Canadian Conservation Institute
Institut canadien de conservation

CCI Notes 16/6

Processing Contemporary Black-and-White Photographic Films and Papers for Maximum Permanence

Introduction

Correctly processing contemporary black-and-white photographs contributes significantly to their longevity. Therefore, processing must be carried out judiciously. Correctly processed black-and-white silver gelatin films and fibre-base prints, while essentially stable to dry heat and visible light, are nevertheless susceptible to image deterioration when exposed to aggressive chemicals.

Pollutants such as hydrogen peroxide or hydrogen sulphide may originate from external sources, but other residual chemicals in a photographic film or paper may result from poor processing procedures. For example, chemical compounds used in the fixing step during processing may cause black-and-white photographs to discolour. If residual fixing salts are allowed to remain in the photograph, they may seriously jeopardize its permanence. This has been the subject of numerous intensive discussions in the photographic literature over the years.

This Note summarizes traditional procedures for processing silver gelatin photographic films and fibre-base papers for maximum permanence. More recent recommendations are also presented, including adding a toner treatment to the conventional processing sequence.

The Photographic Process

Unexposed black-and-white film or paper contains silver salts (silver halides) as the light-sensitive material embedded in a gelatin layer. Silver halides are white, but slowly turn yellow, then brown, and finally black when exposed to light. It is not necessary to expose modern photographic materials to light for a long time: a fraction of a second is usually sufficient for films, and a few seconds is enough for paper prints. Brief exposure creates an invisible "latent image" that can be made visible by treatment in a chemical solution known as "developer."

The following five steps in *conventional* processing of exposed black-and-white film or paper yield photographs that are free of harmful processing chemicals: development, stop bath, fixing step, washing, and drying. In recent years, a post-processing treatment known as *toning* has been performed to increase the stability of the silver image.

Development

Developers are often made according to complex formulae, and are mixed and sold ready for use. They are available either in solid form, which must be dissolved in water, or as a liquid concentrate, which must be diluted with water. The development step may take several minutes for films and between 60 and 120 seconds for papers. During development, exposed silver halides are converted to black elemental silver particles to form the visible picture. Pictures are developed at a specified temperature, usually 20°C.

Stop Bath

Both the choice of the developer and the development time can affect important image characteristics such as contrast. Development is stopped by treating the film or paper for 15–30 seconds in a stop bath, which is usually a 2% solution of acetic acid in water.

Fixing Step

At this point in the process, the film or paper still contains unexposed — and therefore undeveloped —

light-sensitive silver halides that must be removed. The fixing and subsequent washing steps are therefore crucial for the permanence of the developed photograph.

A fixing bath dissolves unexposed silver halides, thereby removing them from the picture. A fixing bath contains sodium thiosulphate or ammonium thiosulphate, and may also be called a *hypo bath*. As silver halides dissolve in the fixing bath, complex compounds containing silver salts and thiosulphate are formed. If the fixing is not complete, residual silver halides and silver thiosulphate compounds will remain in the film or print. This can cause black and white tones to turn yellow and brown. The washing step will not remove these compounds because they are only soluble in a fresh fixing solution. Therefore, a two-bath fixation is necessary. In the first fixing bath, the silver thiosulphate complexes are formed, and most are dissolved. In the second fixing bath, all remaining silver thiosulphate complexes are dissolved and removed. The procedure leaves only pure fixing solution in the gelatin layer and, in the case of prints, also in the paper base.

There are two kinds of fixing solutions in common use: normal fixers, which generally have gelatin-hardening properties; and rapid fixers, which may contain hardeners.[1]

Normal fixers with hardening properties (e.g. Eastman Kodak's F-5 type) work slowly because the hardening of the gelatin causes them to penetrate and diffuse the gelatin layer slowly. Normal fixers have a beneficial effect on the stability of the gelatin layer. Rapid, non-hardening fixers are more efficient than hardening fixers, and are washed out of films and papers more quickly. Residual amounts of either type of fixer will damage image stability.

