United States Patent Office

2,944,899

Patented July 12, 1960

2,944,899

STABILIZATION OF PHOTOGRAPHIC SILVER HALIDE EMULSIONS

Rudolph E. Damschroder and Herbert B. Cowden, Rochester, N.Y., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

No Drawing. Filed Oct. 4, 1956, Ser. No. 613,816

7 Claims. (Cl. 96—95)

This invention relates particularly to gelatin silver halide emulsions which are stabilized against hardening upon aging for long periods of time or because of storage under adverse conditions of temperature or humidity or a combination of these conditions.

It is a well known practice in the manufacture of gelatin silver halide emulsions to harden the emulsions to facilitate handling during the coating and processing operations. However, a number of photographic processes are known which require that the gelatin silver halide emulsions be substantially unhardened. One such photographic process is the inbibition dye printing process in which an unhardened gelatin silver halide emulsion is exposed, developed under conditions of tanning development, the unexposed areas washed out with hot water, the relief image remaining on the support then dyed up and the dye transferred imagewise to an imbibition printing blank. Obviously it is desirable in that process for the initial gelatin silver halide emulsion to remain unhardened as long as possible in order for the emulsion to be available for instant use.

Another process also requiring a substantially unhardened gelatin silver halide emulsion is the colloid transfer process of the Yutzy and Yackel U.S. Patents 2,596,756, granted May 13, 1952, and 2,716,059, granted August 23, 1955. In these processes a substantially unhardened gelatin silver halide emulsion is exposed to a subject developed in the presence of a gelatin tanning silver halide developing agent, then the developed emulsion layer while moist is pressed against an absorbent support to transfer a stratum of the unhardened image area to the receiving sheet to form a positive image thereon.

A well known problem encountered in all such processes utilizing unhardened gelatin silver halide emulsions results from the inability to maintain the emulsion in the unhardened condition over a reasonable period of time particularly under adverse conditions of storage. For example, in the case of unhardened emulsions coated on ordinary photographic paper support, the ingredients in the paper stock tend to harden the emulsion prematurely. Even when extreme care is taken to provide a support for the emulsion free of gelatin hardening agents, the emulsion tends to harden over a period of time and become useless for the purpose intended.

The emulsion hardening problem is further complicated in the preferred processes of U.S. Patents 2,596,756 and 2,716,059 above by the presence in the unhardened emultions of gelatin tanning silver halide developing agents such as 3,4-dihydroxydiphenyl, 2,5-dihydroxydiphenyl, 2,3-dihydroxydiphenyl or 5,6,7,8-tetrahydronaphthohydroquinone alone or in combination with substantially non-tanning silver halide developing agents such as 4-methoxy-1-naphthol, N-methyl-p-aminophenol-x-sulfonic acid, p-hydroxyanilinomethane sulfonic acid, pyrogalloldimethyl ether or 8-hydroxy-1-naphthol. Such tanning developing agents tend to accelerate the hardening of the gelatin emulsion upon aging and thus render the

emulsion less useful for the intended purpose. Moreover, on aging of the emulsions the substantially non-tanning self-coupling developing agents such as 4-methoxy-1-naphthol undergo oxidation and self-coupling to cause the formation in the emulsion of an undesirable bluish coloration, and because of the light absorption of the bluish coloring material a loss of light sensitivity of the emulsion takes place.

We have discovered that the tendencies for all of the mentioned unhardened emulsion systems to become prematurely hardened either due to unknown constituents of the supports or due to known factors such as the presence of developing agents in the emulsions, can be very greatly alleviated by incorporating into the emulsions certain cyclic compounds containing activated methylene groups. A further unexpected and fortuitous result of the use of these cyclic compounds in the emulsions of U.S. Patent 2,716,059 containing the self-coupling developing agents such as 4-methoxy-1-naphthol, resides in the fact that such emulsions containing the cyclic compounds do not develop the mentioned blue coloration or loss in sensitivity upon aging.

As an illustration of the effectiveness of these compounds when the compound 5,5-dimethylcyclohexanedione-1,3 was used in an unhardened emulsion coated on a paper stock which had previously caused substantial emulsion hardening, the element was found not to have changed its photographic characteristics after incubation for 28 days at 120° F. and 42 percent relative humidity. The same emulsion free of the compound and coated on the same stock was useless in less than seven days storage under ordinary room conditions.

