United States Patent Office 2,991,177 Patented July 4, 1961

2,991,177

METHOD OF INCORPORATING COUPLER WITH DIMETHYL FORMAMIDE IN HYDROPHILIC COLLOIDS

Curt B. Roth and Fritz W. H. Mueller, Binghamton, N.Y., assignors to General Aniline & Film Corporation, New York, N.Y., a corporation of Delaware

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4 Claims. (Cl. 96—97)

This invention relates to a method of incorporating photographic chemical compounds particularly hydrophobic color couplers in hydrophilic colloids, especially sensitive silver-halide photographic emulsions.

The manufacture of photographic emulsions requires that numerous adjuncts be brought into operative association in order to produce modern photographic films and papers. Such adjuncts include chemical and optical sensitizers, color-forming components, antioxidants, masking and filter dyes, bleach-out dyes, stabilizers, and the like.

The manner by which these materials are incorporated into photographic emulsions presents numerous unique problems and much effort and research have been directed toward their solution, and this is particularly true with regard to the incorporation in photographic emulsions of couplers or color formers which react with the oxidation products of certain developing agents to yield dye images.

One of the earliest processes for using color formers in this manner was suggested in U.S. Patent 1,055,155, issued to Rudolf Fischer in 1912. This was a system of three color photography in which the couplers or color-forming compounds were located in three different emulsion layers wherein each coupler was capable of yielding a color complementary to the sensitivity of the layer in which it was incorporated. Although the Fischer process was theoretically feasible, it did not prove successful in practice, a fact attributable mainly to the shortcomings of the couplers then available which tend to wander from the emulsions in which they were incorporated with consequent color degradation of the final dye images. Numerous improvements followed the advent of the original Fischer patent, particularly as regards couplers and the techniques for incorporating them in photographic colloids. By synthesizing couplers containing a bulky group, i.e., a long chain alkyl radical (see U.S. Patent 2,186,-849) attached to the molecule, their tendency to diffuse out of their respective sensitive emulsion layers was greatly retarded. These long-chain non-diffusing couplers also contained a salt-forming group, i.e., a carboxyl or sulfo group, in order that they could be incorporated in a photographic emulsion in the form of soluble alkali metal salts.

While the above process produces excellent dye images free from color degradation, the preparation of long-chain high molecular weight couplers containing salt-forming groups poses difficulties in chemical synthesis. An alternate process of incorporating color formers in photographic colloids makes use of a dispersion technique. One of the advantages of this method is that couplers may be used which contain no salt-forming groups.

A further advantage of the above method arises from the fact that a heterogeneous system is produced wherein the minute dispersed particles of coupler constitute a discontinuous phase while the photographic hydrophilic colloid is the continuous medium. An interface thus exists between the coupler particles and the continuous hydrophilic colloid phase, an arrangement that operates to retard wandering of the coupler.

One of the earliest proposals employing the aforesaid dispersion technique of incorporating color formers or couplers in emulsion layers is described in Martinez

U.S. Patent 2,269,158. According to this method, the coupler and a water-insoluble colloid such as a resin or a cellulose ester is dissolved in a volatile solvent and the resulting mixture dispersed in a gelatin emulsion. After removal of the volatile solvent either as a separate step or in the natural process of drying the coated emulsion layer, the coupler-resin mixture remains behind distributed throughout the photographic gelatin emulsion as minute particles. The presence of the resin was claimed to retard diffusion of the coupler without recourse to increasing the molecular weight or bulk of the coupler by the use of long-chain groups.

One of the main disadvantages in processes of this type is attributable to the solid nature of the final particles containing the coupler. Since the solid colloid material has limited solvent action for the coupler and the dye produced therefrom, there is a tendency for the coupler or dye or both to crystallize on aging of the final emulsion coating. The separation or crystallization of the coupler decreases the reactivity towards dye formation during photographic development while the crystallization of the dye diminishes the brilliance of the colored images.

Another method of incorporating couplers is disclosed in U.S. Patent 2,322,027. In the method described therein, the couplers are dissolved in water-immiscible, oily type solvents or "crystalloids" and the resulting solution added to an aqueous phase containing a dispersing agent such as gelatin or a higher fatty alcohol sulfate. The mixture is then passed through a homogenizing apparatus wherein is formed a dispersion of the oily coupler solution in the aqueous medium. In some instances, the dissolution of the coupler in the oily solvent is facilitated by an ancillary low-boiling water-immiscible solvent which is subsequently removed by evaporation.

The above dispersion of coupler is then mixed with a gelatino silver-halide emulsion and coated in the usual manner to produce a system in which particles of coupler, surrounded by an oily membrane, are distributed throughout the gel matrix.

This system of combining couplers in a photographic emulsion requires elaborate and expensive equipment, i.e., heavy colloid mills for the manufacture and handling of coupler dispersions in large quantities. In order to provide for adequate dye density, the minute oily droplets must contain a high percentage of dissolved coupler. Such concentrated solutions can only be obtained by employing couplers possessing high solubility in the oils, a factor which poses difficulties in synthesizing large amounts of these compounds in pure form. In addition, this procedure does not always produce dispersions of sufficiently small particle size with the result that the sharpness of the photographic images suffers. Finally, the coated films containing coupler-oil dispersions, as above described, often display a hazy appearance due to the difference in refractive indices between the coupler-oil mixture and the photographic colloid, i.e., gelatin.

It is, therefore, an object of this invention to provide a method for incorporating chemical compounds in photographic emulsions.

