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MICRODISPERSIONS OF PHOTOGRAPHIC COLOR COUPLERS

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This invention relates to color photography and particularly to a method for dispersing color couplers in photograpic emulsions.

Photographic color couplers are either of the water-insoluble type which are dissolved in a hydrophobic solvent and dispersed in the photographic emulsion as described in Jelley and Vittum U. S. Patent 2,322,027, or of the water solubilizable type which are dissolved in aqueous alkaline solutions and mixed with the emulsion. The latter type contains solubilizing groups, e. g., sulfonic acid or carboxylic acid which permit formation of soluble sodium or other water-soluble salts.

Unfortunately, all of these non-diffusing solubilized couplers have a strong tendency to react with gelatin when they are in solution, raising the viscosity of the mixtures. A large amount of gelatin compared to the weight of couplers must first be mixed with the alkaline solution of the coupler before it cn be mixed with a gelatino-silver halide emulsion. This increases the coating thickness or conversely decreases the dye density which can be obtained for a given coating thickness. A further disadvantage of the solubilized couplers is that because of their homogeneous or continuous nature in solution packets cannot be made successfully from them by the method of Godowsky U. S. Patent 2,698,794. A certain proportion of soluble coupler remains free in the external or continuous phase giving rise to color contamination when single layer mixed packet coatings are processed photographically.

It is therefore an object of the present invention to provide a novel means of incorporating couplers containing acid groups in photographic emulsions. A further object is to provide a method for making fine dispersions of couplers in photographic emulsions. A still further object is to provide a method for producing photographic dye images of higher contrast and maximum density than those usually obtained. Other objects will appear from the following description of our invention.

These objects are accomplished by dissolving the acid form of a coupler containing an acid group, e. g., carboxyl or sulfonic acid, in a water-soluble or water-miscible solvent for the acid form of the coupler, then adding water and a wetting or dispersing agent to the coupler solution to form a microdispersion or suspension of coupler in the aqueous medium. The water-soluble or water-miscible solvent is then removed and the coupler dispersion incorporated in a hydrophilic colloidsilver halide emulsion.

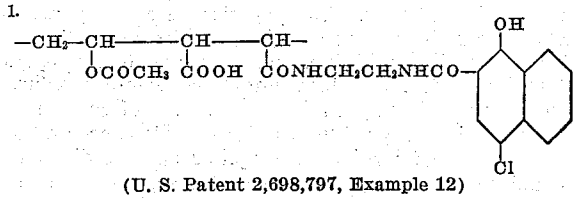
By "microdispersion" we mean an extremely finely-divided suspension or dispersion of the coupler, approaching a sol in degree of fineness. Mechanical grinding or milling is not required to attain the fine particle size desired, but the sol that forms is a stable entity.

Couplers used in our process are color-forming compounds capable of coupling with the oxidation product of a primary aromatic amino developing agent on photographic development. Such couplers will be described more fully hereinafter.

Water-miscible solvents for the coupler used in our process include acetone, methyl or ethyl alcohols, acetonitrile, dimethyl formamide and dioxane.

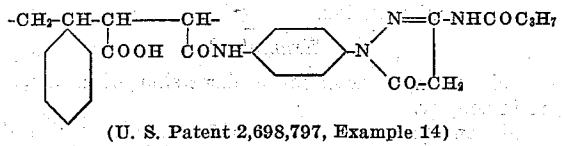
The following couplers can be used according to the process of our invention:

1.



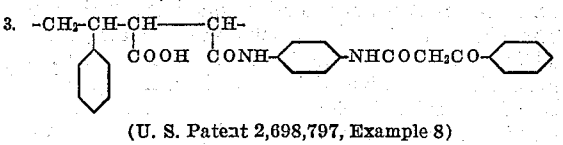
(U. S. Patent 2,698,797, Example 12)

2.



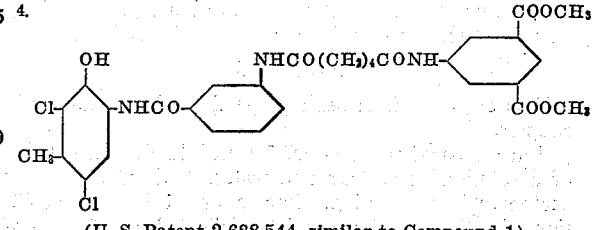
(U. S. Patent 2,698,797, Example 14)

3.



