

2,852,382

## COUPLER DISPERSIONS FOR COLOR PHOTOGRAPHY CONTAINING PROTEIN POLYMERS

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No Drawing. Application August 11, 1955

Serial No. 527,872

14 Claims. (Cl. 96-97)

This invention relates to photographic silver halide emulsions containing novel polymeric compositions in combination with color couplers, i. e., a color-forming compound capable of reacting with a primary aromatic amino developing agent on photographic development.

This application is a continuation-in-part of our copending applications Serial Nos. 426,551 (now U. S. Patent 2,763,625, issued September 18, 1956) and 426,552 (now U. S. Patent 2,831,767, issued April 22, 1958), both filed April 29, 1954, and Serial No. 398,236 (now abandoned), filed December 14, 1953.

In Fierke and Chechak U. S. application Serial No. 476,561, filed December 20, 1954 (now U. S. Patent 2,801,171, issued July 30, 1957), there is described a method for preparing photographic emulsions containing dispersions of couplers or color-forming compounds in which the ratio of coupler solvent to coupler is less than 1:1, e. g., 1/2:1 or 0:1. When these low ratios of coupler solvent to coupler are used, certain couplers produce on photographic development dyes which are shifted in hue from the desired normal hue and which have low contrast and/or low maximum density.

Accordingly, it is an object of our invention to provide photographic silver halide emulsions in which these undesirable effects of hue shift and contrast loss, as well as loss of maximum density, are overcome. Another object is to provide photographic silver halide emulsions containing couplers or color-forming compounds and polymeric compositions of a novel type. Other objects will become apparent from the following description and examples.

In general, the above objects are accomplished by preparing a photographic silver halide emulsion containing both a coupler and a polymeric composition resulting from the polymerization of a protein material with at least one monoethylenically-unsaturated compound containing the  $-\text{CH}=\text{C}-$  group. The polymeric composition employed in the instant invention can wholly or partially constitute the vehicle employed in the photographic silver halide emulsion, or these polymeric compositions can be employed together with a coupler or color-forming compound to wholly or partially replace the coupler solvent used in the process of application Serial No. 476,561. Alternatively, the polymeric compositions employed in our invention can be used both in the photographic silver halide emulsion and in the coupler compositions or dispersion, which is intermixed with the photographic silver halide emulsion.

The novel polymeric compositions employed in the instant invention can be prepared according to the methods outlined in our copending applications Serial Nos. 398,236; 426,551 and 426,552 mentioned above. These polymeric compositions contain from about 5 to 95 percent by weight of protein material and from about 95 to 5 percent by weight of the polymerized monoethylenically-unsaturated compound mentioned above.

The saturated protein component which is employed in preparing the polymeric materials of this invention can be an unsubstituted protein such as gelatin, hydrolyzed gelatin, glue, casein, soybean protein, or the like, or it can be an acylated protein such as succinyl protein, phthalyl protein, or acetyl protein prepared by reacting

an organic acid anhydride or chloride with a protein such as glue, gelatin, casein, or the like. Such acylated protein derivatives are known to the art, and the preparation of a phthalic anhydride derivative of gelatin suitable for use in practicing the invention is described in Yutzy and Frame, U. S. Patent No. 2,525,753. Other protein derivatives can be prepared in similar fashion by reacting any of the well known proteins with any of the saturated organic acid anhydrides. Thus, for example, a method of preparing derivatives of other proteins than gelatin is described in the Lowe and Gates U. S. Patent 2,691,582, issued October 12, 1954. Since such unsubstituted proteins and saturated acyl protein derivatives are well known in the art, and such proteins and protein derivatives are all suitable for use in practicing this invention, it is not intended that this invention shall be limited to the particular materials described herein with reference to certain preferred embodiments of the invention. One advantage of this invention resides in the fact that the protein which can be employed need not be in a highly purified state such as was necessary with photographic gelatin alone. Thus, lower grades of gelatin, glue, casein, or the like can be satisfactorily employed in practicing the invention since the graft polymers obtained therefrom do not adversely affect photographic emulsions.

The polymerizable monomer or monomers which is graft polymerized with the protein material can be any of the well known olefinic polymerizable monomers including vinylic monomers and diolefinic monomers. Thus, for example, the vinylic monomer (or monomers) can include styrene, substituted styrenes, acrylic acid esters, methacrylic acid esters, vinyl ethers, vinyl ketones, vinylidene chloride, vinyl chloride, vinyl esters, acrylonitrile, substituted acrylonitriles, vinyl pyridines, acrylamides, allylamines, and similar well known vinylic monomers. Similarly, polymerizable diolefins, such as 1,3-butadiene, isoprene, chloroprene, 2,3-dimethyl-1,3-butadiene and similar diolefinic monomers are entirely suitable for use in practicing the instant invention.

