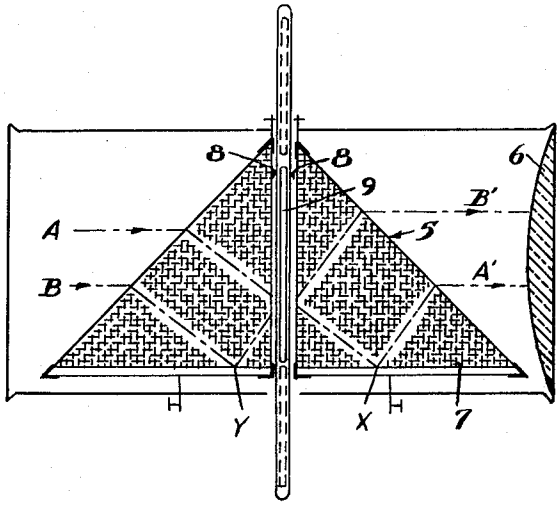
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METHOD OF DEVELOPING MULTILAYER COLOR FILMS

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Inventor
Andre Kurt Schwerin
By Fetherstonhaugh & Co.
Attorneys

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METHOD OF DEVELOPING MULTILAYER COLOR FILMS

Andre Kurt Schwerin, Montreal, Quebec, Canada, assignor to Miracol-R Ltd., Montreal, Quebec, Canada

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This invention relates to the art of colour photography and, more particularly, to the positive reproduction of coloured images directly onto sheets of opaque material coated with multi-layer emulsions commonly referred to as integral tripack.

The principal object of this invention is to make direct colour prints of the photographed object without the employment of intermediate negative or positive colour transparencies.

A further object is to provide a novel colour developing process for the multi-layer emulsion coated print material which will develop a high emulsion speed or high sensitivity in the emulsion.

A particular advantage of my colour developing process is that the emulsion coated print material may now be directly subjected to high speed exposures and then processed to produce a high degree of sensitivity in the emulsions.

Another advantage is that a high colour reproduction fidelity can be attained by subjecting the print to my developing process.

A further advantage is that the processing time, with the employment of my developing process, is greatly reduced.

A still further advantage is in a new developing process which renders excellent half-tones without any colour fog.

A still further advantage is that my new developing process renders the colour transparency films obsolete, thereby greatly reducing the cost of colour photography.

It is common practice in the art to reproduce colour prints directly onto multi-layer emulsion print material. But insofar as I am aware, this has only been accomplished with the employment of an intermediate colour transparency which serves to translate to the print material the colour image absorbed by the transparency from the original image through photographic exposure to said image.

The print material employed in the reproduction of colour prints has an opaque base of a cellulose acetate or nitrate derivative which is coated with a multi-layer emulsion consisting basically of three superimposed layers of light sensitive emulsions of well known silver halide composition. The emulsion constituting the upper layer is sensitized to bluish light by the

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introduction of a blue sensitive colorant such as oxopseudocyanine. The emulsion constituting the middle layer is sensitized to greenish light by the introduction of a green sensitive colorant such as pseudocyanine and the emulsion constituting the lower layer is sensitized to reddish light by the introduction of a red sensitive colorant such as carbocyanine. The colorants listed above are only given by way of example. These colorants were selected from an extensive list of colorants given in a standard text book. The colorants above selected are known to have the desired properties but there are other well known colorants in the list which have the desired properties in equal or lesser degrees and therefore may be substituted for the selected colorants. The emulsions have incorporated therein non-diffusing colour formers or couplers in alcoholic solutions. These non-diffusing colour formers serve to combine with oxidation products of a color developer of well known constituents having, for example, a hydrochloride salt of di-ethyl-paraphenylendiamine to form insoluble dyes when the sheet or film is subjected to a colour print developing process. The colour former employed in the blue sensitive emulsion may be, for example, an alcoholic solution of di-(benzoyl-acetic-acid) benzidine, forming a yellow dye. The colour former employed in the green sensitive emulsion may be, for example, an alcoholic solution of 1-(para-stearyl-amino-phenyl)-3 methyl-5 pyrazolene, forming a red dye, and the colour former employed in the red sensitive emulsion may be, for example, an alcoholic solution of di-(1-oxy-2-naphthoyl) benzidine, forming a blue dye.

