

Patented Dec. 5, 1944

2,364,374

UNITED STATES PATENT OFFICE

2,364,374

COLOR PHOTOGRAPHIC MATERIALS

Edward B. Knott, Wealdstone, Harrow, England,
assignor to Eastman Kodak Company, Roch-
ester, N. Y., a corporation of New Jersey

No Drawing. Application July 3, 1941, Serial No.
400,925. In Great Britain July 23, 1940

5 Claims. (Cl. 95—7)

This invention relates to improvements in color photography and more particularly to the manufacture of photographic elements containing color formers, also referred to as coupling components.

It is well known to produce images by developing a silver salt image in presence of a coupling component, by which I mean a compound which, during the production of the silver image by the photographic development, couples with the oxidation products of the developing agent where they are formed. If such coupling components are added to the developer solution, or incorporated in the emulsion layer, the dye which is thus formed by coupling is deposited in the gelatin or other silver halide carrier adjacent to the metallic silver grain. It is desirable that the dyes formed should not readily wander from the place of formation and it is accordingly desirable that they should be insoluble in water. They are probably not physically attached to the silver grain. At all events the silver may be subsequently bleached out of the carrier layer leaving a pure dye image.

When the coupling components are incorporated in the emulsion it is important that they should not wander or diffuse to any substantial extent during processing. If an emulsion containing a coupling component is adjacent to or near to another emulsion not containing a coupling component or containing a different coupling component it is equally important that diffusion or wandering of the coupling component or any of them should not take place at any time prior to the processing, e. g. during coating.

Numerous proposals have been made to produce coupling components which will not wander or diffuse from the emulsions in which they are incorporated. In some of these proposals attempts were made so to alter the coupling components that they would have an affinity for gelatin. In others, groups of high molecular weight were introduced into the coupling components. Although it has been proposed to cause coupling components to be absorbed on to the silver halide grains with the object of avoiding diffusion, most of the methods proposed have involved chemical synthesis of a more complex coupling component from a simpler coupling component. When this is done there is usually an undesirable tendency for the absorption range to become wider and the absorption curve to become flatter, resulting in less pure dye images.

It is pointed out in Schinzel U. S. Patent 2,306,410, that it is not necessary for the coupling component to be soluble. It is possible for coupling development to take place with alkaline coupling development even if the coupling component is insoluble therein, and accordingly, it can be insoluble in water. The use of insoluble coupling components is of advantage in that they

show little or no tendency to wander from the emulsion layer or the emulsion grain in which they are incorporated but their insolubility in water frequently makes it difficult for them to be dispersed in adequate amounts and to an adequately fine degree in the emulsion. If they are not adequately dispersed then the dye which is formed tends to be produced in localized spots resulting in a granular appearance which impairs the photographic reproduction.

When coupling components are incorporated in photographic silver salt emulsions it is necessary that they should be present in fine dispersion but adequate concentration in order that satisfactory color density and good brilliance of color be produced on coupling development. In Martinez U. S. Patent 2,269,158, there is described a color photographic element having a plurality of differentially color-sensitive photographic emulsions on a support, at least one of which emulsions consists of silver halide emulsified in a water-soluble binder such as gelatin having distributed through it fine, discrete particles of a water-insoluble water-permeable binder (such as a resin) containing color coupler.

I have now found, and this forms the subject of the present invention, that color couplers can with advantage be incorporated in photographic silver salt emulsions by precipitation in the presence of salts of salt-forming water-insoluble binders such as natural or artificial gums or resins. I may use water-soluble salts such as those of alkali metals, ammonium, etnanolamine, or of other strong organic bases or water-insoluble salts of alkaline earth metals or of other metals whose presence in photographic emulsions is not deleterious, or of organic bases of complex structure or high molecular weight such as quinine or cinchonine.

According to one feature of the present invention, therefore, there is provided a photographic silver salt emulsion containing a salt of a salt-forming water-insoluble binder such as a natural or artificial gum or resin, and a color coupler. According to a further feature of the invention there is provided a method of incorporating a color coupler in a photographic silver salt emulsion which consists in precipitating an insoluble salt of a salt-forming water-insoluble binder such as a natural or artificial gum or resin associated with color coupler in such emulsion, preferably from a solution of such insoluble salt containing color coupler in an organic solvent for both. The emulsion may, however, contain the cation of the insoluble salt in which case the solution of coupler in organic solvent may contain the gum or resin itself or preferably a water soluble salt thereof. Suitable organic solvents are methanol, ethanol or acetone.

The present invention may be used in making

the elements described in Martinez U. S. Patent No. 2,269,158, granted January 6, 1942, and the methods described or claimed therein may be employed with salts of salt-forming water-soluble or water-insoluble binders such as gums or resins.

