

UNITED STATES PATENT OFFICE

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PROCESS FOR THE PRODUCTION OF PHOTOGRAPHIC COLOR IMAGES

Alfred Fröhlich and Wilhelm Schneider, Dessau, Germany, assignors to General Aniline & Film Corporation, New York, N. Y., a corporation of Delaware

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This invention relates to the production of photographic color images.

It is known to use for the production of photographic color images silver halide emulsions having color formers fast to diffusion which may be added in dissolved form to the photographic silver halide emulsion, but which cannot thereafter be washed out of the emulsion. Such color formers fast to diffusion were obtained from simple dyestuff components by introducing certain substituents preventing diffusion or by binding dyestuff components onto compounds fast to diffusion. As substituents preventing diffusion there were proposed inter alia substantive groups, radicals of high polymeric carboxylic acids, carbon chains with more than 5 carbon atoms, sterols and the like. Furthermore there were introduced into these color formers groups increasing water solubility, such as sulfo- or carboxyl groups, in order to render the color formers soluble in water or alkali and thus to facilitate their incorporation into the emulsion.

This invention has as an object an improved method for making photographic color images.

A further object is a method for improving the manufacture of color formers fast to diffusion.

Still further objects will be apparent from the following description.

It has been found that for the production of photographic color images there may be advantageously used such color formers fast to diffusion, which are obtained by condensation of aromatic hydroxy-aldehydes with phenols in the presence of acids or alkalies. The condensation of these compounds may be accomplished according to the prescriptions given for benzaldehyde and phenol by Losew, Petrow and Kotrelew in "Promyschlennostj Organitscheskoj Chmii," volume III, Number 4, 1937, pages 210-212.

For the condensation for instance there is suited as the hydroxyaldehyde salicylic aldehyde, as the phenol for instance the simple phenols, p- and m-cresol, and xylene. The condensation products thus obtained are feebly colored powders, easily soluble in diluted alkalies. The solutions showing a pH-value of 9-12 may be added to the photographic emulsion at any point of the manufacturing process. If necessary, these compounds may be added previously to a gelatin solution, whereupon this gelatin may be subjected to a washing process before it has solidified and before it is cut into small cubes, in order to dissolve out eventually uncondensed parts of the reaction components. The gelatin thus

treated is then added to the photographic emulsion. The silver halide emulsion thus obtained, which, before casting, may be subjected to a short washing process, is worked up into photographic layers in a manner known per se, said layers being arranged on one or both sides of a support, if necessary, on top of one another and being sensitized for different spectral regions.

The silver halide emulsions, however, may be worked up also in a different manner. According to U. S. Patent 2,186,730, there may be arranged for instance on a support differently sensitized emulsions bearing various color formers in the form of minute particles.

The manufacture of the color images can be accomplished in various ways, for instance according to U. S. patent application Ser. No. 111,250, filed November 17, 1936, and U. S. Patents 2,179,228, 2,179,238, 2,186,730, 2,178,612 and 2,186,849. The images may be formed in the exposed emulsion layers by simple color forming development or reversal development according to U. S. Patents 2,229,137 and 2,179,234. The color formers according to this invention, moreover, may be employed together with other color formers fast to diffusion within the different emulsion layers, according to U. S. Patents 2,179,238, 2,178,612, 2,186,849, 2,186,850, 2,179,244 and 2,186,732.

Example I

94 grams of phenol and 84 grams of salicylic aldehyde are heated to boiling and after adding 1 gram of gaseous hydrochloric acid, the whole is boiled under reflux for three hours. The condensation product thus obtained is dissolved in 200 cc. of glacial acetic acid and precipitated with 3 liters of ether. A feebly red powder soluble in alkalies is obtained.

3 grams of this powder are dissolved in 300 cc. of water, while adding 0.5 gram of sodium hydroxide and the whole is added to 1 kg. of a silver halide emulsion. After casting and drying, the layers thus obtained are exposed to light and developed with p-amino dimethyl aniline. A blue dyestuff image is obtained.

If the silver image is transformed into a β -naphthalene-antidiazotate silver image and the latter is brought into a feebly acid solution, a red azo-dyestuff-image is obtained.

Example II

100 grams of p-cresol and 84 grams of salicylic aldehyde are heated to boiling in a reflux condenser for 5 hours and a feeble current of gaseous HCl is slowly conducted therethrough. The

condensation product thus obtained is diluted with 100 cc. of ether and precipitated with 1 liter of benzine. Dissolution in a small amount of ether and precipitation with benzine are repeated three times. A grey powder is then obtained, soluble in alkalis with a feebly yellow color.

5 grams of this powder are dissolved in 300 cc. of water, while adding 0.5 gram sodium hydroxide, and added to 1 kg. of a silver halide emulsion. When treated according to Example I, a blue dyestuff image is obtained.

Example III

100 grams of m-cresol and 84 grams of salicylic aldehyde are heated to boiling under reflux for 5 hours and a feeble current of gaseous HCl is slowly conducted through the reaction mixture. The condensation product thus obtained is diluted with 100 cc. of ether and precipitated with 1 liter of benzine. Dissolution in a small amount of ether and precipitation with benzine are repeated three times. A grey powder is then obtained, which is soluble in alkalis with a feebly yellow color.

5 grams of this powder are dissolved in 300 cc. of water, while adding 0.5 gram of sodium hydroxide, and added to 1 kg. of a silver halide emulsion. When treated according to Example I, a blue dyestuff image is obtained.

Example IV

100 grams of 1-2-3-xyleneol and 84 grams of salicylic aldehyde are heated to boiling under reflux for 5 hours and a feeble current of gaseous HCl is conducted therethrough. The condensation product thus obtained is diluted with 100 cc. of ether and precipitated with 1 liter of benzine. Dissolution in a small amount of ether and precipitation with benzine are repeated three times. A grey powder is then ob-

tained which is soluble in alkalis with a feebly yellow color.

5 grams of this powder are dissolved in 300 cc. of water, while adding 0.5 gram of sodium hydroxide, and added to 1 kg. of a silver halide emulsion. When treated according to Example I, a blue dyestuff image is obtained.

We claim:

1. A color photographic silver halide emulsion containing as the color former the condensation product of p-cresol with salicylic aldehyde.

2. A color photographic silver halide emulsion containing as the color former the condensation product of m-cresol with salicylic aldehyde.

3. A color photographic silver halide emulsion containing as the color former the condensation product of 1,2,3-xyleneol with salicylic aldehyde.

4. A silver halide emulsion for color photography containing as a color former the product obtained by the condensation of a substance selected from the class consisting of phenol and its nuclear substituted alkyl derivatives with an aromatic hydroxy aldehyde.

5. Compositions as defined in claim 4 wherein the hydroxyaldehyde is an ortho-aldehyde of the benzene series.

6. Compositions as defined in claim 4 wherein the hydroxyaldehyde is ortho-hydroxybenzaldehyde.

7. In a process of producing color photographic images by color forming development, the improvement which comprises developing an exposed silver halide emulsion with an aromatic primary amino developer in the presence of the condensation products of a substance selected from the class consisting of phenol and its nuclear substituted alkyl derivatives with a hydroxybenzaldehyde.

ALFRED FRÖHLICH.
WILHELM SCHNEIDER.