The multi-layer emulsion print material has been in commercial use in the trade for printing from colour transparencies and are readily identifiable by persons in the trade according to their trade names. Several manufacturers are engaged in the production of the print material and although the exact formulae for producing them remain a trade secret, they all contain the basic ingredients outlined above, or their equivalents. However, since this invention is not concerned with the production of the multi-layer emulsion print material but rather with the employment of these commercial products in a novel manner, it is thought that the above description

of their basic ingredients will be sufficient for those skilled in the art to identify them.

As previously stated, the conventional colour print on the multi-layer emulsion print material is produced from colour transparencies. These transparencies generally have a high degree of colour or tone contrast ranging from 2.0 to 3.0. Consequently, the gradation of the multi-layer emulsion print material must be very slow. The sensitivity of this print material is also slow. That is to say, the light exposure of the colour transparency to the coated material must be for a relatively long period of time to permit the layers of emulsion to properly absorb the correct amount of colour from the transparency so as to reproduce as closely as possible the actual colours of the original photographed image.

By conventional processing or development of this coated print material after the image has been reproduced thereon the normal speed or sensitivity of the emulsion on the material is about the same as a medium bromide paper, that is, about 3°–4° American Standards Association. Thus, it will be seen that such a low emulsion speed or low sensitivity is not normally receptive to high speed exposures. If one were to expose such a coated print material directly, even with prolonged exposure time and to process it by ordinary known formulae, i. e., those published by various photographic manufacturers, one would obtain a picture result which would be nearly black. In prolonging the time of the bath in the first developer for as much as two hours, the multi-layer emulsion prints show an intense bluish or greenish colour fog. And, of course, with direct photographing, the pictured image, such as it is, will be laterally reversed.

The manner in which the present invention overcomes all of the above disadvantages will be more readily understood from the following detailed description, reference being had to the accompanying drawing in which—

The single figure represents digrammatically a prism according to my invention positioned before a camera lens.

My primary concern has been to devise a means whereby a colour image may be photographed directly onto a multi-layer emulsion print material of the character above described by exposure of said print material which is enclosed in any conventional camera to the colour image. The material may be arranged in camera in any conventional manner, for example, as a single exposure print or may be in the form of a plurality of prints on a roll, depending on the type of camera employed. Normally, the image produced would be laterally reversed. However, to correct this, optical adjustment is required. This is accomplished by mounting a prism 5 before the lens 6. The prism is mounted in such a way that its base 7 is parallel to the optical axis of the lens in a position to obtain the maximum angle of deviation. Thus an image before the camera will have one side designated A reflected off the prism base at point X to appear before the lens 6 in the lateral reverse position indicated A'. Similarly the other side of the image designated B will be reflected off the prism base at point Y to appear before the lens in the lateral reverse position indicated at B'. The lens will then laterally transpose the image portions designated A' and B' so that the resultant image on the multi-layer emulsion print material will correspond to the original image.

The prism employed in my invention is of a

transparent plastic composition such as polymers of methyl methacrylate, which is coloured throughout with a yellowish-brown dye of a type which is non-soluble in water, non-fading and is suitable for chromatic correction. Such a coloured prism can be made suitable for lights of different colour temperatures such as sunlight, photo flood, flashlight, etc.

It is often desirable to produce sharper chromatic definition to compensate for different colour temperatures and chromatic variations of the print material. This is normally accomplished by placing coloured gelatine filters before the lens. To accomplish the best results the prism is divided in two, as indicated at 8, so that a filter 9 may be vertically positioned between the two halves of the prism to intercept optical paths of the image passing through the prism. A conventional filter disc with a plurality of filters for different compensations arranged thereon may be mounted for rotation in any suitable manner to position any selected filter thereon between the prism halves in the optical paths of the image.

After exposure to a colour image, the multi-layer emulsion print material is then removed from the camera and is subjected to my developing process. The processing, which is of prime importance to this invention, introduces above all a new formula for the first developer which produces a very high increase of emulsion sensitivity, permitting exposure times equal to or shorter than those used with the employment of the conventional colour transparencies. For example, the speed calculated in A. S. A. degrees, for outdoor picture taking, is about 32° A. S. A. and for indoor picture taking, with photoflood lamps of 3400° Kelvin, is about 25° A. S. A. With photoflood lamps and a light level about 720 foot candles, pictures can be taken directly with a lens aperture of f:6.8 at an exposure time of one-tenth of a second. Outdoor pictures can be taken in sunlight with a lens aperture of f:8 at an exposure time of one-twenty-fifth of a second.