Typical monomers which can be employed in practicing the invention include ethyl acrylate, n-propyl acrylate, isopropyl acrylate, isobutyl acrylate, n-amyl acrylate, isoamyl acrylate, n-hexyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, n-decyl acrylate,  $\beta$ -cyanoethyl acrylate,  $\beta$ -chloroethyl acrylate, n-butyl acrylate, 2-methoxyethyl acrylate, 2-ethoxyethyl acrylate, 2-butoxyethyl acrylate, and similar alkyl acrylates wherein the alkyl group contains from 1 to 10 carbon atoms; methacrylates containing from 1 to 10 carbon atoms, and preferably from 4 to 10 carbon atoms in the alkyl group, such as n-butyl methacrylate, n-hexyl methacrylate, 2-ethylhexyl-methacrylate, n-octyl methacrylate, ethyl methacrylate, methyl methacrylate and the like; styrene monomers such as styrene or a substituted styrene such as o-methyl styrene, m-methyl styrene, p-methyl styrene, 2,4-dimethyl styrene, 2,5-dimethyl styrene, 3,4-dimethyl styrene, 3,5-dimethyl styrene, 2,4,5-trimethyl styrene, 2,4,6-trimethyl styrene, 2,4,5-trimethylstyrene, o-ethylstyrene, m-ethylstyrene, p-ethylstyrene, 3,5-diethylstyrene, p-n-butylstyrene, m-sec-butylstyrene, m-tert-butylstyrene, p-hexylstyrene, p-n-heptylstyrene, p-2-ethylhexylstyrene, o-fluorostyrene, m-fluorostyrene, p-fluorostyrene, o-chlorostyrene, m-chlorostyrene, p-chlorostyrene, 2,3-dichlorostyrene, 2,4-dichlorostyrene, 2,5-dichlorostyrene, 2,6-dichlorostyrene, 3,4-dichlorostyrene, 3,5-dichlorostyrene, 2,3,4,5,6-pentachlorostyrene, m-trifluoromethyl styrene, o-cyanostyrene, m-cyanostyrene, m-nitrostyrene, p-nitrostyrene, p-dimethylaminostyrene, and similar styrene derivatives; acrylonitrile monomers such as acrylonitrile or a substituted acrylonitrile, such as methacrylonitrile,  $\alpha$ -chloroacrylonitrile,  $\alpha$ -bromoacrylonitrile, trifluoromethylacrylonitrile,  $\alpha$ -trifluoromethylcarboxy acrylonitrile, and the like; vinyl es-

ters, such as vinyl acetate, vinyl propionate, vinylbutyrate, or the like; vinyl pyridines, such as 4-vinyl pyridine, 2-methyl-5-vinyl pyridine and the like; vinyl ketones such as methylvinyl ketone, ethylvinyl ketone, and the like; vinyl ethers such as methylvinyl ether and the like; alkenyl esters such as isopropenyl acetate and the like, and similar well known polymerizable unsaturated monomers, such as acrylic acid, allylamine, acrylamide, methacrylamide, N-alkyl acrylamides, such as N-methyl acrylamide and N-methyl methacrylamide, and the like.

The polymeric solutions or hydrosols of this invention are prepared by polymerization in an aqueous system with or without a micell-forming surface-active agent. The use of a surface-active agent facilitates the dispersion of the monomer in the water. The surface-active agents which can be employed in practicing the invention include the cationic surfactants, anionic surfactants, and amphoteric surfactants. Such surface-active materials which form micells are well known in the art, and it is not intended that the invention shall be limited to the particular surfactants which are particularly described herein. Any of the other micell-forming surface-active agents can be employed in practicing the invention with advantageous results. Typical surfactants which can be employed in practicing the invention are the salts of the higher fatty acids, such as sodium stearate, potassium stearate, sodium palmitate, potassium palmitate, sodium laurate, potassium laurate, sodium myristate, potassium myristate, and the like; salts of higher fatty alcohol sulfates such as the sodium or potassium lauryl sulfates, sodium or potassium di-(2-ethylhexyl) sulfosuccinates, sodium or potassium cetyl sulfates, sodium or potassium stearyl sulfates, and the like; salts of aromatic sulfonic acids, such as the sodium or potassium salts of an alkyl naphthalene sulfonic acid; high molecular weight quaternary ammonium salts containing the radical  $C_{15}H_{31}$  or  $C_{17}H_{35}$ ; and similar well known micell-forming surface-active agents.

The polymerization is facilitated by the use of a polymerization catalyst. Such polymerization catalysts are well known in the art, and any of the well known catalytic materials or combinations such as are commonly employed in promoting emulsion polymerizations can be used. Thus, for example, the per-catalysts are entirely suitable, including the organic peroxides, such as benzoyl peroxide, acetyl peroxide, lauroyl peroxide, tert. butyl hydroperoxide, and hydrogen peroxide; persulfates, such as sodium, potassium or ammonium persulfates, or persulfuric acid itself; perborates, such as sodium or potassium perborates; water-soluble salts of percarbonic acid; water-soluble salts of perphosphoric acid; water-soluble salts of sulfo-peracids; and similar well known per-catalysts. If desired, the redox-type catalysts can be used in practicing the invention, and in some cases, this may be desirable in order to carry out the reaction at a lower temperature or in a shorter time than can be obtained using an oxygenated catalyst alone.

The polymerization is desirably effected at an elevated temperature. Usually, a temperature of about 85° C. is satisfactory since the polymerization ordinarily occurs within a period of about one hour at this temperature. It will be understood, however, that higher or lower temperatures can be employed in accordance with well known polymerization practice. The polymerization time will, of course, depend upon the other variable factors, such as the kind and concentration of catalyst, the temperature of polymerization, the nature of the polymerizing reactants, and similar variable factors. When the polymerization is effected at an elevated temperature, it may be necessary to effect the polymerization in a reaction system provided with a reflux condenser or in a closed pressure system. Such expedients are well known in the art and do not form a limiting part of the present invention.