Rapid fixers work more efficiently, particularly if they do not contain hardeners. Rapid fixers also require shorter washing times than do normal fixers. For example, it is generally accepted that a type of photographic enlarging paper called bromide paper can be fixed completely in about 25 seconds in a rapid fixer. However, one manufacturer, Ilford Inc., recommends a fixing time of 60 seconds in a non-hardening fixer for its fibre-base enlarging paper Ilfobrom Galerie. Always follow the specific instructions given by manufacturers with regard to their products.

The effectiveness of a fixing bath can be tested using a fixer test solution such as Kodak FT-1. Another way to ensure that a fixing bath is sufficiently fresh is to replace it after a given number of prints have been treated in it (e.g. fifty 8" x 10" prints in a one-bath fixing step per gallon of fixer, or two hundred 8" x 10" prints in a two-bath fixing sequence per gallon of fixer). Recommended fixing times are about 5 minutes in each bath, with good agitation, if using a normal hardening fixer.

The presence of residual silver salts in a processed film or print (i.e. the effectiveness of the fixing procedure) can be measured using a qualitative silver test, such as Kodak Residual Silver Test Solution ST-1.

Washing

After the fixing step, residual fixing solution must be removed from photographs. Otherwise, compounds containing sulphur atoms may react with the finely divided image silver to form yellow or brown silver compounds, particularly in the presence of high relative humidity and high temperatures.

Remove residual fixing salts or hypo by washing films and prints in running water for extended periods of time. Recommended washing times are generally shorter for films than for papers because papers have sponge-like properties and tend to retain chemicals. Double-weight papers require longer washing times than do single-weight papers. It is not necessary to use special print washers, as is often advocated in popular photographic literature, if washing is done in running water and if prints are prevented from sticking together during washing. Do not wash films or prints any longer than necessary, and never leave them in a wash-water tank overnight.

The effectiveness of a washing procedure depends on the type of fixer used in processing; the weight (or thickness) of the paper; and the temperature, pH (acidity), flow, and salt content of the wash water.

To estimate the amount of residual hypo in films and papers, use a qualitative test (e.g. the Kodak Hypo Test Solution HT-2) in conjunction with a reference sample (e.g. the Kodak Hypo Estimator). The iodine-amylase, methylene blue, and silver sulphide methods specified in *ISO 18917:1999* (International Organization for Standardization 1999) will give more precise and detailed determinations of residual processing chemicals. Test for residual silver and hypo on an additional reference print or film sheet.

Using a wash-aid or a hypo clearing agent will accelerate the washing process. These salt solutions increase the polarity of the wash water, thereby making it easier to remove fixing salts. Never use washing aids known as hypo eliminators; they contain hydrogen peroxide in an aqueous ammonia solution, and can harm modern photographic materials.

Drying

The last step in processing is air-drying the photograph on a fibreglass screen in a clean, dust-free environment to prevent it from picking up external impurities. Over-drying causes curling. Once prints are dry, place them in Melinex 516 sleeves.

Post-processing Treatments

Since the 19th century, the process of toning has been considered an optional treatment step after normal processing is complete. In the toning process, the image-forming silver particles in a photograph react with another metal salt to form silver compounds or alloys.[2] A toning treatment has two major effects: it may change the image tone, and it generally increases the permanence of the picture. (Some rarely used toning processes change only the tone of the picture. This Note is concerned with permanent pictures, so only those toners that increase the longevity of the photograph will be discussed.)

Selenium salts solutions were introduced as toners almost 80 years ago. Hundreds of formulae have been proposed throughout the history of photography. Sepia toning produces permanent pictures of chemically inert silver sulphide. Toning in a bath of gold salts is effective, but the high price of gold has prevented its widespread use in photographic processing.

Poly-Toner, produced by the Eastman Kodak Company, has also been used. The Image Permanence Institute (Rochester, NY) has proposed the use of a polysulphide toner to increase the permanence of silver images, particularly in microfilm.

