United States Patent Office 3,748,130
Patented July 24, 1973

3,748,130

NOVEL PHOTOGRAPHIC PRODUCTS AND PROCESSES

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No Drawing. Filed Aug. 9, 1971, Ser. No. 170,344
Int. Cl. G03c 5/54, 7/00, 1/34
U.S. Cl. 96—29 D 13 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to photographic silver halide emulsions containing sodium hypochlorite.

BACKGROUND OF THE INVENTION

It is well known in the photographic art that light-sensitive silver halide emulsions, due to factors encountered in manufacturing, storage and the like, tend to fog to some degree. In addition, various additives, such as booster developers incorporated in the emulsion or certain sensitizing dyes, while providing certain advantageous characteristics to the emulsions, often produce fog, sometimes to such a degree that the additives can be used only sparginly or not at all.

To counteract the fog-producing phenomena, antifoggants and stabilizers are generally employed. Although various materials have been employed to counteract fog, such materials often have the additional tendency to adversely effect speed of the emulsion. It is believed that the speed loss is effected by a non-discriminatory attack on the sensitivity centers of the silver halide grains as well as the fog centers.

A novel additive for reducing fog levels has now been found which is not susceptible to the deficiencies of the prior art.

SUMMARY OF THE INVENTION

Photographic silver halide emulsions are stabilized against fog by the addition of sodium hypochlorite thereto. Conventional silver halide emulsions often employ additives which may result in some degree of fog but which are desirable in the emulsion for other purposes. In the past, a certain level of fog from such additives has been tolerated to obtain the benefits accruing from the additive. It has now been found, however, that by the addition of sodium hypochlorite to the emulsion, stability of the thus-formed negative with respect to fog is greatly enhanced to a degree that permits the employment of additives which, though desirable for other reasons, are generally poor, or not suitable for use at all because of the fog level generated.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a photographic silver halide emulsion having incorporated therein a stabilizing amount of sodium hypochlorite. It has been found that sodium hypochlorite can be incorporated in emulsions at a level sufficient to produce a marked reduction in fog level, to a point where additives, which heretofore could not be employed because of excessive fog production, can now be used satisfactorily. In addition, the levels of the sodium hypochloride which can be employed advantageously do not adversely effect emulsion speed. It is believed that the antifoggant of the present invention preferentially attacks the fog centers but not the sensitivity centers, i.e., potential latent image sites, of the silver halide grains.

While not intending to be bound by theory, it is believed that the oxidation potential of the sodium hypochlorite, in the quantities used possesses an oxidation potential sufficient to oxidize the fog centers but not the sensitivity centers. The presence of OCl in solution establishes a redox buffer which destroys existing fog sites and inhibits the formation of new fog sites, while at the same time does not adversely effect sensitivity centers. The specific amount employed must be determined empirically for each emulsion and for each new additive, since the specific degree of fog produced will vary with each of the enumerated changes to the emulsion.

The antifoggants of the present invention are particularly useful in silver and color diffusion transfer proceses, and especially in color diffusion transfer processes of the dye developers type as well as in conventional silver halide processes.

Generally, in diffusion transfer processes, an exposed silver halide emulsion is developed and, under the control of the development, an imagewise distribution of image-forming components is formed which is transferred, at least in part, to a superposed image-receiving layer to form the transfer image thereon. In silver diffusion transfer processes, an exposed silver halide emulsion is developed with a silver halide developing agent in the presence of a silver halide solvent such, for example, as a thiosulfate or thiocyanate. Almost concurrently with the development of the latent image, the silver halide solvent reacts with the silver halide in unexposed and undeveloped areas to form a soluble, mobile silver complex. At least a portion of the silver complex is transferred to a print-receiving layer where it is precipitated to form the positive image. Suitable examples of such processes are disclosed in patents such as U.S. Patent No. 2,647,056 to Edwin H. Land.