The polymeric compositions of our invention which contain 60 percent or less of hydrophilic material material

are generally obtained in the form of polymeric hydrosols, while those compositions containing more than 60 percent hydrophilic material are generally obtained in the form of solutions, the particle size of which is considerably smaller than those particles found in the polymeric hydrosols. However, for the purposes of the present invention, each of these types of compositions can be advantageously employed. Those polymeric compositions containing in excess of 60 percent hydrophilic material are readily soluble in warm water and can be redispersed from a dried film of the polymer. Thus, it is possible to dry these particular polymeric solutions and store them for prolonged periods of time in dried form. The dried polymers can thereafter be readily dispersed in warm water and used in emulsion formulas of the instant invention in the same manner as the original aqueous solution or dispersion. Because of its inherent water solubility or dispersibility, the polymeric composition need not be mixed with gelatin prior to drying. For such storage purposes, the protein component is preferably an unsubstituted or acylated gelatin, hydrolyzed gelatin, glue, casein, or soy protein. The casein is particularly useful when it has first been modified by treating in solution with hydrogen peroxide at an alkaline pH and at an elevated temperature to cause some oxidation. The protein can be completely unmodified, however, and such unmodified proteins give entirely satisfactory results. Any of the acyl protein derivatives can be employed providing such derivatives do not contain any ethylenic or carbon-to-carbon unsaturation, which would cause the derivative to enter into a copolymer reaction with the monomer or monomers, rather than the graft polymerization.

We have found that the polymeric compositions of our invention, which we shall call graft polymers, can be mixed directly with aqueous solutions of gelatin, or similar naturally occurring hydrophilic colloidal protein materials, which have been rendered soluble or dispersible in water. The hydrosols or solutions employed in our invention are compatible with protein in all proportions and they can be used alone or with varying amounts of another protein, such as from 5 to 95 percent by weight of gelatin or other protein materials. The coatings which are obtained from the polymeric compositions of our invention when used alone, or in admixture with gelatin or the like, have good optical clarity. That is, by using a graft polymer, polymeric compositions are obtained which have a refractive index quite similar to that of the unmodified protein material. Such compatibility cannot be realized by using physical mixtures of the protein material and ordinary homopolymers or copolymers. However, small amounts of such conventional homopolymers or copolymers can also be added to the compositions employed in our invention, inasmuch as the graft polymerization increases the compatibility of such ordinary homopolymers or copolymers for any other unmodified protein material which might be present. This compatibility is not present ordinarily, in the absence of the graft polymers employed in our invention.

The properties of the polymeric compositions employed in the invention will depend, of course, on the particular ingredients going into the polymerization. Generally speaking, the alkyl acrylates containing from 2 to 10 carbon atoms in the alkyl group, the alkyl methacrylates containing from 4 to 10 carbon atoms in the alkyl group and the diolefins (butadiene, isoprene, chloroprene, and the like) give polymeric compositions having moderate flexibility. Other monomers, such as styrene, substituted styrenes, acrylonitrile, substituted acrylonitriles, methyl methacrylate, ethyl methacrylate, vinyl acetate, vinylidene chloride, isopropenyl acetate, and the like give polymeric compositions of somewhat lower flexibility but of considerably greater film strength.

The polymeric compositions of the instant invention can be combined with the coupler or color-forming compound directly, by using the method described in the

Fierke and Chechak application Serial No. 476,561 mentioned above, or these polymeric compositions can be first mixed with the silver halide dispersion, and this dispersion combined with such dispersions as are described in the Fierke and Chechak application. Alternately, the polymeric compositions of our invention can wholly or partially replace the vehicle, such as gelatin, used in preparing the silver halide dispersion itself.

The coupler dispersion employed in our invention and containing the novel polymeric composition can be made by dissolving the coupler in a low-boiling organic solvent for the coupler, e. g., ethyl acetate, dispersing the solution in gelatin (or the graft polymer composition), then adding gelatin (or graft polymer) and the polymeric composition. The coupler dispersion in gelatin can be added to a solution of the protein material and monomers before emulsion polymerization. The dispersion containing the polymeric composition can be chilled and dried for storage, or can be added immediately to a gelatino-silver halide emulsion, or other silver halide emulsion using one of the graft polymers of our invention as a vehicle. If dried, the dispersion is re-melted before adding to the silver halide emulsion. The coupler dispersion can also contain a high boiling crystalloidal organic solvent for the coupler, e. g., di-n-butylphthalate, which can be added at any stage during the preparation of the dispersion.

Typical couplers or color-forming compounds which can be employed in our invention have been described in Jelley and Vittum U. S. Patent 2,322,027. Other couplers which can be employed include the following:

- (1) 1-hydroxy-2-[ $\delta$ -(2',4'-di-tert.amylphenoxy)-n-butyl]-naphthamide (U. S. Patent 2,474,293)
- (2) 1-hydroxy-4-phenylazo-4'-(p-tert.-butylphenoxy)-2-naphthanilide (U. S. Patent 2,521,908)
- (3) 2-(2,4-di-tert.amylphenoxyacetamino)-4,6-dichloro-5-methyl phenol (Graham U. S. application Serial No. 285,544)
- (4) 3-( $\alpha$ -di-tert.amylphenoxy-n-butyrylamino)-4,6-dichloro-5-methyl phenol
- (5) 6-{ $\alpha$ -{4-[ $\alpha$ -(2,4-di-tert.amylphenoxy)butyramido]-phenoxy}acetamido}-2,4-dichloro-3-methyl phenol
- (6) 2-[3'-(2'',4''-diamylphenoxy)-acetamido]-benzamid-4-chloro-5-methyl phenol
- (7) 1-(2',4',6'-trichlorophenyl)-3-[3'-(2'',4''-di-tert.-amylphenoxyacetamido)-benzamido]-5-pyrazolone (U. S. Patent 2,600,788)
- (8) 1-(2',4',6'-trichlorophenyl)-3-[3'-(2'',4''-di-tert.-amylphenoxyacetamido)-benzamido]-4-(p-methoxyphenylazo)-5-pyrazolone
- (9) N-(4-benzoylacetaminobenzenesulfonyl)-N- $\gamma$ -phenyl-propyl-p-toluidine (U. S. Patent 2,298,443)
- (10)  $\alpha$ -o-Methoxybenzoyl- $\alpha$ -chloro-4-[ $\alpha$ -(2,4-di-tert.-amylphenoxy)-n-butyramido]-acetanilide (McCrosen U. S. application Serial No. 295,806)
- (11)  $\alpha$ -{3-[ $\alpha$ -(2,4-di-tert.amylphenoxy)acetamido]-benzoyl}-2-methoxyacetanilide
- (12) 3-benzoylacetamido-4-methoxy-2',4'-di-tert.amylphenoxy-acetanilide
- (13) [4-benzoylacetamido-3-methoxy-2',4'-di-tert.amylphenoxy-acetanilide

