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COLOUR PHOTOGRAPHIC PROCESS

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1 Claim. (Cl. 96—55)

This invention relates to a colour photographic process.

After the colour development step in the processing of exposed gelatino-silver halide colour photographic materials, when the desired degree of development has been attained, the colour photographic materials are usually treated in a "stop-bath" to prevent further development reaction occurring in the gelatino-silver halide emulsion layers. Such a stop-bath may consist, for example of an aqueous solution of a weakly acidic substance such as sodium bisulphite or an aqueous solution of a buffer substance, such as a phosphate buffer or an acetic acid/acetate buffer, but acid hardening stop baths such as acid solutions of alum or chrome alum which also harden the gelatine to some extent may also be used with advantage. It is known that alkaline solutions of formaldehyde are more effective as gelatine hardening agents than these acid hardening stop-baths but they do not effectively arrest development. Acid solutions of formaldehyde are not effective as gelatine hardening agents.

In our British specification No. 723,171 a process is described for the colour correction of a cyan coloured colour photographic image layer formed by exposing a light-sensitive layer containing a cyan colour former, to the light from a coloured object, colour developing to form a cyan image in the exposed parts of the layer and bleaching and fixing the developed silver, which comprises treating the layer at a stage subsequent to the colour development, with formaldehyde in the presence of a primary aromatic amine to form the leuco derivative of a masking dyestuff by reaction with the residual colour former in the unexposed parts of the layer and subsequently oxidising this leuco derivative to form the colour correcting masking dyestuff image.

The treatment with formaldehyde can be effected immediately after colour development by adding formaldehyde to the stop-bath used after the development step, and examples are given in which the formaldehyde is added to an acetic acid/sodium acetate stop-bath or, instead of a stop-bath, there is used an aqueous solution of formaldehyde and sodium carbonate. When however an alkaline solution of formaldehyde is used after the colour development step, the formaldehyde reacts with the residual developer in the photographic material to form the insoluble aldehyde-anil.

Also in British specification No. 698,046 there is described an improved process for colour correction in colour photography which comprises developing with an aromatic amine as colour developer, an exposed multilayer photographic material comprising 3 differently sensitised gelatino-silver halide emulsion layers, one such layer containing a yellow, one a magenta and the other a cyan colour former, wherein the magenta colour former is a water-soluble yellow styryl dyestuff which contains a substituent rendering the compound fast to diffusion and which is derived from a p-N-substituted-amino-benzaldehyde and a reactive methylene compound, and subsequently treating the photographic material with

a substance capable of liberating the p-N-substituted-amino-benzaldehyde from the p-N-substituted-amino-benzylidene derivative of the aromatic amine used as colour developer. As a substance capable of liberating p-N-substituted-amino-benzaldehyde, formaldehyde is mentioned and in one example the formaldehyde is added to an acetic acid/sodium acetate stop bath.

We have now found that an alkaline solution of formaldehyde containing a sulphite is not only effective in stopping development and hardening the gelatine without precipitating the developer amine as an insoluble anil but also in facilitating the formation of colour correcting masks, by the processes of British specification No. 723,171 and British specification No. 698,046.

According to our invention therefore we provide an improved colour photographic process which comprises developing with an aromatic amine as colour developer, an exposed colour photographic material comprising differently sensitised gelatino-silver halide emulsions containing colour formers, and subsequently treating the colour photographic material with an alkaline solution of formaldehyde and an inorganic sulphite.

The mixture of formaldehyde and sulphite used in the process of our invention is surprisingly more effective in arresting development than either of these two substances used separately.

The colour photographic material may contain the differently sensitised emulsions containing colour formers in different layers, for example it may be of the kind described in British specification No. 723,171 or in British specification No. 698,046, or it may contain two or more differently sensitised emulsions dispersed in the same layer.

The aromatic amine used as colour developer may be for example an N:N-dialkyl-p-phenylenediamine which may be substituted in the nucleus, such as N:N-diethyl-p-phenylenediamine, N-ethyl-N-hydroxyethyl-p-phenylenediamine and 5-diethylamino-2-amino-toluene.

As an inorganic sulphite there may be used for example sodium sulphite, which may be formed if desired in situ in the alkaline formaldehyde solution by adding sodium bisulphite to this solution.

