

PATENT SPECIFICATION



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COMPLETE SPECIFICATION.

Improvements in Processes for the Production of Colour Photographs.

We, LEOPOLD DAMROSCH MANNES and LEOPOLD GODOWSKY, Jr., citizens of the United States of America, residing respectively at 111, East 81st Street, and 8, West 76th Street, City, County and State of New York, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement :—

This invention relates to improvements in color photography. Heretofore, colors on the finished negative and positive were obtained by coloring the silver image by processes of metallic toning (conversion to insoluble and colored metallic salts) or dye-toning (converting the silver image to a metallic salt acting as mordant for aniline dyes). These methods, while practicable, have certain disadvantages which are in a large measure overcome by the present process.

The main object of the present invention is to substitute a method of color development for such color-toning or dye-toning, this method of color-development being applicable for all the so-called "primary" colors used, in color photography.

It has been proposed for the purpose of producing color photographs to form layers of emulsions sensitized to record different color values, incorporating in them color formers. It has also been proposed for the same purpose to use developers containing substances which become coupled with those oxidation products of the developer which are formed whilst developing and forming colored bodies soluble with difficulty.

The method of producing colored photographs of the present invention comprises forming in layers of emulsion sensitized respectively to record different color values, superimposed latent images of different color sensations, simultaneously developing and then fixing said images, then successively forming color images in the different layers by bleaching and re-developing with developers containing re-

spectively different color formers.

It is understood that the number of layers of differently sensitized emulsion to be treated is not limited to two or three, though three layers is generally the maximum number desired.

A method for carrying out the process of the invention is to separate the treatment of the developed, fixed and washed film or plate for subsequent coloring by methods of controlled diffusion of chemical solutions. The coatings may be simultaneously bleached in potassium ferricyanide and the upper one (or two in the case of triple coating) alone redeveloped by controlled diffusion of a concentrated developer. The undeveloped lower layer, still containing an image-record in silver ferrocyanide, may be developed by immersion in a color-forming developer as described above which will not affect the redeveloped silver of the upper layer or layers. The plate, or film, may be fixed in sodium thiosulphate, washed, and then dried, and the remaining layer or layers bleached to silver ferrocyanide for redevelopment in another color-forming developer, and so on to the third coating in the case of three-color photography. After the three steps of coloring, the remaining metallic silver formed in the color development is removed by solution in sodium thiosulphate and potassium ferricyanide, or some other solvent of silver. The colored negative is printed on a similarly coated positive which in turn is color-developed substantially as described for the negative.

Instead of this method of separation by controlled diffusion of concentrated redeveloper, the negative may be treated as follows :

The plate or film is developed, fixed and dried. The top layer is converted to silver ferrocyanide by controlled diffusion of potassium ferricyanide in solution. Treatment with a color developer will then affect this bleached layer only. The silver may be removed from this top image-record by controlled diffusion of any suitable silver-solvent. The lower

layers are successively treated in this manner using a different color developer for each, until only pure color records remain.

Obviously this method depends on controlled diffusion of the potassium ferricyanide employed.

In the case of triple-coating for three-color photography it is often desirable for reasons of balance, to coat the red-sensitive layer between the green-sensitive layer which is next to the support and the blue-sensitive layer on top containing the yellow dye. It is also practicable to coat twice only, having the lower layer red-sensitive and the upper green-sensitized, and then before exposure removing the color sensitizer near the surface, using, for instance, an alcoholic or partially alcoholic solution of yellow dye and displace the green sensitizer. This gives a sensitive element substantially blue-sensitive at the surface, green-sensitive below, and red-sensitive near the support. As the layer of the blue record is somewhat thin and allows of separate treatment by controlled diffusion, a master positive may be made by reflected light exposure, i.e., rephotographing, to be used later, for example, in preparing an imbibition matrix for applying the yellow color to the finished print. After reflection printing the surface record may be dissolved and removed after drying and the remaining lower layers treated for the two colors only. This method of treatment of the exposed plate may also be applied to triple coatings.

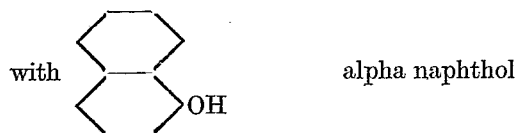
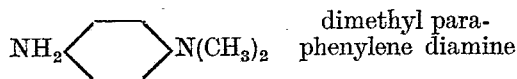
The term "color-former" here used refers to organic compounds acting as couplers in connection with certain developers in photographic processes, thus forming colored compounds, usually insoluble in water, in the presence of the finely divided silver being reduced by the developing agent. This, in general, distinguishes them from leuco-bases and rather classifies them as intermediate couplers in a dye-forming process.

Phenols, naphthols, cresols, nitrophenylacetoneitriles, ethyl acetoacetate, and their halogenated or sulphonic acid compounds are typical members of this type of color-former.

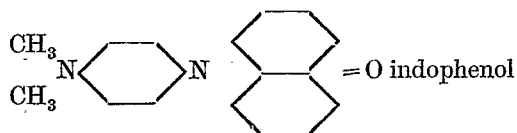
Paraphenylenediamines and paramidophenols are typical developers used in conjunction with the color-formers. The colored compounds so formed belong to the class, for instance, of indophenols, indoanilines, and indamines.

In further explanation of the term "color-forming compounds" we would say that this term is intended to describe any substances which, though not dyes or leuco compounds of dyes, can form dyes by chemical combination with the oxida-

tion or reaction product derived from the developer in the chemical reaction which takes place upon the development of the photographic image, said oxidation or reaction product being formed mainly through the action of the developer in reducing the developable salts in a photographic emulsion layer. Thus, any compound such as leuco-malachite green or indigo-white which can form a dye through mere oxidation does not fall into this class. A specific example of color-former action as we intend to describe it in our application is given by the reaction between alpha naphthol, a typical color-former, and dimethyl paraphenylene diamine, a photographic developer. The oxidation product of the developer reacts with alpha naphthol in this case to form a dye, indophenol. As the oxidation of the developer takes place first where actual development occurs (i.e. where the photographic image is developed) the dye is formed in situ with the photographic image. This reaction is as follows:—



as oxidized in the development reaction



Hydrogen is removed in the process from both the naphthol and the diamine. This indophenol dye is otherwise known as naphthol blue.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

The method of producing a color photograph comprising forming in superimposed layers of emulsion sensitized respectively to record different color values, superimposed latent images of different color sensations, simultaneously developing and then fixing said images, then successively forming color images in the different layers by bleaching and redeveloping with developers containing respectively different color-formers.

Dated this 28th day of May, 1932.

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