High boiling coupler solvents which can be used in conjunction with the polymeric materials of our invention, in addition to the di-n-butylphthalate mentioned above, are organic crystalloidal solvents which are substantially water-insoluble, have low molecular weight and a boiling point above 175° C., in addition to high solvent action for the coupler and dyes formed from it. Also, such solvents should be permeable to photographic developer oxidation products. Additional examples of such products are methyl, ethyl, propyl, etc., phthalates, triphenylphosphates, tricresylphosphates, etc.

Low boiling solvents for the coupler or color-forming compound include methyl, ethyl, propyl, butyl and like

acetates, isopropyl acetate, ethyl propionate, sec. butyl alcohol, carbon tetrachloride, chloroform, methyl isobutylquinone,  $\beta$ -ethoxyethyl acetate,  $\beta$ -butoxy- $\beta$ -ethoxyethyl acetate, tetrahydrofurfural adipate, and the like.

The following examples will serve to illustrate more fully the manner of practicing our invention.

#### EXAMPLE 1

100 grams of the coupler 1-(2',4',6'-trichlorophenyl)-3-[3'-(2'',4''-di-tert.-amylphenoxyacetamido)-benzamidol-5-pyrazolone (coupler No. 7) were dissolved in 250 cc. of ethyl acetate at the reflux temperature of ethyl acetate. This solution was poured into a solution containing 800 cc. of 10 percent gelatin solution and 100 cc. of 5% Alkanol B (alkylnaphthalene sodium sulfonate) solution and then milled 5 times in a colloid mill. 50 cc. of water was used to rinse the mill. The dispersion was set up on a chill plate at 40° F., noodled and air dried at 78° C. and 50 percent relative humidity. Dry weight of the dispersion was 193 grams.

Using the method described in Gates et al. U. S. application Serial No. 398,236, there was slowly added to a stirred solution of 3.18 parts of potassium persulfate in 650 parts of water at 85° C. a mixture of 188 parts of n-butyl acrylate and 46 parts of acrylonitrile and a solution of 100 parts of succinyl glue in 350 parts of water, the glue being a succinic anhydride reaction product with the glue and having a succinyl content of 5 percent. The addition was carried out over a period of 30 minutes and the mass was held for 30 minutes at 85° C. A hydrosol of the three components was thereby produced.

7.9 grams of the coupler dispersion and 85 cc. of the hydrosol were added to a portion of a gelatino-silver halide emulsion containing 0.046 mole of silver halide. After coating on a film support, the material was exposed and developed in a primary aromatic amino developer and was found to produce a satisfactory dye image.

#### EXAMPLE 2

8 grams of the coupler used in Example 1 and 2 grams of di-iso-octyl hydroquinone were dissolved in 25 cc. of ethyl acetate at the reflux temperature of ethyl acetate. This solution was poured into a solution containing 136 cc. of 10 percent gelatin solution and 16 cc. of 5% Alkanol B solution and then milled 5 times in a colloid mill. 50 cc. of water was used to rinse the mill.

8.4 grams of the coupler dispersion and 45 cc. of the polymeric hydrosol prepared as described in Example 1 were added to 133 grams of a gelatino-silver halide emulsion containing 0.03 mole of silver halide. A similar coating was made of the coupler dispersion added to the silver halide emulsion without polymeric hydrosol. These two emulsions were coated on film support, exposed and processed in a developer of the following composition:

	Grams
p-Amino diethylaniline sulfate.....	2
Sodium sulfite, anhydrous.....	5
Sodium carbonate, anhydrous.....	20
Potassium bromide.....	2
Water to 1 liter.	

The following results for speed, gamma and maximum density were obtained:

	Speed	Gamma	Max. density
Coating without hydrosol.....	X.....	1.05	0.66
Coating with hydrosol.....	X+0.4 log E.....	2.0	1.68

This table clearly shows that the addition of the polymeric hydrosol to the coupler dispersion increased the contrast, improved the speed and also raised the maximum density of the processed films.

### EXAMPLE 3

A coupler dispersion in gelatin was made as described in Example 1, using instead of the coupler of Example 1, the coupler 1-hydroxy-2-[8-(2',4'-di-tert. amylphenoxy)-n-butyl]-naphthamide.

To a stirred solution of 0.37 gram of potassium persulfate in 442 cc. of distilled water at 85° C. there were added 36 grams of n-butyl acrylate, 15 grams of styrene and a solution of 11 grams of glue and 11 grams of the gelatin dispersion containing 20.5 grams of coupler in 200 cc. of distilled water. These materials were added over a period of 9 minutes. The reaction mixture was stirred for 1 hour longer at 85° C. and then cooled and filtered.