A further object is to provide a method of incorporating hydrophobic chemical compounds, i.e., those having no solubilizing groups in a hydrophilic photographic colloid.

A further object is to provide a method of incorporating hydrophobic color formers in a hydrophilic photographic colloid which obviates the need for high energy homogenizing equipment.

A further object of the invention involves the uniform distribution of a hydrophobic color former in a hydrophilic photographic colloid while insuring that the

color former is unassociated with any oily or resinous dispersion.

A further object of this invention comprises a light-sensitive silver-halide emulsion containing uniformly distributed through the gel matrix, hydrophobic color formers unassociated with any oily or resinous dispersion.

Other objects will appear hereinafter as the description proceeds.

These objects are accomplished by dissolving the chemical compounds particularly hydrophobic color formers in a dialkylformamide such as dimethylformamide and then mixing this solution in a hydrophilic photographic colloid followed by removal of the solvent.

In preparing photographic emulsion with the solutions of the color formers in dialkylformamide, two general methods can be used. In the first of these, the dialkylformamide solution of the color former is added directly to a melted gelatino silver-halide emulsion while stirring with a laboratory type mixer such as a Waring Blendor. In the second method, the solution of coupler in dialkylformamide is first dissolved in an aqueous solution of a water-soluble colloid, such as gelatin, and the resulting mixture combined with a melted gelatino silver-halide emulsion.

The above process produces an even distribution of color former in the colloid carrier of the light-sensitive photographic emulsion unassociated with any photographically inert material, particularly oily or resinous dispersants. That such a result should be obtained is rather startling since it has been our experience that attempts to mix solutions of chemical compounds in photographic hydrophilic colloids, wherein the solvent is water-soluble, causes a precipitation of the compounds and/or a coagulation of the colloid by the solvent.

In the preferred embodiment of this invention, the coupler is dissolved in dimethylformamide and the temperature adjusted to 40° C. This solution is then added to an aqueous gelatin solution and thoroughly agitated in a laboratory type mixer or stirrer. The resulting mixture is combined with a gelatino silver-halide emulsion, chilled, washed with cold water to remove the dimethylformamide, and the sensitive emulsion then coated in the usual manner on a conventional base such as those of cellulose acetate, polyester (polyethylene terephthalate) or polycarbonate, paper, glass, or the like.

In some instances, it may be desirable to remove the dimethylformamide by evaporation rather than washing of the noodled emulsion. This is effected by coating the gelatino silver-halide emulsion containing the coupler as prepared above and allowing the dimethylformamide to escape by evaporation during the drying of the coated emulsion. If the latter operation is desired, one of the polyester or polycarbonate film bases should be used since dimethylformamide causes a swelling or softening of the cellulose acetate film bases.

The photographic coatings, when prepared as above described, produce on color development very sharp, highly transparent colored images and display no deleterious effects such as desensitization or fogging.

An even more surprising feature of our procedure concerns the manner by which the dialkylformamide solution of the color former blends or mingles with the hydrophilic photographic colloid. It was to be expected that the dialkylformamide solution would be dispersed or emulsified when agitated with the hydrophilic colloid. However, examination with high power optical equipment fails to reveal the presence of discrete particles or globules of the color former dispersed throughout the continuous phase of the hydrophilic colloid. In fact, the aforesaid dialkylformamide solutions actually appear to dissolve in the hydrophilic colloid so that in effect one obtains a solution of a hydrophobic color former in the said hydrophilic colloid. As a consequence, a virtually grainless dye image results upon color development since no "dye clumps" due to color former aggregates or coalescence of oil droplets containing color former can occur.

It is thus possible to dissolve color formers in photographic emulsions without the necessity of providing for the usual solubilizing groups such as sulfonic and carboxylic groups in said couplers.

Another unexpected feature of our invention concerns the removal of the dimethylformamide by washing the noodled emulsion. In many cases, the dimethylformamide solvent could be completely washed out of the noodled emulsion without removing any of the color former itself.

Since the manner of incorporating color formers in photographic emulsions as described herein does not require such ancillary substances such as crystalloids or resins, photographic films prepared in accordance with the present invention are free from the hazy or frosty appearance which characterizes films using the dispersion methods of the prior art.

The color couplers used herein may be any of the hydrophobic or lypophilic variety which contain long-chain residues to render them non-diffusing in photographic emulsions, and they do not contain any solubilizing groups such as sulfonic or carboxylic acid groups.

By "coupler" is meant the type of a color-forming compound containing a reactive methylene or phenolic hydroxyl group capable of reacting with the oxidation products of primary aromatic amino coupling developers.

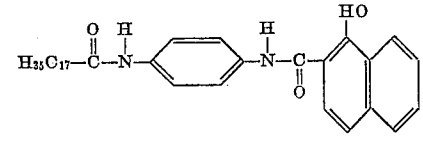
Couplers which can be used according to our invention are those of the type disclosed in U.S. Patent 2,186,849 in which, however, the solubilizing group is dispensed with; U.S. Patents 2,298,443; 2,322,027; 2,369,489; 2,474,293; 2,600,788; U.S. application Serial No. 681,884, filed by Robert F. Coles on September 4, 1957, and U.S. application Serial No. 693,509, filed by Robert F. Coles and Heinz Schulze on October 31, 1957.

