made to standard, universally adopted sizes, the work can be sent, framed and exposed at any time in the best conditions, safely and quickly.

The function of mounting is to protect the print during its conservation and to show it in the best possible way when it has to be presented or exhibited.

As there is intimate contact between the work and its mount, special attention must be paid to the quality of the materials used³⁵. When using a colored mat, the dye may migrate to the print when the humidity level is high.

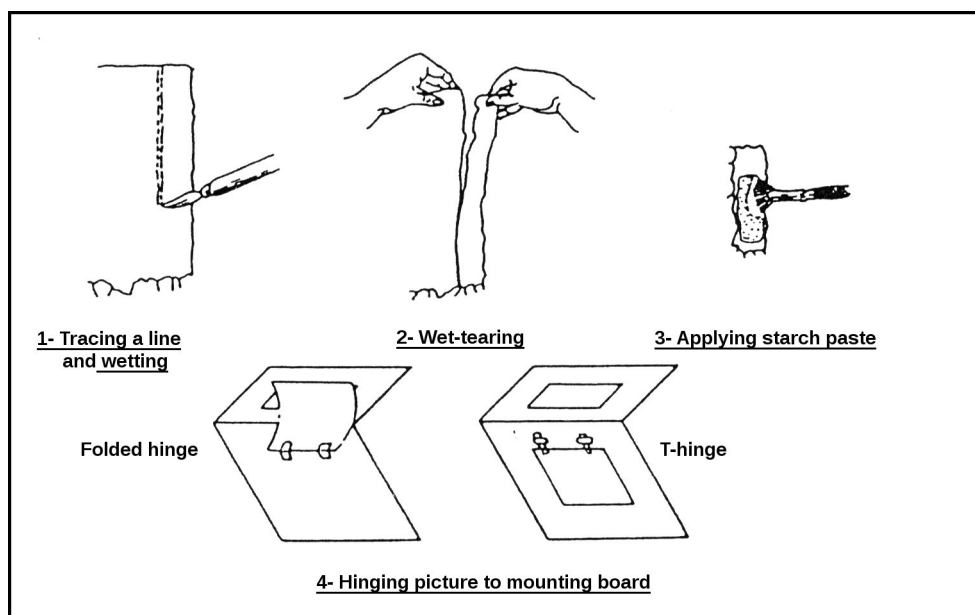
In the absence of a backing or mounting board, the backside of the print is in direct and intimate contact with the back of the frame, which is usually made of Unalit or MDF (Medium Density Fiber). These materials are quite corrosive and can very quickly cause an irreversible yellowing of the framed photographic print.

³⁵ Bertrand Lavédrine - Deterioration of Some Contemporary Prints. In: Topics in Photographic Conservation, American Institute for Conservation Photographic Materials Group, vol.6, 1995.

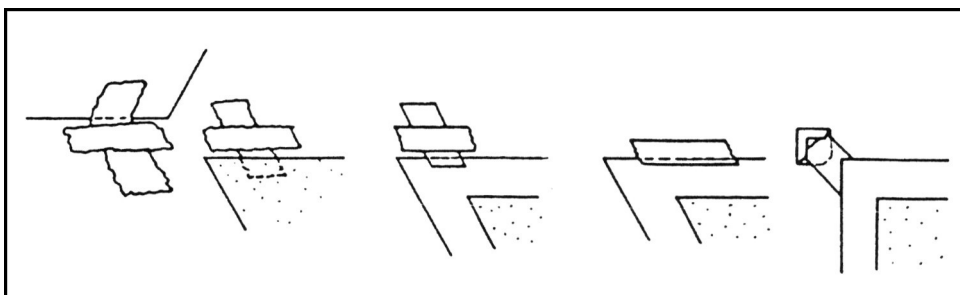
Generally, the window of the mat is cut before fixing the print on the mounting board, which facilitates the correct placement of the print.

The conservation munting

When maximum permanance is to be guaranteed for a print, it is mounted using clear polyester or acid-free adhesive photo wedges, or acid-free paper hinges with reversible glue. How to make paper hinges with Japanese paper is shown in the following figure.

