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C. BUTEMENT

2,197,994

COLOR PHOTOGRAPHY

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Fig. 1.

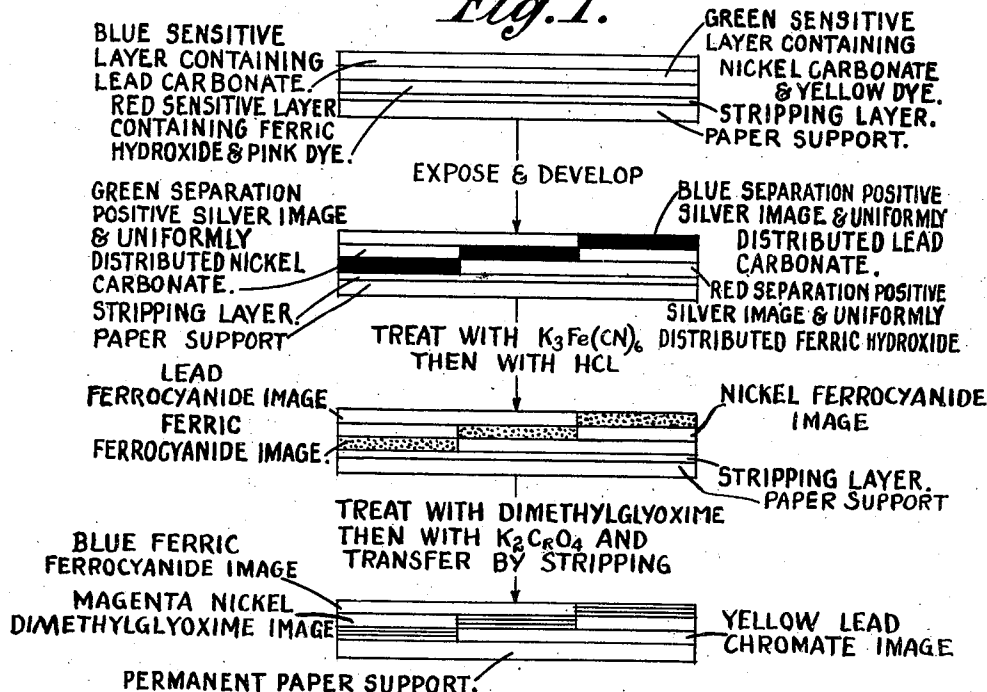


Fig. 2.

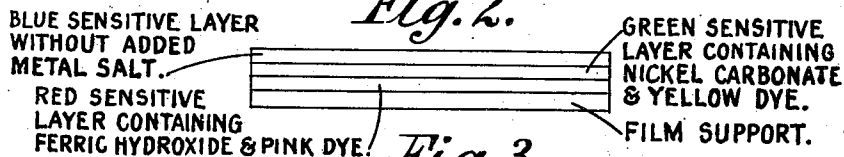


Fig. 3.

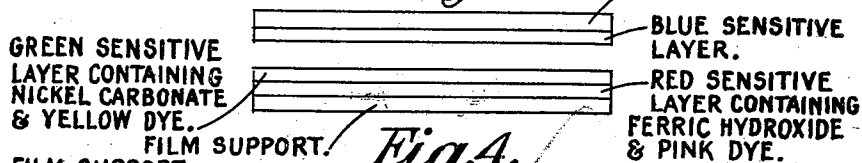


Fig. 4.

