PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Process of Colour Photography

We, LEOPOLD DAMROSCH MANNES and LEOPOLD GODOWSKY, Jr., both of Kodak Park, Rochester, State of New York, United States of America, citizens of the United States of America, do hereby declare the nature of this invention to be as follows:—

This invention relates to a method of producing photographic images in colour and may be employed in connection with various processes of producing photographs in natural colours.

One of the processes to which the improved method of producing coloured images is particularly applicable is the so-called "mixed grain" process wherein the photographic element consists of the usual transparent support having on one face thereof a single emulsion made up of intermixed silver halide grains differentially sensitized to different parts of the spectrum. When a photographic element of this character is exposed in a camera, latent images recording different colour sensations in the object photographed will be formed by the differently sensitized grains of emulsion, and if the element be then processed to develop and differentially colour such images a photograph in approximately natural colours will be produced.

The improved procedure of producing coloured photographic images may be employed with advantage in colouring the respective images of this process.

The improved process is particularly applicable to the now widely used amateur motion picture processes wherein the film originally exposed in the camera is developed into a positive for use in the projector. In the practice of this process the film is exposed in the camera in exactly the same manner as an ordinary film and when processed according to the present invention, produces a positive film in substantially natural colours adapted for projection in an ordinary projecting machine without the use of colour filters, gratings, prisms, or other adjuncts difficult of operation.

The following is the improved procedure.

A suitable support—e.g. glass or film—is provided on one side with a coating of photographic emulsion composed of two batches, one of which has been sensitized to one of the two colours which are to be used to colour the resulting picture, while the other batch has been similarly sensitized to the other colour. In accordance with the particular process herein described, the emulsion to be used is divided into two substantially equal parts, and one of the parts is made sensitive to orange-red light by the application of some such dye-sensitizer as pinacyanol or naphthacyanol, and the other part is sensitized to green light by the use of a dye-sensitizer such as pinaflavol. After the emulsion is sensitized by the addition of the dye, excess dye is removed by washing, so that the emulsions when mixed will allow each separate silver halide grain to retain its own colour sensitivity unimpaired by contact or juxtaposition with a grain which has been sensitized to the opposite colour.

After each of the two parts of the batch has been separately colour-sensitized and washed as described, they are mixed together and stirred sufficiently to insure a uniform mixture of the two separate parts throughout the batch and then spread on the film or other support in a layer which need be no thicker than the ordinary emulsion layer for black and white work.

The emulsion may be prepared as above described without further treatment, but in order to get effective colour separation with the emulsion just described it is desirable that the exposure be made through a yellow filter in order to remove most of the blue-violet rays, for the reason that the dye sensitizers which make the mixed particles of the two batches of emulsion sensitive to orange-red and green, respectively, do not equally affect the normal sensitization of the silver salt to the blue-violet rays. By employing a yellow filter effective colour separation can be obtained, but the resulting picture is not in all respects a faithful reproduction of the natural colours because of the loss of the blue-

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violet component. To avoid the use of the yellow filter and the resulting loss of the blue-violet rays one preferably reduces the relative sensitivity to the blue-violet rays the batch of emulsion which has been orange-red-sensitized before mixing with the other batch.

This latter step is preferably carried out by soaking the emulsion at about 20° C. for ten minutes in a solution consisting of Indian yellow in water, to which some silver nitrate is added, the ingredients being in the following proportions:

Distilled water	-	10 ounces
Indian yellow	-	100 grains
Silver nitrate	-	2 grains

After soaking as described, the emulsion is washed with pure water until any excess is removed to thereby avoid partial reduction in sensitivity of the green-sensitized half of the emulsion when the two batches are mixed together. The Indian yellow may be used without the silver nitrate, but it is preferred to use the nitrate for the reason that the mixture of the nitrate with the Indian yellow causes the ingredients of the Indian yellow to combine more readily with the silver halide grains in the emulsion and thereby produce a more effective reduction in sensitivity than can otherwise be obtained.

To maintain equality of the photochemical characteristics of the orange-red-sensitized portion of the emulsion and the green-sensitized portion, it is preferable to similarly treat the green-sensitized part with a solution of silver nitrate and water, but this step is of course not necessary and the balance may obviously be obtained by other expedients.

