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FINAL RINSE BATH FOR COLOR PROCESS

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ABSTRACT OF THE DISCLOSURE

A bath comprising water, dye stabilizing agent and an alkoxy substituted polyoxyethylene wetting agent is used advantageously as the final rinse in processing photographic elements, particularly in processing color photographic elements because this bath leaves the processed photographic element free of water spots, scum, foam as well as stabilizing the image against the formation of stains.

This invention relates to photographic processing baths and more particularly to anti-stain baths which do not deposit processing scum on the processed photographic elements passed through the said baths and to photographic processes in which the said anti-stain baths comprise the final rinse.

The production of color pictures by color processing image-exposed multi-layer photographic elements is well known. For example, Mannes et al. in U.S. Patent 2,252,718 describe a well known color photographic system in which the photographic element comprises a support coated in succession with a red-sensitive silver halide emulsion layer, a green-sensitive silver halide emulsion layer, a bleachable yellow filter layer, and a blue-sensitive silver halide layer is image exposed and then processed. Color reversal processing involves a negative silver image development, washing, selective reexposure of the bottom red-sensitive layer, cyan development of that layer with an alkaline solution containing a color developing agent and a cyan-forming coupler, washing, selective reexposure of the blue-sensitive layer, yellow development of the blue-sensitive layer with an alkaline solution containing a color developing agent, and a yellow-forming coupler, washing, fogging and magenta development of the green-sensitive layer with an alkaline solution containing a color developing agent and a magenta-forming coupler, washing, followed by treatment with a potassium ferricyanide bleach bath, a sodium thiosulfate fix, washing and drying.

Multilayer photographic elements having the color-forming couplers incorporated in the silver halide emulsion layers are described in patents, such as, Jelley and Vittum U.S. Patent 2,322,027, issued June 15, 1943, Mannes et al. U.S. Patents 2,304,939 and 2,304,940 issued Dec. 15, 1942, etc. Color processing of these elements usually involves the simultaneous color development of the three silver halide emulsion layers with an alkaline solution containing a color developing agent, washing, hardening, washing, treatment with a potassium ferricyanide bleach bath, a sodium thiosulfate fix, washing and drying.

It is known to use formaldehyde in the final wash or rinse of these color processes in order to stabilize the processed element against the formation of stains in the element during the drying step or during subsequent storage. It is also known to use a wetting agent in the final rinse to prevent the adhesion of water droplets with subsequent spotting of the dried photographic element. The use of a wetting agent is particularly advantageous where the color material is processed by hand using Nikor reels, or on sheet film hangers, or on strip immersion machines, such as, 10E and Pako machines.

Many of the known wetting agents have a tendency to form scum or processing dirt that is deposited on the processed element as streaks, spots or over the entire surface of the dried element. This problem is particularly troublesome on the support side of 35 mm. color elements that do not have a gel pelloid coating. It is frequently necessary to clean processed 35 mm. films before mounting them in order to remove water spots if insufficient wetting agent has been used in the final rinse bath or to remove scum or dirt from the processed films if enough wetting agent is used to prevent water spots. Certain of the available wetting agents cannot be used in final rinse baths because of the detrimental effect they have on dye stability. Other wetting agents are unusable because of foam problems.

New final rinse baths are desired which will not produce water spots, scum, foam and yet which will prevent the formation of stains and not have detrimental effects on image dye stability.

It is, therefore, an object of our invention to provide an improved final rinse bath (and concentrated composition for preparing said bath) which will prevent the formation of stains and which will prevent the formation of water spots and scum deposits on the processed film.

Another object of our invention is to provide a color process using our final rinse bath to produce color pictures that are free from stains, water spots and scum.

Still other objects will be apparent from a consideration of the following specification and claims:

These and other objects of our invention are accomplished by using in color processes a final rinse bath comprising water, a dye stabilizing agent and a wetting agent included in those represented by the formula:

$$RO-\left[\begin{array}{c}CH-CHO\\ | \quad\quad |\\ R_1 \quad R_2\end{array}\right]_n H$$

wherein R represents an alkyl group that has from 8 to 18 carbon atoms in either a straight chain or a branched chain, e.g., octyl, iso-octyl, nonyl, decyl, dodecyl, tridecyl, pentadecyl, octadecyl, etc.; R_1 and R_2 each represent the same or a different group, such as, the hydrogen atom, or an alkyl group having from 1 to 6 carbon atoms, e.g, methyl, ethyl, propyl, hexyl, etc.; and n represents an integer of from 6 to 20.