Generally, in carrying out color diffusion transfer processes, a silver halide emulsion is exposed to create therein a latent image. The latent image is developed and concurrently with and under control of this development, an imagewise distribution of suitable color-providing material, usually comprising one or more dyes or dye intermediates, is formed. At least, a portion of these color-providing materials is transferred to a superposed image-receiving layer to form a colored positive image thereon. As examples of such processes, mention may be made of the processes disclosed and claimed in U.S. Patent No. 2,983,606, issued May 9, 1961 to Howard G. Rogers, wherein dye developers (i.e., compounds which are both dyes and silver halide developing agents) are the color-providing materials; U.S. Patents Nos. 2,647,049; 2,661,-293; 2,698,244; 2,698,798; 2,802,735; 3,148,062; 3,227,-550; 3,227,551; 3,227,552; 3,227,554; 3,342,294; 3,330,-655; 3,347,671; 3,352,672; 3,364,022; 3,443,939; 3,443,-940; 3,443,941; 3,443,943; etc., wherein color diffusion transfer processes are described which employ color coupling techniques comprising, at least in part, reacting one or more color developing agents and one or more color formers or couplers to provide a dye transfer image to a superposed image-receiving layer and those disclosed in U.S. Patents Nos. 2,774,668 and 3,087,817, wherein color diffusion transfer processes are described which employ the imagewise differential transfer of complete dyes by the mechanisms therein described to provide a transfer dye image to a contiguous image-receiving layer, and thus including the employment of image-providing materials in whole or in part initially insoluble or nondiffusible as disposed in the film unit which diffuse during processing as a direct or indirect function of exposure.

As pointed out above, the antifoggants of the present invention are especially useful in color diffusion transfer processes employing dye developers, i.e., compounds which are both dyes and silver halide developing agents. Generally, in carrying out such processes, the dye developers are preferably disposed in the photosensitive element in a separate alkali-permeable layer contiguous with

the silver halide emulsion layer. After exposure, the photosensitive element is permeated with an alkaline processing solution which solubilizes the dye developer. As a consequence of the development, the dye developer is immobilized in exposed areas. In unexposed and partial exposed areas of the emulsion the dye developer is unreacted and diffusible and thus provides an imagewise, mobile distribution of the dye developer. At least a portion of the imagewise distribution of the dye developer is transferred to a superposed image-receiving layer to form the positive image thereon.

Multicolor images may be obtained using color image-forming components such as, for example, the previously-mentioned dye developers, in diffusion transfer processes by several techniques. One such technique contemplates the use of a photosensitive silver halide stratum comprising at least two sets of selectively sensitized minute photosensitive elements arranged in the form of a photosensitive screen. Transfer processes of this type are disclosed in U.S. Pats. Nos. 2,968,554 and 2,983,606. Another process for obtaining multicolor transfer images utilizing dye developers employs an integral multilayer photosensitive element, such as is disclosed in U.S. Pat. No. 3,345,163 issued Oct. 3, 1967, wherein at least two selectively sensitized photosensitive strata are superposed on a single support and are processed, simultaneously and without separation, with a single, common image-receiving layer. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum and a blue-sensitive silver halide emulsion stratum, said emulsions having associated therewith, respectively, for example, a cyan dye developer, a magenta dye developer and a yellow dye developer. The dye developer may be utilized in the silver halide emulsion layer, for example, in the form of particles, or it may be employed as a layer behind the appropriate silver halide emulsion strata. Each set of silver halide emulsion and associated dye developer strata may be separated from other sets by suitable interlayers, for example, by a layer of gelatin or polyvinyl alcohol.

The sodium hypochlorite may be effectively located in one or more silver halide emulsion layers and/or adjacent layers of a film unit. Particularly effective results are achieved by incorporating the sodium hypochlorite directly into the emulsion layers. The sodium hypochlorite is preferably added directly to the melted diluted emulsion as a water solution prior to the addition of the sensitizing dye and surface active agent, although such order of addition is not critical.

In order to illustrate the advantageous properties obtained by means of the present invention, a series of emulsions were evaluated employing additives which can be detrimental to the emulsion stability. The effect of sodium hypochlorite on such systems will be noted.

To a silver iodobromide emulsion comprising about 2% iodide was added Dye No. 4 sensitizing dye. The emulsion had a pH of 6.3 and pBr of 2.4 before dilution and coating. The sodium hypochlorite was added at the indicated concentration and the emulsion was coated on a base of cellulose triacetate. This film was air dried, exposed on a sensitometer and processed with a processing solution (Type 42, Polaroid Corporation, Cambridge, Mass.) and an image-receiving sheet from a Type 47 film assembly (Polaroid Corporation). The negative and image-receiving element were maintained in superposed position for 15 seconds, after which they were stripped apart. The photographic characteristics of the resulting positive print were measured on an automatic densitometer.