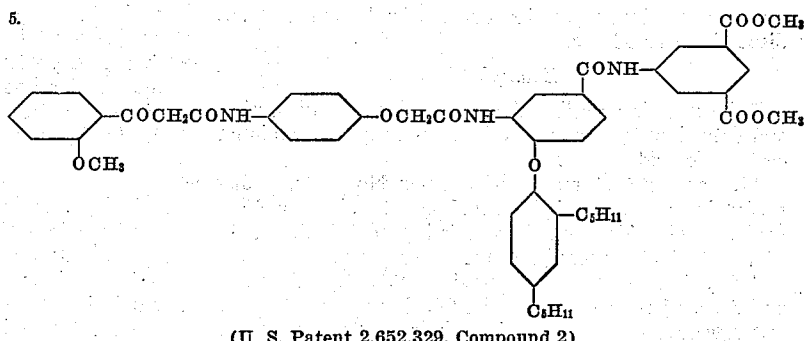
(U. S. Patent 2,698,797, Example 8)

4.



(U. S. Patent 2,688,544, similar to Compound 1)

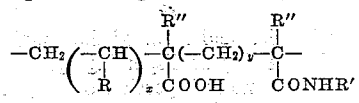
5.



(U. S. Patent 2,652,329, Compound 2)

Other couplers described in U. S. Patents 2,652,329, 2,688,544 and 2,698,797 may be used in place of those

listed above. The couplers of U. S. Patent 2,698,797 are resin couplers having the recurring structure



where R is hydrogen, phenyl, alkyl, alkoxy, carboxyalkyl, or acyloxy, x and y are 0 or 1, R' represents a color-forming group including an aryl group, capable of reacting with the oxidation product of a primary aromatic amino developing agent on photographic development, and R'' is hydrogen or an alkyl radical, e. g., methyl or ethyl.

Example 1

This example describes the preparation of a coupler dispersion from a cyan resin coupler.

Twenty grams of coupler No. 1 were dissolved by warming to 50° C. in a mixture of 450 cc. of acetone and 50 cc. of water. One cc. of a 1% acetone solution of Alkaterge-C (substituted oxazoline) was added and the solution cooled to room temperature (75° F.). To this solution there was added by pouring in rapidly without further stirring, 160 cc. of water containing 0.1 cc. of Aerosol OT (dioctyl ester of sodium sulfosuccinic acid). A turbid suspension of colloidally dispersed coupler formed immediately. The particles were barely resolvable under the microscope at 900 times magnification. The suspension was left exposed to air at room temperature for 24 hours at which time the volume had reduced to 200 cc. with only a minimum amount of acetone left in it. This corresponds to a 10% solids concentration. No further stabilization was required and the dispersion could be stored at room temperatures up to 85° F. for over a year without evidence of crystallization, coalescence or sedimentation.

Example 2

This example describes a dispersion of a magenta resin coupler.

Fifteen grams of coupler No. 2 were dissolved in 450 cc. of an acetone-water solution containing 90% acetone. Three cc. of a 1% acetone solution of Alkaterge-C were added and the solution filtered to remove undissolved material. A solution of 150 cc. of water containing 0.2 cc. of Aerosol OT solution was poured into the coupler solution to form a microdispersion. Acetone was removed by room temperature evaporation over three days. The final volume of microdispersion was 150 cc.

Example 3

This example describes a dispersion of a yellow resin coupler.

Ten grams of coupler No. 3 were dissolved in 200 cc. of a solution of acetone and water, 90% of which was acetone, without heating. One cc. of a 1% acetone solution of Alkaterge-C was added followed by 100 cc. of distilled water added without further stirring. Acetone was removed by evaporation and the final volume of the dispersion was 100 cc.

Example 4

This example describes the preparation of a dispersion and emulsion from a non-resin cyan coupler containing carboxylic acid groups.

17.2 grams (0.2 mole) of coupler No. 4 were dissolved in 80 cc. of ethyl alcohol and 10 cc. of a 20% sodium hydroxide solution by stirring at 60° C. for 30 minutes. This hydrolyzes the ester groups and the yellow solution was then diluted to 400 cc. with water and 5 cc. of concentrated hydrochloric acid in 50 cc. of water were added slowly with stirring. The precipitate of the dicarboxylic acid of the coupler was filtered off with the aid of a vacuum pump, washed twice with slightly acid water, then dried at room temperature for several days. A tan-colored solid was obtained.