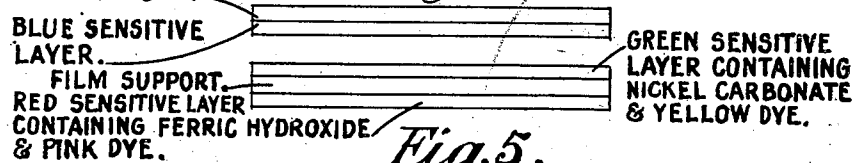
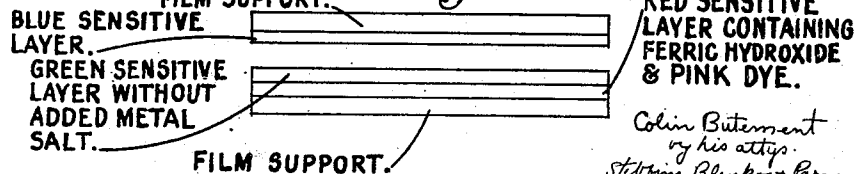


Fig. 5.



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UNITED STATES PATENT OFFICE

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COLOR PHOTOGRAPHY

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3 Claims. (Cl. 95—2)

This invention consists in improvements in or relating to color photography and has for its object the provision of a new or improved light sensitive material which may be used either for taking or for copying and which may be processed to produce an image in color and more particularly, in magenta. A further object of the invention is to provide a method of processing the new or improved material. Still further objects are the provision, in one form of the invention, of new or improved light sensitive material which may be processed, after exposure, to produce an additional colored image or images which combine with the magenta image to give a multi-color photograph and the provision of a method of processing this form of the material.

It is already known to incorporate in a silver halide emulsion layer organic color formers which react during development of the silver image by a suitable developer with the products of development to produce dyed gelatine images. It has also been proposed to provide light sensitive material for use in the production of multi-color photographs consisting of three super-imposed layers of emulsion sensitised respectively to light covering the three wave-length regions customary in the three-color process and each containing a color former of the kind described above and so selected that on development and bleaching of the silver images colored images are produced in the three subtractive primary colors.

Further, it is known that colored images may be produced by treating the silver salts produced by bleaching a silver image with solutions of certain metal salts which react with the silver salts to produce colored metal compounds. The metals and the salts of them which may be used to produce the desired colors are well known.

The present invention provides light sensitive photographic material for use in the production of colored images, comprising a silver halide emulsion layer carried on a support and containing a nickel compound (such as nickel carbonate or nickel hydroxide) which is substantially inert to the silver halide but which may, by chemical treatment after exposure, development and bleaching of the silver halide, be converted to one of the salts of nickel which is known to react with the silver salts produced by bleaching the silver image to provide a reaction product which is colored or may, by further treatment, be converted into a colored product.

The invention also provides light sensitive photographic material for use in the production of

colored images comprising a plurality of light sensitive layers carried on a support and sensitised to different regions of the spectrum, each layer containing a compound of one of the known metals hereinbefore referred to which is substantially inert to the silver halide but which may, by chemical treatment after exposure, development and bleaching of the silver halide, be converted to a compound of the metal which is known to react with the silver salts produced by bleaching the silver image to provide a reaction product which is colored or may, by further treatment, be converted into a colored product, the metal compounds originally incorporated in the layers being selected to provide products of different colors, and one of the compounds being a compound of nickel. In a preferred form of the invention, there are three emulsion layers containing metal compounds sensitised respectively to light of the three wave-length regions customary in the three-color process and the metal compounds are so selected that the images which they produce are in colors complementary to the wave-length regions to which their respective emulsion layers are sensitised.

In one form of a multi-color material according to the invention, the metal compounds initially added are such that they are all converted to salts which will react with the silver salts by treatment of the material with a single solution.

The invention includes the method of treating photographic material as described above which has been exposed and developed to form a colored picture which comprises the steps of bleaching the silver image or images, converting the metal compound or the metal salt in each layer when there is more than one layer containing the metal compound, into a salt of the metal which will react with the silver salts produced by bleaching the silver image to provide a reaction product which is colored or may, by further treatment, be converted into a colored product and allowing or causing the salts to react in that way.

The material according to the invention may be used for taking in the camera or it may be used for printing and, with the selection of suitable metal salts, it may be arranged to provide all the images in two, three or four color processes or it may be arranged to provide only some of the images and other processes be relied upon to provide the remaining images. The further description of the invention will be directed to the application of it to three-color processes.