Included among the typical wetting agents used to advantage in our final rinse baths are the following compounds:

Octyloxy polyethoxy ethanol
Isooctyloxy polyethoxy ethanol
Decyloxy polyethoxy ethanol
Dodecyloxy polyethoxy ethanol
Tridecyloxy polyethoxy ethanol
Pentadecyloxy polyethoxy ethanol
Octadecyloxy polyethoxy ethanol
Tridecyloxy polypropoxy propanol

The preferred wetting agents have a cloud point that is at about the processing temperature or below the processing temperature. By cloud point we mean the temperature at which an aqueous solution of the wetting agent just starts to become cloudy.

The wetting agents are used in our final rinse baths over a wide range of concentrations, e.g., from about 0.01 to about 0.50 g./l. Our wetting agents prevent the formation of water spots even when used at very low concentrations at which most other wetting agents are ineffective. The optimum concentration of the wetting agents in the final rinse bath will depend upon the particular wetting agent, the processing equipment, water hardness, and the characteristics of the photographic element. The optimum concentration of the wetting agent for a given

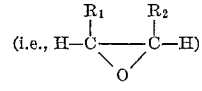
process is readily determined by methods well known in the art.

Any of the dye stabilizing agents known to be useful in the final rinse baths for color processing to prevent the formation of stains in the processed photographic elements may be used to advantage in our final rinse baths. Useful dye stabilizing agents include aliphatic aldehydes, e.g., formaldehyde, paraformaldehyde, acetaldehyde, aldol, crotonaldehyde, propionaldehyde, etc.

The dye stabilizing agents are used to advantage over a wide range of concentrations, e.g., from about 1 ml./l. to 100 ml./l. of the rinse bath. A preferred range is from about 10 ml./l. to about 30 ml./l. The optimum concentration is readily determined by methods well known in the art.

Concentrated liquid compositions containing our wetting agents either with or without the dye stabilizing agents are used to advantage for preparing the operating final rinse baths by the appropriate dilution with water and addition of the dye stabilizing agent if this is not included in the concentrate. The concentrate can be made up to about 130 times the concentration of the operating solution, i.e., the final rinse bath used in color processing.

Our wetting agents can be readily prepared by reactions well known in the art. In general, the alkylene oxide



is reacted with an alcohol having the formula ROH in which R, R_1 and R_2 are as defined previously. A number of wetting agents are available commercially.

The dye stabilizing agents are well known compounds and are either readily available or can be prepared by well known methods.

Although our final rinse bath is used to advantage in the processing of black-and-white photographic products, it is particularly useful as the final rinse in processes for color photographic products. The color products may have images of any of the various types of dyes used in color photography including indophenols, indamines, indoanilines, azomethines (including quinone-imines) which are formed by the reaction of a color-forming coupler and an oxidized primary phenylenediamine color developing agent. The photographic element may have a paper support, an opaque film support or a transparent film support such as are conventionally used in photographic materials.

The final rinse time may be varied considerably providing there is sufficient time for enough of the dye stabilizing agent to penetrate the layers of the photographic element containing the dye images. Usually a momentary immersion of the wet processed photographic element in the final rinse bath is sufficient. The optimum time can be determined readily by methods well known in the art.

Our invention is further described by the following examples which are intended to illustrate but not limit the invention.

Example 1

Strips of a multilayer color photographic film were image exposed and processed through the following steps:

preharden	stop
neutralize	wash
negative development	bleach
stop	fix
wash	wash
reexposure	stabilize (final rinse bath)
color developer	dry

The strips were given identical processing except as to the wetting agent used in the final rinse bath. The final rinse bath consisted of water with 10 ml./l. of 37% formaldehyde and the wetting agent indicated in the following table.

Strip No.	Wetting Agent in Final Rinse	Condition of Film
1	None	Water spots.
2	Nonylphenoxy polyethoxy ethanol.	Scum, no water spots.
3	Tridecyloxy polyethoxy ethanol, 0.14 ml./l.	No scum, no water spots.

