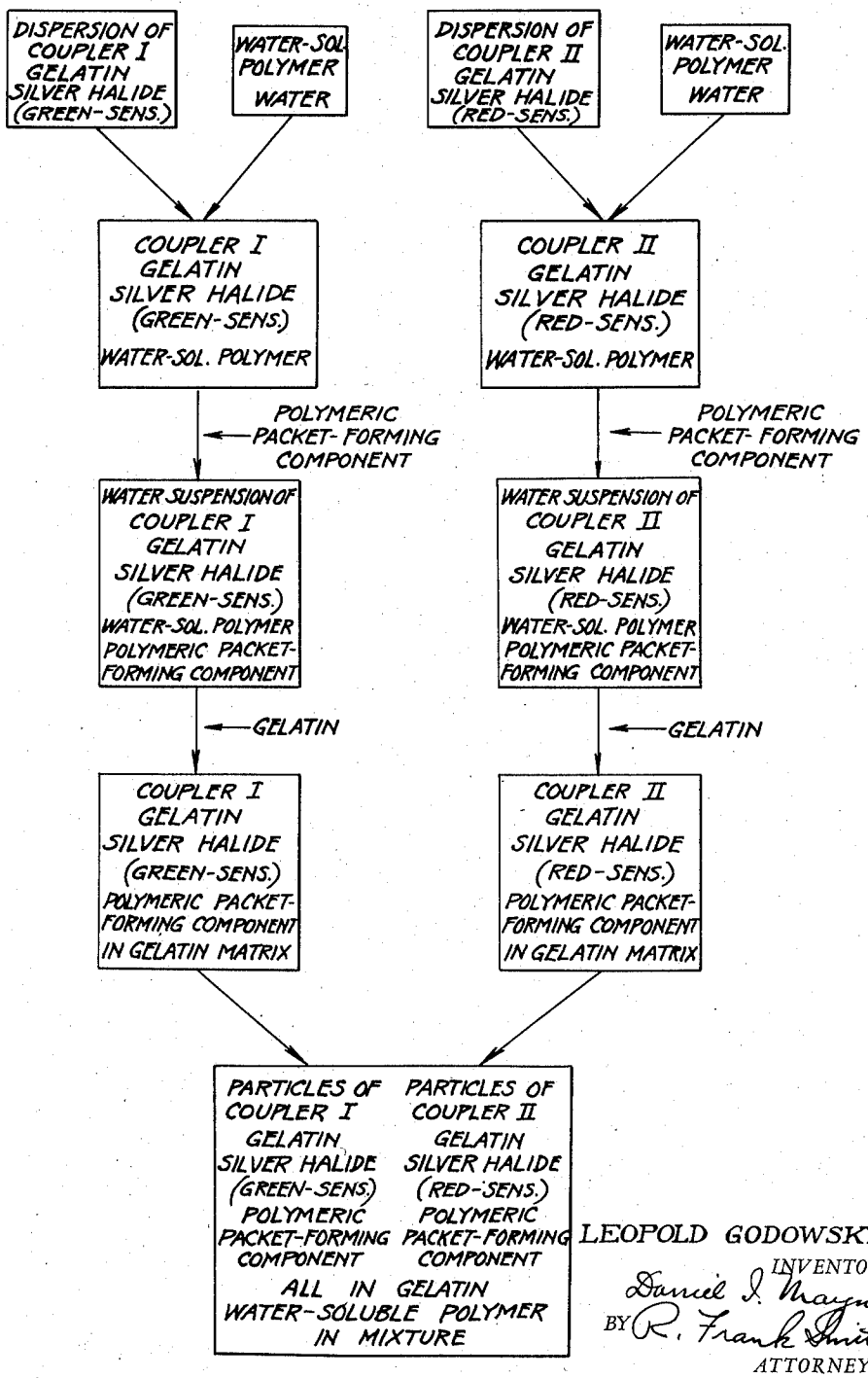
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PHOTOGRAPHIC LAYERS CONTAINING THE REACTION PRODUCT OF AMMONIA ON A STYRENE-MALEIC ANHYDRIDE COPOLYMER

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LEOPOLD GODOWSKY
INVENTOR

BY Daniel J. Mayne, R. Frank Smith
ATTORNEYS.