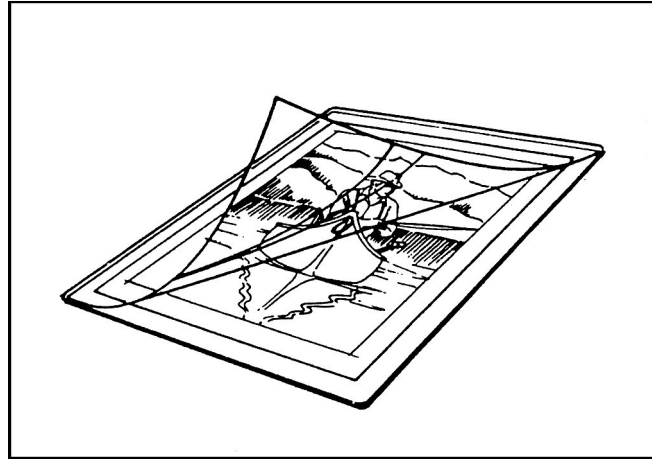


The Japanese paper is cut by tearing it along a line moistened with water. The print is then centered under the window and secured with paper hinges and starch glue.



Above, the most used reversible adhesion options for photographic conservation purposes.

The most fragile documents can be placed safely in assemblies whose back is formed by a stiff cardboard without acid on which a sheet of polyester is fixed on two sides by means of a special double-sided adhesive tap, as shown the following figure.



This kind of wallet, made to the dimensions of the acid-free storage box, is very convenient for storing precious prints for which mounting is not desired. The electrostatically charged polyester sheet maintains indeed the print without glue.

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Method (b) is particularly suited for preventing moisture to penetrate into aluminum frames. Here the back is protected by a polyester sheet (8) and the whole is sealed on all four sides with a strip of plastic or linen. It should be noted, however, that a completely airtight seal is undesirable as, in case of significant temperature changes, any imbalance between moisture inside and outside the frame can cause condensation. The frame should be able to "breathe" and to adapt to changes in temperature and humidity.

If the print is very large, which complicates the use of a mat, method (c) can be used, where a spacer (9) or a small wooden frame is used to prevent contact with the window. If this contact can not be avoided, plexiglass is used instead of glass, because glass reacts to atmospheric conditions, allowing condensation inside the frame, which can stain the print.

When cleaning a frame, never spray detergent on the frame or window. Moisture could penetrate the frame and stain the mat or print, or cause a dangerous increase in moisture in the frame. Instead, use a soft cloth moistened with a little cleaning agent.

If a print remains permanently framed, it is advisable to open the frame periodically and make sure that no problem did occur. This can be done every 10 years or so. Even if all the elements are in perfect condition, it is better to clean the window inside. It is amazing how glass can tarnish when the frame remained closed for some time.

The prints can never be mounted between two glass plates, with or without mounting. This method encourages the formation of mold, and in case the glass would be broken, the print will almost certainly be damaged. If a document must remain visible on both sides, acrylic is used instead of glass.

The use of non-reflective glass is not recommended because, to be effective, the print must be in contact with the glass.

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16. Exposure to light

Influence of light

Of all the external elements acting on a paper object, light is perhaps the least known and probably the most misunderstood. It should be kept in mind that light, in all its forms, is weakening works of art on paper, whether they are photographic prints or images produced by other techniques.

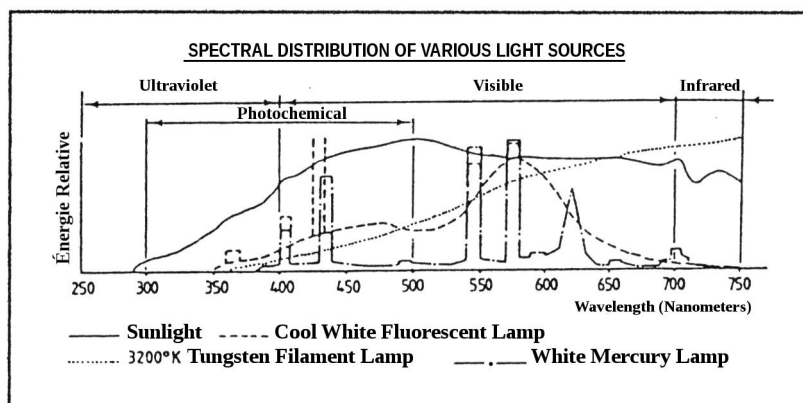
The degradation of the image does not stop automatically when the light falls below a certain level. The fading is not reversible either. When a piece of paper is placed in complete darkness, the degeneration process stops, but this does not in any way enhance the contrast of the image, nor return it to its original state.

Light is needed to see the image, but any excess that accelerates its fading should be avoided. One standard is to use the same level of light that is needed to read a text.

It must be remembered that the human eye is not able to estimate a quantity of light because it adapts very quickly to large changes in intensity. A quantity of light must therefore be measured by means of an instrument.

