Aug. 19, 1952 I. B. CURRENT 2,607,686

PROCESS OF OBTAINING COLD SEPIA TONES

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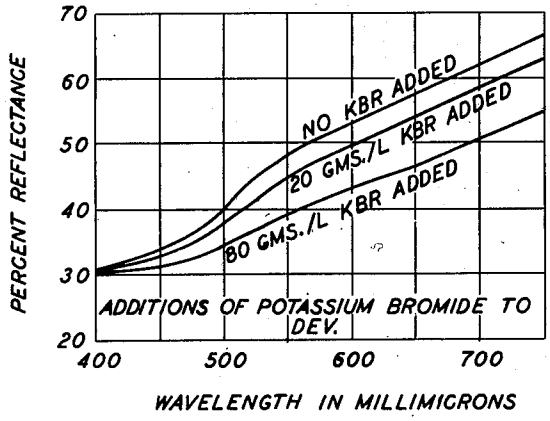


Fig. 1

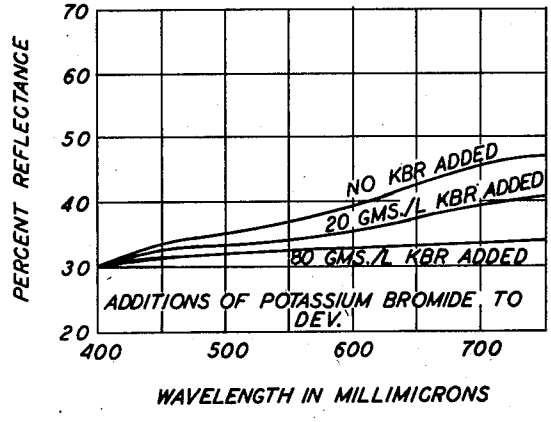


Fig. 2

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PROCESS OF OBTAINING COLD SEPIA TONES

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6 Claims. (Cl. 95—88)

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This invention relates to the toning of developed photographic prints and particularly to an improved process of obtaining cold sepia tones by sulfur or selenium toning of developed chloride and chloro-bromide emulsions.

It is known in the photographic art that metallic silver, which forms the image of a photographic print or transparency, can be replaced with a compound of silver or other metal, such as sulfur, selenium, gold, tin and the like, by the toning process. The most generally used toning process consists of converting the metallic silver to silver sulfide or silver selenide to produce what are commonly known as "sepia" prints which range in color from a yellowish brown to a shade approaching purple. Sulfide and selenide toning methods may be either direct, in which the silver image is converted at once into an image of silver sulfide or silver selenide, or indirect, in which the silver image is first converted to a silver halide by bleaching, and then transformed into a sulfide or selenide image in a bath containing soluble sulfide or selenide.

The color of a sulfide-toned print depends upon the sizes and structures of the grains of which the image is composed. A coarse grained structure in the original silver print generally gives a tone tending toward the purple, while a fine grained print generally produces a toned print of a yellowish brown shade. For this reason, both the nature of the emulsion with which the print is made, and the processing procedure used in making a silver print have a bearing upon the color of the print after toning has been carried out. For example, the development of the silver print has a very important effect upon the color of the toned print. If a print is overexposed and underdeveloped, the grain structure is finer and the color of the toned print tends toward the yellow.

Considerable time and effort have been expended by investigators in devising satisfactory methods of obtaining uniformly the desired shades in sulfide and selenide toned prints. In the field of portrait and pictorial photography, the positive emulsions used have been formulated to produce only a relatively warm tone upon development. However, many photographers also desire to use the same paper for sepia toning, but are disappointed by the extremely warm or yellowish sepia tones obtained, despite the fact that bromide emulsions tend to produce somewhat colder tones than either chloride or chloro-bromide emulsions.