Examples of color couplers incorporated in photographic emulsions by our method are the following:

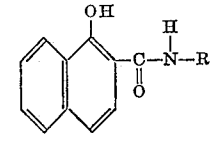
COUPLERS PRODUCING CYAN IMAGES

1-hydroxy-N-(p'-stearamidophenyl)-2-naphthamide

(1)



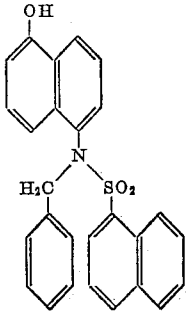
(2)



wherein R is a tertiary alkyl group of from 18 to 24 carbon atoms.

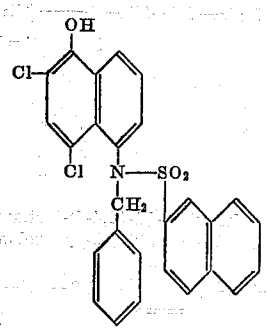
5-(N-benzyl-1-naphthylsulfonamido)-1-naphthol

(3)



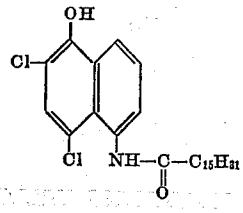
5-(N-benzyl-1-naphthylsulfonamido)-2,4-dichloro-1-naphthol

(4)



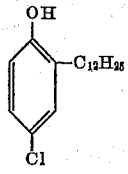
2,4-dichloro-5-palmitamido-1-naphthol

(5)



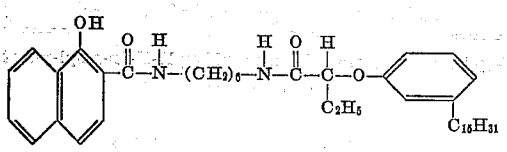
4-chloro-2-laurylphenol

(6)



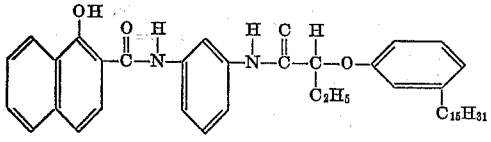
N-(1-hydroxy-2-naphthoyl)-N'-[α(3-pentadecylphenoxy)-n-butyryl]-1,6-hexanediamine

(7)



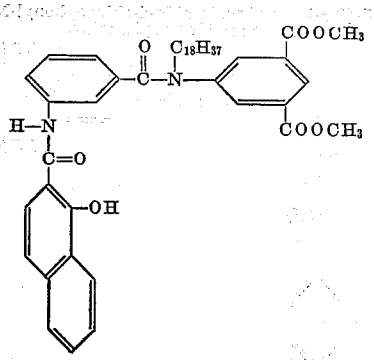
N-(1-hydroxy-2-naphthoxyl)-N'-[α-(3-pentadecylphenoxy)-n-butyryl]-m-phenylenediamine

(8)



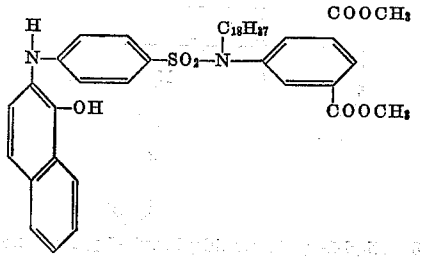
1-hydroxy-3'-[N-(3,5-dicarbomethoxyphenyl)-N-(octadecyl) carbamyl]-2-naphthanilide

(9)



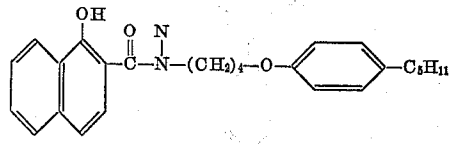
N'-(3,5-dicarbomethoxyphenyl)-N'-octadecyl-N⁴-(hydroxy-2-naphthyl)sulfanilamide

(10)



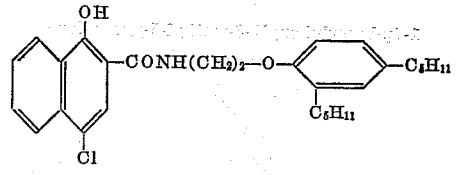
1-hydroxy-2-[δ-(p-tert.amylphenoxy)-n-butyl]naphthamide

(11)



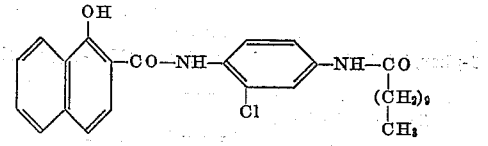
1-hydroxy-2-[β-(2',4'-di-tert.amylphenoxy)-ethyl]-4-chloro-naphthamide

(12)



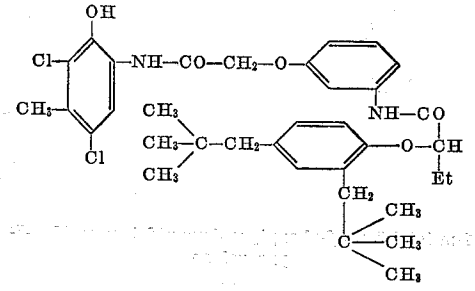
2-chloro-N-(1-hydroxy-2-naphthoyl-N'-undecylyl)-p-phenylenediamine

(13)



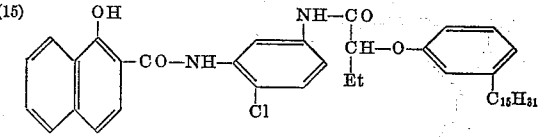
2,6-dichloro-2-{3-[α-(2,4-ditert.amylphenoxy)-n-butyramido] phenoxyacetamido}-5-methylphenol