The concentration of sulphite in the mixed solution required to completely obviate the precipitation of the anil of the developer amine will depend largely on the nature and the concentration of the developer amine, but, in general, a concentration of between 0.1% and 1% is convenient and satisfactory in practice but concentrations outside these limits may sometimes be used and the invention is not restricted to the use of such concentrations.

The concentration of formaldehyde is not critical but should be such that after reaction with the sulphite there is sufficient free formaldehyde left in solution to ensure effective hardening of the gelatine and, when desired, to form colour correcting masks, for example by the processes described in British specification No. 698,046, and British specification No. 723,171. In general satisfactory results are obtained when the quantity of formaldehyde added to the stop-bath solution is between 0.3% and 4% of the total weight of the stop-bath solution.

The alkalinity of the stop-bath solution may be adjusted as desired by the addition of sodium carbonate, or sodium bicarbonate or other buffer substances. If desired suitable restrainers such as potassium bromide can be added to the stop-bath solution. For example 20 parts of potassium bromide may be added to a solution made up by dissolving in water, 12 parts of anhydrous sodium sulphite, 25 parts of 37% aqueous formaldehyde solution, 7 parts of sodium bicarbonate and 2 parts of sodium carbonate monohydrate and the solution may be made up to 1,000 parts with water and used as a stop-bath solution. Substances which react with silver halide

such as sodium thiosulphate may also be added if desired.

The invention is illustrated but not limited by the following example in which the parts are by weight:

Example

A multilayer light sensitive material is made up as follows:

A transparent support material is coated with a layer of red sensitive gelatino-silver halide emulsion containing 10 grams per litre of the sodium salt of 1-hydroxy-2 - naphthoylamino - 2' - (N - methyl - N - octadecylamino)-benzene-5'-carboxylic acid. Upon this layer there is coated a green sensitive gelatino-silver halide emulsion containing 10 grams per litre of the sodium salt of the yellow styryl dyestuff 1-(4'-phenoxy-3'-sulpho-phenyl)-3-heptadecyl - 4 - di - (ethylcarboxymethyl) - amino - benzylidene-5-pyrazolone which serves as a magenta colour former. A layer of colloidal silver in gelatin is now coated on to act as yellow filter layer and finally as the top layer there is coated a blue sensitive gelatino-silver halide emulsion containing 10 grams per litre of the sodium salt of 3-(p-anisoylacetamido)-4-(N-methyl-N-octadecylamino)-benzoic acid. The film is exposed to the light from a coloured object and then developed in a solution of the following composition:

	Parts
p-N:N-diethylamino-aniline sulphate	2.5
Sodium sulphite, anhydrous	2
Hydroxylamine hydrochloride	1
Sodium carbonate, anhydrous	30
Potassium bromide	0.75

Water to make up to 1000 parts.

The film is then transferred to a stop bath of the following composition:

	Parts
Sodium sulphite, anhydrous	12
Formaldehyde, 37% aqueous solution	25
Sodium bicarbonate	7
Sodium carbonate	2
Potassium bromide	20

Water to make up to 1000 parts.

At this stage the hardened film contains the first developed silver, the azomethine dyestuff images in the three layers which were originally light sensitive, the yellow styryl dyestuff masking image in the magenta layer and the leuco form of the red dyestuff masking image in the cyan layer.

The material is subjected to a short wash and then transferred to a first fixing bath of the following composition:

	Parts
Sodium thiosulphate	200
Sodium sulphite, anhydrous	2
Sodium acetate	20
Acetic acid, glacial	10

Water to make up to 1000 parts.

The film is washed and the developed silver is bleached in a bleaching bath of the following composition:

	Parts
Potassium ferricyanide	100
Potassium bromide	25
Sodium dihydrogen phosphate	50

Water to make up to 1000 parts.

The film is further washed and fixed in a bath having the same composition as the first fixing bath. The film is finally washed and dried.

What we claim is:

An improved colour photographic process which comprises developing with a primary aromatic amine as colour developer, an exposed colour photographic material comprising differently sensitized gelatino-silver halide emulsions containing colour formers capable of reaction with the oxidation product of said developer to form a dye, and immediately after colour development, without intervening process steps, treating the colour photographic material with an alkaline stop-bath containing from 0.3% to 4% by weight of formaldehyde and from 0.1% to 1% by weight of an inorganic sulphite, the quantity of the inorganic sulphite in said bath being insufficient to react with all the formaldehyde therein and subsequently fixing and bleaching the colour photographic material.

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