2495

Published May 4, 1943

Serial No. 394,290

ALIEN PROPERTY CUSTODIAN

COLOR COUPLERS FOR COLOR DEVELOPMENT

Pierre Bruylants, Winxele-Velthem (Lowen), and Philibert Leopold Jozef Raymond Merckx, Berchem-Antwerp, Belgium; vested in the Alien Property Custodian

No Drawing. Application filed May 20, 1941

Our invention relates to color photographic images and to means for producing same. More particularly our invention relates to a process and material for color development in connection with color photography and it includes also the images obtained therewith.

It is an object of our invention to provide for an improved process of producing color photographic images by means of color couplers.

It is another object of our invention to provide for developing compositions which contain color couplers for the production of color photographic images.

Other objects of our invention are new and particularly useful color couplers as well as photographic emulsions or sensitive layers, in which such color couplers are incorporated, and photographic materials comprising a sensitive layer with a content of such a color coupler.

Still other objects of our invention will appear as the specification proceeds.

It is known that color photographic images can be obtained by the use of such developers that form colored and insoluble oxidation products during development, the product thus formed coloring the gelatine adjacent to the developed silver. It is also known that coloured images can be formed by the addition to the developing agents of certain products, called color couplers, which couple with the oxidation products of the developing agent and thus form coloring substances.

Hitherto many chemical compounds have been either used or proposed as color couplers. Among others have become known substituted and unsubstituted phenols and naphthols, nitrophenylacetonitriles, derivatives of acetamids, distinguished by the presence of an acidic methylene group, isoxazolones and cumaranones.

United States Letters Patent No. 1,969,479 to Seymour discloses amongst others photographic developers containing as a color coupler a hydrazone of an acyl acetic acid ester.

As far as we are aware, no theory hitherto has been put forward in connection with the process of color development that allows to anticipate with practical certainty whether or not a given product is a color coupler. This is the reason why the search for useful color couplers is, as a rule, largely guided by empirism.

Despite the great number of color couplers already known it has not always been possible to find such color couplers which, with the oxidation product of the developing agent, give the desired tone more particularly with regard to the colors already formed or still to be formed in the other layers of a photographic material comprising several layers. The fact that it is desirable only to use such color couplers which form coloring substances insoluble in water and which simultaneously resist to the subsequent photographic baths restrains considerably the number of the color couplers that can be used.

Now we have found a new class of color couplers very useful for color development. This new class of color couplers includes the mono- and poly-hydrazones being the products of condensation of one or more hydrazides, which contain at least one reactive methylene group, with compounds containing also one or several reactive methylene groups. These new color couplers contain thus at least two reactive methylene groups separated from each other by a chain comprising what we call the hydrazine radical =N—NH—, and they may for instance on principle be produced by the condensation of an acyl hydrazine with a keto compound containing at least one reactive methylene group; no pyrazolone derivatives are formed during this condensation reaction, as the analysis of the products shows.

Examples of our new color couplers are:

(1) $CN-CH_2-CONH-N=C(CH_3)-CH_2-COOC_2H_5$

cyanacetylhydrazone of acetoacetic ethyl ester

(2) $C_6H_5-CO-CH_2-C(=N-NH-CO-CH_2-CN)-COOC_2H_5$

or

$C_6H_5-C(=N-NH-CO-CH_2-CN)-CH_2-CO-COOC_2H_5$

cyanacetylhydrazone of benzoyl pyruvic ethyl ester

(3) $CONH-N=C(CH_3)-CH_2-CO-C_6H_5$ and $CONH-N=C(CH_3)-CH_2-CO-C_6H_5$

or

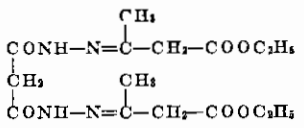
$CONH-N=C(C_6H_5)-CH_2-CO-CH_3$ and $CONH-N=C(C_6H_5)-CH_2-CO-CH_3$

malonylhydrazone of benzoylacetone

(4) $C_6H_5-C(=N-NH-CO-CH_2-C_6H_4-NO_2)-CH_2-COOC_2H_5$

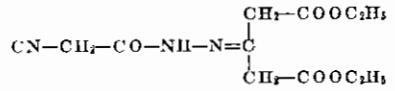
para-nitrophenylacetylhydrazone of benzoyl acetic ethyl ester

(5)



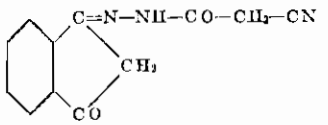
malonylhydrazone of acetoacetic ethyl ester

(6)



cyanacetylhydrazone of acetone dicarboxylic diethyl ester

(7)



monocyanacetylhydrazone of diketohydrinden

These compounds can be obtained by the methods described in "Berichte der deutschen Chemischen Gesellschaft" vol. 27, p. 688, vol. 40, p. 712, and vol. 41, p. 643.

On development with diethyl paraphenylenediamine as developing agent in conjunction with one of the above color couplers, we get with the compound cited in

Example 1: an orange color
Example 2: a red color
Example 3: a yellow color
Example 4: a magenta color
Example 5: a magenta color
Example 6: an orange color
Example 7: a magenta color

The new color couplers allow to obtain during development particularly beautiful and bright colors.

Our color couplers may be added to a developing bath containing a fair amount of a sulfite.

Another advantage of this invention is that the new color couplers are generally soluble in weak bases, such as carbonates, so that they can be added to the developing baths without the intervention of organic solvents. Usually the developing baths are only slightly colored.