(14)



4-chloro-N-(1-hydroxy-2-naphthoyl)-N'-[α-(3-pentadecyl-phenoxy)-n-butyryl]-m-phenylenediamine

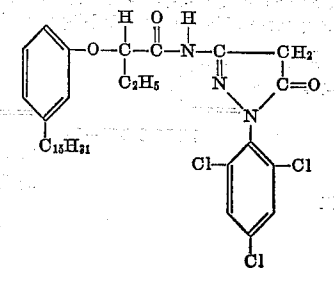
(15)



COUPLERS PRODUCING MAGENTA IMAGES

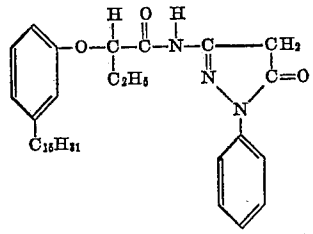
3-α-(3'-pentadecylphenoxy)-n-butyramido-1-(2',4',6'-trichlorophenyl)-5-pyrazolone

(1)



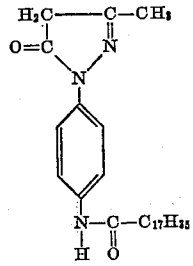
3-α-(3′-pentadecylphenoxy)-n-butyramido-1-phenyl-5-pyrazolone

(2)



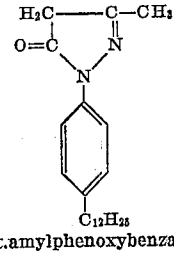
3-methyl-1-(p-stearamidophenyl)-5-pyrazolone

(3)



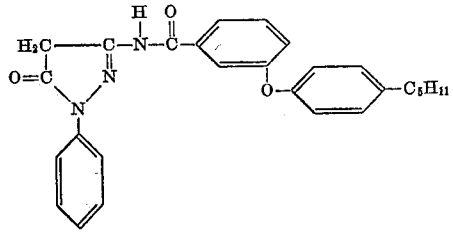
1-(p-laurylphenyl)-3-methyl-5-pyrazolone

(4)



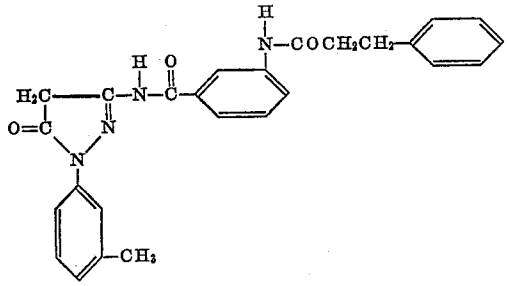
1-phenyl-3-(p-tert.amylphenoxybenzamido)-5-pyrazolone

(5)



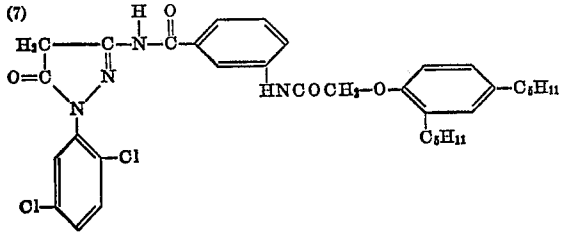
1-m-tolyl-3-(m-β-phenylpropionamidobenzamido)-5-pyrazolone

(6)



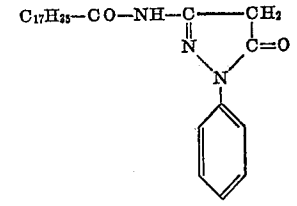
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(7)



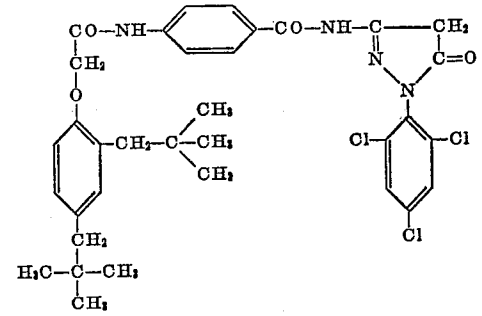
1-phenyl-3-stearamido-5-pyrazolone

(8)



1-(2,4,6-trichlorophenyl)-3-[4-(2,4-di-tert.amylphenoxyacetamido)benzamido]-5-pyrazolone

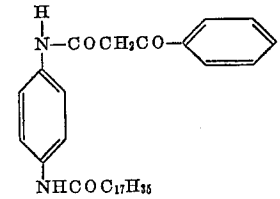
(9)



COUPLERS PRODUCING YELLOW IMAGES

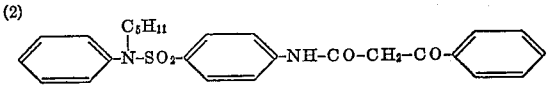
m-Stearamidobenzoylacetanilide

(1)



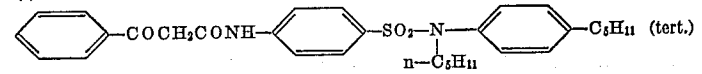
N-(p-benzoylacetamidobenzenesulfonyl)-N-iso-amylaniline

(2)



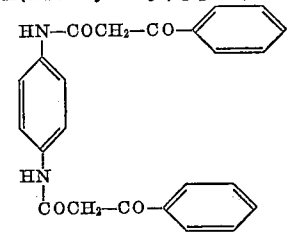
N-(p-benzoylacetamidobenzenesulfonyl)-N-(n-amyl-p-tert. amylaniline)