It has always been taught by the art that for greatest uniformity of color and depth of tone, the prints should be developed prior to toning in a developer containing a specified amount of a soluble bromide for a fixed period of time. As a consequence of this understanding, several print developers containing specified amounts of a soluble bromide have been devised for various positive emulsions. For bromide and fast chloro-bromide papers, an Amidol (di-hydrochloride of 2,4-diaminophenol) developer containing one gram of potassium bromide is generally used. A Metol-glycine-hydroquinone (p-methylamino-phenol sulfate, p-hydroxyphenylglycine, and hydroquinone) developer containing from 3 to 4 grams of potassium bromide is generally used for chloride and chloro-bromide papers, whereas for some chloride and slow chloro-bromide papers, a Metol hydroquinone developer containing from 1½ to 2 grams of potassium bromide is generally used. For some bromide and chloro-bromide papers, a glycine-hydroquinone developer containing as high as 4 grams of potassium bromide has been recommended.

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In developing positive chloride and chloro-bromide emulsions with developers normally used, i. e., those containing from 0.5–4 grams of potassium bromide per liter, warmer tones are obtained after sulfur or selenium toning. Despite the fact that these emulsions are available in a wide range of speeds, from the slow chloride type to the fastest papers, substantially equal in speed to the fastest bromides, they all may yield upon development with the recommended print developers, followed by sulfur or selenium toning, prints of warmer than desired character.

It is an object of the present invention to provide a method whereby cold sepia tones are obtained by the toning of chloride and chloro-bromide emulsions.

Other objects and advantages will appear hereinafter.

I have found that contrary to recognized understandings and established procedures, chloride and chloro-bromide positive emulsions, which normally yield warm tones upon sulfur or selenium toning, yield colder sepia tones by first developing the exposed chloride and chloro-bromide positive emulsion with any black and white print developer containing from 20 to 80 grams of potassium bromide per liter of developer. With normal or slightly increased developing time, the prints are altered so that almost any degree of colder (deeper brown) sepia and even bluish-black tones are obtained on sulfur or selenium toning. This unexpected result appears to be due to the high concentration of potassium bromide in the developer, which pos-

sibly has the effect of replacing or converting part or all of the chloride of a chloride or chloro-bromide emulsion to bromide in addition to a change in the size of the silver halide crystals due to aggregation of the small grains or grain growth (compared to an Ostwald ripening effect), to give a tone effect more nearly approaching that available from a bromide paper.

The amount of potassium bromide to be added to the developer is governed by the kind of paper selected for making the print and the color tone desired. For a slow chloro-bromide and a fast chloro-bromide or a chloride paper of moderate speed, as little as 20 grams per liter of potassium bromide is sufficient to produce a noticeable effect after development from 4 to 8 minutes followed by toning. A concentration of 50 grams per liter of potassium bromide has been found to produce satisfactory cold tones after toning. Above 80 grams per liter of added potassium bromide, the restraining action may be so great that the effect of the conversion of the halide in the paper cannot be realized and a warmer than normal tone may result. The exact limits of potassium bromide concentration are dependent, therefore, upon the type of emulsion, i. e., whether a chloride or a chloro-bromide emulsion, the desired tone, and the developing time, all of which can be very readily ascertained by simple trial experiments.

The developers which may be used in accordance with the present invention are those which are normally employed for developing out positive silver halide emulsions. As illustrative examples of the reducing agents contained in such developers, the following are given:

(*a*) p-Methylaminophenol sulfate and hydroquinone
(*b*) Glycin (p-hydroxyphenylglycine)
(*c*) Adurol (2-brom-1,4-dihydroxybenzene)
(*d*) Eikonogen (hydrated sodium amino naphthol sulfonate)
(*e*) Amidol (2,4-diaminophenol dihydrochloride)
(*f*) Chlorhydroquinone (2-chloro-1,4-dihydroxybenzene)

Print developers containing the foregoing reducing or developing agents are available in photographic literature and need not be reproduced herein.

As pointed out above, the developing time of the exposed print may vary from 4 to 8 minutes. The usual developing time with developers of this type, without the high concentration of potassium bromide, normally used for developing exposed positive emulsions varies from 1½ to 5 minutes. With the same developers containing from 20 to 80 grams of potassium bromide a minimum developing time of about 2 minutes may be necessary to yield satisfactory results. The developing time must, in some cases depending upon the type of print paper, be extended from 5 to 10 minutes to overcome the restraining effect of the potassium bromide, otherwise the result may yield warmer tones than would be obtained without the bromide addition. This makes the developing time an important variable when using, prior to toning, a developer containing a high concentration of potassium bromide, but if it is extended enough, usually not more than 8 to 10 minutes, reasonably reproducible colder toning results will be obtained with warm tone printing papers.