A great advantage offered by the new class of color couplers is that owing to their wide diversity the most varying tones ean be obtained, which is of utmost importance for the mutual adaptation of the different dyes formed by color development in a material with two or more layers.

Still another advantage of the new color couplers is that they can quite easily be rendered free from diffusion from one layer into another, which is very important when they are to be incorporated in the emulsion directly. To this purpose condensation with hydrazides containing a sufficient amount of carbon atoms suffices.

Our new color couplers can moreover be kept a long time, which is not always possible with the known hydrazones deriving from acetoacetic acid esters.

Thus, the invention comprises the color couplers defined above as well as the improved process of producing color photographic images by means of these color couplers. Furthermore the invention comprises the improved process of forming color photographic images by the incorporation in the photographic emulsion, before or after coating, of a color coupler as defined above and development of such an emulsion after exposure. The invention also comprises a photographic emulsion, which contains a color coupler as defined above and preferably such a color coupler which derives from a hydrazide containing a sufficient number of carbon atoms to substantially prevent diffusion, as well as a photographic material comprising one or several layers formed of such an emulsion. The invention further includes the process of developing a latent photographic image by means of a color developer comprising in addition to an aromatic amino developing agent a color coupler as above defined, and it includes also a color developer containing these substances. The invention also includes a process or method of color development which comprises developing a latent photographic image by means of an aromatic amino developer in the presence of color couplers as above defined, and eliminating the silver image which is formed during development so that a clear and transparent color image remains.

Our invention further includes photographic elements having at least one layer containing a clear and transparent image composed essentially of the product resulting from the coupling "in situ" during development of color couplers as above defined, with the oxidation product of an aromatic amino developing agent.

The aromatic compounds which may be used as developing agents in the present invention include the mono-, di- and tri-amino-aryl compounds. Among the mono-amino developing agents may be mentioned amino-phenols and amino-cresols and their halogen derivatives and amino-naphthols.

The developing agents preferably used and giving the best results in connection with the present invention are the aromatic ortho- and para-diamines, such as ortho- and para-phenylenediamines. These developing agents may be substituted in one amino group or in the ring or in one amino group and in the ring, forming different compounds such as:

Diethyl-para-phenylenediamine,
Monoethyl-para-phenylenediamine,
Dimethyl-para-phenylenediamine, and
3-amino-6-dimethylamino-toluene.

These compounds are usually kept in the salt form, such as hydrochloride or sulfate.

By color development we not only mean the formation of a colored image by the interaction, during the photographic developing process, of a developer and a color coupler but also the formation of a colored image by the action of an insoluble oxidising agent, such as for instance silver ferricyanide, present in a photographic layer, on a developing bath which contains, besides the reducing and the other usual constituents, a color coupler as described above. This color coupler according to our invention may also be present in the emulsion.

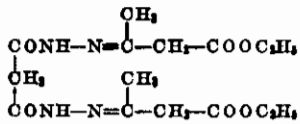
The following developer solutions may for instance be used to give a color image according to our invention:

FORMULA 1

A

Diethyl-para-phenylenediamine hydrochloride	grams	2
Sodium sulfite cryst	do	10
Sodium carbonate cryst	do	60
Sodium hydroxide	do	2
Water	ccm	1000

B



grams__ 2

For use B is added to A.

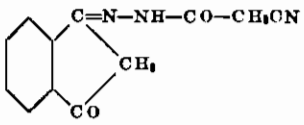
The developing bath prepared in conformity with formula 1 gives a magenta color; the absorption maximum of this color is in the correct theoretical position, viz. at 5.500 A and the color has a good transparency for the blue part of the spectrum.

FORMULA 2

A

Diethyl - para - phenylenediamine hydrochloride	grams__	4
Sodium sulfite cryst	do____	5
Sodium carbonate cryst	do____	20
Sodium hydroxide	do____	1
Water	ccm__	1000

B



grams__ 2

Acetone ccm__ 50

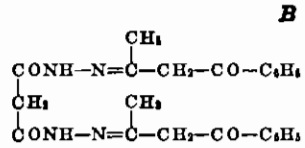
For use B is added to A.

FORMULA 3

A

3-amino-6-dimethylaminotoluene hydrochloride	grams__	4
Sodium sulfite cryst	do____	5
Potassium carbonate	do____	30
Sodium hydroxide	do____	0.5
Water	ccm__	1000

B



grams__ 2

Acetone ccm__ 60

For use B is added to A.

Organic solvents, for instance acetone, alcohols or the like, may be used to dissolve the color couplers, but as already stated the color couplers can be added to the developing bath without the intervention of organic solvents.

The invention is in no way limited to the use of the color couplers in the developing solution itself. Thus, as above stated, one of the essential products, viz. the color coupler, which during the development form the dye, can also be added to the photographic emulsion, before or after coating, for instance by adsorption upon the silver salts. The other ingredients of the color forming baths, containing chiefly the aromatic amino-developer, may be applied later, during the developing process, as a bath.

The present invention may be utilized in the formation of colored photographic images on plates or papers as well as on film, employing gelatine or other carriers for the silver halide.

The developing process may be used for the developing of photographic material provided with one or several sensitive layers, which are applied on one side or on both sides of the support.

The silver image formed during development can easily be eliminated. For this purpose a bath, of course, must be used which has no harmful effect upon the dye. Thus, a bath consisting of a solution in water of potassium ferricyanide and sodium thiosulfate easily eliminates the silver without destroying the dye.

Various changes may be made in the details described in the above specification without departing from the scope of the invention.

PIERRE BRUYLANTS.
PHILIBERT LEOPOLD JOZEF RAYMOND MERCKX.