103.5 cc. of the polymeric hydrosol dispersion containing the coupler were added to a gelatino-silver halide emulsion containing approximately 0.046 mole of silver halide. The emulsion was coated on film base and after exposure and processing as in Example 2 was found to produce a dye density of satisfactory contrast.

### EXAMPLE 4

A coupler dispersion was made as described in Example 1, using N-(4-benzoylacetylaminobenzenesulfonyl)-N-(γ-phenylpropyl)-p-toluidine (coupler No. 9) instead of coupler No. 7.

A hydrosol was made as described in Example 1, containing 16 percent glue, 59 percent n-butyl acrylate and 23 percent styrene instead of the components listed in Example 1.

8 grams of the coupler dispersion and 24 cc. of the hydrosol were added to a portion of a gelatino-silver halide emulsion containing 0.046 mole of silver halide, and this was coated on film base (coating C).

A similar emulsion was made without the hydrosol, and this was separately coated on film base (coating B).

A separate coupler dispersion was made by dissolving 8 grams of coupler No. 9 in a solution of 25 cc. of ethyl acetate and 16 cc. of di-n-butyl phthalate at the reflux temperature of ethyl acetate. This mixture was then poured into a solution of 65 cc. of 10 percent gelatin solution and 8 cc. of 5% Alkanol B solution at 50° C., stirred for about one minute and run through a colloid mill five times, after which the mill was rinsed with 25 cc. of water. The dispersion was set up on a chill plate at 40° F., noodled and air dried at 78° C. and 50 percent relative humidity.

8 grams of this coupler dispersion and 24 cc. of the hydrosol were added to another portion of the gelatino-silver halide emulsion, and this was coated on film base (coating A).

There were thus produced a coating having a coupler to high-boiling coupler solvent (di-n-butyl phthalate) ratio of 1:2 (A), a coating having a coupler to coupler solvent ratio of 1:0 (B), these coatings not containing hydrosol, and a coating having a coupler to coupler solvent ratio of 1:0 and a coupler to hydrosol solids ratio of 1:2 (C). These coatings permitted a comparison to be made between coatings having a coupler to coupler solvent ratio of 1:2 and 1:0, and a coating to which the hydrosol had been added.

These coatings were exposed and developed in the developer of Example 2, and showed the following peak dye absorption, gamma and maximum density:

Coating	Ratio of Coupler to Coupler Solvent	Ratio Coupler to Hydrosol Solids	Peak Absorption, mμ	Gamma	Maximum Density
A-----	1:2	-----	456	1.43	1.82
B-----	1:0	-----	464	0.45	0.30
C-----	1:0	1:2	464	1.21	1.60

This shows that shift in peak dye absorption and the

loss in contrast and maximum density when a low coupler solvent to coupler ratio is used, can be corrected by incorporating the hydrosol in the emulsion.

In Examples 5-8 below, the beneficial effect of the graft polymers of our invention, when incorporated in a silver halide emulsion as the vehicle therefor, is shown. The log E speed, density in terms of D max., and gamma for the coatings of Examples 5-8 are given, and compared with a check coating prepared in exactly the same manner except that gelatin alone was used as the vehicle for the silver halide emulsion. The silver halide emulsion employed in each example was a positive silver bromide emulsion and contained approximately 0.03 mol. of silver. The same color coupler was employed in each of the coatings of Example 5-8 and also in the check coating. This coupler was of the same type as coupler No. 9 above. The results are given in Table I below.

### EXAMPLE 5

125 g. of coupler No. 9 were dissolved in 350 cc. of ethyl acetate at the reflux temperature. This solution was poured into a solution containing 1000 cc. of 10% gelatin solution and 125 cc. of Alkanol B (alkylnaphthalene sodium sulfonate) solution and then milled five times in a colloid mill. The mill was then rinsed out with 50 cc. of water and the dispersion was set up on a chill plate at 40° F., noodled, and air dried. Dry weight of the dispersion was 237.5 g.

6.6 g. of the above coupler dispersion were added to a portion of silver bromide emulsion containing approximately 0.03 mol. of silver halide and having an emulsion vehicle consisting of 60% gelatin and 40% of a graft polymer composed of n-butyl acrylate, styrene, and succinyl glue. After coating on a film support, the material was exposed and developed in a primary aromatic amino developer, and the speed, density and gamma measured. The results are given in Table I below.

The graft polymer used in Example 5 was prepared as follows:

To a stirred solution of 1.27 g. of potassium persulfate in 850 cc. of water at 85° C. was added dropwise a solution of 40 g. of 5% succinyl glue in 150 cc. of water, together with a solution composed of 150 g. of n-butyl acrylate and 64 g. of styrene. The additions were complete in 19 minutes and the reaction mixture was stirred and heated at 85° C. for 45 more minutes to give the desired polymer.

### EXAMPLE 6

This coating was made and processed exactly as the coating in Example 5 above, except that a graft polymer composed of gelatin and n-butyl acrylate was employed in place of the graft polymer in Example 5. The speed, density and gamma for the coating are given in Table I below.

The graft polymer used in Example 6 was prepared as follows:

To a stirred solution of 260 g. of photographic gelatin, 4.0 g. of potassium persulfate and 2.0 g. of sodium bisulfite in 3600 cc. of water at 45° C. were added dropwise 140 g. of n-butyl acrylate over a period of 20 minutes. The reaction mixture was stirred at 45° C. for one hour and cooled before use.

### EXAMPLE 7

The coating in this example was made exactly as that described in Example 5 above, except that a graft polymer composed of gelatin and ethyl acrylate was employed in place of the graft polymer of Example 5. The speed, density and gamma for the coating was measured in exactly the same manner as that in Example 5, and the results are given in Table I below.

