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MANUFACTURE OF MULTICOLOR
PHOTOGRAPHS

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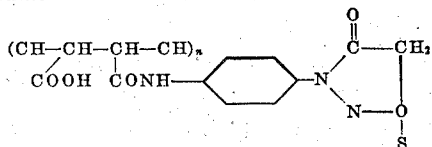
My present invention relates to the manufac-
ture of multicolor photographs.

One of its objects is an improved process of
producing multicolor photographs. Another ob-
ject is a process of producing a multicolor photo-
graph by a single development in color. Another
object is a process of producing a multicolor
photograph by a single exposure and a single de-
velopment in color. Further objects will be seen
from the detailed specification following here-
after.

It has long been known that one can develop
exposed photographic silver halide emulsions to
a color-picture instead of the usual black silver-
picture by using either certain developers (pyro-
gallol, indoxyl, thioindoxyl or the like) which are
oxidized to sparingly soluble colored bodies by
exposed silver halide, or by adding to certain
developers, for example para-dimethyl-amino-
aniline, substances which couple to form spar-
ingly soluble colored bodies with the oxidation
products of the developer produced during the
development. In the latter case it has been pro-
posed to incorporate the coupling components in
the sensitive layer itself. Although, obviously,
these processes have been conceived particularly
for the purpose of multicolor photography, they
have not passed into practice because they are
much too detailed. For this reason, lately a vari-
ant of the second process referred to above has
been proposed, which requires a large number of
successive treatments with liquid of a three-layer
film.

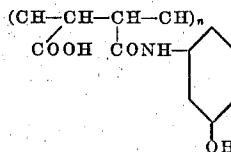
The present invention relates to the treatment
of a photographic layer in a simple manner to
produce two-color or multicolor pictures without
any developing operation in excess of that for
normal black-and-white development.

Layers suitable for the invention are of the
kind which have been described in the co-pend-
ing application Ser. No. 90,726 filed July 15, 1936.
They are silver halide emulsions, to which has
been added, for example, a substance obtainable
by the reaction of a compound which by known
reactions is capable of forming dyestuffs, for ex-
ample an amine, a phenol, an aminophenol, a
naphthol or an amino-naphthol, or a compound
having a reactive methylene-group, with a high-
ly polymeric carboxylic acid or a derivative there-
of, for instance, the condensation product from
polyvinyl-maleic-acid-anhydride and p-amino-
phenyl-3-methylpyrazolon having probably the
formula:



and the condensation product from polyvinyl-

maleic-acid-anhydride and m-aminophenol hav-
ing probably the formula:



So also the silver halide emulsion layers described
in the copending application Ser. No. 72,718 filed
April 11, 1936, may be used. These contain as
coupling components for the color development
such compounds as are fast to diffusion in the
binding agent used, for instance the gelatin or
the like. Suitable groups which determine such
fastness to diffusion are, for instance, diphenyl,
stilbene, azoxy-benzene, hydroxynaphthoic acid
amide, diaryl-urea, benzthiazole and certain
phenols, aminophenols containing substituents in
the 3:5-position and the like. Color-forming
components in which these groups are introduced
are, for example, phenols, anilines, naphthols,
naphthylamines, amino-naphthols; also all sub-
stances which have a reactive methylene-group,
for example an acetoacetic ester, a cyanoacetic
ester, a benzoyl-acetic ester, hydrindene, pyrazo-
lone, cumaranone. Further suitable components
are for instance α -hydroxynaphthoic-acid-benzi-
dide, di-(α -hydroxynaphthoic-acid-amino)-stil-
bene, dibenzoylacetic - benzdide, 2,3 - hydroxy-
naphthoic-acid-amino-benzoylacetic-anilide, di-
 α -hydroxynaphthoylaminobenzoylaminophenyl-
urea, α -hydroxy-naphthoylaminio-I-acid, m-hy-
droxyphenyl-(2) amino-methylbenzthiazole, α -
hydroxynaphthoic-acid-dianisidide, α -hydroxy-
naphthoic-acid-dichloro-benzidide, α -hydroxy-
naphthoic-acid-benzidide-dicarboxylic - acid, di-
lm - hydroxyphenylaminocarboxyl - diphenyl or
the like.

Finally, there are applicable according to the
invention emulsion layers in which there are in-
corporated color-formers containing an aliphatic
hydrocarbon chain of more than 5 carbon atoms.
Such layers are described in the co-pending ap-
plication Ser. No. 94,340 filed August 5, 1936. All
these layers have the property that the incor-
porated color-former is converted into dyestuff
by a secondary process during the color develop-
ment and is more strongly held in the light-sen-
sitive layer, which generally comprises gelatin,
than has been the case with the bodies hitherto
proposed for the purpose; thus they withstand
the usual photographic baths. Neither in this
treatment nor in the subsequent washing with
water are they dissolved or washed off. Only
under these conditions is it possible to conduct
in a single operation a development of all the
contributory colors in three superimposed layers.