It is interesting to note that an appreciable number of patents indicate that diketones are gelatin hardeners and that U.S. Patent 2,725,305 in particular shows that cyclic 1,2-diketones are gelatin hardening agents in contrast to the above cyclic 1,3-diketone.

Some cyclic compounds which are useful in emulsions are tabulated in the following table. The first four compounds tabulated are by far the more effective as regards their behavior in preventing undue hardening of gelatin emulsion layers and the mentioned tendency of certain emulsions to develop the blue coloration. In the table is indicated the effectiveness of each compound as regards the prevention of hardening of gelatin emulsions in general as well as the effectiveness in preventing the development of blue emulsion coloration in the presence of 4-methoxy-1-naphthol.

Compound	Prevents	
	Hardening	Blue Coloration
5,5-dimethylcyclohexanedione-1,3	+	+
dicyclohexanone oxalyldihydrazone	+	+
4-cyano-5-phenylcyclohexanedione-1,3	+	+
5-phenylcyclohexanedione-1,3	+	+
3-dicyanomethylene-5,5-dimethylcyclohexanone.	+	+
3-dicyanomethylene-1-methyl-1-cyclohexene	−	+
dicyanomethylene cyclohexane	−	+
1-dicyanomethylene-1,2,3,4-tetrahydronaphthalene.		
2-methyl-1-phenyl-4,6-(1H, 5H) pyrimidine dione.	−	+
1-dicyanomethylene indan	−	+
(1-cyano-1-ethoxycarbonylmethylene)-cyclopentane.	−	+

The following compounds do not affect the mentioned blue coloration but are effective for preventing emulsion hardening: cyclohexanone oxime, 2,4-pentanedione dioxime and 2,5-hexanedione dioxime.

The compound 5,5-dimethylcyclohexanedione-1,3 above is the most effective compound both for the prevention of emulsion hardening on aging and the development of the blue coloration which occurs from the oxidizing and self-coupling of 4-methoxy-1-naphthol on aging of the emulsion. This compound is known in the art as dimedone" and will be referred to as such hereinafter.

The following related compounds have been found to be ineffective or only slightly effective in the prevention of emulsion hardening or the prevention of the mentioned blue coloration in spite of their similarity in structure to the above compounds.

2,4-pentanedione
2,4-di(dicyanomethylene)pentane
N-(4-benzoylacetamidobenzenesulfonyl)-N-(α-phenylpropyl)-p-toluidine
2-bromo-5,5-dimethylcyclohexanedione-1,3

From the above table it will be apparent that a single compound can be selected which will simultaneously prevent both emulsion hardening and the development of the mentioned blue coloration. However, it may be desirable in certain instances to employ two or more of the compounds which give a single effect. Thus one compound which strongly inhibits gelatin hardening but not the bluing of the emulsion may be employed in conjunction with another compound whose single effect is to prevent emulsion bluing. Accordingly, the hardening and bluing effects mentioned can be controlled separately depending upon requirements of the particular emulsion. The compounds can be used in emulsions in amounts of the order of about 1 to 20 grams per mol of silver halide. The higher amounts in some cases tend to slow down the gelatin tanning which occurs during the silver halide development.

The following examples illustrate the use of the mentioned compounds in unhardened gelatin silver halide emulsions:

Example 1

A high-contrast silver chloride emulsion containing 1 mole of silver chloride and 340 grams of gelatin was melted at 40° C. and the following additions made: 200 grams of 15 percent aqueous saponin solution, 5 grams of dimedone dissolved in 50 cc. of methanol, and 900 grams of a dispersion made by dissolving 45 grams 4-phenyl catechol (3,4-dihydroxydiphenyl) and 19.3 grams of 4-methoxy-1-naphthol in 129 grams of tricresyl phosphate at about 80° C. and pouring it into a rapidly stirring solution of 64.3 grams of gelatin and 64 grams of 8 percent aqueous saponin solution in 579 cc. of water at 50° C. This mixture was coated over 500 square feet of an unhardened gelatin-sized paper base. The product resulting was processed as described in U.S. Patent 2,716,059 by first exposing to a line or halftone subject, then developing with a solution of sodium carbonate after which the developed paper was pressed against a paper transfer sheet to transfer a stratum of the unhardened image areas to the receiving sheet. A sample of the same light-sensitive paper which had been incubated for 28 days at 120° F. and 42 percent relative humidity was found to give comparable prints whereas a similar paper made in the same manner but omitting dimedone from the emulsion had become hardened sufficiently to impair the print quality greatly and the emulsion had assumed an objectionable bluish color.