To obtain this high emulsion speed the composition of the formula of the first developer is listed herebelow, giving specific quantities in the left hand column with variations in the right hand column, as follows:

Water ---------- cc--	1,000	
Sodium sulphite ---------- grams--	50	±25
Hydroquinone ---------- do----	15	±5
Sodium thiocyanate ---------- do----	3.0	±0.5
Potassium bromide ---------- do----	3.5	±1.0
Sodium hydroxide ---------- do----	20	±5.0
Benzotriazole ---------- do----	0.75	±0.1
Ascorbic acid ---------- do----	0.75	±0.1
Sodium sulphate ---------- do----	15	±10

The formula will have a pH value of 12.4.

The variation of the quantity of any ingredient will bear, for the most part, a relation to the variation of the quantities of certain other ingredients.

The sodium hydroxide in the above mentioned proportion acts as a strong accelerator which produces a complete first developing in about six minutes at a temperature of 80° F. but in the conventional formulae the sodium hydroxide at the elevated temperature of the base normally produces two inconveniences. First, the softening of gelatine; second, intense colour fog. To reduce the softening of the gelatine, the quantity of sodium sulphite, which, in the conventional formulae is about 100 grs., is reduced in the present formula. Thus the oxidation products of my

developer (sulpho-quinone) which are not neutralized have the property of gelatine tanning counteracting the softening effect of the alkali.

The developing substance in the above formula is hydro-quinone, but this substance can be replaced by, for example, para-aminophenol or other reducing substances giving an elevated contrast necessary by reason of the soft gradation of the utilized material.

The formula also contains a solvent for the silver halide composition, such as silver bromide, in a relatively elevated quantity, said solvent being the sodium thiocyanate.

The principal difficulty in processing the multi-layer emulsion print material when a photograph is taken directly thereon, consists of a heavy bluish or greenish colour fog which is produced by the decomposition of a small quantity of non-insulated silver bromide in the different emulsion layers. To decrease this fog, I have added a relatively high quantity of potassium bromide to the first developer. (In the conventional developing processes the complete disappearance of colour fog has ordinarily been obtained by the addition of one or more organic compounds like para-nitrobenziminazol, or other well known compounds.) However, these organic compounds are not sufficient to produce desired results in my formula.

In my formula, I use a mixture of benzotriazole and ascorbic acid. Experience shows that the proportionate quantities given in this formula are a decisive factor. Equal portions of 0.5 gram per 1000 cc. gives only indecisive results, but with approximately 0.75 gram each per 1000 cc. the colour fog is completely obliterated. By increasing the quantities of the above mentioned mixture the result stays the same but the sensitivity of the emulsion is rapidly decreased in proportion to the excess quantities. Thus, the critical quantities of this added mixture will be 0.75 gram each per 1000 cc. At this concentration, the speed of the emulsion will not be affected. The mixture may, however, vary in proportions to the extent of ±0.1 providing that the total quantity is 1.50 grams approximately, without substantially affecting the anti-fog properties or the sensitivity of the emulsions.

After the processing in the first developer, the multi-layer emulsion material often shows certain dichroic fog produced by the solvent action of the sodium hydroxide on the silver halide composition. To prevent this kind of fog, the above formula contains an inert substance such as sodium sulphate or the like which does not enter into the developing action, but which tends to coagulate the colloidal silver as it forms. The emulsion sheet is processed in the first developer mentioned above for six minutes at 80° F. and is then introduced in a stop bath (for example, citric acid, 35 grams per 1000 cc.), and washed for one minute in a translucent tank, permitting at the same time the second exposure. After this, the sheet is processed for 6 minutes at 80° F. in a colour developer of known constituents, for example, hydrochloride salt of di-ethyl-paraphenylen-diamine. There are other colour developers containing, for example, 2-amino-5-diethyl - aminotoluene chlorhydrate. These are, however, well known in the art, and form no part of this invention beyond the necessity of employing any suitable colour developer in the completion of the printing process after the print has been subjected to my first developer process. The print is then introduced into a new stop bath, washed and the silver image formed is subsequently removed by a Farmer reducer solution in which the formed silver bromide is eliminated by a hypo bath.