Many natural or artificial gums or resins contain acid radicals or salt-forming hydroxyl groups. Metals which may be used to form salts for the present invention, are magnesium, calcium, strontium, barium, aluminum, cadmium, manganese, zinc, cerium, nickel, cobalt and thorium. This list is illustrative only. Resins which will form water-soluble or water-insoluble salts—suitable for use in the present invention—are whole lac, hard lac, soft lac, hydrolysed lac (see for example Ayres, Batley and Knott U. S. Patent 2,199,978, granted May 7, 1940), colophony, dammar, mastic, sandarach and glycerol-phthalic anhydride. This list is also illustrative only. Instead of resins we may use, as the salt-forming water-insoluble binder, cellulose esters of polybasic acids having free carboxylic groups e. g. cellulose phthalate or cellulose acetate-phthalate (see for example Malm U. S. Patent 1,884,035, granted October 25, 1932). Artificial resins which form salts are well known (see for example U. S. Patent 2,161,788, granted June 13, 1939).

The following examples illustrate the manufacture of silver salt emulsions according to the invention. In Examples 1 and 2 water-soluble salts of resins are used. In Examples 3 and 4 water-insoluble salts of the resins are precipitated in the emulsion.

Example 1

To 250 cc. of emulsion containing the equivalent of 15 grams silver nitrate is added 30 cc. of an alcoholic solution containing 1 per cent p-nitrophenacetoneitrile and 10 per cent sodium salt of colophony. When such emulsion is developed with a color developer containing p-amino diethylaniline as the developing agent, a well-dispersed and brilliant dye image is obtained.

Example 2

As Example 1 but using the sodium salt of soft lac instead of the sodium salt of colophony.

Example 3

To 250 cc. of emulsion containing the equivalent of 15 grams silver nitrate is added 5 cc. of a 10 per cent aqueous solution of cadmium nitrate. After thorough mixing 30 cc. of an alcoholic solution containing 1 per cent 1-phenyl-3-methyl-5-pyrazolone and 10 per cent sodium salt of colophony are slowly added with agitation.

Example 4

As Example 3 but using instead of the cadmium nitrate 5 cc. of a 10 per cent nickel chloride solution.

In the case that water-insoluble salts of the resins are used, as in Examples 3 and 4, treatment of the film with ammonia after color development will render the resin soluble, so that it may be removed.

The employment of salts of gums or resins according to the invention possesses many advantages:

(a) If the refractive index of a resin and of the water-soluble water-permeable binder into which such resin is to be incorporated are materially different, a bloom or matte surface may be pro-

duced. This can often be remedied by employing a metallic salt, according to the present invention, which has a refractive index closer to that of the binder.

(b) The employment of salts of gums or resins is particularly useful in cases where the color couplers are added to the emulsions in the form of aqueous solutions (e. g. in alkali such as caustic soda).

(c) The presence of salts of gums or resins in association with color coupler tends to reduce the tendency of the color coupler to wander from the emulsion in which it is incorporated. This is particularly important in the case of emulsions of silver salts in water-soluble binders such as gelatin and particularly important also where two or more emulsions are present on the same side of a single support and have to be differentially processed to color.

Some metallic salts of resins employed in the present invention can be dissolved in organic solvents such as alcohol, for example the cadmium and magnesium salts of colophony and soft lac. This enables them to be added in such solution to the emulsions using the same procedure as for resins themselves.

This invention is particularly useful with color couplers of limited solubility as defined in Vittum and Weissberger U. S. application Serial No. 314,679, filed January 19, 1940.

Numerous variations may be made in my invention within the scope of the appended claims.

I claim:

1. The method of preventing the diffusion in photographic gelatino-silver halide layers, of color couplers which couple with the oxidation product of primary aromatic amino color developers, which comprises mixing the color coupler with the gelatin and an appreciable amount of a water-insoluble salt of a resin.

2. The method of preventing the diffusion in photographic gelatino-silver halide layers, of color couplers which couple with the oxidation product of primary aromatic amino color developers, which comprises mixing the color coupler with the gelatin and an appreciable amount of a water-insoluble salt of a natural resin.

3. The method of preventing the diffusion in photographic gelatino-silver halide layers, of color couplers which couple with the oxidation product of primary aromatic amino color developers, which comprises mixing the color coupler with the gelatin and an appreciable amount of a water-insoluble salt of a synthetic resin.

4. The method of preventing the diffusion in photographic gelatino-silver halide emulsion layers, of color couplers which couple with the oxidation product of primary aromatic amino color developers, which comprises mixing the color coupler with the emulsion and an appreciable amount of a water-insoluble salt of a resin.

5. The method of preventing the diffusion in photographic gelatino-silver halide emulsion layers, of color couplers which couple with the oxidation product of primary aromatic amino color developers, which comprises mixing with said emulsion a solution of a water-soluble salt of a water-insoluble binder and a color coupler, and precipitating in said emulsion a water-insoluble salt of said water-insoluble binder, having said color coupler associated therewith.

EDWARD B. KNOTT.