The plate or film coated with the emulsion thus described is exposed in an ordinary camera for an interval depending upon the speed of the silver salt forming the emulsion, the treatment above described adding but little to the time of exposure than an untreated emulsion of the same original speed would require.

The next step in the process is to develop the film. Any suitable developer may be used for this purpose, preferably a "soft working" developer, to give detail and harmonious colour rendering.

It is also desirable that a developer be selected which produces a minimum of relief effect in the gelatin. To this end caustic alkalis should not be used. Sodium carbonate is preferable as an alkali, and as little as possible should be used. "Metol" and "glycin" are suitable as developing agents, as are also "acid amidol" developers. As will be later explained, it is essential that development at this stage be carried out completely, that is, that none of the latent images be left undeveloped.

The next step in the process is to expose the developed film to a uniform red light. By this step all of the red-sensitive particles not exposed and developed out in the original exposure and first development are exposed.

After exposure to red light, as above described, the film is treated with a colour-forming developer, that is, one which forms a coloured insoluble precipitate in the gelatin in situ with the silver image simultaneously formed. A colour-forming developer producing a blue-green colour is employed. A suitable ingredient as developing agent is dimethyl-para-phenylen-diamine-hydrochloride reacting with alpha-naphthol as coupler or indoxyl, or paraphenylene-diamine-hydrochloride with trichlor-naphthol. After this development the emulsion is well washed.

The effect of this step is to develop and simultaneously colour blue-green, the latent images formed by the exposure to red light as above described.

The next step in the process is to expose the film to white or blue-green light to thereby form latent images in the remaining unexposed particles, namely, the blue-green sensitive particles which were unaffected by the exposure to red light.

The film is then developed with an orange-red colour-forming developer, including such couplers as thio-indoxyl, or para-nitro-benzyl-cyanide with dimethyl-para-phenylene-diamine. The film is then well washed to remove the excess. Both emulsions throughout now contain both direct and reversal metallic silver images. In addition, the reversal image formed in the blue-green sensitive emulsion contains an orange-red image, while the reversal image formed in the orange-red sensitive emulsion contains a blue-green image.

The final step in the process is to dissolve out all the silver images. Any suitable solvent such as potassium ferricyanide with hypo may be used for this purpose.

The resulting picture is a true positive of the object photographed in natural colours so far as such colours can be reproduced by any two-colour process. Suppose the object photographed to be a colour card containing a section of a shade predominantly orange-red and slightly blue-green. On exposure and development both emulsions will contain silver images but the image in the blue-

green sensitive emulsion will be of an intensity corresponding to the proportion of blue-green in the colour on the colour card. Likewise the extent to which the blue-green sensitive emulsion is unexposed corresponds to the proportion of orange-red colour in the colour on the card. Hence, when this portion of the emulsion is completely exposed by exposure to white light and subsequently developed with the orange-red colour-forming developer, the resultant orange-red image will be of an intensity corresponding with the conversion effected by the second exposure only. In other words, the images which are reproduced in colour are not the images produced by the original exposure, but the images produced by the subsequent exposures to red light and white. These images are in intensity the complements of the objects in the scene photographed and must therefore be coloured respectively with the opposite colour.

The above described process is also applicable to three-colour work by utilizing an emulsion made up of three batches instead of two, the particles of each batch being sensitized to record one of the three colours.

The expression "natural colour picture" is used in the foregoing specification to mean a photographic picture of any kind including prints and projected pictures, wherein the objects appear in approximately their real colours.

Dated this 20th day of November, 1935.

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COMPLETE SPECIFICATION

Process of Colour Photography

We, LEOPOLD DAMROSCH MANNES and LEOPOLD GODOWSKY, Jr., both of Kodak Park, Rochester, State of New York, United States of America, citizens of the United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a method of producing photographic images in natural colours and may be employed in connection with various processes of producing photographs in natural colours. It is particularly useful for producing positives in colours by direct exposure in the camera.

It is known—see Seymour United States Patent No. 1,897,866—to sensitize two silver bromide emulsions with suitable green and red sensitizers and either to mix such emulsions and apply to a support or to apply the emulsions in separate layers on a support, to expose through a yellow filter which absorbs the blue violet rays, develop in an ordinary developer, then remove the developed negative silver image, treat with a chemical sensitizer, expose to light of a colour which will affect the remaining silver halide grains of only one of the emulsions, develop in a colour forming developer so chosen that the colour it forms is complementary to the colour whose value it represents, expose to light and develop similarly in another colour-forming developer and remove the silver images with a suitable solvent such as potassium ferri-cyanide with hypo.