In the preferred form of this application of

the invention the material consists of three emulsion layers sensitised to red, green and blue respectively applied in the order stated to a support, the red-sensitive emulsion containing a pink water-soluble dye such as acid magenta and a metal compound which upon subsequent treatment forms the blue constituent of the finished print, the green-sensitive emulsion containing a yellow water-soluble dye such as auramine and a metal compound which upon subsequent treatment forms the magenta constituent of the finished print and the blue-sensitive emulsion layer containing a metallic compound which upon subsequent treatment forms the yellow constituent of the finished print. The dyes may, if desired, be contained in separate layers applied to the sensitised emulsion layers instead of being incorporated in said emulsion layers.

The metal compound in the blue-green image emulsion layer (i. e., the red-sensitive emulsion) may be a ferric compound, e. g., ferric hydroxide or ferric carbonate; the metal compound in the magenta image emulsion layer (i. e., the green-sensitive emulsion) may be a nickel compound, e. g., nickel carbonate or nickel hydroxide, while the metal compound in the yellow image layer may be a lead salt such as lead carbonate.

After exposure of the coated support under suitable conditions, the print is developed as in normal black and white printing, fixed and then bleached. The metal compounds in the sensitive layers are thereafter converted to compounds which are blue, magenta and yellow respectively and the print may then be stripped from its support and applied to another support with the colored layers in the reversed sequence.

Following is a description by way of example of one method of carrying the invention into effect in the production of a colored print from a three-color mosaic negative transparency. The method is illustrated in Figure 1 of the accompanying diagrammatic drawing which shows the print, in section, at four stages in the method and sets out briefly the intermediate process steps.

The paper or other support is first coated with a stripping layer and then with a layer of emulsion sensitised to red (for example with Dicyanin or Pinacyanol). This layer also contains a proportion of ferric hydroxide and a pink, water-soluble, dye acid magenta. A second layer of emulsion sensitised to green (for example with Pinaverdol or Erythrosin) and containing a proportion of nickel carbonate and a yellow water-soluble dye such as auramine is applied to the first and this is followed by a blue-sensitive emulsion layer containing a proportion of lead carbonate. The coated material is shown at the first stage in Figure 1. The proportions of ferric hydroxide, nickel carbonate and lead carbonate added to the layers are just sufficient to convert all the silver salts by the treatment later described.

The composite printing sensitive material is exposed in contact with the multi-color transparency and upon development of the print three positive images will be formed, one in each layer of the emulsion and each recording only one color of the transparency. This composite print which is shown diagrammatically at the second stage in Figure 1, and at this stage is black and white, is fixed, washed as in the normal black and white process, is then bleached in a ferricyanide bath which converts the silver in each of the layers into silver ferrocyanide and washed

and dried. The print is then treated with dilute hydrochloric acid which converts the ferric hydroxide in the bottom layer into ferric chloride and this combines with the silver ferrocyanide in this layer to form a blue image of ferric ferrocyanide. Simultaneously, the nickel carbonate in the second layer is converted to soluble nickel chloride which forms nickel ferrocyanide with the silver ferrocyanide in this layer. After washing, this is converted to the magenta nickel dimethylglyoxime by treatment with a solution of the composition given later of dimethylglyoxime and triethanolamine. The print is then treated with a solution of potassium chromate which converts the lead ferrocyanide in the top layer into yellow lead chromate. The print is now at the third stage shown in Figure 1. The print may then be transferred to a permanent base and the original paper support stripped off, as shown at the fourth stage in Figure 1.