It can be seen that strip 3 which received our process had no scum deposited on it, while strip 2 which was processed outside the process of our invention had scum on it that required cleaning before the picture was suitable for use. Strip 1 was unsatisfactory because of water spots and required cleaning to remove the spots.

Example 2

Example 1 was repeated but using a final rinse bath containing 7 ml./l. of 37% formaldehyde containing the indicated wetting agent.

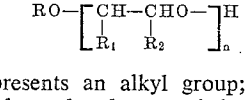
Strip No.	Wetting Agent in Final Rinse	Condition of Film
1	None	Water spots.
2	Nonylphenoxy polyethoxy ethanol 1.9 ml./l.	Scum.
3	Tridecyloxy polyethoxy ethanol 1.4 ml./l.	No scum, no water spots, no dye stains.
4	Tridecyloxy polyethoxy ethanol 0.14 ml./l.	No scum, no water spots, no dye stains.

Similarly, other final rinse baths of our invention that contain other wetting agents and dye stabilizing agents are used to advantage in stabilizing the dye images and leaving the processed and dried photographic element free of water spots and scum. The final rinse baths of our invention are valuable for use in color photographic processing because they not only stabilize the color images but produce a good color photograph that does not need to be cleaned before it is satisfactory for use.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

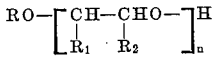
1. In a process of color photography in which an image-exposed photographic element comprising at least one silver halide emulsion layer is developed to produce a silver and dye image, washed, bleached, fixed, washed, bathed in a final rinse to prevent the formation of stains, the said improvement comprising the method for preventing the formation of processing scum in the final rinse and the deposition of said scum on the processed photographic element by the use of a final rinse comprising water, a dye stabilizing agent and a wetting agent having the formula:



wherein R represents an alkyl group; R_1 represents a group selected from the class consisting of the hydrogen atom and an alkyl group having from 1 to 6 carbon atoms; R_2 represents a group selected from the class consisting of the hydrogen atom and an alkyl group having from 1 to 6 carbon atoms; and *n* represents an integer of from 6 to 20.

2. In a process of color photography in which an image-exposed photographic element comprising at least one silver halide emulsion layer is developed to produce a silver and dye image, washed, bleached, fixed, washed, bathed in a final rinse to prevent the formation of stains, the said improvement comprising the method for preventing the formation of processing scum in the final rinse and the deposition of said scum on the processed photographic element by the use of a final rinse comprising water, about 10 ml./l. of 37% formaldehyde, and

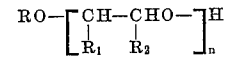
from about 0.01 to about 0.50 g./l. of a wetting agent having the formula:



wherein R represents an alkyl group; R_1 represents a group selected from the class consisting of the hydrogen atom and an alkyl group having from 1 to 6 carbon atoms; R_2 represents a group selected from the class consisting of the hydrogen atom and an alkyl group having from 1 to 6 carbon atoms; and *n* represents an integer of from 6 to 20.

3. In a process of color photography in which an image-exposed photographic element comprising at least one silver halide emulsion layer is developed to produce a silver and dye image, washed, bleached, fixed, washed, bathed in a final rinse to prevent the formation of stains, the said improvement comprising the method for preventing the formation of processing scum in the final rinse and the deposition of said scum on the processed photographic element by the use of a final rinse comprising water, about 10 ml./l. of 37% formaldehyde, and from about 0.01 to about 0.50 g./l. of tridecyloxy polyethoxy ethanol containing an average of about 12 ethoxy units per molecule.

4. In a process of color photography in which a completely processed wet photographic element containing a dye image and substantially no silver and substantially no silver halide is bathed in a final rinse to stabilize the dye image, the improvement comprising the method for preventing the formation of processing scum in the final rinse and the deposition of said scum on the processed photographic element by the use of a final rinse comprising water, a dye stabilizing agent and a wetting agent having the formula:



wherein R represents an alkyl group; R_1 represents a group selected from the class consisting of the hydrogen atom and an alkyl group having from 1 to 6 carbon atoms; R_2 represents a group selected from the class consisting of the hydrogen atom and an alkyl group having from 1 to 6 carbon atoms; and *n* represents an integer of from 6 to 20.

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J. TRAVIS BROWN, *Acting Examiner.*