The graft polymer employed in Example 7 was prepared in the following manner.

9

To a stirred solution of 260 g. of photographic gelatin, 4.0 g. of potassium persulfate and 2.0 g. of sodium bisulfite in 6000 cc. of water at 45° C. were added dropwise 140 g. of ethyl acrylate over a period of 30 minutes. The reaction mixture was stirred at 45° C. for 75 minutes and cooled before use.

## EXAMPLE 8

The coating of this example was prepared in exactly the same manner as that of Example 5 above except that a graft polymer composed of gelatin and ethyl acrylate was employed in place of the graft polymer used in Example 5. The speed, density, and gamma for the coating was made in exactly the same manner as that in Example 5 and the results are given in Table I below.

The graft polymer employed in Example 8 was identical to that employed in Example 7, except that the graft polymer contained 40% by weight of ethyl acrylate instead of the 35% by weight, which was used in Example 7.

Table I

Example	Log E Speed	D Max.	Gamma
Check.....	X	0.30	0.26
5.....	X-.12	1.34	0.99
6.....	X-.06	1.40	1.00
7.....	X-.15	1.40	0.97
8.....	X-.15	1.52	0.99

In Examples 9 and 10 below, graft polymers of the above-mentioned type were employed in the coupler dispersion in place of the gelatin as shown in Examples 1-8 above. The same positive silver chlorobromide emulsion was used in Examples 9 and 10, and this emulsion had gelatin as the emulsion vehicle. It contained approximately 0.0281 mol. of silver halide. The Log E speed, density in terms of D max., and gamma for each of the coatings are given in Table II below. These results are compared with a check coating containing usual photographic gelatin in place of the graft polymer, which was used in the coupler dispersions in Examples 9 and 10.

## EXAMPLE 9

A solution of 8 g. of coupler No. 9 in 25 g. of ethyl acetate was added to a 10% solution containing 46 g. of a graft polymer prepared in exactly the same manner as that used in Example 6 above, and 8 cc. of 5% Alkanol B solution. The resulting mixture was passed through a colloid mill five times, set on a chill plate, noodled and dried. The dried product was obtained as hard, transparent noodles that could be readily redispersed by plumping in water and warming to 40° C.

16.9 g. of the above dispersion were added to the gelatino-silver-chlorobromide emulsion containing 0.0281 mol. of silver. After coating on a film support, the material was exposed and developed in a primary aromatic amino developer, and the speed, density and gamma for the coating measured. The results are given in Table II below.

## EXAMPLE 10

The coating of this example was prepared in exactly the manner shown in Example 9, except that the graft polymer employed in Example 7 was employed instead of the graft polymer used in Example 9. The speed, density and gamma for the coating is given in Table II below.

Table II

Example	Log E Speed	D. Max.	Gamma
Check.....	X	0.30	0.45
9.....	X+.06	1.58	1.14
10.....	X-.06	1.55	1.21

10

The coatings in Examples 11 and 12 were obtained in exactly the same manner as those in Examples 9 and 10 above, i. e., the graft polymers were employed in the coupler dispersions rather than in the silver halide emulsion, as in the case of Examples 5-8. The log E speed, density in terms of D max., gamma and fog for the various coatings are given in Table III below. These coatings were compared with a check which contained gelatin in place of the graft polymers employed in the coupler dispersions of Examples 11 and 12.

## EXAMPLE 11

8.0 g. of coupler No. 9 were dissolved in ethyl acetate and this solution was poured into a solution containing 46 g. of a graft polymer composed of gelatin, acrylamide, n-butyl acrylate and styrene, and 8 cc. of a 5% Alkanol B solution. The resulting mixture was milled five times in a colloid mill, chill set, noodled and air dried.

21.2 g. of the above dispersion were added to a solution of a negative gelatino-silver-bromiodide emulsion containing approximately 0.044 mol. of silver halide. After coating on a film support, the material was exposed and developed in a primary aromatic amino developer. The speed, density and gamma for the coating are given in Table III below.

The graft polymer employed in Example 11 was prepared as follows:

To a stirred solution of 240 g. of photographic gelatin in 3000 cc. of water containing 4.0 g. of potassium persulfate and 2.0 g. of sodium bisulfite at 45° C. was added dropwise a solution of 40 g. of acrylamide in 100 cc. of water, together with a solution composed of 90 g. of n-butyl acrylate and 30 g. of styrene. The additions were complete in 15 minutes and the reaction mixture stirred at 45° C. for one hour and cooled before use.

## EXAMPLE 12

This coating was prepared in exactly the same manner as that in Example 11, except that only 13.7 g. of graft polymer (same polymer as used in Example 11), in admixture with 16 g. of an ordinary copolymer composed of n-butyl acrylate and styrene was employed in place of the single graft polymer employed in Example 11. The speed, density and gamma and fog for the coatings are given in Table III below.

Table III

Example	Log E Speed	D. Max.	Gamma	Fog
Check.....	X	0.22	0.13	0.15
11.....	X+.05	0.87	0.44	.08
12.....	X+.30	0.71	0.35	.06

The copolymer employed in Example 12 was prepared as follows:

90 g. of n-butyl acrylate, 38 g. of styrene and 1.28 g. of benzyl peroxide in 200 g. of triethyl acetate were refluxed for 18 hours and the solution assayed. 41 g. of solution contained 16 g. of polymer.

The check coatings in Tables I, II and III were prepared in exactly the manner shown in Fierke and Chechak U. S. application Serial No. 476,561, filed December 20, 1954.