This complete multi-step processing lasts only about twenty minutes as compared with the conventional developing processes in which the first developer calls for immersion periods of from 60 to 90 minutes. My processing can be done by hand or by an automatic developing machine.

From the foregoing it will be appreciated that, with the exception of the water, benzotriazole and ascorbic acid, the quantities of the ingredients should preferably be increased or decreased proportionately. Or, if not increased proportionately, certain factors must be taken into consideration. The sodium hydroxide must be in a proportion which at 80° F., will serve as a strong accelerator. The sodium sulphite must be in a proportion which when combined with the hydro-quinone will produce tanning of the gelatinous substance of the emulsions sufficient to counteract the softening effect of the sodium hydroxide. The hydro-quinone must be in a proportion which will give elevated contrast to the gradation of the emulsions. The sodium thiocyanate must be in an elevated quantity. And the sodium sulphate must be sufficient to coagulate the formation of colloidal silver in the emulsions. Thus if a formula called for maximum quantities of the remainder of the following ingredients, it would not be practical to use the specified minimum quantity of one or more of sodium hydroxide, sodium sulphite, hydro-quinone, sodium thiocyanate or sodium sulphate. The ingredient or ingredients not increased proportionately would have to be in a quantity or quantities, within the specific limits which would bring about the above outlined results.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a method of producing positive photographic colour images of opaque subjects, the steps which comprise direct exposure to an opaque subject without the medium of a color transparency of a photographic material of an opaque base carrying superimposed silver halide emulsion layers differently sensitized to blue, green and red, and containing colour formers, subjecting the exposed material to a multi-stage developing process including a first developer containing the following ingredients in the following proportions:

Water	cc.	1000
Sodium sulphite	grams	25 to 75
Hydro-quinone	do	10 to 20
Sodium thiocyanate	do	2.5 to 3.5
Potassium bromide	do	2.5 to 4.5
Sodium hydroxide	do	15 to 25
Benzotriazole	do	0.65 to 0.85
Ascorbic acid	do	0.65 to 0.85
Sodium sulphate	do	5 to 25

said photographic material being immersed in the first developer for six minutes with the temperature of said developer at 80° F. to increase to a high degree the sensitivity of the emulsions, immersing said material in a stop bath, simultaneously washing and subjecting said material to light exposure, further processing the material in a colour developer, washing in a second stop bath and then removing the silver formed in the emulsions during the first and second developer stages.

2. In a method of producing colour positive photographic colour images of opaque subjects, the steps which comprise photographically producing an image of the subject on a photographic material of an opaque base carrying superimposed silver halide emulsion layers differently sensitized to blue, green and red, and containing colour formers, subjecting the exposed material to a multi-stage developing process including a first developer containing the following ingredients in the following proportions:

Water	cc..	1000
Sodium sulphite	grams..	25 to 75
Hydro-quinone	do....	10 to 20
Sodium thiocyanate	do....	2.5 to 3.5
Potassium bromide	do....	2.5 to 4.5
Sodium hydroxide	do....	15 to 25
Benzotriazole	do....	0.65 to 0.85
Ascorbic acid	do....	0.65 to 0.85
Sodium sulphate	do....	5 to 25

said photographic material being immersed in the first developer for six minutes with the temperature of said developer at 80° F. to increase to a high degree the sensitivity of the emulsions.

3. A method according to claim 2, in which the benzotriazole and ascorbic acid are introduced as a mixture in equal proportions of 0.75 gram.

4. A method according to claim 2, in which the benzotriazole and ascorbic acid are introduced as a mixture in proportions of from 0.65 to 0.85 gram, the total quantities not exceeding 1.5 grams.

5. In a method of producing positive photographic colour images of opaque subjects, the steps which comprise photographically producing the image of the subject on photographic material of an opaque base carrying superimposed silver halide emulsion layers differently sensitized to blue, green and red, and containing

colour formers, and then subjecting said material to a multi-stage developing process, including the first developer containing the following ingredients:

Water	cc..	1000
Sodium sulphite	grams..	50
Hydro-quinone	do....	15
Sodium thiocyanate	do....	3.0
Potassium bromide	do....	3.5
Sodium hydroxide	do....	20
Benzotriazole	do....	0.75
Ascorbic acid	do....	0.75
Sodium sulphate	do....	15

said photographic material being immersed in said developer for six minutes with the temperature of the developer at 80° F.

ANDRE KURT SCHWERIN.

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