(3)



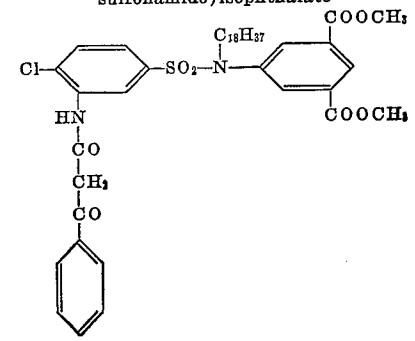
N,N′-di(ω-benzoylacetyl)-p-phenylenediamine

(4)



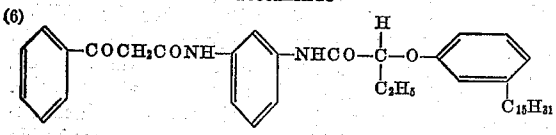
Dimethyl 5-(3-α-benzoylacetamido-4-chlorophenyl-N-octadecylsulfonamido)isophthalate

(5)



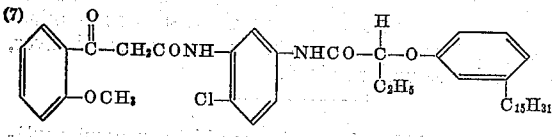
α-Benzoyl-3-[α-(3'-pentadecylphenoxy)-n-butyramido] acetanilide

(6)



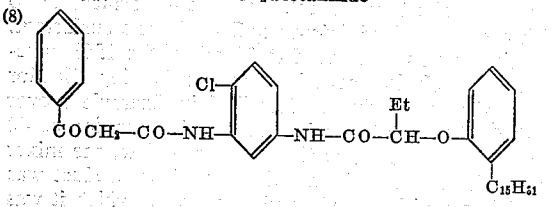
6-chloro-α-(2'-methoxybenzoyl)-3-[α-(3-pentadecylphenoxy)-n-butyramido]acetanilide

(7)



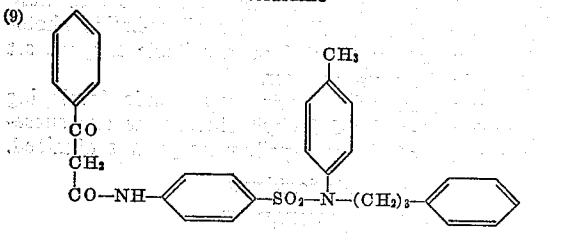
α-Benzoyl-6-chloro-3-[α-(3'-pentadecylphenoxy)-n-butyramido]acetanilide

(8)



N-(p-benzoylacetamidobenzenesulfonyl)-N-(γ-phenylpropyl) toluidine

(9)



Anti-oxidants suitable for use in this invention are typified in the following list:

3-tert.-butyl-4-hydroxyanisole
3-n-butyl-4-hydroxyanisole
3-iso-butyl-4-hydroxyanisole
3-(alpha-methyl)-propyl-4-hydroxyanisole
3,5-di-tert.-butyl-4-hydroxytoluene
Di-tert.-butyl-p-cresol
2,6-di-tert.-butyl-4-methylphenol
2,2'-methylenebis[6-tert.-butyl-4-methylphenol]
2,2'-methylenebis[6-tert.-butyl-4-ethylphenol]
2,2'-dimethyl-6,6'-di-tert.-butyl-p,p-biquinone

Although we prefer to use the customary gelatino silver-halide emulsion, other water-soluble colloidal materials, suitable for preparing photographic emulsions can be used and in this connection reference is made to polyvinyl alcohol, casein, etc.

Couplers

EXAMPLE I

0.720 gram of 1-(2,4,6-trichlorophenyl)-3-[4-2,4-ditert. amylphenoxyacetamido)benzamido]-5-pyrazolone (magenta coupler of Formula 9) was dissolved in 4 ml. of dimethylformamide using mild heating to facilitate dissolution. The temperature of the resulting clear solution was then adjusted to 40° C., to which was then added 4 drops of Tergitol NPX. This solution was then added to 29 ml. of an 8% aqueous gelatin solution maintained at 40° C. in a kitchen type Waring Blendor. The speed of the Waring Blendor was regulated by a Veritran unit.

The addition of the dissolved coupler to the aqueous gelatin is rather critical and was carried out as follows: the dimethylformamide solution of coupler was added to the aqueous gelatin through a special funnel over a period of 30 seconds while the Blendor was run at a setting of 15 volts.

The above mentioned special funnel consists of a small Pyrex glass funnel of 37 mm. (inside diameter) whose stem had been drawn out to a capillary of 1 mm. (inside diameter). The ring of the stem was 40 mm. The stem was packed with cotton or glass wool to filter out mechanical impurities. The use of such a funnel resulted in a small constant flow rate and gave satisfactory reproducible results.

After mixing for 30 seconds at 15 volts, the mixer was then run for 30 seconds at 120 volts. At the end of this period, a 15 minute stirring period at 50 volts was maintained during which time 5 drops of 6 N sodium hydroxide was added. A final stirring at 50 volts for 15 seconds was then carried out and the mixture poured into a small dish. After chilling, the gelled product was cut into small noodles and then washed for 18 hours with cold water. The washed noodles were remelted at 40° C. and then mixed with 50 g. of a gelatino silver-halide emulsion followed by coating on a suitable support, set and dried in a manner well-known in the art.