The present invention is illustrated by the accompanying drawing in which Figs. 1 and 2 represent spectrophotometric reflectance curves indicating the relative proportions of light of different wavelengths that are reflected from the toned areas. In other words, the curves are graphic presentations of the relative color of the tones at an arbitrarily chosen medium density (0.5) at wavelength 400 at which the start of the curves are selected. Although these curves do not show the effects of higher and lower densities which also influence the color of the tone prints, they serve, however, to show the relative toning effects. The higher the right hand part of the curves extend, the more reddish or warmer the tones they represent become. A curve straight across with no "ups" or "downs" would represent a practically neutral or gray tone. The color of the tone is represented by the shape of the curve and even relatively minor variations in the curve shape may be detected in the actual print by an experienced eye.

These curves were obtained by adjusting toned photographic print wedges in the spectrophotometer until the toned deposit gave a reflectance reading of 30% at a wavelength of 400 millimicrons.

Fig. 1 indicates the nature of the tones obtained on a slow chloro-bromide paper with a two minute development in a high energy developer containing no potassium bromide and 20 and 80 grams per liter respectively, and the subsequent conversion of the silver image into the silver sulfide image.

Fig. 2 illustrates the toning effect on a fast chloro-bromide paper resulting from 8-minute development in a low energy developer containing no potassium bromide and 20 and 80 grams of potassium bromide per liter respectively, and subsequent conversion of the silver images into selenide images.

The following examples will serve to specifically describe the invention as applied to warm tone printing papers, i. e., chloride and chloro-bromide positive emulsions. These examples should not be construed as limiting or restricting the present invention, but should be considered merely as illustrative.

Example I

Three specimens of a warm tone chloro-bromide projection paper of moderate speed were exposed. The first paper was developed in a developer solution of the following composition for 5 minutes at 68° F.:

Hot water (125° F.)	cc	750
p-Methylaminophenol sulfate	grams	5
Sodium sulfite	do	40
Hydroquinone	do	6
Sodium carbonate (monohydrate)	do	40

Water to make 1 liter.

The second and third exposed papers were developed in two separate developing solutions prepared as above, except that the developing solutions contained in addition 20 and 80 grams of potassium bromide per liter, respectively.

After fixing and washing, the developed prints were toned to completion for 30 minutes at 72° F. with a direct sepia toner of the following composition:

Liver of sulfate	grams	2

Water to make 1 liter.

The toned prints were washed for 20 minutes and dried.

A spectrophotometric curve of the resulting image in each of the three prints at a density of about 0.5, was obtained as illustrated in Fig. 1.

From these curves, it will be observed that the addition of 20 and 80 grams of potassium bromide, respectively, per liter of developer produces excellent colder tones when followed by direct sepia toning.

Example II

Three sheets of a fast chloro-bromide emulsion projection paper were individually exposed through a negative. The first exposed print was developed for 8 minutes at 68° C. in a developer solution of the following composition:

Hot water (125° F. or 52° C.)	cc	750
p-Methylaminophenol sulfate	grams	3.5
Hydroquinone	do	11.5
Sodium sulfite (anhydrous)	do	45
Sodium carbonate (monohydrate)	do	78
Water to make 3 liters.		

The second and third exposed papers were developed in two separate developing solutions prepared as above, except that the developing solutions contained in addition 20 and 80 grams of potassium bromide per liter, respectively.

After short-stopping, fixing, washing, and drying, the developed prints were toned for 10 minutes at 72° F. in a solution prepared as follows:

100 grams of sodium sulfite are dissolved in a small amount of water, then 10 grams of powdered selenium metal dissolved in this solution, and the volume brought up to 1 liter. The clear part of the solution may be decanted or filtered from any sediment remaining and used as a direct toning solution.

The toned prints were washed for 15 minutes in flowing water and then dried.

Spectrophotometric curves of the resulting three images, at a density of about 0.5, were obtained as illustrated in Fig. 2. These curves illustrate the somewhat less cold toning effects resulting from the development with bromide additions.