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PHOTOGRAPHIC LAYERS CONTAINING THE REACTION PRODUCT OF AMMONIA ON A STYRENE-MALEIC ANHYDRIDE COPOLYMER

Leopold Godowsky, Westport, Conn., assignor to Eastman Kodak Company, Rochester, N. Y., a corporation of New Jersey

Original application April 15, 1950, Serial No. 156,066, now Patent No. 2,698,794, dated January 4, 1955. Divided and this application June 23, 1954, Serial No. 438,667

3 Claims. (Cl. 96—97)

This invention relates to color photography and particularly to mixed packet photographic emulsions.

This application is a division of my application Serial No. 156,066, filed April 15, 1950, now U. S. Patent 2,698,794.

There have been many prior suggestions of mixed grain photographic emulsions, that is, photographic systems in which differently sensitized silver halide grains are incorporated in a single photographic emulsion layer and used to produce differently colored photographic images in the layer. Mixed grain systems have a number of advantages, chief among which is the simplicity of coating a single emulsion layer rather than several layers. Other advantages are the improved definition obtained by having the differently sensitized particles juxtaposed in a single layer, and the simplification of processing which is generally obtained.

Prior mixed grain photographic methods have not been successful either because it was impossible to secure color separation with them, that is, effectively to prevent color formation around unexposed silver halide grains, or because the colored particles formed in the process were too grainy.

It is, therefore, an object of the present invention to provide a method and sensitive material for mixed packet color photography according to which difficulties in the prior art are overcome and a practical result is achieved. By "mixed packet" I mean a process or an emulsion in which differently color-sensitive silver halide grains having color-formers associated therewith are incorporated in a single photographic layer for the purpose of producing differently colored photographic images in that layer by a single exposure.

These objects are accomplished by first dispersing a color-forming compound in a peptized silver halide emulsion, preferably a gelatino-silver halide emulsion. The emulsion may contain the normal amount of gelatin, or a lower amount than usual may be present. For example, the gelatin content may be from 4 to 200 grams or more per 100 grams of silver halide. The emulsion containing the coupler dispersion is then mixed with a suitable water-dispersible polymer which does not react with gelatin, and to the mixture there is added a solution of a polymeric packet-forming component. Two or more of the resulting packet dispersions which contain silver halide sensitized to different spectral regions, are then mixed with additional gelatin or another water-soluble

polymer to form the mixed packet emulsion, preferably by adding the gelatin or polymer to each packet dispersion separately before mixing them.

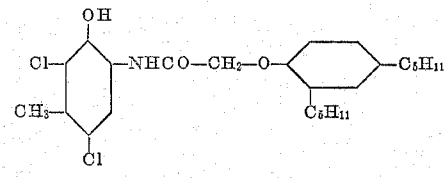
The accompanying drawing is a flow sheet illustrating the steps in my process.

My invention involves the use of a silver halide emulsion containing a non-diffusing color-forming compound or coupler which is reactive with the oxidation product of a primary aromatic amino developing agent to form a dye image. These couplers are preferably incorporated in the emulsion as described in Jelley and Vittum U. S. Patent 2,322,027, but may be directly dispersed in the colloid carrier. The couplers are incorporated in the emulsion by dissolving them in a substantially water-insoluble solvent for the coupler, and dispersing the solution in gelatin and adding it to a gelatino-silver halide emulsion.

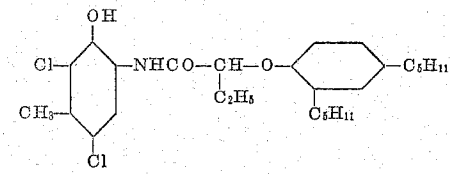
The silver halide used in these emulsions may be optically sensitized, and ordinarily two or more emulsions sensitive to different regions of the visible spectrum will be employed.