The light used for printing is obtained from a discharge lamp of the kind shown under the registered trade-mark "Osira." The lamp provides light which, in addition to the normal mercury vapour spectrum giving prominent lines in the green and blue region, embodies the spectrum of cadmium vapour giving the well known cadmium red line. The composite radiation from the lamp is filtered by the use of a didymium-chloride liquid filter or a glass filter which has the same property of absorbing radiation wavelength bands in regions where there may be excessive overlap in the spectral transmission of the primary filter elements of the mosaic screen. Exposure is carried out in one of three ways. The light produced by the lamp may be arranged after passing through the filter to illuminate diffusely the original and copy materials in contact, or successive exposures varying in time may be made incorporating successively standard commercial tri-chromatic filters between the filter described above and the master transparency or a rotating filter disc can be used between the filter described above and the master, the disc being provided with tri-chromatic filters selected as to their dimensions or densities to give the desired relative exposures.

In a modified form of the process described in the above example, the uppermost layer (the blue-sensitive yellow image layer) consists of a normal emulsion with no added metal salt as shown in Figure 2, the image being toned yellow by any suitable yellow toner. For example, a lead salt may be introduced into the layer and then converted to a yellow image by first converting the silver image to silver ferrocyanide and then converting it to lead ferrocyanide by treatment in the following solution of a soluble lead salt:

Lead acetate.....	gms..	40
Glacial acetic acid.....	ccs..	100
Water to make.....	ccs..	1000

The material is then washed well and treated in a 1% solution of potassium chromate to convert the lead ferrocyanide to yellow lead chromate.

Alternatively, the silver ferrocyanide may be treated with a 2% solution of mercuric potassium iodide to convert it to the yellow mercury salt. As the layer of mercury salt is somewhat opaque it is generally desirable, when this process is used, to transfer the entire print to a fresh support so that the blue layer is on top and the yellow at the bottom.

In a further modified form of the above ex-

ample the red-sensitized layer containing ferric hydroxide and the green-sensitized layer containing nickel carbonate are coated on one support and the blue-sensitive layer is coated on a separate support. The red- and green-sensitized layers may either be coated on the same side of the support as shown in Figure 3, in which case the emulsions should be well washed after sensitizing to remove surplus dye and to prevent wandering of the dyes, or the layers may be coated on opposite sides of the support as shown in Figure 4.

After exposure, the red- and green-sensitized layers are treated as before by development, fixing, bleaching in a ferricyanide bath to form silver ferrocyanide, and bathing in hydrochloric acid to convert the ferric hydroxide to ferric chloride, which combines with the silver ferrocyanide in its layer to form blue ferric ferrocyanide, and also to convert the nickel carbonate to nickel chloride, which forms nickel ferrocyanide in its layer. The nickel ferrocyanide is then as before, converted to nickel dimethylglyoxime to give blue and magenta images respectively in the two layers.

The independent blue-sensitive layer is developed and toned yellow by any convenient means, such as those described above and the combined blue and magenta images are then secured to the yellow image to provide the complete picture.

It is preferred to use silver chloride emulsions for the several layers which contain metal salts but silver bromide emulsions may be used and when a separate blue-sensitive layer is used and is toned yellow, it is convenient to use a bromide emulsion for this layer.

According to another example of the invention, a red-sensitized layer containing ferric hydroxide is coated on a support as described above and on top of this is coated a green-sensitized layer without added metal salt as shown in Figure 5. The blue-sensitized layer is applied to a separate support and is treated as described above.

After exposure, the red- and green-sensitized layers are developed, fixed and bleached in a ferricyanide bath as before. The layers are then treated for about 5 minutes in a bath of:

Parts by weight

Saturated chrome alum solution.....	90
Hydrochloric acid (sp. gr. 1.16).....	10
Nickel chloride solution (20%).....	40

The treatment in this solution converts the image in the bottom layer to blue ferric ferrocyanide as before and converts the silver ferrocyanide in the upper layer to nickel ferrocyanide.

