

UNITED STATES PATENT OFFICE

2,367,548

HARDENING AND STAIN PREVENTION
PROCESS IN COLOR PHOTOGRAPHYPaul W. Vittum, Rochester, N. Y., assignor to
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corporation of New JerseyNo Drawing. Application September 4, 1942,
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9 Claims. (Cl. 95-88)

This invention relates to photographic hardening baths and particularly to baths of use in color photography for hardening and preventing the staining of gelatin emulsion layers.

In processing color films having gelatin emulsion layers by means of color-forming development methods, it is usually desirable at some stage in the process to harden the emulsion layers of the film. For instance, in the color process disclosed in the prior U. S. Patent No. 2,252,718, granted August 19, 1941, to Mannes et al., it is convenient to harden the emulsion layers following color-forming development and prior to removal of the silver images with ferricyanide and hypo solutions. I have found that the usual hardening solutions used for this purpose have a deleterious effect upon the dye images which may be traced to the presence of sulfite in the hardening bath. It appears that dye images formed from coupler compounds giving azomethine, indoaniline and indophenol dyes are particularly susceptible to attack by sulfite and the effect produced is a destruction of a portion of the dye image and rendering the remaining dye image unstable. Similarly, in processing color films having coupler compounds incorporated in the emulsion layers, constructed, for example, as described in Jelly and Vittum U. S. Patent 2,322,027, granted June 15, 1943, Mannes et al., U. S. Patents 2,304,939 and 2,304,940, granted December 15, 1942, it is desirable to harden the emulsion layers subsequent to color-forming development and prior to removal of silver from the films. With these films the presence of sulfite in the hardening bath adversely affects the dye images as described.

In processing the above films it is also observed that there is a tendency for stain to be produced in the emulsion layers when the color-developed films are treated with ferricyanide or other oxidizing solutions used for the removal of silver from the layers. It is believed that this stain results from the oxidation of traces of the color-forming development compounds retained in the layers following color-forming development.

I have found that by the addition of acid to the hardening bath used prior to treatment of the above films with oxidizing solutions for the removal of silver, stain may be reduced. The acid apparently removes from the solution layer any color-forming developer compound extracted from the developer by the emulsion layers. Therefore, no developer compound is available

for oxidation to stain in the subsequent treatment with oxidizing solutions if the hardening bath is acid.

It is, therefore, one object of my invention to provide emulsion hardening baths having no deleterious effect upon color developed dye images and which will prevent the formation of stain.

Another object is to describe color processes in which the hardening and stain preventing baths of my invention are particularly useful. Other objects will appear hereinafter.

The following example will illustrate a typical hardening bath contemplated by my invention.

Example

15	Sodium acetate.....	grams--	15.0
	Acetic acid (28 per cent).....	cc--	47.0
	Boric acid.....	grams--	7.5
	Potassium alum.....	do--	15.0
20	Water to.....	cc--	1000.0

As shown, the baths of my invention may contain a buffer compound, an organic acid, a gelatin hardening agent and boric acid. Instead of the particular buffer compound shown in the example, one may use other compounds of similar activity such as citrate, borate, etc. Similarly, other organic acids and gelatin hardening agents such as chrome alum may be used in the formula. It is not necessary that the formula contain boric acid; however, the compound may be used where accelerated hardening is desired.

I will now describe a color process in which a bath of my invention is especially useful. A color film carrying sensitive emulsion layers containing coupler compounds and, if desired, crystalloidal materials as described in the Jelly and Vittum application above-mentioned, and in which the coupler compound for forming a cyan image in the red sensitive emulsion layer is, for example, an acyl-o-aminophenol, such as acetamino phenol, is exposed in the usual manner to a colored scene. Following exposure the film is developed in a color developer of the following composition:

2-amino-5-diethylamino toluene	
HCl.....	grams-- 2
Sodium sulfite.....	do-- 2
20 Sodium carbonate.....	do-- 20
Potassium bromide.....	do-- 2
Water to.....	cc-- 1000