The following couplers are suitable for use according to my invention:

Cyan couplers:

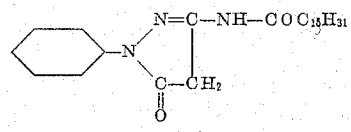


2-(2',4'-tert.amylphenoxy)-acetylamino-4,6-dichloro-5-methylphenol

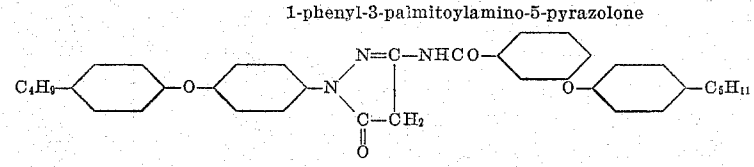


2-[α-(2',4'-tert.amylphenoxy)-n-butyrylamino]-4,6-dichloro-5-methylphenol

Magenta couplers:

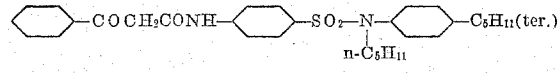


1-phenyl-3-palmitoylamino-5-pyrazolone

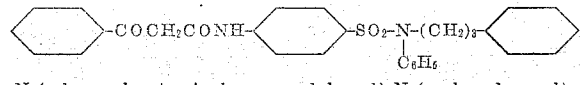


1-[p-(p'-tert.butylphenoxy)-phenyl]-3-[m-(p-tert.amylphenoxy)-benzoylamino]-5-pyrazolone

Yellow couplers:



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



N-(p-benzoylacetaminobenzenesulphonyl)-N-(γ-phenylpropyl)-aniline

After making the dispersion of coupler in gelatino-silver halide emulsion, the dispersion is added to a water solution of a water-soluble polymer or water-soluble salt

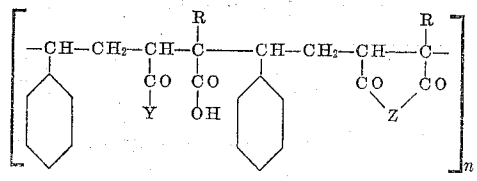
of a polymeric material containing salt-forming acid groups, such as the copolymer of methacrylic acid and methyl-α-methacrylate (Minsk, Weyerts and McDowell U.S. Patent 2,391,181) algin (alkali metal salts of polymeric d-mannuronic acid), carboxy methyl cellulose (Collins, Freeman and Anthonisen U. S. Patent 2,278,612), and cellulose sulfate (Belgian Patent 448,249). The water-soluble polymer is mixed with the gelatin of the dispersion and acts as a modifying agent, so that small packets, each containing appropriately sensitized silver halide and color-forming coupler, can be formed.

To the mixture of dispersion and water-soluble polymer or salt, mentioned above, there is then added, preferably with stirring, an aqueous solution of a polymeric packet-forming component or gelatin reactant, or vice versa. The polymeric packet-forming component consists of a polymeric carbon chain having recurring phenyl groups and carboxyl groups, and preferably also carboxylic acid amide groups or imide groups or both and is used as the water-soluble salt, such as the ammonium, sodium, potassium or lithium salt. The polymeric packet-forming component is preferably an interpolymer of styrene and an α,β-unsaturated carboxylic acid, part of whose carboxyl groups may have been converted to amide or imide derivatives or both, such as interpolymers of styrene-maleic acid, styrene-acrylic acid, styrene-methacrylic acid or styrene-itaconic acid.

The mixture of coupler-silver halide dispersion, water-soluble polymer and polymeric packet-forming component now consists of particles or packets of gelatin, associated with polymeric packet-forming component, containing silver halide and coupler, the packets being dispersed in an aqueous medium containing additional gelatin or another film-forming water-soluble polymer. This is finally mixed with at least one other similarly made packet dispersion containing differently-sensitized silver halide and a different coupler to form the finished mixed grain emulsion. The finished emulsion is then ready for coating on a suitable support, such as glass, cellulose ester, or paper.