Five grams of this dicarboxylic acid were dissolved in 200 cc. of acetone by warming to 40° C. for 10 minutes with rapid stirring. The solution was filtered clear of a small amount of insoluble residue and 0.1 cc. of a 1% acetone solution of Alkaterge-C was added. The solution was cooled to 25° C. and 500 cc. of distilled water was poured in rapidly to form a turbid colloidal dispersion of very small particles. This dispersion was left exposed to the air overnight in a large evaporating dish in order to remove the acetone. To the residual aqueous suspension of 500 cc. total volume there was added 50 cc. of melted phthalic anhydride gelatin (prepared by reacting 20 grams of phthalic anhydride with 100 grams of gelatin in the manner described in Example 1 of Yutzy and Frame U. S. Patent 2,525,753) in 10% solution and the mixture stirred for 15 minutes. This gelatin suspension was cooled to 60° F. and 1–N sulfuric acid was added dropwise to reduce the pH to between 4.0 and 4.4 to cause the phthalic anhydride gelatin dispersion of coupler to flocculate. After settling for 4 hours, the water was decanted and the remaining solid was heated to 104° F. to coagulate the dispersion and drive off the remaining water. Ten cc. of a 10% solution of sodium citrate was added and the mixture stirred at 104° F. in order to raise the pH of the gelatin and redisperse the colloidal suspension of coupler.

A quantity of 9.4 grams of this microdispersion containing equal parts of the dicarboxylic acid and the phthalic anhydride gelatin was diluted with 5% sodium citrate solution to a volume of 30 cc. and a pH of about 6.5. A silver chloride emulsion was made containing 80 grams of gelatin per mol of silver, and 4.3 cc. of the coupler dispersion were mixed with 10 cc. of the emulsion while stirring at 40° C. Nine grams of a 20% solution of hard gelatin and 6 cc. of water were added followed by 0.5 cc. of 7.5% saponin solution and 0.3 cc. of mucochloric acid solution. This volume of 30 cc. was spread over glass plates with an area of 140 square inches.

In order to serve as a check, a quantity of the microdispersion of coupler before adding the silver halide emulsion, was dissolved with sodium hydroxide to convert the acid to the sodium salt, then buffered with sodium citrate at a pH of about 8.5. Gelatin was then added for coating and setting. A quantity of this coupler dispersion was mixed with the silver halide emulsion as in the case of the acid form of the coupler.

Both coatings were exposed and processed in a developer bath of the following composition:

2-amino-5-diethylamino toluene HCl	grams	2
Sodium sulfite	do	2
Potassium bromide	do	2
Sodium carbonate	do	20
Benzyl alcohol	cc.	10
Water to	liter	1

Upon comparing the acid microdispersion with the sodium salt dispersion, we found that the color density produced by the acid microdispersion was slightly higher than that produced by the dispersion of sodium salt of the coupler and that the dye image of the acid microdispersion more nearly corresponded to the tone reproduction curve of the developed silver image.

Example 5

This example describes a dispersion and emulsion of a non-resin yellow coupler.

A dispersion was made of 17.7 grams of coupler No. 5 in a mixture of 80 cc. of methyl alcohol, 50 cc. of ethyl alcohol and 30 cc. of acetone. Ten cc. of a 20% sodium hydroxide solution were added to dissolve and hydrolyze the ester. The solution was stirred at 60° C. for 30 minutes, diluted to 400 cc. with distilled water and 1 gram of sodium sulfite was added. The solution was left standing overnight to insure complete hydrolysis.

The acid was recovered from the solution by precipitation with hydrochloric acid and filtering as described in Example 4.

Five grams of the dicarboxylic acid were dissolved in acetone and dispersed in the same manner as described in Example 4. Soon after the suspension formed, 10 cc. of a 5% aqueous solution of polyvinyl pyrrolidone was added as a stabilizing agent to minimize coalescence during the removal of acetone.

The dispersion was incorporated in a silver chloride emulsion as described in Example 4 and comparison with a dispersion of the sodium salt of the coupler indicated satisfactory color reproduction.

Example 6

This example describes a dispersion of cyan resin coupler packets.