Example 2

A coating was made in the manner of Example 1 except upon a paper support sized with a resin of commercial origin which resin had the property of completely hardening gelatin emulsions coated thereon after only 7 days aging under ordinary room conditions. The coated element was incubated 28 days at 120° F. and 42 percent relative humidity and found to produce good prints in the process described in Example 1.

Example 3

The procedures of Example 1 were carried out except that in making the emulsion the saponin solution was first added to the silver halide emulsion followed by a dispersion made by dissolving 45 grams of 4-phenyl catechol, 19.3 grams of 4-methoxy naphthol and 5 grams of dimedone in 129 grams of tricresyl phosphate at about 80° C. and pouring it into a rapidly stirring solution of 64.3 grams gelatin and 64 grams 8 percent aqueous saponin solution in 574 cc. of water at 55° C.

Coatings of this emulsion made upon paper and processed as described in Example 1 exhibited the same improved stability upon aging.

A further utility for the mentioned cyclic compounds is in silver halide emulsions of conventional hardness which contain coupler compounds of the types well known in color photography and which emulsions are designed for use in color development processes of photography. That is, it has been found that if coupler-containing emulsions coated upon variously sized paper stocks are aged for long periods of time or if the aging has been accelerated by application of adverse conditions of temperature and humidity, the coupler compounds are prevented to a certain extent from coupling with the color developing agent with the detrimental effect that losses in dye density are sustained. This effect is illustrated in the following example:

Example 4

A gelatin silver chlorobromide emulsion containing a coupler compound producing a yellow dye upon color development was coated on a paper support containing a low concentration of melamine-formaldehyde resin size. The emulsion coating contained the following amounts of ingredients per square foot of coating surface:

	Mg.
Silver halide (calc. as silver)	120
3-benzoylacetamino-4-methoxy-2',4'-di-(tert.-amylphenoxy)acetanilide (McCrossen et al. U.S. patent application Serial No. 575,099, filed March 30, 1956)	160
Gelatin	390

Several coatings were made of this emulsion varying the concentration of dimedone in each coating as shown in the following table. The coatings were then exposed on a sensitometer and developed to dye images using a conventional color developing composition containing a phenylenediamine type of color developing agent. The loss in yellow dye density for each coating is shown in the table.

Sample	Grams Dimedone per mole Silver Halide	D-max Loss after Incubation 6 Days 120° F., 42% RH
		Percent
1	0	9
2	1	7.5
3	2	1.8
4	5	0

From the above discussion it will be apparent that one effect that the cyclic compounds have upon emulsions in general is to effectively prevent a loss in image density whether this was manifest by effectively lower emulsion speeds, loss in D-max or other characteristics.

The emulsions containing the cyclic stabilizing compounds and which are particularly adapted to use in the processes of U.S. Patent 2,596,756 and 2,716,059 are substantially unhardened as defined in those patents. That is, the emulsion should be no harder than would be the case with gelatin containing about 0.25 ounce of formaldehyde solution (40 percent diluted 1:3 with water) or 0.7 gram dry formaldehyde per pound dry gelatin freshly coated or 0.1 ounce of the solution per pound

dry gelatin for a sample aged 3 to 6 months under average room conditions. Also, as described in U.S. Patent 2,716,059 auxiliary non-tanning silver halide developing agents may be present in the emulsion layer together with the cyclic stabilizing compounds or the non-tanning developing agent may be employed in the alkaline solution which is used to initiate development of the unhardened and exposed emulsion containing the tanning developing agent and the cyclic stabilizing compounds.

When employing the unhardened emulsions containing tanning developing agent and cyclic stabilizing compound in the colloid transfer process described in Example 1, any of the techniques disclosed in U.S. Patent 2,596,756 may be employed for improving the optical density of the print. For example, the print while still moist from the transfer operation may be exposed to light of suitable intensity and duration with the result that added silver density will become apparent. However, it is preferable to perform the transfer from the developed emulsion layer to a receiving sheet of the type disclosed in the Chan et al. U.S. patent application Serial No. 530,638, filed August 25, 1955, now U.S. Patent 2,865,745, granted December 23, 1958, having on its surface a mixture of a silver halide fogging agent and a compound retarding the tanning of the gelatin in the presence of fogged silver halide and gelatin tanning silver halide developing solution. For example, a mixture of (1) either thioacetamide, dithiooxamide, dithiobiuret, thiosemicarbazide or thiourea and (2) either sodium formaldehyde bisulfite, sodium formaldehyde sulfoxalate, 2,4-dihydroxybenzoic acid, sodium benzene sulfinate, borophosphate, aminomethane sulfonic acid or borax. A preferred mixture is about 5 to 50 milligrams of thiourea and 10 to 50 milligrams of sodium formaldehyde bisulfite per square foot of surface.