The following sensitizing dyes were employed:

Dye 1.—5,5',6,6'-tetrachloro - 3,3' - disulfopropyl-1,1'-diethylbenzamidazolo-carbocyanine betaine sodium salt;

Dye 2.—3-carboxymethyl-1'-ethylthia-2'-cyanine betaine;

Dye 3.—5,6'-dimethoxy - 3-carboxymethyl-1'-ethylthia-2'-cyanine betaine;

Dye 4.—5,5',6,6' - tetrachloro - 3,3' - disulfoisobutyl-1,1'-diethylbenzimidazolo-carbocyanine betaine sodium salt.

The results are summarized in the following table.

TABLE 1

Example	Sodium hypochlorite concentration	$D_{max.}$ values (silver) Initial	$D_{max.}$ values (silver) After 16 days at room temperature
Control	0	0.47	0.32
1	1.25×10^{-5} mg./g. silver	0.86	0.61
2	1.25×10^{-4} mg./g. silver	0.95	1.35
3	1.25×10^{-3} mg./g. silver	1.15	1.43

As well as providing the indicated result, it will be noted that a long term improvement has also been achieved.

Another set of emulsions were evaluated as follows:

To a silver iodobromide emulsion comprising 2% iodide was added the indicated sensitizing dyes and a booster developer (methylphenylhydroquinone) as a 4.6% oil dispersion at a level of about 0.25 g./g. of silver. The emulsion had a pH of 6.3 and a pBr of 2.4 before dilution and coating. The sodium hypochlorite was added at a concentration of 12.5×10^{-3} g./g. silver. The emulsions were coated on a base of cellulose triacetate having coated thereon a magenta dye developer 2-[p-(2'',5''-dihydroxyphenethyl)-phenylazo]-4-isopropoxy-1-naphthol at a concentration of 3 g./g. of silver. This film was air dried, exposed on a sensitometer and processed with a processing solution (Type 108, Polaroid Corporation, Cambridge, Mass. and an image-receiving sheet from a Type 108 film assembly (Polaroid Corporation). The negative and image-receiving element were maintained in superposed position for 60 seconds, after which they were stripped apart. The photographic characteristics of the resulting positive print were measured on an automatic densitometer.

TABLE 2

System	$D_{max.}$ values (magenta): No booster, no sodium hypochlorite — 24 hours room temperature	No booster, no sodium hypochlorite — 6 days 120° F.	Methylphenyl hydroquinone—no sodium hypochlorite — 24 hours room temperature	Methylphenyl hydroquinone—no sodium hypochlorite — 6 days 120° F.	Methylphenyl hydroquinone sodium hypochlorite — 24 hours room temperature	Methylphenyl hydroquinone sodium hypochlorite — 6 days 120° C.
Control (no dye)	2.24	1.99	2.15	2.09	2.17	2.12
4. Dye 1 (1.3 mg./g. silver)	2.19	1.66	2.03	1.97	2.22	2.19
5. Dye 2 (1.3 mg./g. silver)	2.23	1.99	F	F	2.20	2.21
6. Dye 3 (1.3 mg./g. silver)	2.22	2.07	0.96	0.97	2.25	2.21
7. Dye 1 (0.5 mg./g. Ag)						
Dye 2 (0.4 mg./g. Ag)	2.19	1.84	F	F	2.22	2.20
Dye 3 (0.8 mg./g. Ag)						
8. Dye 1 (0.4 mg./g. Ag)						
Dye 2 (0.32 mg./g. Ag)	2.26	2.00	F	F	2.20	2.20
Dye 3 (0.64 mg./g. Ag)						

NOTE.—F indicates total fog.

From the foregoing it will be noted that the booster alone is responsible for an increase in fog over the control. When employed with Dyes 2 and 3, the combination of dyes and booster results in almost total fog in both cases. Similarly, combinations of dyes with the booster resulted in total fog. However, in each case suppression of the fog to levels, in many cases as good as the experiments without booster, and in some instances better, is achieved. It also should be noted that even in negatives subjected to accelerated aging conditions, the $D_{max.}$ values remained high indicating effective fog suppression.

Although the antifoggant properties of the sodium hypochlorite were illustrated in diffusion transfer processes, it should be understood that they are equally effective in conventional photographic products and systems.