On development of the above emulsion with a primary aromatic amino developing agent such as 2-amino-5-diethylaminotoluene and subsequent removal of silver, a magenta image was obtained.

EXAMPLE II

30 milliliters of a 15% aqueous gelatin solution were placed into a speed mixer. With the mixer running at 30 volts, 4 drops of Tergitol #4 were added to the above mixture over a period of 5 seconds. The mixer was then run for 10 seconds at 30 volts. To this homogeneous mixture was then added a solution of 0.720 g. of 3-α-(3'-pentadecylphenoxy) - n - butyramido - 1 - (2',4',6' - trichlorophenyl)-5-pyrazolone (magenta coupler of Formula 1) in 8 ml. of dimethylformamide, to which had been added 4 drops of Tergitol NPX. As soon as the addition was complete, the mixer was run for 30 seconds at 120 volts. Then, 6 drops of a 20% aqueous sodium hydroxide solution were added over a period of 5 seconds with the mixer running at 90 volts. Mixing was continued for 10 seconds at 90 volts. 0.6 milliliter of a 5% aqueous saponin solution was then added over a period of 5 seconds with the mixer running at 90 volts. Mixing was continued for 10 seconds at 90 volts. The product was then poured into a dish and allowed to cool. The gelatinous product was then cut into noodles and washed for 18 hours with cold water. The noodles were then remelted at 40° C., and the melt added to 50 g. of photographic emulsion in darkness and coated in the usual manner.

On development of the above emulsion with a primary aromatic amino developing agent such as 2-amino-5-diethylaminotoluene and subsequent removal of silver, a magenta image was obtained.

EXAMPLE III

0.650 gram of 1-phenyl-3-stearamido-5-pyrazolone (magenta coupler of Formula 8) was dissolved in 5 ml. of dimethylformamide by gentle warming. The temperature of the resulting solution was adjusted to 40° C. and then added with stirring to a melted gelatino silver-halide photographic emulsion while keeping the temperature at about 40° C. The composition was then coated in a manner well-known to the art on a clear plastic film base such as polyethylene ester and the dimethylformamide allowed to evaporate from the aforesaid coating during the drying operation.

On development of the above emulsion with a primary aromatic amino developing agent such as 2-amino-5-diethylaminotoluene and subsequent removal of silver, a magenta image was obtained.

EXAMPLE IV

1.0 gram of 2-chloro-N-(1-hydroxy-2-naphthoyl-N'-undecylyl)-p-phenylenediamine (cyan coupler of Formula 13) was dissolved in 9.3 ml. of dimethylformamide to which had been added 5 drops of Tergitol NPX. The

resulting solution of coupler was then added through the special funnel to 40 ml. of a 15% aqueous gelatin solution in a Waring Blendor to which had been previously added 5 drops of Tergitol #4. The addition was carried out over a period of 30 seconds with the mixer running at 40 volts. After the addition, mixing was continued for 60 seconds at 120 volts. The milky white product was then poured into a dish, cooled and allowed to chill. The gelled product was then cut into noodles followed by washing for 18 hours in cold water. The excess water was drained off and the noodles melted and combined with 50 g. of a photographic silver-halide emulsion and coated in the manner previously described.

On development of the above emulsion with a primary aromatic amino developing agent such as 2-amino-5-diethylaminotoluene and subsequent removal of silver, a cyan image was obtained.

EXAMPLE V

0.720 gram of 2,6-dichloro-2-{3-[α-(2,4-di-tert.amylphenoxy)-n-butyramido]phenoxyacetamido} - 5 - methylphenol (cyan coupler of Formula 14) was dissolved in 4 ml. of dimethylformamide to which had been added 6 drops of Span 80 as a surfactant. This solution of coupler was then added through a special funnel described in Example I to 30 ml. of the 15% gelatin to which had been added 4 drops of Tween 20 contained in a Waring Blendor. The addition was carried out over a period of 15 seconds with the mixer running at 40 volts. Mixing was then completed by stirring for 30 seconds at 120 volts. To the mixture was now added 3 drops of 20% aqueous sodium hydroxide and mixing followed by agitation for 30 seconds at 120 volts. The milky white product was then poured into a dish, cooled and allowed to chill. The gelled product was then cut into noodles and washed with cold water as previously described. After draining, the noodles were removed and combined with 50 g. of a photographic silver-halide emulsion followed by coating on a suitable support, set and dried in the usual manner.

On development of the above emulsion with a primary aromatic amino developing agent such as 2-amino-5-diethylaminotoluene and subsequent removal of silver, a cyan image was obtained.

EXAMPLE VI

0.720 gram of 4-chloro-N-(1-hydroxy-2-naphthoyl)-N'-[α - (3 - pentadecylphenoxy)-n-butyryl]-m-phenylenediamine (cyan coupler of Formula 15) was dissolved in 9 ml. of dimethylformamide to which had been added 5 drops of Span 80 as a dispersant. This solution was then added over a period of 30 seconds to 30 ml. of a 15% aqueous gelatin solution contained in a Waring Blendor set at 40 volts; mixing was continued for 30 seconds at 120 volts. Then, 0.6 ml. of a 5% aqueous solution of Saponin was added over a period of 5 seconds with the mixer set at 100 volts. Mixing was continued for an additional 10 seconds at 100 volts. The milky white product was poured into a dish and allowed to cool wherein the gelatinous product was cut into noodles and washed for 18 hours with cold water in the usual manner. The noodles were then melted up at 40° C. with 50 g. of a photographic emulsion and then coated.