It will be appreciated from the following description of our invention that the process of the present invention differs from this known process inter alia in that in the present process no intermediate removal of the developed negative silver image and subsequent chemical sensitizing are effected.

It is also known—see Seymour United States Patent No. 1,900,870—in a two colour photographic process involving the use of superposed differentially colour sensitized layers sensitized to green and red, after exposure in an ordinary camera using a yellow colour filter to screen out the blue violet portion of the spectrum, to develop in an ordinary developer, wash, expose to a red light, develop in a blue green colour forming developer, wash, expose to a white light, develop in a red colour forming developer, wash and remove the silver images by bleaching, fix in hypo and wash.

The present process is distinguished from that process inter alia in that in the present process differentially colour sensitized superposed layers are not employed.

The process to which the improved method of producing coloured images is applicable is the so-called "mixed grain" process wherein the photographic element consists of the usual transparent support having on one face

thereof a single emulsion made up of intermixed silver halide grains differentially sensitized to different parts of the spectrum. When a photographic light sensitive material of this character is exposed in a camera, latent images recording different colour sensations in the object photographed will be formed by the differently sensitized grains of emulsion, and if the material be then processed to develop and differentially colour such images a photograph in approximately natural colours will be produced.

The improved procedure of producing coloured photographic images is employed with advantage in colouring the respective images in this process.

The improved process is particularly applicable to the now widely used amateur motion picture processes wherein the film originally exposed in the camera is developed into a positive for use in the projector. In the practice of this process the highly sensitive film is exposed in the camera in exactly the same manner as an ordinary film and when processed according to the present invention, produces a positive film in substantially natural colours adapted for projection in an ordinary projecting machine without the use of colour filters, gratings, prisms, or other adjuncts difficult of operation.

The method of the invention of producing a colour photograph in natural colours comprises exposing to a light image a photographic light sensitive material comprising mixed sets of differentially sensitized grains sensitized to cover substantially the visible spectrum, developing said sensitive material in an ordinary photographic developer without fixing, exposing the sensitive material to light of a colour which affects one only of the set of differentially sensitized grains, developing in a colour forming developer to produce a colour complementary thereto and similarly exposing the sensitive material to light of another colour and developing again in another complementary colour forming developer, and so on, for any more of the sets of differentially sensitized grains and finally dissolving out all the original silver images and the silver images produced by the colour forming developers.

In carrying out the improved procedure, one proceeds as follows:

A suitable support—e.g. glass or film—is provided on one side with a coating of a highly sensitive photographic emulsion composed of two batches, one of which has been sensitized to one of the two colours which are to be used to colour the resulting picture, while the other batch has been similarly sensitized to the other colour. In accordance with the particular process herein described, the emulsion to be used is divided into two substantially equal parts, and one of the parts is made sensitive to orange-red light by the application of some such dye-sensitizer as pinacyanol or naphthacyanol and the other part is sensitized to green light by the use of a dye-sensitizer such as pinaflavol. After the emulsion is sensitized by the addition of the dye, excess dye is removed by washing, so that the emulsions when mixed will allow each separate silver halide grain to retain its own colour sensitivity unimpaired by contact or juxtaposition with a grain which has been sensitized to the opposite colour.

After each of the two parts of the batch has been separately colour-sensitized and washed as described, they are mixed together and stirred sufficiently to insure a uniform mixture of the two separate parts throughout the batch and then spread on the film or other support in a layer which need be no thicker than the ordinary emulsion layer for black and white work. It will be noted that the emulsions are highly sensitive and particularly suitable for rapid camera exposures. The emulsions do not contain any colour formers.

In order to get effective colour separation with the emulsion just described in accordance with one feature of the invention the batch of emulsion which has been red-sensitized before mixing with the other batch is dyed to reduce the effective sensitiveness of the emulsion to blue-violet rays.