Twenty grams of coupler No. 1 were dissolved by warming to 50° C. in 350 cc. of a mixture of 90% of acetone and 10% of water, 1 cc. of a 1% acetone solution of Alkaterge-C was added and the solution filtered clear. To this solution there was added by pouring in rapidly without further stirring, 200 cc. of distilled water containing a few drops of dilute Aerosol OT solution. Acetone was evaporated from this solution by heating to 40° C. The final volume was 250 cc. equivalent to 8% coupler concentration. 6.25 cc. of this dispersion was stirred together with 12 cc. of a 10% solution of gelatin (melting point 182 to 400° F.) at 40° C. To this solution there was added, in order, 6.4 grams of a silver chlorobromide emulsion (80 mol percent chloride) which had been red-sensitized, 10 cc. of water and 12 cc. of the copolymer of methyl-α-methacrylate and methacrylic acid at pH 8. After stirring for 5 minutes, 2.2 cc. of the ammonium salt of styrene-maleic anhydride resin in 5% aqueous solution were added and the mixture stirred mechanically for 25 minutes during which time packets were formed and hardened. A 10% calcium acetate solution, 2½ cc., was added, followed by 5 cc. melted 20% hard gelatin. The mixture appeared as an excellent dispersion of packets less than 4 microns in diameter.

Example 7

This example describes a dispersion of magenta resin coupler packets.

A packet dispersion was made as in Example 6, using 8.3 cc. of a 9% aqueous micro dispersion of coupler No. 2 and 6.4 grams of a green-sensitized silver chlorobromide emulsion.

Example 8

This example describes a mixed packet coating.

A mixed packet coating was formed by mixing 7.5 grams of the cyan packet emulsion of Example 6 with 5.8 grams of the magenta packet emulsion of Example 7, 5 grams of 20% hard gelatin solution and 0.5 cc. of a 10% gelatin dispersion of di-tert.-octyl hydroquinone in di-n-butylphthalate. The total volume was coated over an area of ½ square foot.

This coating was exposed through a standard test chart and developed in the developer of Example 4. The dye density and color separation obtained from this coating were satisfactory.

Yellow coupler packets were also made from coupler No. 5 as well as mixed packets of coupler No. 1 and coupler No. 5.

Example 9

This example describes a dispersion of non-resin cyan coupler packets.

A dispersion was made by dissolving 6.6 grams of the free acid of coupler No. 4 (prepared as described in Example 4) in 300 cc. of acetone with moderate heating. To this solution there was added 0.1 cc. of a 1% solution of Alkaterge-C and the solution filtered clear of a small amount of suspended matter. Eight hundred cc. of distilled water were added followed by 10 cc. of a 5% aqueous solution of polyvinyl pyrrolidone. The acetone was allowed to evaporate by leaving the suspension exposed to air overnight. To the dispersion there was then added 66 grams of melted 10% phthalic anhydride gelatin solution and the whole dispersion diluted to 1000 cc. while stirring during one hour. After cooling to 60° F., 1 cc. of 1-N sulfuric acid was added slowly to flocculate the phthalic anhydride gelatin. Water was removed by decantation and the residue redispersed by stirring at 40° C. with 10 cc. of a 10% sodium citrate solution.

6.5 grams of the coupler dispersion were mixed with 5 grams of 20% phthalic anhydride gelatin at 40° C. and the mixture buffered with 2 cc. of 10% sodium citrate solution. A red-sensitized gelatino-silver chloride emulsion containing one mol of silver in 2040 grams of emulsion, 10.2 grams of the emulsion being used, was added and mixed with the coupler dispersion with stirring during five minutes. Packets were formed by adding 2.5 cc. of a 2% aqueous solution of the ammonium salt of styrene-maleic anhydride resin and stirring for 15 minutes. The packets were then stabilized with 2 cc. of a 10% calcium acetate solution. An excellent dispersion of small spherical packets resulted.

Example 10

This example describes a dispersion of non-resin yellow coupler packets.

Packets were formed from the microdispersion of Example 5 by mixing 7.6 grams of the coupler dispersion with 10.1 grams of 20% phthalic anhydride gelatin, 4 cc. of a 10% sodium citrate solution and 10 grams of a gelatino-silver chlorobromide emulsion (2 mol percent chloride) containing one mol of silver in 999 grams of emulsion. Five cc. of a 2% aqueous solution of the ammonium salt of styrene-maleic anhydride resin were added and the packets which formed were stirred for 15 minutes at 40° C. Finally, 4 cc. of a 10% calcium acetate solution were added. A good dispersion of spherical packets somewhat larger in diameter than the cyan packets of Example 9 was obtained.

Example 11

This example describes the preparation of a packet coating of cyan and yellow couplers.

