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PROCESS OF FORMING COLORED IMAGES BY MEANS OF ARYL HYDRAZONES OF GLYOXYLIC ACID AMIDE

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This invention relates to colour photography and particularly to the production of coloured images in silver halide photographic emulsion layers.

The usual photographic developers for silver halide photographic emulsions result simply in the formation of a silver image, and if this is removed substantially no image remains. Certain types of developer, however, for example pyrogallol, used in the absence of any preservative such as sodium sulphite, not only form a silver image but also a coloured image which remains when the silver image is removed. In British Patent No. 15,055 of 1912 there is listed a large number of compounds which will develop exposed silver halide emulsions to silver images and, at the same time, form a coloured image, in situ with the silver image, which can be revealed by bleaching out the silver with, for example, Farmer's reducer.

According to the present invention a process of colour photography includes the step of forming a coloured image in a photographic emulsion layer carrying an image in a reducible silver salt by developing such image in the presence of a strong alkali and at a temperature of at least 20° C. by means of a compound of the general formula:

$$R—NH—N=CH—CO—NH_2$$

where R is a substituted or unsubstituted aromatic nucleus, and thereafter removing residual silver and silver salts from the layer.

In the preferred procedure a photographic element including a photographic emulsion layer carrying an image in a reducible silver salt is developed by treatment with an aqueous solution of the said compound containing sodium hydroxide or potassium hydroxide, followed by removal of the residual silver and silver salts.

The developing compounds employed according to this invention may be generically defined as the aryl hydrazones of the amides of glyoxylic acid. They may be produced by various methods, for example:

(*a*) An aromatic amine is diazotised and added to an ice-cold ethyl alcohol solution of cyanacetic ester in the presence of sodium acetate. A precipitate of the aryl azo cyanacetic ester usually appears, but if it does not, owing to solubility in the solvent medium, it can be thrown down by the addition of sodium carbonate. This precipitate is separated, washed and dried. The dried precipitate is then hydrolysed, for example by boiling it in two molecular equivalents of potassium hydroxide, 6% aqueous solution, for an hour or more. The product, which is an aryl hydrazone glyoxylic amide, may then be crystallised out from the aqueous solution and is preferably recrystallised from water, aqueous ethyl alcohol or

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benzene solution in the presence of decolourising carbon.

(*b*) An aryl hydrazine is condensed with dichlor acetic acid and the product methylated by treatment with dimethyl sulphate. This yields the methyl ester which in turn may be converted to the amide by treatment with concentrated ammonia.

The group R may be any aryl or substituted aryl group, e. g. a benzene, naphthalene, anthracene, phenanthrene, or anthraquinone residue which may be substituted by hydroxy, alkoxy, hydroxyalkyl, amino, substituted amino, nitro, sulphonic or carboxylic acid groups or halogen atoms. Thus, using method (*a*) aromatic amines which may be employed are, for example, aniline, o-, m- and p-chloranilines and nitroanilines, anilines substituted with two or more nitro or chlor groups, p-alkoxyanilines and p-alkylthiolanilines, naphthylamines, amino naphthol sulphonic acids, amino anthraquinones, sulphanilic and anthranilic acid.

Specific examples of developing compound according to this invention are—

Phenyl hydrazone of glyoxylic acid amide, M. Pt. 176° C.

p-Ethoxy phenyl hydrazone of glyoxylic acid amide, M. Pt. 176° C.

p-Methyl-thiol phenyl hydrazone of glyoxylic acid amide, M. Pt. 178° C.

β-Naphthyl hydrazone of glyoxylic acid amide, M. Pt. 143° C.

Variation in the substitution of the phenyl ring (i. e. the group R) has an important effect on the colour of the image obtained and some effect on the development activity. The simple phenyl hydrazone of glyoxylic acid amide combines at a high degree of development activity with the production of a yellow image, and for that reason is generally preferred.

The colour development is conveniently effected by treating the photographic element with a solution of the compound in ½ to 2% caustic soda solution for a period of 10 to 15 minutes at 23–30° C. However, these concentrations, times and temperatures are not limitative and wide variations may be made from them, though as already indicated a temperature above 20° is necessary.

While the invention may be applied to the development of any silver salt image, it is of the greatest value in the formation of colour images in situ with silver images developed from silver chloride, ferricyanide and chromate. Silver bromide and silver iodobromide latent images do not develop so easily with the developing agents of this invention.