When the coupler dispersions shown in Examples 11 and 12 above were added to a silver halide emulsion containing a graft polymer as the emulsion vehicle, improved results were also obtained, as compared with a gelatino-silver-halide emulsion containing a conventional coupler dispersion wherein the coupler peptizer was gelatin.

As mentioned above, graft protein polymers containing from about 5 to 75% by weight of protein material have been found to be particularly useful in practicing our invention, although graft polymers containing in excess of 75% by weight of protein material can also be employed to advantage.

What we claim as our invention and desire secured by Letters Patent of the United States is:

1. A photographic silver halide emulsion capable of producing a dye image having improved contrast and dye density upon exposure and development with a primary aromatic amine developing agent, comprising a silver halide emulsion containing an organic material selected from the group consisting of a color-forming compound capable of reacting with said developing agent on photographic development and a composition comprising (a) an organic color-forming compound capable of reacting with said developing agent on photographic development and (b) an organic crystalloidal solvent for said organic color-forming compound, said solvent having a boiling point above 175° C. and being permeable to the oxidation products of said developing agent formed during photographic development, and a polymeric composition resulting from the polymerization of a mixture of (1) 5 to 95% by weight of a protein material selected from the group consisting of unsubstituted proteins and saturated acylated proteins and (2) from 95 to 5% by weight of at least one monoethylenically-unsaturated compound containing the  $-\text{CH}=\text{C}-$  group, said photographic silver halide emulsion containing less than about one part of said organic crystalloidal solvent per part of said color-forming compound.

2. A photographic silver halide emulsion capable of producing a dye image having improved contrast and dye density upon exposure and development with a primary aromatic amine developing agent, comprising a silver halide emulsion containing an organic material selected from the group consisting of a color-forming compound capable of reacting with said developing agent on photographic development and a composition comprising (a) an organic color-forming compound capable of reacting with said developing agent on photographic development and (b) an organic crystalloidal solvent for said organic color-forming compound, said solvent having a boiling point above 175° C. and being permeable to the oxidation products of said developing agent formed during photographic development, and a polymeric composition resulting from the polymerization of a mixture of (1) 5 to 95% by weight of a protein material selected from the group consisting of unsubstituted proteins and saturated acylated proteins and (2) from 95 to 5% by weight of at least one ester of an acid selected from the group consisting of acrylic acid and methacrylic acid, said photographic silver halide emulsion containing less than about one part of said organic crystalloidal solvent per part of said color-forming compound.

3. A photographic silver halide emulsion capable of producing a dye image having improved contrast and dye density upon exposure and development with a primary aromatic amine developing agent, comprising a gelatino-silver halide emulsion containing an organic dispersion of a color-forming compound capable of reacting with said developing agent on photographic development, and a dispersion of a polymeric hydrosol resulting from the emulsion polymerization of a mixture of (1) 5 to 60% by weight of a protein material selected from the group consisting of unsubstituted proteins and saturated acylated proteins, (2) a flexibilizing component selected from the group consisting of alkyl acrylates in which the alkyl group contains from 2 to 10 carbon atoms, alkyl methacrylates in which the alkyl group contains from 4 to 10 carbon atoms, butadiene, isoprene, and chloroprene, and (3) a strengthening component selected from the group consisting of styrene, substituted styrenes, acrylonitrile, substituted acrylonitriles, vinyl acetate, vinylidene chloride, and isopropenyl acetate, said flexibilizing component and said strengthening component comprising from 95 to 40% by weight of said mixture, and said silver halide emulsion being substantially free of organic crystalloidal solvent for said color-forming compound, said solvent having a boiling point above 175° C. and being permeable to the

oxidation products of said developing agent formed during photographic development.

4. A photographic silver halide emulsion capable of producing a dye image having improved contrast and dye density upon exposure and development with a primary aromatic amine developing agent, comprising a gelatino-silver halide emulsion containing an organic dispersion of a color-forming compound capable of reacting with said developing agent on photographic development, and a dispersion of a polymeric hydrosol resulting from the emulsion polymerization of a mixture of (1) 5 to 60% by weight of a saturated acylated protein, (2) an alkyl acrylate in which the alkyl group contains from 2 to 10 carbon atoms, and (3) acrylonitrile, said acrylate and said acrylonitrile comprising from 95 to 40% by weight of said mixture, and said silver halide emulsion being substantially free of organic crystalloidal solvent for said color-forming compound, said solvent having a boiling point above 175° C. and being permeable to the oxidation products of said developing agent formed during photographic development.

5. A photographic silver halide emulsion capable of producing a dye image having improved contrast and dye density upon exposure and development with a primary aromatic amine developing agent, comprising a gelatino-silver halide emulsion containing an organic dispersion of a color-forming compound capable of reacting with said developing agent on photographic development, and a dispersion of a polymeric hydrosol resulting from the emulsion polymerization of (1) 5 to 60% by weight of succinyl glue, (2) n-butyl acrylate, and (3) acrylonitrile, said acrylate and said acrylonitrile comprising from 95 to 40% by weight of said mixture, and said silver halide emulsion being substantially free of organic crystalloidal solvent for said color-forming compound, said solvent having a boiling point above 175° C. and being permeable to the oxidation products of said developing agent formed during photographic development.