In the process there is provided a multilayer

film consisting, for instance of two or three light-sensitive layers arranged on one or both faces of a single support and selectively color-sensitized, and capable of being developed to a color corresponding with its range of color sensitivity; this film is exposed in a photographic or cinematographic camera and then developed with a normal black and white developer to produce a negative. For this development there must only be used a developer which does not react with the coupling components incorporated in the layers, for instance, amidol, para-methylaminophenol, or hydroquinone. After the development of the black and white negative the film, without being fixed, is exposed to the general illumination, whereupon the residual silver halide is developed with a color-forming developer, for instance para-dimethylamino-aniline. The general illumination and color development following the first black-and-white development may advantageously be combined by merely conducting the color development in bright light.

In the second developing operation there is produced in each layer of the multicolor film a picture in the component color allotted to this layer; for example, in a 3-layer film there are obtained at once 3 component pictures of correct color and superimposed. After the second development the silver present in the layers may be removed by any of the usual solvents for silver. It is also possible to remove already the silver formed in the first developing operation by means of the known silver dissolving agents.

The process may similarly be conducted for producing copies by copying, optically or in contact, an exposed film made by the process above described, enlargement or diminution being used if desired, on such a material and developing to a colored positive picture in the manner described.

As a specific example, a support, for instance a Celluloid film, carries on its front face an orthochromatically color-sensitized layer in which is incorporated diphenylcarboyl-4,4'-di-(para-amino-1-phenyl-3-methyl-5-pyrazolone) as a red developing component. Over this layer is a not specially sensitized layer which contains as the yellow developing component dibenzoylacetic-benzidide-3,3'-dicarboxylic acid and at the same time a yellow filter color, for example tartrazine. On the back of the film is a layer of emulsion which is sensitive to red light and contains as the blue developing component 4,4'-di-1-hydroxy-2-naphthoylamino)-diphenyl. Then this film is exposed and first developed for 10 minutes in an amidol developer (200 cc. of water, 1 gram of amidol, 10 grams of sodium sulfite crystals, 0.2 gram of potassium bromide) and then washed for 5 minutes and further developed for 10 minutes in daylight with dimethylaminoaniline (200 cc. of water, 2 grams dimethylaminoaniline, 6 grams calcined sodium carbonate); after washing for 15 minutes and then removing silver by means of Farmer's reducer, for example 200 cc. of water, 20 grams of sodium thiosulfate and 2 grams of potassium ferri-cyanide, a colored positive is obtained.

What I claim is:

1. A process of producing multicolor photographs which comprises producing a multilayer film having incorporated in the several gelatine silver halide emulsion layers a dye component capable of forming a dye with a developer adapted

for color development, said dye components although soluble in aqueous photographic developing solutions being of such molecular constitution that they are incapable in such dissolved form of diffusing in gelatine in any photographic treating bath, exposing said multilayer film to a colored object, developing the exposed film in a developer not capable of forming a color with said dye components, exposing said multilayer film a second time, simultaneously developing all the layers of the exposed film in a developer capable of forming dyes with said dye components and removing the developed silver from said film.

2. A process of producing multicolor photographs which comprises producing a multilayer film having the emulsion layers arranged in superposition on the same side of the support and having incorporated in the several gelatine silver halide emulsion layers a dye component capable of forming a dye with a developer adapted for color development said dye components although soluble in aqueous photographic developing solutions being of such molecular constitution that they are incapable in such dissolved form of diffusing in gelatine in any photographic treating bath, exposing said multilayer film to a colored object, developing the exposed film in a developer not capable of forming a color with said dye components, exposing said multilayer film a second time simultaneously developing all the layers of the exposed film in a developer capable of forming dyes with said dye components and removing the developed silver from said film.

3. A process of producing multicolor photographs which comprises producing a multilayer film having incorporated in the several gelatine silver halide emulsion layers a dye component capable of forming a dye with a developer adapted for color development, said dye components although soluble in aqueous photographic developing solutions being of such molecular constitution that they are incapable in such dissolved form of diffusing in gelatine in any photographic treating bath, exposing said multilayer film to a colored object, developing the exposed film in a developer not capable of forming a color with said dye components, and then simultaneously developing all the layers of said film in bright light in a developer capable of forming a dye with said dye components and removing the developed silver from said film.

4. A process of producing multicolor photographs which comprises producing a film having one side coated with an orthochromatically sensitized silver halide emulsion layer containing diphenyl - 4,4' - (para - amino - 1 - phenyl - 3 - methyl-5-pyrazolone) and this emulsion layer with a silver halide emulsion layer which has not been specially sensitized and containing dibenzoylacetic-benzidide-3,3'-dicarboxylic acid and a yellow filter dye, and the other side with a silver halide emulsion layer sensitized to red and containing 4,4'-di-(1 - hydroxy-2-naphthoylamino)-diphenyl, exposing this film to a colored object, simultaneously developing all the layers of the exposed film in an amidol developer, washing said film, simultaneously developing all the layers of said film in daylight with a dimethylaminoaniline developer and removing the silver by means of Farmer's reducer.

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