The following example illustrates the invention:

Example

Photographic paper bearing a silver chloride emulsion, of the type commonly known as "gaslight" paper, was exposed to an object and thereafter developed for 15 minutes at 30° C. in a developing bath of the following composition:

Phenyl hydrazone of glyoxylic acid amide	gm. 3
Caustic soda	gm. 5
Water to make	litre 1

The paper was then washed, fixed in 20% hypo solution, washed again, and thereafter bathed in Farmer's reducer solution. The product carried a yellow negative image of the original object.

The invention is of particular value in the production of colour photographs by the three-colour subtractive process where the image corresponding to the record of the blue aspects of the object photographed is required to be produced as a yellow image. Moreover, by reason of the greater development activity of the developing agents of this invention for silver chloride images, as compared with silver bromide images, it is possible to process a multilayer photographic material of which one emulsion layer is silver chloride and the others silver bromide to cause development of the former without any substantial effect on the latter.

As an example of such a process the following is instanced. A multilayer photographic material is produced comprising a colourless transparent support bearing in succession (i) a red-sensitive silver bromide emulsion, (ii) a green-sensitive silver chloride emulsion, a yellow filter layer, and (iii) a blue-sensitive silver bromide emulsion. The yellow filter layer is either of the type which is resistant to ordinary development conditions or, if it is discharged under such conditions the layer contains a colourless substance which may be converted to a yellow colour (U. S. application Serial No. 667,992, filed May 7, 1946).

This material is exposed to a coloured object and developed so that negative records in silver (and complementary records in silver halide) corresponding to the red, green and blue aspects of the original object are formed in layers (i), (ii) and (iii) respectively. If the yellow filter layer has been discharged by this treatment, it is again converted to a yellow layer by the method indicated above. The material is then exposed to white light entering through the support, thus rendering the silver halide in layers (i) and (ii) developable. It is then developed first in a developer according to this invention, producing a yellow image in layer (ii), and then with an N.N.-dialkyl-p-phenylene diamine developer containing a colour-former which combines with the oxidation product of such developer to give a blue-green image in layer (i). A suitable colour-former is 2:4-dichlor-α-naphthol.

The material is then re-exposed with white light from the front, i. e. with light incident on layer (iii), and developed in an N.N.-dialkyl-p-phenylene diamine developer containing a colour-former yielding a magenta image, e. g. 1-p-nitrophenyl-3-methyl - 5 - pyrazolone. The material is then treated with Farmer's reducer, which removes the silver images, and with an agent to discharge the colour of the yellow filter layer leaving a false-colour record of the original object.

This record is printed on to a similar photographic material and similarly processed. The printed record thus obtained is a true colour record of the original object.

The foregoing process is only one example of the application of this invention, and it may be generally stated that in all known processes where a yellow image is produced by the development of a silver chloride, ferricyanide or chromate image by means of an aromatic primary amino developing agent in the presence of a colour-former which couples with the oxidation products of such developing agent, the process may be varied by forming the yellow image by the method of this invention.

What we claim is:

1. A process of colour photography which includes the step of forming a coloured image in a photographic emulsion layer carrying an image in a reducible silver salt by developing such image, in the presence of a caustic alkali and at a temperature of at least 20° C., by means of a compound of the general formula

$$R—NH—N=CH—CO—NH_2$$

where R is an aromatic nucleus, and thereafter removing residual silver and silver salts from the layer.

2. A process of colour photography which includes the step of forming a coloured image in a photographic emulsion layer carrying an image in a reducible silver salt by developing such image, in the presence of a caustic alkali and at a temperature of at least 20° C., by means of a compound of the general formula

$$R—NH—N=CH—CO—NH_2$$

where R is an aryl radical, and thereafter removing residual silver and silver salts from the layer.

3. A process of colour photography which includes the step of forming a coloured image in a photographic emulsion layer carrying an image in a reducible silver salt by developing such image, in the presence of a caustic alkali and at a temperature of at least 20° C., by means of the beta-naphthyl hydrazone of glyoxylic acid amide, and thereafter removing residual silver and silver salts from the layer.

4. A process of colour photography which includes the step of forming a coloured image in a photographic emulsion layer carrying an image in a reducible silver salt by developing such image, in the presence of a caustic alkali and at a temperature of at least 20° C., by means of the phenyl hydrazone of glyoxylic acid amide, and thereafter removing residual silver and silver salts from the layer.

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