On development of the above emulsion with a primary aromatic amino developing agent such as 2-amino-5-diethylaminotoluene and subsequent removal of silver, a cyan image was obtained.

EXAMPLE VII

0.720 gram of α-benzoyl-6-chloro-3-[α-(3'-pentadecylphenoxy)-n-butyramido] acetanilide (yellow coupler of Formula 8) was dissolved in 8 ml. of dimethylformamide to which had been added 6 drops of Tergitol NPX. This solution of coupler was then added through the special funnel described in Example I to 30 ml. of a 15% aqueous gelatin solution to which had been added 6 drops of Tergitol #4 contained in a Waring Blendor. The aforesaid addition was made over a period of 30 seconds with the mixer running at 40 volts. After the addition was complete, the Blendor was run for 30 seconds at 120 volts. The product was then poured into a dish, chilled, and the gelled product cut into noodles with a knife. The noodles were washed with cold water, drained, remelted and combined with a photographic silver-halide emulsion and coated.

On development of the above emulsion with the primary aromatic amino developing agent such as 2-amino-5-diethylaminotoluene and subsequent removal of silver, a yellow image was obtained.

EXAMPLE VIII

0.720 gram of N-(p-benzoylacetamidobenzenesulfonyl)-N-(γ-phenylpropyl)toluidine (yellow coupler of Formula 9) was dissolved in 10 ml. of dimethylformamide to which had been added 6 drops of Span 80 as a surfactant. This mixture was then added to 30 ml. of the 15% aqueous gelatin solution contained in the Waring Blendor through the special funnel described in Example I over a period of 20 seconds with the Blendor running at 40 volts. As soon as the addition was complete, the mixer was run for 30 seconds at 120 volts. The product was poured into a dish and allowed to gel after which it was cut into noodles and washed for 18 hours in cold water. After draining off the excess water, the noodles were remelted and added to 50 g. of a silver-halide photographic emulsion and coated on a suitable support, set and dried in the usual manner.

On development with a primary aromatic developing agent such as 2-amino-5-diethylaminotoluene and subsequent removal of silver, a yellow image was obtained.

Antioxidants

EXAMPLE IX

2.0 grams of 2,5-di-tert.butylhydroquinone were dissolved in 30 ml. of dimethylformamide containing 4 drops of Tergitol NPX. This solution added to 5 ml. of a 2% aqueous gelatin solution, 5 ml. formamide and 5 ml. of an aqueous 1% sodium carboxy methyl cellulose (medium viscosity) solution and 4 drops of Tergitol #4. The addition was made very slowly to the carefully and very efficiently stirred hydrophilic phase. After the mixing was complete, the product was diluted to 100 ml. with freshly distilled dimethylformamide. This solution was then added to photographic emulsions which required the presence of an antioxidant. Smooth, even coatings were obtained upon coating onto a film base. By varying the volume used, concentrations of from 0.025 g. to 0.40 g. per 50 g. of photographic emulsion were very satisfactorily incorporated.

EXAMPLE X

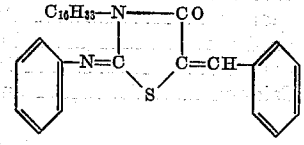
2.0 grams of 2-lauroylhydroquinone were dissolved in 30 ml. of dimethylformamide and 4 drops of Tergitol NPX. This solution was added to 5.0 ml. of a 2% aqueous gelatin solution, 10 ml. of formamide and 5 ml. of a 1% aqueous sodium carboxy methyl cellulose solution. The addition was made very slowly to a carefully stirred aqueous phase. After the addition was complete, the volume was increased to 100 ml. with dimethylformamide. The antioxidant solution was used as shown in Example IX.

Ultraviolet absorbers

EXAMPLE XI

Into a Waring Blendor were poured 60 ml. of a 15% aqueous gelatin solution. The mixer was started at 40 volts and over a period of 5 seconds with the mixer running at 40 volts were added 5 drops of Tergitol #4. Mixing was continued for 10 seconds at 40 volts. To this white, homogeneous mixture was added, over a period of 5 seconds with the mixer running at 50 volts, 0.6 ml. of an 8% aqueous Saponin solution. Mixing was

continued for 10 seconds at 50 volts. Then, over a period of the 50 seconds with the mixer running at 60 volts was added, through a special funnel, a solution consisting of 0.40 g. of the ultraviolet absorber of the following formula (described in U.S. Patent 2,739,971):



in 14 ml. of dimethylformamide and 5 drops of Tergitol NPX. After the addition was complete, mixing was continued for 30 seconds at 120 volts. The white, opaque product was poured into a dish and cooled. The gelled product was then cut into noodles, and the noodles washed for 18 hours with cold water. The noodles were remelted at 40° C. and 0.6 ml. of an 8% aqueous Saponin solution and 2 drops of Pluronic L–61 added. The mixture was then coated onto a suitable film base in the usual manner.