In the preparation of the system described above, that is, gelatin, water-soluble polymer, and packet-forming component, the ingredients must be present in a fairly definite ratio. If the gelatin is present in approximately 0.7% aqueous solution (an appropriate concentration for making an emulsion), then the water-soluble polymer should be present in an amount from about 1 to 2 times that of the gelatin, and the packet-forming component should be present in an amount from 0.01 to 0.5 times that of the gelatin. Within these ranges the three-component systems exhibit a definite degree of optical turbidity. If this turbidity is measured in optical density per cm. of mixture at 30° C., using orange-colored light, of about 5800 A. U., the optical density is greater than 0.05, and is generally of the order of 0.1.

Suitable polymers of styrene with maleic acid or its derivatives are represented by the following formula:



Y=OH, NH_2, NHR', NR'$_2$

Z=NH, NR', OH groups on each carbon atom to which Z is attached

R=H, CH_3, C_2H_5

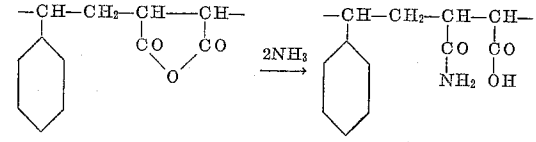
R'=alkyl of less than 6 carbon atoms

n=the number of units in the polymer chain

It will be understood that the above structural formulas

are illustrative only, and are not limiting as to ratios and unit arrangements of constituents.

The polymeric packet-forming components of the first structural formula above may be prepared by forming an interpolymer of styrene and maleic anhydride, and then treating the polymer with ammonia, a primary or secondary amine, or water, as indicated by the following formula using ammonia:



Formation of these polymers is described in Condo, Krister and Lundquist U. S. Patent 2,286,062 and McDowell and Kenyon U. S. Patent 2,313,565.

In order to ascertain the packet-forming components which are suitable for use in my process, the following test may be made:

A solution or dispersion of the polymeric compound to be tested, gelatin, and the sodium salt of methylmethacrylate-methacrylic acid polymer is made up in water so that the final concentrations are gelatin, 0.7%; methylmethacrylate-methacrylic acid salt, 1.67 times the amount of gelatin; and polymeric compound, 0.1 to 0.5 times the amount of gelatin. The gelatin is a deashed calfskin gelatin having an isoelectric point of approximately 4.8. The polymeric compound is added as an approximately 2% solution in ammonium hydroxide of pH 7.5. When vigorously stirred, this mixture is characterized by its ability to scatter or diffuse light transmitted through it. With polymeric compounds suitable for my process, the mixture must exhibit an optical density of at least 0.05 per centimeter of mixture, when measured at 30° C. with orange-colored light of approximately 5800 Angstrom units wave length.

The packet-forming components were prepared as follows:

Example 1.—Styrene-maleic anhydride interpolymer

Into a 12-liter all glass reflux outfit equipped for anhydrous conditions the following were measured:

234 gm. distilled styrene
220.5 gm. maleic anhydride
3188 ml. dry benzene
4.25 gm. benzoyl peroxide

The reaction mixture was heated on a steam bath for a total of two hours although the major portion of the reaction was completed in less than twenty minutes after the steam had been turned on. When the reaction mixture had cooled to room temperature, the solids were separated by filtration, washed with dry benzene and put to dry in a vacuum oven at 60° C.

Example 2.—Polystyrene-maleamic acid polymer

50 gm. of polystyrenemaleic anhydride were added gradually to 250 ml. of 28% ammonium hydroxide in a 500 ml. Erlenmeyer flask with stirring from a mixer to form a slurry. After stirring for eighteen hours at room temperature a viscous, clear colorless dope was obtained. 300 gm. of this dope was diluted to approximately 2% solids with water and 48% hydrobromic acid was added to it until it was just acid to Congo red. The solid that was formed was separated by filtration, and leached with absolute alcohol until the wash solutions were bromide free. The solids were put to dry in an oven at 60° C.

20 gm. of the solid were doped to form a 5% dope by weight in water made alkaline with 13 ml. of 20% sodium hydroxide. pH=8.63.

Example 3.—Polystyrene-maleamic acid ammonium salt

The following reagents were put to reflux in an all glass reflux outfit equipped with a mechanical stirrer.