Cyan, magenta and yellow dye images are thus

developed in the respective emulsion layers. It is found that if the emulsion layers of the developed film are now hardened in a hardening bath of composition shown in the above example prior to removal of silver from the layers, the dye images are not affected and any color-forming developer compound in the layers will be removed; otherwise, a hardening bath, containing sulfite especially if applied prior to removal of silver will adversely affect the dye images. After hardening the emulsions the film is treated with ferricyanide and hypo solutions to remove silver and any silver halide in the layers. Color negatives thus produced may be printed onto a similarly constructed color film or paper having coupler compounds incorporated in the emulsion layers, and the exposed photographic elements then developed with a color-forming developer of the above composition to form subtractive dye images in the respective emulsion layers. Then, in the manner of my invention, the emulsion layers are hardened with a hardening bath such as shown in the above example followed by removal of silver and silver halide from the element. A multi-color image which is a positive in respect to the original scene is thus obtained.

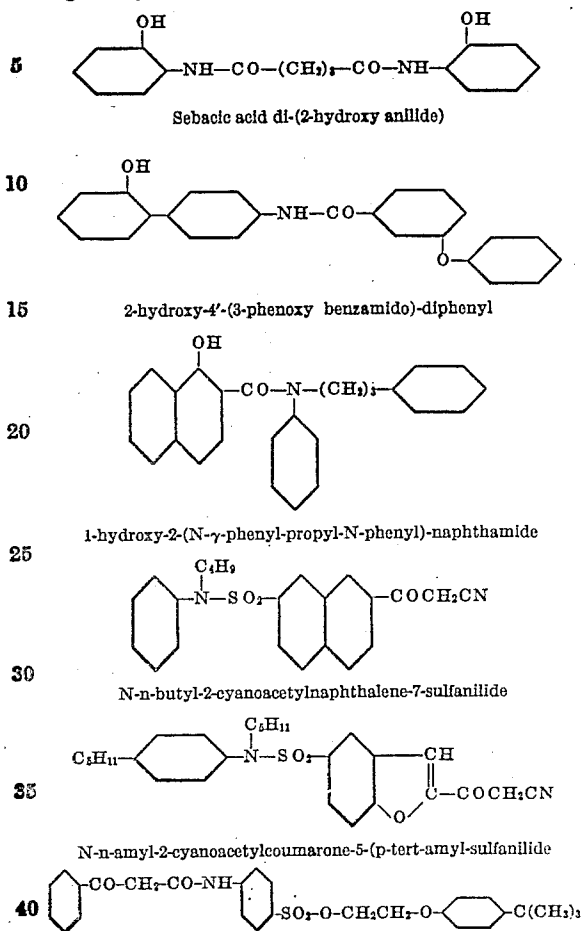
A color film constructed as described in the Mannes et al. U. S. Patents 2,304,939 and 2,304,940 above-cited may be processed in a similar manner to give a color negative which may be printed onto a similarly constructed positive color film and processed as described to a color positive using the hardening bath before removal of silver and silver halide.

A film constructed as described in the above Mannes et al. U. S. Patent No. 2,252,718 is processed as described therein using a hardening bath according to my invention as follows: after exposure, negative development, and reversal exposure and color-forming development of the respective emulsion layers, the film is treated with a hardening bath compounded as described under the above example, followed by removal of the silver images and silver halide using ferricyanide and hypo solutions. The hardening bath functions as above-described to harden the emulsion layers and to remove color-forming developer compound from the emulsion layers.

Color films containing coupler compounds and, if desired, crystalloidal or porosity modifying materials as described in the Jelly and Vittum Patent 2,322,027, and Mannes et al. Patents 2,304,939 and 2,304,940 above, may also be processed by the reversal process of color photography as follows using a hardening bath according to my invention: after exposure of the film it is developed to a black-and-white negative in MQ developer, and then the emulsion layers are selectively re-exposed and color developed to produce subtractive dye images in the layers. Following this, a hardening bath of composition, such as shown in the above example, is used to harden the emulsion layers and to remove any developer compound in the layers. Film is then treated with ferricyanide and hypo solutions to remove silver and any silver halide in the layers.