Accordingly, when the developed emulsion layer is pressed against the receiving sheet, the unexposed or less exposed regions of the emulsion adhere to the receiving sheet and at the same time the fogging agent commences to fog the unexposed silver halide and the gelatin tanning retarder such as sodium formaldehyde bisulfite tends to stop tanning development of the emulsion layer. Thus, additional copies are readily obtainable from the same developed emulsion layer independent of the speed of the operator by merely rewetting the emulsion and repeating the transfer operation.

The other receiving elements described by the Chan et al. invention can be employed in conjunction with the process illustrated in Example 1 above. For example, a paper stock translucentized with α-methyl styrene can be coated with a mixture of the mentioned silver halide fogging agents and retarders for gelatin tanning. Using a stabilized emulsion as described in the above examples, a print may then be obtained on the translucent base which readily lends itself to use in other reproduction processes.

Another process in which it is advantageous to use the cyclic stabilizing agents such as dimedone in a substantially unhardened emulsion is a silver halide diffusion transfer process of the type in which a substantially unhardened gelatin silver halide emulsion is coated upon a hardened hydrophilic organic colloid layer, such as hardened gelatin, containing a silver precipitating agent such as colloidal silver, silver sulfide, zinc sulfide, etc. In the process the emulsion is exposed, developed in the presence of a silver halide solvent such as hypo with the result that the residual undeveloped silver halide in the unhardened emulsion transfers imagewise to the underlying layer as a soluble silver salt and there forms an argental image. Thereafter the outer unhardened emulsion layer can be removed with warm water leaving a positive image on the support. The cyclic compounds such as dimedone in preventing emulsion hardening insure the removability of the emulsion layer even after aging of the original sensitive element for long periods of time.

What we claim is:

1. A photographic emulsion comprising a mixture of gelatin, silver halide and a stabilizing agent of the class consisting of 5,5-dimethylcyclohexanedione-1,3; 4-cyano-5-phenylcyclohexanedione-1,3; 5-phenylcyclohexanedione-1,3; 3-dicyanomethylene-5,5-dimethylcyclohexanone and 2-methyl-1-phenyl-4,6-(1H, 5H) pyrimidine dione.

2. The emulsion of claim 1 wherein the gelatin is substantially unhardened.

3. The emulsion of claim 1 wherein the gelatin is substantially unhardened and the emulsion further contains a gelatin tanning silver halide developing agent.

4. The emulsion of claim 1 wherein the gelatin is substantially unhardened and the emulsion further contains a mixture of a gelatin tanning silver halide developing agent and a substantially non-tanning silver halide developing agent.

5. A photographic emulsion comprising a mixture of substantially unhardened gelatin, silver halide, and 5,5-dimethylcyclohexanedione-1,3.

6. A photographic emulsion comprising a mixture of substantially unhardened gelatin, silver halide, a gelatin tanning silver halide developing agent, 4-methoxy-1-naphthol and a compound preventing the formation of blue coloration in the emulsion upon aging selected from the class consisting of 5,5-dimethylcyclohexanedione-1,3; 4-cyano-5-phenylcyclohexanedione-1,3; 5-phenylcyclohexanedione-1,3; 3-dicyanomethylene-5,5-dimethylcyclohexanone; and 2-methyl-1-phenyl-4,6-(1H, 5H) pyrimidine dione.

7. A photographic emulsion comprising a mixture of substantially unhardened gelatin, silver halide, a gelatin tanning silver halide developing agent, 4-methoxy-1-naphthol and 5,5-dimethylcyclohexanedione-1,3.

References Cited in the file of this patent

UNITED STATES PATENTS

742,405	Eichengrun et al.	Oct. 27, 1903
2,214,446	Albers et al.	Sept. 10, 1940
2,444,607	Heimbach	July 6, 1948
2,675,314	Vittum et al.	Apr. 13, 1954
2,716,059	Yutzy et al.	Aug. 23, 1955
2,735,769	Allen et al.	Feb. 21, 1956