Conditions were maintained anhydrous by calcium chloride tubes on all openings to the atmosphere.

49 gm. maleic anhydride (Eastman white label)
52 gm. distilled styrene
1500 ml. dry toluene
2.0 gm. benzoyl peroxide

The reaction mixture was heated for 2½ hours on a steam bath without stirring and then allowed to cool to room temperature. A small sample of the solids was withdrawn, washed with fresh benzene, and put to dry for analysis and viscosity purposes.

The stirrer was turned on and dry ammonia was bubbled into the reaction mixture continuously for 3½ hours. During this time the temperature within the reaction mixture rose from a starting temperature of 23° C. to 45° C. and then returned to 23° C. The solids were filtered off on a Büchner funnel, washed with toluene, and put to dry in a vacuum oven at 60° C. over night.

The residual toluene was then extracted with absolute alcohol by stirring the product with 2–3 l. portions of absolute ethyl alcohol and filtering onto a Büchner funnel. The product was then dried as above.

Forty grams of the polymer were gradually added to 200 ml. of water in an Erlenmeyer flask with mechanical stirring. The solution was kept slightly alkaline by the portion-wise addition of 28% NH_4OH. The pH was never allowed to exceed eight. A clear colorless dope was obtained which was then adjusted to 15% solids by weight by the addition of distilled water. The pH of this solution was 6.38.

A two-color emulsion was made as follows:

Example 4

Separate red-sensitive and green-sensitive silver bromoiodide emulsions were made containing 33 grams of gelatin per 100 grams of silver halide.

A cyan coupler dispersion was made by dissolving 4.375 grams of the coupler 2-[α-(2,4-di-tert.-amylphenoxy)-n-butyrylamino]-4,6-dichloro-5-methyl phenol and 0.27 gram of dioctyl hydroquinone in 5 cc. of n-butylphthalate at 150° C. adding the solution to 5 cc. of a 5% solution of Alkanol B dispersing agent in 25 cc. of 10% gelatin solution, and dispersing it therein.

A magenta coupler dispersion was made by dissolving 2.75 grams of the coupler 1-(p-p'-tert.butyl-phenoxyphenyl)-3-[m - (p - tert.amylphenoxy)benzoylamino] - 5-pyrazolone and 0.21 gram of dioctyl hydroquinone in 7.9 cc. of n-butylphthalate at 165° C., adding the solution to 5 cc. of a 5% solution of Alkanol B in 25 cc. of 10% gelatin solution, and dispersing it therein.

Six grams of the red-sensitive emulsion containing 0.4 gram of silver halide and 0.13 gram of gelatin were added to 8 grams of the cyan coupler dispersion and mixed with a fast stirrer for 10 minutes, Twelve cc. of a 10% solution of a copolymer of methacrylic acid and methyl-α-methacrylate (sodium salt) were mixed with 100 cc. of distilled water. The emulsion-coupler dispersion was added to the copolymer solution, and this was stirred for 10 minutes more. To this mixture there were added 4 cc. of a 0.5% solution of the ammonium salt of styrene-maleamic acid polymer and the whole dispersion was stirred at 42° C. for one hour. Then 50 cc. of an 18% solution of gelatin were added and mixed.

A similar dispersion was made using 6 grams of the green-sensitive emulsion containing 0.4 gram of silver halide and 0.13 gram of gelatin, and 8 grams of the magenta coupler dispersion instead of the red-sensitive emulsion and cyan coupler.

The two final dispersions were mixed together and coated, and after exposure and development in a p-phenylenediamine type color developer, gave satisfactory cyan and magenta images in the portions exposed to red and green light, respectively.

What I claim is:

1. Photographic gelatin layers which contain in a minor amount the reaction product of ammonia on a copolymer containing as the main monomers styrene and maleic acid anhydride.

2. A gelatino-silver halide emulsion containing dispersed particles of the reaction product of ammonia on a styrene-maleic acid anhydride copolymer.

3. A photographic gelatin layer containing a dispersion of packets of the reaction product of ammonia on a styrene-maleic acid anhydride polymer, said packets containing silver halide.

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