The packet dispersions of Examples 9 and 10 were mixed and coated, exposed to a color chart and developed in the developer of Example 4. A two-color coating of satisfactory contrast was produced.

A three-color mixed packet coating using cyan, magenta and yellow couplers was also made, and exposed and developed as above. A photographic record which showed good separation of the three colors was obtained.

Example 12

This example illustrates the preparation of a coupler dispersion without the use of a dispersing agent.

Two grams of the acid form of coupler No. 5 (formed by hydrolysis and subsequent acid precipitation as described in Example 5) were dissolved in 80 cc. of acetone at room temperature, then insolubilized in the form of an extremely finely divided microdispersion by pouring in rapidly 200 cc. of distilled water. Then 1 cc. of a 5% solution of polyvinyl pyrrolidone was added and the acetone removed by evaporation.

While we have described our invention as being applied to the microdispersion of couplers containing acid groups, microdispersions may also be prepared by our method using oil-soluble couplers of the type disclosed in Jelley and Vittum U. S. Patent 2,322,027. Compounds other than couplers such as antistain agents and ultra-violet absorbers may also be dispersed in gelatin by our method.

It will be understood that the examples included herein are illustrative only and that our invention is to be taken as limited only by the scope of the appended claims.

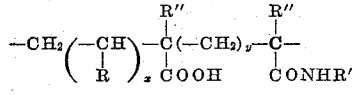
What we claim is:

1. The method of making a dispersion in gelatin of a water-insoluble color coupler capable of coupling with the oxidation product of a primary aromatic amino developing agent and containing at least one carboxyl group, which comprises dissolving said carboxyl-containing coupler in a water-miscible solvent for said coupler, then adding water and a dispersing agent to the solution of coupler and water-miscible solvent until said coupler is precipitated as a dispersion, removing said water-miscible solvent from said dispersion, and incorporating the dispersion in gelatin.

2. The method of making a dispersion in gelatin of a water-insoluble color coupler capable of coupling with the oxidation product of a primary aromatic amino developing agent and containing at least one carboxyl group, which comprises dissolving said carboxyl-containing coupler in acetone, then adding water and a dispersing agent to the solution of coupler and acetone until said coupler is precipitated as a dispersion, removing said acetone from said dispersion, and incorporating the dispersion in gelatin.

3. The method of making a dispersion in gelatin of a water-insoluble color coupler capable of coupling with the oxidation product of a primary aromatic amino developing agent and containing at least one carboxyl group, which comprises dissolving said carboxyl-containing coupler in acetone, then adding water and the dioctyl ester of sodium sulfosuccinic acid to the solution of coupler and acetone until said coupler is precipitated as a dispersion, removing said acetone from said dispersion, and incorporating the dispersion in gelatin.

4. The method of making a packet photographic emulsion which comprises dissolving in a water-miscible solvent for the coupler, a coupler compound having the recurring structure



where R is selected from the class consisting of hydrogen, phenyl, alkyl, alkoxy, carboxyalkyl and acyloxy radicals, x and y are selected from the class consisting of 0 and 1, R′ represents a coupler including an aryl group, capable of reacting with the oxidation product of a primary aromatic amino developing agent on photographic development, and R″ is selected from the class consisting of hydrogen and an alkyl radical, adding water and a dispersing agent to the solution thus formed to precipitate the carboxyl-containing coupler, removing said water-miscible solvent by evaporation, adding to the dispersion, in order, gelatin, gelatino-silver halide emulsion, the copolymer of methyl-α-methacrylate and methacrylic acid, and the ammonium salt of styrene-maleic anhydride copolymer, and stirring the mixture until packets are formed.

5. The method of making a dispersion of a water-insoluble color coupler capable of coupling with the oxidation product of a primary aromatic amino developing agent and containing at least one carboxyl group, which comprises dissolving said carboxyl-containing coupler in a water-miscible solvent for said coupler, then adding water to the solution of coupler and water-miscible solvent until said coupler is precipitated as a dispersion, and removing said water-miscible solvent from said dispersion.

References Cited in the file of this patent

UNITED STATES PATENTS

2,280,722	Schneider et al.	Apr. 21, 1942
2,304,940	Mannes et al.	Dec 15, 1942
2,322,027	Jelley et al.	June 15, 1943
2,403,721	Jelley et al.	July 9, 1946
2,478,400	Jelley et al.	Aug. 9, 1949
2,652,329	McCrossen et al.	Sept. 15, 1953
2,698,794	Godowsky	Jan. 4, 1955