Recently, toning using such products as Kodak Rapid Selenium Toner or Kodak Poly-Toner has become accepted as an *essential part* of a processing sequence designed to produce permanent photographs. This is due to changes in the properties of silver particles in contemporary black-and-white photographic materials, and the presence of increasing amounts of air pollution in the environment.

Details of the processing steps outlined above are summarized in Table 1.

Processing Resin-coated (RC) Papers

The paper support in resin-coated (RC) papers is coated on both sides with a thin layer of polyethylene plastic. One side is then coated with a silver halide gelatin layer, which forms the photographic picture. The plastic coating gives these RC papers properties similar to those of films. The processing solutions cannot be soaked up by the paper base, but penetrate only into the gelatin layer. RC papers can therefore be processed rapidly (i.e. in a few minutes).

Table 1. Summary of processing sequences and recommended processing times for each step

Step	Film	Fibre-base paper
1. Development	Varies from 4 to 9 minutes according to film type and manufacturer's recommendations; agitation at regular intervals.	Between 60 and 120 seconds; constant agitation.
2. Stop bath	15 seconds.	30 seconds.
3. Fixing	5 minutes in a hardening fixer; 2 minutes in a non-hardening rapid fixer; agitation at regular intervals.	(i) First fixing bath: 5 minutes with regular agitation. (ii) Second fixing bath, which must contain fresh fixing solution: 5 minutes with regular agitation.
4. Washing	(i) Rinse for 5 minutes. (ii) Treat in hypo clearing agent for 2 minutes. (iii) Wash for 5 minutes.	(i) Rinse for 5 minutes. (ii) Treat in hypo clearing agent for 3 minutes.* (iii) Wash for 20 minutes.†
5. Toning	(i) Treat in Eastman Kodak Rapid Selenium Toner (dilution in water 1:20) for 3 minutes. (ii) Wash for 10 minutes in running water.	(i) Treat in Eastman Kodak Rapid Selenium Toner (dilution in water 1:20) for 3 minutes. (ii) Wash for 20 minutes in running water.
6. Drying	Dry, suspended in air in a dust-free environment.	Dry, emulsion side down, on a fibreglass screen in a dust-free environment.

* Hypo clearing agent treatment times given are for double-weight papers. Shorten these times by one-third to one-half for single-weight papers.

† Washing times given are for double-weight papers. Shorten these times by one-third to one-half for single-weight papers.

The following steps comprise a typical processing sequence: develop for 60 seconds, rinse in water, fix for 30 seconds, wash for 2 minutes, and dry in a special electrical dryer for 30 seconds. Total processing time is 4 minutes. Some manufacturers make processing machines for RC papers that have the developer already built into the gelatin layer (developer-incorporated papers). These processors make a well-processed dry RC paper print in 55 seconds. Although selenium toning increases their image stability, RC papers should not be used for pictures that are intended for long-term preservation.

Endnotes

1. Hardeners are chemical compounds that strengthen the gelatin's resistance to the processing solutions. Complex laboratory procedures have measured the effect of hardeners on the properties of gelatin and have confirmed that gelatin treated in such solutions is "hardened" (i.e. is somewhat strengthened in its stability) during processing.

2. An alloy is a chemical component formed from two or more metals. Bronze, for example, is an alloy of copper and tin.

Suppliers

Note: The following information is provided only to assist the reader. Inclusion of a company in this list does not in any way imply endorsement by the Canadian Conservation Institute.

All processing chemicals recommended by specific manufacturers for their products are available at good photographic stores, as are the following materials, which are suggested for general use:

Kodak F-5 Fixer; Kodak Hypo Clearing Agent; Kodak Poly-Toner; Kodak Rapid Selenium Toner:
local photographic stores

or

Kodak Canada
3500 Eglinton Avenue West
Toronto ON M6M 1V3
Canada
tel.: 416-766-8233 or 1-800-465-6325
fax: 416-766-5814
wwwca.kodak.com

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