Characteristics of light

When looking at the relative spectral energy distribution of different light sources, it appears that the amount of energy increases as the wavelength decreases.



From wavelengths around 500 nanometers onwards, the electromagnetic force is capable of causing photomechanical damage to organic materials. This damage consists of discoloration, darkening, and structural damage caused by the degradation of molecular complexes. This degradation is not immediately noticeable, but develops slowly by cumulative exposure to light rays.

Visible light from 400 to 500 nm mostly causes discoloration, although microstructural damage may also occur. Ultraviolet energy from 300 to 400 nm causes greater damage.

Protecting from light

There are different ways to protect precious or delicate objects from light. The first and most obvious one is to keep objects in complete darkness. It can be seen below that this is preferably done in acid free boxes guaranteeing safe storage.

Another possibility is to reduce their exposure to light. Damage caused is directly proportional to the amount of light received. If, for example, the exposure time is halved, the possible deterioration is also reduced by half.

Museums manage the exhibition of works of art in a variety of ways. Good practice is, for example, to show the most delicate objects only to authorized persons, and only by appointment. In addition, museums only show their works at specific times and in dimly lit rooms. Most museums organize a rotation so that a specific object will only be visible for a few weeks or months. Ultraviolet radiation can also be eliminated. Finally, the amount of light can be reduced. These examples can be followed by each collector.

Light measurement

The amount of light emitted by a light source is measured in lux. There are more or less sophisticated luxmeters, but below we provide a simple measurement method using a photographic light meter to measure incident light.

The sensitivity scale of the cell is set to 100 ISO. The light meter is placed at the location of the object to be illuminated and the exposure time theoretically required for shooting with an aperture of $f = 4$ is determined. This measurement is converted to lux according to the table below.

Exposure	Lux	<u>Recommended for lighting:</u>
1 sec.	50	The most fragile objects, such as: historical and color emulsions
1/4 sec.	150	Fragile objects such as modern b&w baryta emulsions
1/15 sec.	1250	risk of damage to fragile objects
1/25 sec.	3750	!!!!!!!!!!!!!!

The amount of light can also be estimated using a cell measuring reflected light, and a neutral gray card calibrated at 18%³⁷. The cell is set to 1/30 sec. and the sensitivity to ISO 400. The light reflected by the calibrated gray card is measured. Then the table below is used.

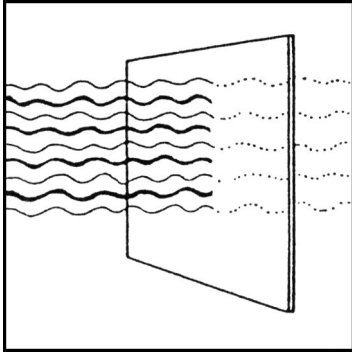
aperture	lux
1,0	16
1,4	32
2,0	63
2,8	125
4,0	250
5,6	500
8,0	1000
11,0	2000
16,0	4000
22,0	8000
32,0	16000
45,0	32150

³⁷ EASTMAN - KODAK - Estimating Luminance and Illuminance Using Reflection-type Exposure Meters and an 18% Gray Card. In: Kodak Tech. Bits, 1984.

Artwork lighting

Each of the three basic light sources, namely: natural light, fluorescent light and incandescent light has its own combination of advantages and disadvantages.

Natural light



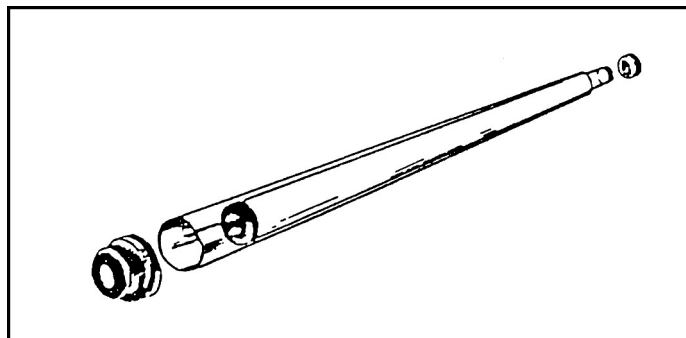
Natural light is rarely used as the sole light source by museums and galleries for the obvious reason that it is almost impossible to control.

Prints should not be installed in direct or reflected natural light. Even indirect light is a danger because, apart from its high intensity, it is also a source of ultraviolet rays which, although invisible, are even more destructive than visible light. Ultraviolet radiation, with wavelengths <400 nm, causes not only a fading of the image, but also a weakening of the paper fibers.