This dyeing step is preferably carried out by soaking the emulsion at about 20° C. for ten minutes in a solution consisting of Indian yellow in water, to which some silver nitrate is added, the ingredients being in the following proportions:

Distilled water	-	10 ounces
Indian yellow	-	100 grains
Silver nitrate	-	2 grains

After soaking as described, the emulsion is washed with pure water until any excess of the dye is removed to thereby avoid partial dyeing of the green-sensitized half of the emulsion when the two batches are mixed together. The Indian yellow may be used without the silver nitrate, but it is preferred to use the nitrate for the reason that the mixture of the nitrate with the Indian yellow causes the ingredients of the Indian yellow to combine more readily with the

silver halide grains in the emulsion and thereby produce a more effective reduction of the relative sensitivity to blue light than can otherwise be obtained.

To maintain equality of the photochemical characteristics of the red-sensitized portion of the emulsion and the green-sensitized portion, it is preferable similarly to treat the green-sensitized part with a solution of silver nitrate and water, but this step is of course not necessary and the balance may obviously be obtained by other expedients.

The gelatin can be tanned in any of the usual ways, either before this solution is mixed with the emulsion or after mixing.

In producing colour photographs the plate or film coated with the light emulsion material thus described is exposed in an ordinary camera, the treatment above described adding but little more to the time of exposure than an untreated emulsion of the same original speed would require.

The next step in the process is to develop the film. Any suitable developer may be used for this purpose, preferably a "soft working" developer, to give detail and harmonious colour rendering.

It is also desirable that a developer be selected which produces a minimum of relief effect in the gelatin. To this end caustic alkalis should not be used. Sodium carbonate is preferable as an alkali, and as little as possible should be used. "Metol" and "glycin" are suitable as developing agents, as are also "acid amidol" developers. As will be later explained, it is essential that development at this stage be carried out completely, that is, that none of the latent images be left undeveloped.

The next step in the process is to expose the developed film to a uniform red light. By this step all of the red-sensitive particles not exposed and developed out in the original exposure and first development are exposed.

After exposure to red light, as above described, the film is treated with a colour forming developer, that is, one which forms a coloured insoluble precipitate in the gelatin in situ with the silver image simultaneously formed. A colour forming developer producing a blue-green colour is employed. A suitable ingredient as developing agent is dimethyl-para-phenylen-diamine-hydrochloride reacting with alpha-naphthol as coupler or indoxyl, or para-phenylene-diamine-hydrochloride with trichlor-naphthol. After this development the emulsion is well washed.

The effect of this step is to develop and simultaneously colour blue-green, the latent images formed by the exposure to red light as above described.

The next step in the process is to expose the film to white or blue-green light to thereby form latent images in the remaining unexposed particles, namely, the blue-green sensitive particles which were unaffected by the exposure to red light.

The film is then developed with an orange-red colour forming developer, including such couplers as thio-indoxyl, or ortho-nitro-benzyl cyanide with dimethyl-para-phenylene-diamine. The film is the well washed to remove the excess. Both emulsions throughout now contain both direct and reversal metallic silver images. In addition, the reversal image formed in the glue-green sensitive emulsion contains an orange-red image, while the reversal image formed in the orange-red sensitive emulsion contains a blue-green image.

The final step in the process is to dissolve out all the silver images. Any suitable solvent such as potassium ferricyanide with hypo may be used for this purpose.

The resulting picture is a true positive of the object photographed in natural colours so far as such colours can be reproduced by any two-colour process. Suppose the object photographed to be a colour card containing a section of a shade predominantly orange-red and slightly blue-green. On exposure and development both emulsions will contain silver images but the image in the blue-green sensitive emulsion will be of an intensity corresponding to the proportion of blue-green in the colour on the colour card. Likewise the extent to which the blue-green sensitive emulsion is unexposed corresponds to the proportion of orange-red colour in the colour on the card. Hence, when this portion of the emulsion is completely exposed by exposure to white light and subsequently developed with the orange-red colour forming developer, the resultant orange-red image will be of an intensity corresponding with the conversion effected by the second exposure only. In other words, the images which are reproduced in colour are not the images produced by the original exposure, but the images produced by the subsequent exposures to red light and white. These images are in intensity the complements of the objects in the scene photographed and must therefore be coloured respectively with the opposite colour.

The process as applied to three-colour work will now be described.