Although, as illustrated in the example, the sodium hypochlorite is directly incorporated in the silver halide emulsion itself, it should be understood that the antifoggant may be incorporated, in part, or in whole, in the processing composition and/or other layers of the film unit, for example, in a permeable layer adjacent the silver halide emulsion. In general, the most efficacious method has been determined to be that of directly disposing the chlorate salt in the silver halide emulsion. For example, the sodium hypochlorite may be advantageously incorporated in the silver halide emulsion during the ripening or sensitivity increasing stage of the emulsion manufacturing process or as a "coating final" just prior to coating the emulsion on a suitable support.

For the production of the photosensitive gelatino silver halide emulsions employed in the present invention, the silver halide crystals may be prepared by reacting a water-soluble silver salt, such as silver nitrate, with at least one water-soluble halide, such as ammonium, potassium or sodium bromide, preferably together with a corresponding iodide, in an aqueous solution of a peptizing agent such as a colloidal gelatin solution; digesting the dispersion at an elevated temperature, to provide increased crystal growth; washing the resultant water-soluble salts by chilling the dispersion, noodling the set dispersion, and washing the noodles with cold water, or alternatively, employing any of the various flocc systems, or procedures, adapted to effect removal of undesired components, for example, the procedures described in U.S. Patents Nos. 2,614,928; 2,614,929; 2,728,662; and the like; after-ripening the dispersion at an elevated temperature in combination with the addition of gelatin and various adjuncts, for example, chemical sensitizing agents of U.S. Patents Nos. 1,574,944; 1,623,499; 2,410,689; 2,597,856; 2,597,915; 2,487,850; 2,518,698; 2,521,926; and the like; all according to the traditional procedures of the art, as described in Neblette, C. B., "Photography Its Materials And Processes," 6th ed., 1962.

Optical sensitization of the emulsion's silver halide crystals may be accomplished by contact of the emulsion composition with an effective concentration of the selected optical sensitizing dyes dissolved in an appropriate dispersing solvent such as methanol, ethanol, acetone, water, and the like, all according to the traditional procedures of the art, as described in Hammer, F. M., "The Cyanine Dyes And Related Compounds."

Additional optional additives, such as coating aids, hardeners, viscosity-increasing agents, stabilizers, preservatives, and the like, for example, those set forth hereinafter, also may be incorporated in the emulsion formulation, according to the conventional procedures known in the photographic emulsion manufacturing art.

The photoresponsive material of the photographic emulsion will, as previously described, preferably comprise a crystal of a silver compound, for example, one or more of the silver halides such as silver chloride, silver iodide, silver bromide, or mixed silver halides such as silver chlorobromide, silver chloroiodobromide or silver iodobromide, of varying halide ratios and varying silver concentrations.

What is claimed is:

1. A photographic product which comprises a plurality of layers including a support layer and a silver halide emulsion layer having associated therewith image-forming material which is processing composition diffusible as a function of the point-to-point degree of silver halide exposure to incident radiation; said silver halide emulsion containing sodium hypochlorite.

2. A product as defined in claim 1 which includes optical sensitizing agents.

3. A product as defined in claim 1 which includes a booster developer.

4. A product as defined in claim 1 wherein said booster developer is methylphenylhydroquinone.

5. A product as defined in claim 1 wherein said emulsion is panchromatically sensitized.

6. A product as defined in claim 1 wherein said image-forming material is a dye image-forming material.

7. A product as defined in claim 6 wherein said dye image-forming material comprises a dye which is a silver halide developing agent.

8. A product as defined in claim 1 including at least two selectively sensitized silver halide emulsion layers each having a dye which dye is a silver halide developing agent of predetermined color associated therewith, each of the dyes soluble and diffusible in processing composition at a first pH as a function of the point-to-point degree of exposure of the respective emulsion associated therewith.

9. A product as defined in claim 1 which includes a layer adapted to receive image-forming material diffusing thereto.

10. A product as defined in claim 9 wherein said film unit is a permanent laminate.

11. A diffusion transfer process which comprises the steps of developing an exposed photosensitive element containing a silver halide emulsion containing sodium hypochlorite therein to form an imagewise distribution of image-forming material in said photosensitive element, and transferring at least a part of said imagewise distribution by diffusion to a superposed image-receiving layer to provide thereon a transfer image.

12. A process as defined in claim 11 wherein said image-forming material is a dye image-forming material.

13. A process as defined in claim 12 wherein the dye image-forming material comprises a dye which is a silver halide developing agent.

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U.S. Cl. X.R.

96—29 R, 77, 95, 110, 120