There are different types of plexiglas filtering UV rays more or less efficiently. This special plexiglass is available in different thicknesses and is mainly used in place of glass for framing, but also for the windows of protected historic buildings.

Fluorescent light

Fluorescent lighting is little used, mainly for aesthetic reasons. It is not suitable for directional lighting and can not effectively isolate an object from its environment.



Fluorescent light may optionally be used in combination with a cylindrical acrylic plastic tube, slid over the fluorescent tube and filtering ultraviolet rays.

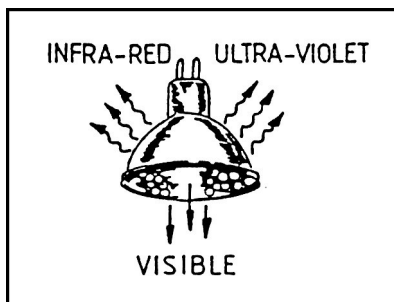
Incandescent light

Incandescent light can be optically focused and is therefore better suited to draw the viewer's attention to the object. Tungsten or halogen lamps that operate at normal mains voltage without a transformer, however, have a high infrared radiation and consume a lot of energy.

Low voltage halogen lamps

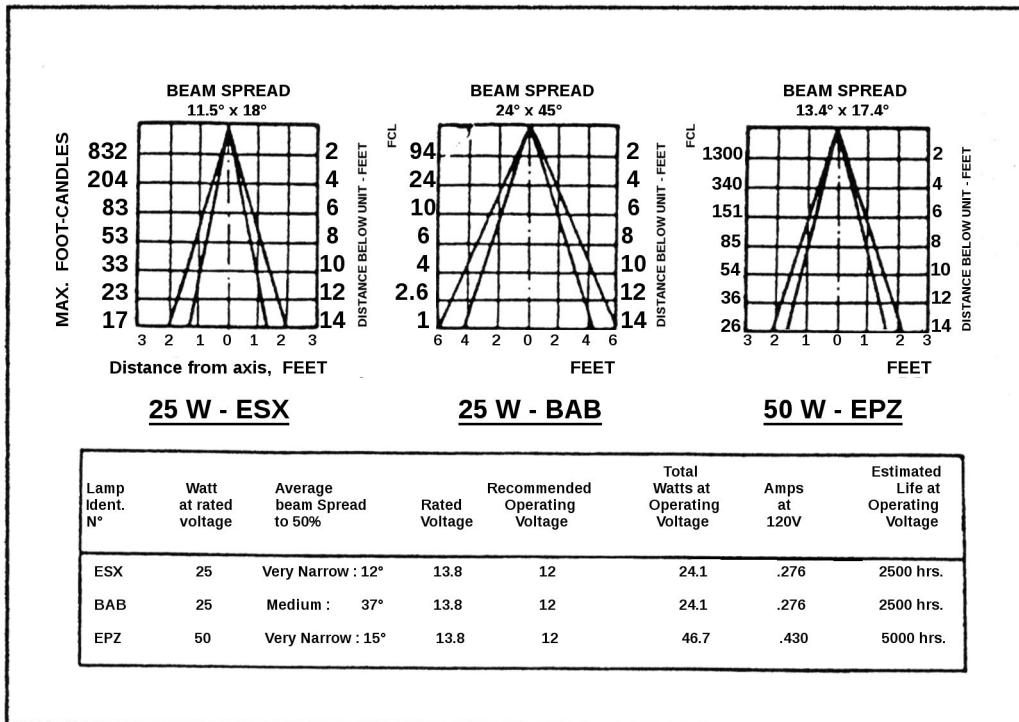
There are low voltage (12V) and low-wattage (25 to 50W) halogen lamps specifically designed for use in exhibition areas. They have several advantages.

The lamps of such lighting systems are equipped with a dichroic reflector consisting of a glass dome covered with a special reflective-transmissive substance. This coating reflects all visible light, while 99% of the dangerous UV and IR rays are absorbed from behind.



In this way, objects sensitive to light and heat, such as historical or modern photo prints, are better protected. This type of lamp produces intense white light with a color temperature of about 3100°K. Normal bulbs usually produce light with a temperature of 2700°K .

With this whiter light, colors stand out better, which is a plus for illuminating artwork. In addition, the light of these lamps hardly fades during their lifespan, so that the available light remains almost constant. These miniaturized lamps are very effective in a low-level lighting system, commonly used in museums and galleries.