In lieu of the developing solutions of the foregoing examples the following developer solution may be employed to yield the same colder tones when followed by direct sepia toning:

Hot water (125° F.)	cc	750
p-Methylaminophenol sulfate	grams	5
Sodium sulfite	do	40
Hydroquinone	do	6
Potassium bromide	do	50
Sodium carbonate (monohydrate)	do	40
Water to make 1 liter.		

Example III

Three sheets of chloro-bromide projection paper were processed up to and including the washing step described in Example I.

After washing the prints were bleached for 5 minutes in a solution of the following composition:

Potassium ferricyanide	grams	50
Potassium bromide	do	10
Water to make 1 liter.		

The bleached prints were washed for 5 minutes and toned, i. e., "redeveloped," in a 1% solution of sodium sulfide in water.

The toned prints were thoroughly washed in water for 30 minutes and dried. Prints of excellent cold sepia tone were obtained.

An optional hardening treatment with an aqueous chrome alum solution may be used on the toned prints prepared as above after some preliminary washing so as to remove most of the sodium sulfide absorbed by the emulsion layer.

Once a particular print developer containing from 20 to 80 grams of potassium bromide per liter has been found which gives the desired sepia tones, all the steps, i. e., developer formula and concentration of potassium bromide should be carefully standardized and made uniform from one time to the next, and frequent renewal of all processing solutions will insure uniformity of tones from day to day. On the other hand, the factors effecting the sepia tones may be put to an advantage in securing almost any degree of warmth and tone, particularly the addition of potassium bromide ranging from 20 to 80 grams per liter to an energetic developer with increased developing time, i. e., from 8 to 10 minutes, which can provide direct sepia tones, considerably colder than Flemish tones available from the same paper with normal print developer and developing time.

While I have herein disclosed the preferred embodiments of my invention, I do not desire to limit myself solely to the specific examples since it will be readily apparent to those skilled in the art that the precise ratios of potassium bromide and the nature of the reducing agent in the print developer may be varied. Any other reducing materials having equivalent properties may be employed without departing from the spirit and scope thereof. Accordingly, therefore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process of obtaining cold sepia tones by toning warm toned positive printing papers of the group consisting of chloride and chloro-bromide papers which consists of exposing and developing said papers with a photographic developer for positive silver halide emulsions comprising an aromatic silver halide developing agent and from 20 to 80 grams of potassium bromide per liter, fixing and washing the developed print, and subsequently toning it with a toner selected from the group consisting of sulfur and selenium toners.

2. A process of obtaining cold sepia tones by toning a warm toned silver chloride emulsion positive printing paper which consists of exposing and developing said paper with a photographic developer for positive silver halide emulsions comprising an aromatic silver halide developing agent and from 20 to 80 grams of potassium bromide per liter, fixing and washing the developed print, and subsequently toning with a toner selected from the group consisting of sulfur and selenium toners.

3. A process of obtaining cold sepia tones by toning a warm toned silver chloro-bromide emulsion positive printing paper which consists of exposing and developing said paper with a photographic developer for positive silver halide emulsions comprising an aromatic silver halide developing agent and from 20 to 80 grams of potassium bromide per liter, fixing and washing the developed print, and subsequently toning with a toner selected from the group consisting of sulfur and selenium toners.

4. A process according to claim 1, wherein the photographic developer consists of the following composition:

Hot water (125° F.)	cc	750
p-Methylaminophenol sulfate	grams	5
Sodium sulfite	do	40
Hydroquinone	do	6

Potassium bromide	grams	20–80
Sodium carbonate (monohydrate)	do	40

Water to make 1 liter.

5. A process according to claim 2, wherein the photographic developer consists of the following composition:

Hot water (125° F.)	cc	750
p-Methylaminophenol sulfate	grams	5
Sodium sulfite	do	40
Hydroquinone	do	6
Potassium bromide	do	50
Sodium carbonate (monohydrate)	do	40

Water to make 1 liter.

6. A process according to claim 3, wherein the photographic developer consists of the following composition:

Hot water (125° F. or 52° C.)	cc	750
p-Methylaminophenol sulfate	grams	3.5
Sodium sulfite (anhydrous)	do	45
Hydroquinone	do	11.5

Potassium bromide	grams	60–240
Sodium carbonate (monohydrate)	do	78

Water to make 3 liters.

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