6. A photographic silver halide emulsion capable of producing a dye image having improved contrast and dye density upon exposure and development with a primary aromatic amine developing agent, comprising a gelatino-silver halide emulsion containing an organic dispersion of a color-forming compound capable of reacting with said developing agent on photographic development, and a dispersion of a polymeric hydrosol resulting from the emulsion polymerization of a mixture of 1 part of succinyl glue, 1.88 parts of n-butyl acrylate and 0.46 part of acrylonitrile, said silver halide emulsion being substantially free of organic crystalloidal solvent for said color-forming compound, said solvent having a boiling point above 175° C. and being permeable to the oxidation products of said developing agent formed during photographic development.

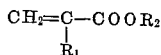
7. A photographic silver halide emulsion capable of producing a dye image having improved contrast and dye density upon exposure and development with a primary aromatic amine developing agent, comprising a photographic silver halide emulsion containing an organic material selected from the group consisting of a color-forming compound capable of reacting with said developing agent on photographic development and a composition comprising (a) an organic color-forming compound capable of reacting with said developing agent on photographic development and (b) an organic crystalloidal solvent for said organic color-forming compound, said solvent having a boiling point above 175° C. and being permeable to the oxidation products of said developing agent formed during photographic development, and a unitary polymeric material resulting from the polymerization of a mixture comprising (A) from 5-95 percent by weight of a protein material selected from the group consisting of unsubstituted proteins and acylated proteins free of olefinic unsaturation, and (B) from 95-5 percent by weight of a mixture of at least two different types of



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polymerizable monomers, said types of monomers being (1) a flexibilizing component selected from the group consisting of alkyl acrylates in which the alkyl group contains from 2 to 10 carbon atoms, alkyl methacrylates in which the alkyl group contains from 4 to 10 carbon atoms, butadiene, isoprene and chloroprene and (2) a strengthening component selected from the group consisting of styrene, substituted styrenes, acrylonitrile, substituted acrylonitriles, vinyl acetate, vinylidene chloride and isopropenyl acetate, said photographic silver halide emulsion containing less than about one part of said organic crystalloidal solvent per part of said color-forming compound.

8. A photographic silver halide emulsion capable of producing a dye image having improved contrast and dye density upon exposure and development with a primary aromatic amine developing agent comprising a photographic silver halide emulsion containing an organic color-forming compound capable of reacting with said developing agent on photographic development, and a polymeric material resulting from the polymerization of a mixture of (1) 60 to 75% by weight of a protein material selected from the group consisting of unsubstituted proteins and saturated acylated proteins and (2) from 40 to 25% by weight of a single polymerizable material represented by the following general formula:



wherein R<sub>1</sub> is a member selected from the group consisting of hydrogen and methyl and R<sub>2</sub> represents an alkyl group of from 1 to 10 carbon atoms, said silver halide emulsion being substantially free of organic crystalloidal solvent for said color-forming compound, said solvent having a boiling point above 175° C. and being permeable to the oxidation products of said developing agent formed during photographic development.

9. A photographic silver halide emulsion capable of producing a dye image having improved contrast and dye density upon exposure and development with a primary aromatic amine developing agent comprising a photographic silver halide emulsion containing an organic color-forming compound capable of reacting with said developing agent on photographic development, and a polymeric material resulting from the polymerization of a mixture of (1) from 60 to 75% by weight of gelatin and (2) from 40 to 25% by weight of an alkyl acrylate in which the alkyl group contains from 2 to 10 carbon atoms, said silver halide emulsion being substantially free of organic crystalloidal solvent for said color-forming compound, said solvent having a boiling point above 175° C. and being permeable to the oxidation products of said developing agent formed during photographic development.

10. A photographic silver halide emulsion as defined in claim 9 wherein said alkyl acrylate is n-butyl acrylate.

11. A photographic silver halide emulsion as defined in claim 9 wherein said alkyl acrylate is ethyl acrylate.

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12. A photographic silver halide emulsion capable of producing a dye image having improved contrast and dye density upon exposure and development with a primary aromatic amine developing agent, comprising a photographic silver halide emulsion containing an organic color-forming compound capable of reacting with said developing agent on photographic development, and a polymeric material resulting from the polymerization of a mixture of (1) 60 to 75% by weight of a protein material selected from the group consisting of unsubstituted proteins and saturated acylated proteins, (2) a flexibilizing component selected from the group consisting of alkyl acrylates in which the alkyl group contains from 2 to 10 carbon atoms, alkyl methacrylates in which the alkyl group contains from 4 to 10 carbon atoms, butadiene, isoprene and chloroprene, and (3) a strengthening component selected from the group consisting of styrene, substituted styrenes, acrylonitrile, substituted acrylonitriles, vinyl acetate, vinylidene chloride, and isopropenyl acetate, said mixture comprising from 40 to 25% by weight of said flexibilizing component and said strengthening component, and said silver halide emulsion being substantially free of organic crystalloidal solvent for said color-forming compound, said solvent having a boiling point above 175° C. and being permeable to the oxidation products of said developing agent formed during photographic development.

13. A photographic silver halide emulsion capable of producing a dye image having improved contrast and dye density upon exposure and development with a primary aromatic amine developing agent, comprising a photographic silver halide emulsion containing an organic color-forming compound capable of reacting with said developing agent on photographic development, and a polymeric material resulting from the polymerization of a mixture of (1) from 60 to 75% by weight of unsubstituted protein, (2) acrylamide, (3) n-butyl acrylate, and (4) styrene, said mixture comprising from 40 to 25% by weight of said acrylamide, said n-butyl acrylate and said styrene, and said silver halide emulsion being substantially free of organic crystalloidal solvent for said color-forming compound, said solvent having a boiling point above 175° C. and being permeable to the oxidation products of said developing agent formed during photographic development.

14. A photographic silver halide emulsion as defined in claim 13 wherein said unsubstituted protein is gelatin.

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