As I have mentioned, the dye images which are most adversely affected by sulfite in a hardening bath are those formed from coupler compounds yielding azomethine, indophenol and indoaniline dyes with color-forming developers. Other coupler compounds giving dye images especially susceptible to sulfite which dye images

should be treated with a hardening bath according to my invention are, for example:



p-tert-butyl phenoxyethyl-p-benzoyl acetaminobenzene sulfonate

It is apparent that the above description is merely illustrative of the various means of accomplishing the objects of my invention and it is to be understood that the disclosure herein is by way of example and that I consider as included in my invention all modifications and equivalents falling within the scope of the appended claims.

What I claim is:

1. In color photography, the method of processing a light-sensitive silver halide gelatin emulsion layer which comprises exposing said layer, developing a dye image in said layer by means of color-forming development, prior to treatment with solutions removing silver from the layer treating said emulsion layer containing a dye image with a hardening bath free of sulfite comprising a photographic gelatin hardening agent, a buffer compound and an organic acid whereby the emulsion layer is hardened and any color-forming developer compound in the layer is removed without affecting the dye image, and removing the silver and any residual silver halide from the layer.

2. In color photography, the method of processing a light-sensitive silver halide gelatin emulsion layer which comprises exposing said layer, developing a dye image in said layer by means of color-forming development, prior to treatment with solutions removing silver from the layer treating said emulsion layer containing a dye image with a hardening bath free of sulfite comprising alum, sodium acetate, acetic acid,

and boric acid whereby the emulsion layer is hardened and any color-forming developer compound in the layer is removed without affecting the dye image, and removing the silver and any residual silver halide from the layer.

3. In color photography, the method of processing a light-sensitive silver halide gelatin emulsion layer containing a coupler compound which comprises exposing said layer, developing a dye image in said layer by means of color-forming development, prior to treatment with solutions removing silver from the layer, treating said layer containing a dye image with a hardening bath free of sulfite comprising a photographic gelatin hardening agent, a buffer compound and an organic acid whereby the emulsion layer is hardened and any color-forming developer compound in the layer is removed without affecting the dye image, and removing the silver and any residual silver halide from the layer.

4. In color photography, the method of processing a light-sensitive silver halide gelatin emulsion layer which comprises exposing said layer, developing a silver image in the exposed layer, exposing the unexposed silver halide in the layer, forming a dye image in the exposed layer by means of color-forming development, treating the layer with a hardening bath free of sulfite comprising a hardening agent for gelatin, a buffer compound and an organic acid whereby the layer is hardened and any color-forming developer compound in the layer is removed without affecting the dye image, and removing the silver and any residual silver halide from the layer.

5. The process according to claim 4 wherein

the hardening bath comprises alum, sodium acetate, acetic acid and boric acid.

6. In color photography, the method of processing a light-sensitive silver halide gelatin emulsion layer containing a coupler compound which comprises exposing said layer, developing a silver image in the exposed layer, exposing the unexposed silver halide in the layer, forming a dye image in the exposed layer by means of color-forming development, treating the layer with a hardening bath free of sulfite comprising a hardening agent for gelatin, a buffer compound and an organic acid whereby the layer is hardened and any color-forming developer compound in the layer is removed without affecting the dye image, and removing the silver and any residual silver halide from the layer.

7. The process according to claim 6 wherein the hardening bath comprises alum, sodium acetate, acetic acid and boric acid.

8. The method of hardening a gelatin emulsion layer containing silver and a color-developed dye image, and removing any developing agent present in the layer, which comprises treating said layer after color-forming development and prior to fixing, with a sulfite-free bath comprising essentially a gelatin hardening agent, an organic acid, and a buffer compound.

9. The method of hardening a gelatin emulsion layer containing silver and a color-developed dye image, and removing any developing agent present in the layer, which comprises treating said layer after color-forming development and prior to fixing, with a sulfite-free bath comprising essentially alum, acetic acid, and sodium acetate.

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