A suitable support—e.g. glass or film—is provided on one side with a coating of photographic emulsion composed of three sets of grains which are sensitive to the three primary colours, blue, green and red respectively. In accordance with the particular process herein described, the emulsion to be used is divided into three batches of substantially equal parts, and one of the parts is made sensitive to red light by the application of a red sensitizer and another part is sensitized to green light by the use of a green sensitizer. After the two batches of emulsion have been sensitized by the addition of the respective sensitizers, excess sensitizer is removed by washing so that when the emulsions are mixed each separate silver halide grain will retain its own colour sensitivity unimpaired by contact or juxtaposition with a grain which has been sensitized to another colour. The batch which has not been colour sensitized is intended to record the blue component.

The three batches are mixed together and stirred sufficiently to insure a uniform mixture thereof and then spread on the film or other support in a layer which need be no thicker than the ordinary emulsion layer for black and white work. The emulsions contain no colour formers.

The two batches which have been colour sensitized may be treated with a yellow dye, for example as described above in the previous example, in order to render these batches effectively insensitive to blue light.

The first step in processing the film is to develop it in any suitable ordinary developer as in the previous example.

The next step is to expose the developed film to a uniform red light. By this step the red-sensitive particles not exposed and developed out in the original exposure and first development are exposed.

After exposure to red light, as above described, the film is treated with a blue-green colour forming developer. A suitable ingredient as developing agent is diethyl-para-phenylene-diamine-hydrochloride with alpha-naphthol as coupler, or indoxyl, or para-phenylene-diamine-hydrochloride with trichlornaphthol. For example, the following developer may be used:

Solution A.

Water	1 litre
Sodium carbonate	10 grm.
Sodium sulphite	5 grm.
Diethyl *p*-phenylene diamine hydrochloride	2 grm.

Solution B.

2:3:4 trichlor alpha naphthol	1 grm.
Methanol	150 ccs.

For use take Solution A 100 ccs. and add thereto 15 ccs. of Solution B. After this development the element is well washed.

The effect of this step is to develop to silver and simultaneously colour blue-green the latent images formed by the exposure to red light as above described.

The next step in the process is to expose the film to green light.

The film is then developed with a magenta colour forming developer such as:

Solution C.

Sodium carbonate	20 grm.
Sodium sulphite	5 grm.
Diethyl *p*-phenylene diamine hydrochloride	10 grm.
Potassium bromide (molar solution)	2 ccs.
Water to	1 litre

In 100 ccs. of this Solution C is dissolved 0.05 grm. of the bromo-thio-indoxyl.

The next step after washing is to expose the film to white or blue light. The film is then developed in a yellow colour forming developer, which, for example, can be made by taking 100 ccs. of the Solution C used for the magenta developer and adding thereto 0.1 grm. benzoyl acetone dissolved in 5 cc. of ethyl alcohol. The film is then well washed to remove the excess. The three emulsions throughout now contain both direct and reversal metallic silver images. In addition, the reversal image formed in the green sensitive emulsion contains a magenta image, while the reversal image formed in the red sensitive emulsion contains a blue green image and the reversal image formed in the blue sensitive emulsion contains a yellow image.

The final step in the process is to dissolve out all the original silver images and the silver images produced by the colour forming developer. Any suitable solvent such as potassium ferri-cyanide with hypo may be used for this purpose.

The resulting picture is a true three colour positive of the object photographed in natural colours.

The expression "natural colour picture" is used in the foregoing specification to mean a photographic picture of any kind including prints and projected pictures, wherein the objects appear in approximately their real colours.

Having now particularly described and ascertained the nature of our said inven-

tion and in what manner the same is to be performed, we declare that what we claim is:—

1. A method of producing a colour photograph in natural colours which comprises exposing to a light image a photographic light sensitive material comprising mixed sets of differentially sensitized grains, sensitized to cover substantially the visible spectrum, developing said sensitive material in an ordinary photographic developer without fixing it, exposing the sensitive material to light of a colour which affects one only of the sets of differentially sensitized grains, developing in a colour forming developer to produce a colour complementary thereto and similarly exposing the sensitive material to light of another colour and developing again in another complementary colour forming developer and so on for any more of the sets of differentially sensitized grains and finally dissolving out all the original silver images and the silver images produced by the colour forming developers.

2. A method of producing colour photographs in natural colours according to claim 1 in which three sets of differentially sensitized grains respectively sensitive to the three primary colours blue, green and red are employed.

3. Method according to either of claims 1 or 2 in which the grains not intended to record the blue component are treated to reduce their effective sensitivity to blue for example by staining with a yellow dye.

Dated this 10th day of December, 1935.

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