The layers are then treated in a bath of:

Parts by weight

Dimethylglyoxime.....	2
Triethanolamine.....	200
Water.....	800

This bath converts the nickel ferrocyanide to the magenta nickel dimethylglyoxime and after clearing in a 1% acetic acid bath and fixing in hypo to remove any remaining silver salts the two layers are transferred to the yellow toned third layer.

As stated above the color filters appropriated to the red-sensitive layer and to the green-sensitive layer may be contained as water-soluble dyes in separate layers applied to the respective emulsion layers, and the layers containing the

dyes may contain compounds which act as precipitating agents for the metallic compounds in contiguous layers, thus preventing the wandering of the metallic compounds from one layer to another.

Although the production of color prints from a colored mosaic transparency developed as a negative has been described above, prints may also be made by reversal from a transparency developed as a normal positive. Further, the invention, in its application to the production of copies, is not restricted to the copying of mosaic additive transparencies but may be applied to the copying of subtractive images.

It will be understood that by the use of a transparent yellow the process may be applied to the printing of transparent positives, e. g., for cinematograph films.

The multilayer film made in accordance with the invention may be exposed in a camera and developed as a negative in complementary colors to the original subject. Prints may then be made on the same material by direct contact or projection printing.

I claim:

1. The method of producing a multi-colored photograph from light sensitive photographic material composed of a support and at least three inseparably superposed light sensitive silver halide emulsion layers which have been exposed to record, respectively, red, green and blue aspects of the subject and which respectively contain a ferric compound, a nickel compound and a lead compound which comprises the steps of developing all the layers to produce silver images, converting all the silver images to silver ferrocyanide, treating the material with hydrochloric acid to convert the ferric compound into ferric chloride, the nickel compound into nickel chloride, and the lead compound into lead chloride, allowing the ferric, nickel and lead chlorides to react with the silver ferrocyanide in their respective layers to produce blue ferric ferrocyanide, nickel ferrocyanide and lead ferrocyanide, treating the material with dimethylglyoxime to convert the nickel ferrocyanide to magenta nickel dimethylglyoxime and treating the material with potassium chromate to convert the lead ferrocyanide to yellow lead chromate.

2. The method of producing a multi-colored photograph which comprises making separation records of the red, green and blue aspects of the subject by exposing light sensitive photographic material having at least three appropriately color sensitive silver halide emulsion layers inseparably carried on a support and containing respectively a ferric compound, a nickel compound and a lead compound, developing the exposed layers to form silver images, converting all the silver images to silver ferrocyanide, treating the material with hydrochloric acid to convert the ferric compound into ferric chloride, the nickel compound into nickel chloride, and the lead compound into lead chloride, allowing the ferric, nickel and lead chlorides to react with the silver ferrocyanide in their respective layers to produce blue ferric ferrocyanide, nickel ferrocyanide and lead ferrocyanide, treating the material with dimethylglyoxime to convert the nickel ferrocyanide to magenta nickel dimethylglyoxime and treating the material with potassium chromate to convert the lead ferrocyanide to yellow lead chromate.

3. The method of producing a multi-colored photograph from light sensitive photographic

material composed of a support and at least three inseparably superposed light sensitive silver halide emulsion layers which have been exposed to record, respectively, red, green and blue aspects of the subject and which contain respectively ferric hydroxide, nickel carbonate and lead carbonate, which comprises the steps of developing all the layers to produce silver images, converting all the silver images to silver ferrocyanide, treating the material with hydrochloric acid to convert the ferric hydroxide into ferric chloride, the nickel carbonate into nickel chlo-

ride, and the lead carbonate into lead chloride, allowing the ferric, nickel and lead chlorides to react with the silver ferrocyanide in their respective layers to produce blue ferric ferrocyanide, nickel ferrocyanide and lead ferrocyanide, treating the material with dimethylglyoxime to convert the nickel ferrocyanide to magenta nickel dimethylglyoxime and treating the material with potassium chromate to convert the lead ferrocyanide to yellow lead chromate.

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