Low voltage halogen lamps can have different lighting angles, which makes it possible to adapt them to a wide variety of exhibition conditions.

To illuminate the framed works and attract the spectator's attention, the radiation level must be 2 to 3 times higher than the general lighting level of the space. Generally, low voltage lamps are mounted in adjustable cylindrical housings, equipped with the necessary voltage transformers and a safety lens. They can be mounted on power supply rails and thus be easily moved, for a very convenient implementation.

Some galleries use bare AC power cables with one or two voltage transformers for the entire plant.

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17. Storage

Archiving boxes

An archive box must form a chemically neutral micro-environment in which photographic prints or negatives can be stored with complete security.

Photographic archivally mounted prints are stored in acid-free cardboard boxes of suitable dimensions.

Let us pause here for a moment to consider the storage of chemically inert plastic pouches in storage boxes.

In the case of unmounted prints, a polyester pouch undoubtedly offers better protection against a series of mechanical damages, and is a positive element in the preservation system. However, in the case of prints mounted on cardboard, there are various factors that may lead to a more nuanced opinion.

In our (rainy) climate, cardboard can sometimes absorb a relatively large amount of moist. When mounted prints are stacked in a box, the set will ultimately have a natural water content proportional to the outdoor humidity rate. Since cardboard is permeable to water and air, the excess humidity in the box will slowly escape into the conservation space, whose relative humidity must be <60%.

But when opting for the additional protection of a polyester pouch enveloping the mounted print, the print in that case is no longer influenced by the ambient storage conditions, and the good conservation of the print can be affected by water deposited on the linings of the pouch, which might cause spots, localized glosses and fungi.

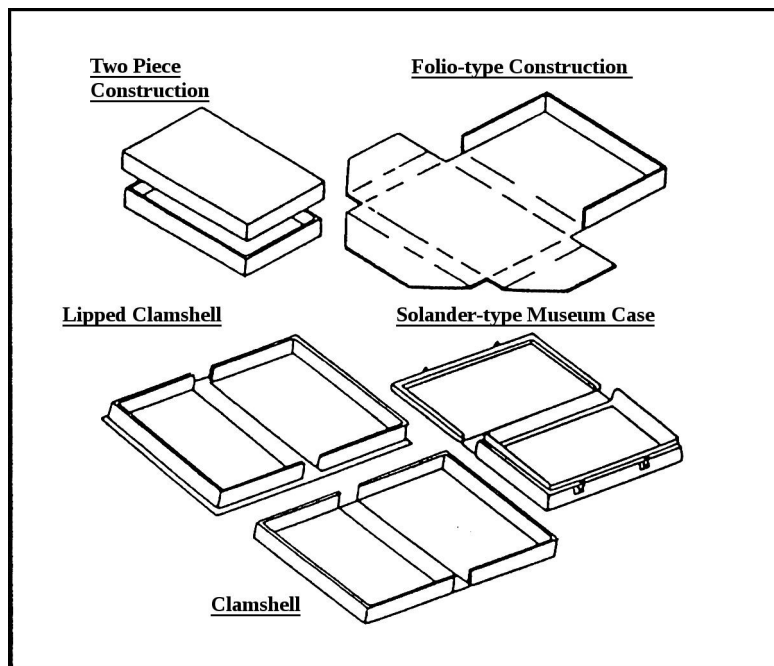
The basic material of most cardboard boxes is usually a 2.5 mm thick, non-deformable cardboard, glue-free between the different layers of paper. The inside of the box is normally covered with a sheet of paper or acid-free polyethylene that prevents the migration of acidic components. The glue used is usually a polyvinyl acetate glue that does not contain free and acidic hydrogen ions that can attack and contaminate the paper.

This inert white material dries into a flexible and transparent film that can also glue plastics.

The outsides of the portfolio boxes can be covered with a wide variety of more or less luxurious materials.

The simplest box is a two-part construction. The "clamshell" type is made of one piece and allows a very practical handling of its content. When the box is open, the upper and lower parts are aligned and thus form a space in which the prints can be moved from right to left without removing them from the box.

The Solander museum boxes are very robust and reinforced with wooden slats. Very popular in the United States, this type of box is almost universally used in museums, hence its name.



Archival boxes designed for long-term preservation are made exclusively of acid-free materials. These sometimes less luxurious boxes can be made of acid-free corrugated cardboard: they are then designed to be assembled by folding, without metal staples.

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“Archival Processing and Care of Fiber Base Photographic Papers”

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