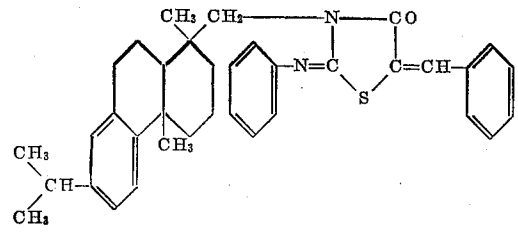
EXAMPLE XII

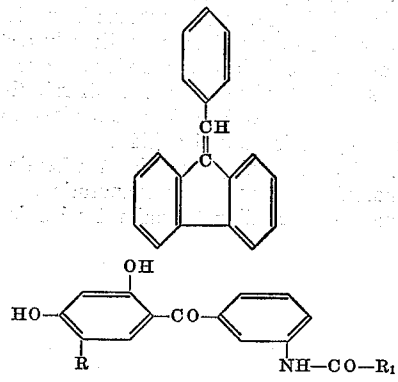
Coated without alkali.—60 milliliters of a 15% aqueous gelatin solution was placed into a Waring Blendor. The mixer was run for 15 seconds at 50 volts. A solution consisting of 2,2'-dihydroxy-4,4'-dimethoxybenzophenone in 5 ml. of dimethylformamide and 15 drops of Span 85 were then added through a special funnel described previously over a period of 30 seconds with the mixer running at 60 volts. The mixing was continued for 45 seconds at 120 volts. The mixture was then poured into a dish and allowed to cool. After chilling, the gelled product was cut into noodles and washed for 18 hours with cold water. The washed noddles were then remelted and coated on a suitable base at 40° C. in the usual manner after the addition of 0.6 ml. of an aqueous solution. A coating was obtained which exhibited a density of 1.425 at 400 millimicrons.

EXAMPLE XIII

Coated in the presence of alkali.—60 milliliters of a 15% aqueous gelatin solution was poured into a Waring Blendor. Over a period of 5 seconds were then added 9 drops of Tween 20 with the mixer running at 50 volts. The mixer was run for an additional 25 seconds at 50 volts. A solution consisting of 2,2'-dihydroxy-4,4'-dimethoxybenzophenone in 5 ml. of dimethylformamide and 6 drops of Span 80 were added through the special funnel, already described, over a period of 30 seconds with the mixer running at 60 volts. Mixing was continued for 30 seconds at 120 volts. Then with the mixer running at 90 volts, 3 drops of a 20% aqueous sodium hydroxide solution was added over a period of 5 seconds. The mixer was run for 25 seconds at 90 volts and the mixture poured into a dish. After chilling, the gelled product was cut into noodles. The noddles were washed for 18 hours with cold water. The washed noodles were drained from the excess water, remelted at 40° C. and then coated in the usual manner at 40° C. after the addition of 0.6 ml. of an aqueous 5% saponin solution. A coating was obtained which exhibited a density of 1.750 at 400 millimicrons.

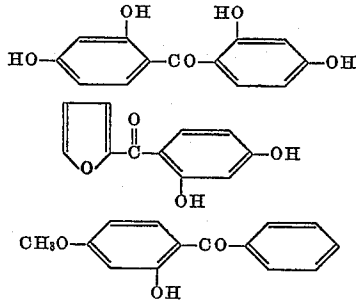
Other examples of ultraviolet absorbers which can be used as above described are the following:





R can be:
Methyl
Ethyl
Propyl
Butyl
Amyl
Hexyl
Dodecyl

R_1 can be:
Aryl
Aryloxymethyl with or without carboxy or sulfonic acid groups



The commercial products used in the examples are defined in the following list:

Span 80 is sorbitan monooleate and is a product of the Atlas Powder Company, Wilmington 99, Delaware.

Span 85 is sorbitan trioleate and is a product of the Atlas Powder Company, Wilmington 99, Delaware.

Tween 20 is polyoxyethylene sorbitan monolorate and is a product of the Atlas Powder Company, Wilmington 99, Delaware.

Tergitol NPX is alkylphenyl polyethylene glycol ether and is a product of the Carbide & Carbon Chemicals Company, 30 East 42nd Street, New York 17, New York.

Tergitol #4 is sodium tetradecyl sulfate and is sold as a 25% solution by the Carbide & Carbon Chemicals Company, 30 East 42nd Street, New York 17, New York.

Pluronic L–61 is a polymer prepared by adding propylene oxide to the two hydroxyl groups of a propylene glycol nucleus until the desired molecular weight is achieved. Ethylene oxide is then added to both ends of the above polymer until the desired ratio of polyoxyethylene to polyoxypropylene units is obtained. Pluronic L–61 is composed of a polyoxypropylene fragment with a molecular weight of 1750 while 10% of the total molecular weight is polyoxyethylene groups.

This product is sold by the Wyandotte Chemical Corporation, Wyandotte, Michigan.

Veritran, model V–I–M, 115 volts, 50–60 cycles, 5 amps., is a product sold by the United Transformer Company, New York, New York.

Waring Blendor is a product sold by the Waring Products Corporation, New York City, and is manufactured by the Winsted H.D.W. Manufacturing Company, Winsted, Connecticut, U.S.A.

We claim:

1. The method of incorporating in a water soluble hydrophilic photographic colloid, a hydrophobic color-forming compound capable of reacting with the oxidation product of a primary aromatic amino developing agent to form a dye which comprises forming a solution consisting of said color-forming compound and dimethyl-

formamide, intimately blending said solution with the photographic colloid, removing substantially all of the dimethylformamide thereby leaving uniformly distributed in the photographic colloid the color-forming compound.

2. The method according to claim 1 wherein the color-forming compound is selected from the class consisting of naphthols, pyrazolones and anilides.

3. The method according to claim 1 wherein the dimethylformamide is removed by evaporation.

4. The method according to claim 1 wherein the dimethylformamide is removed by washing from the gelled photographic colloid.

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