

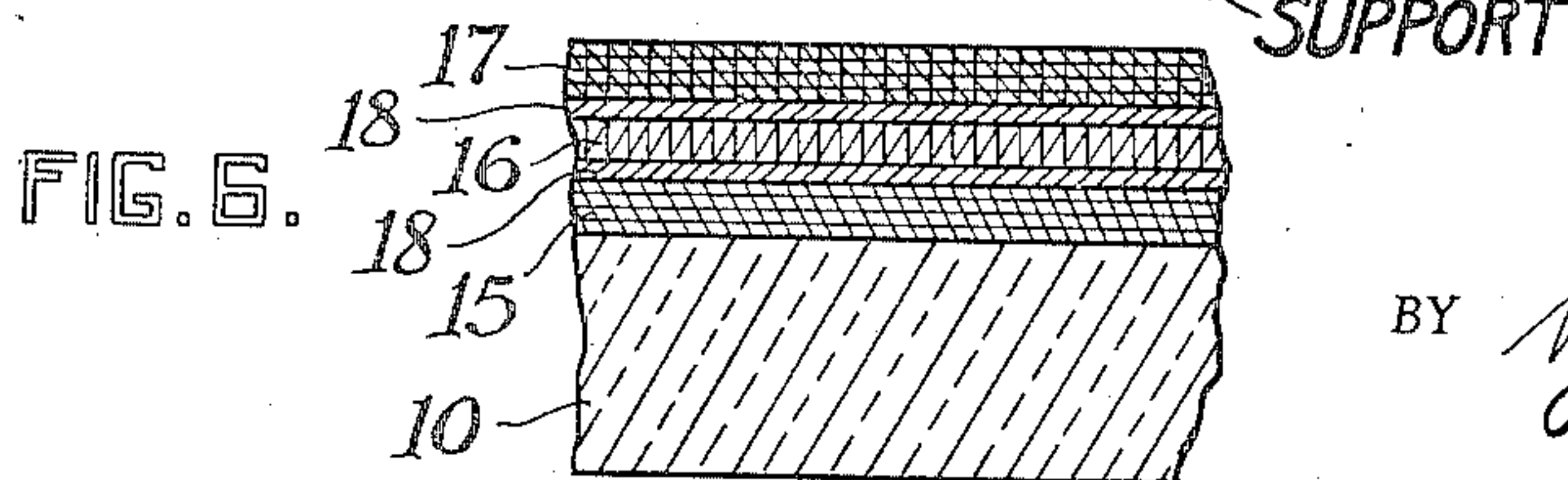
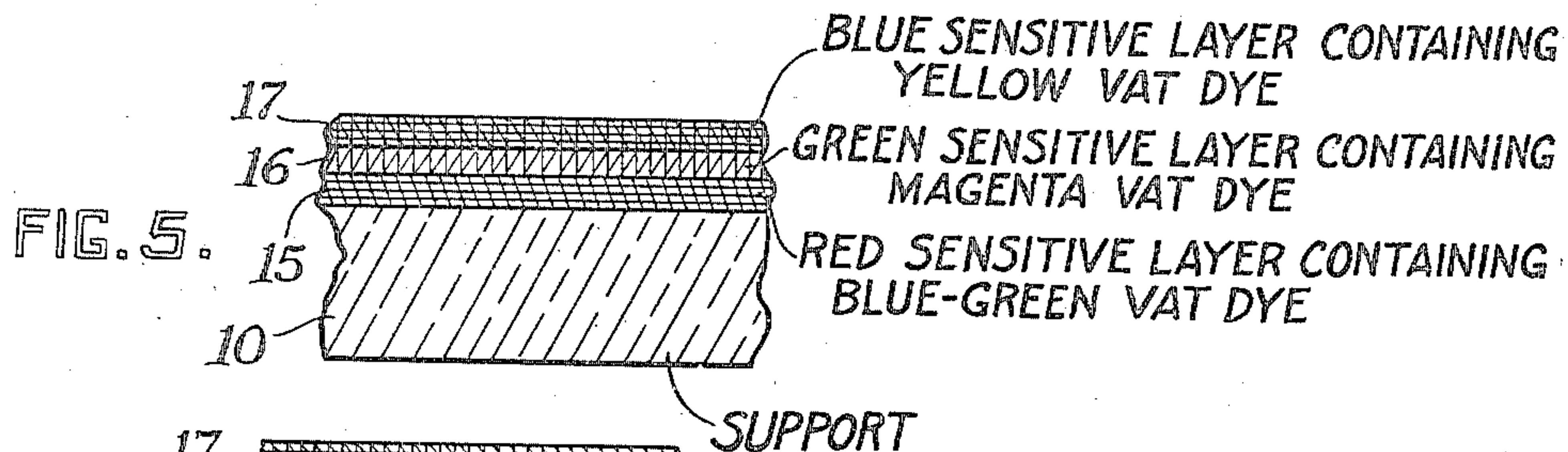
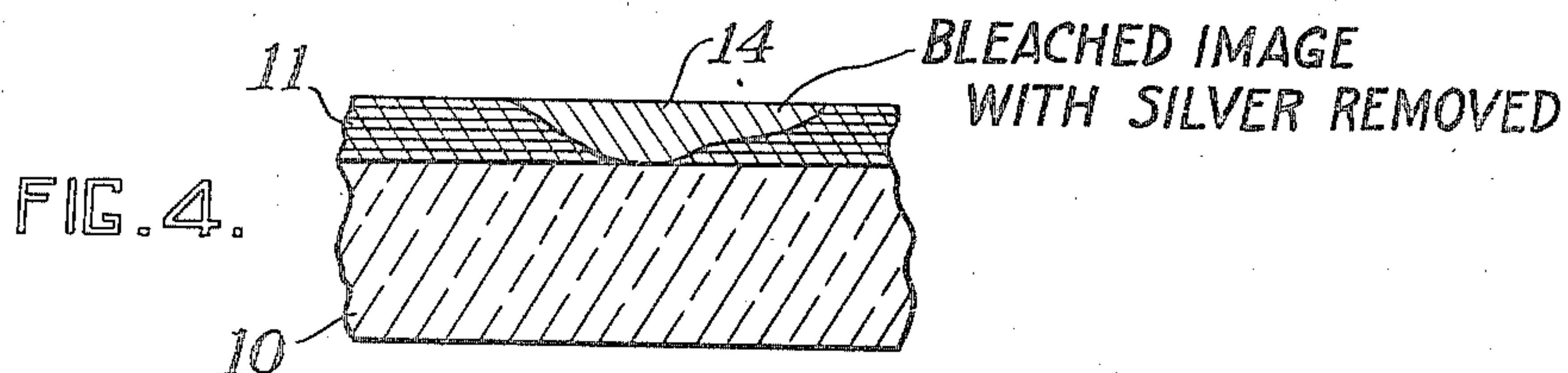
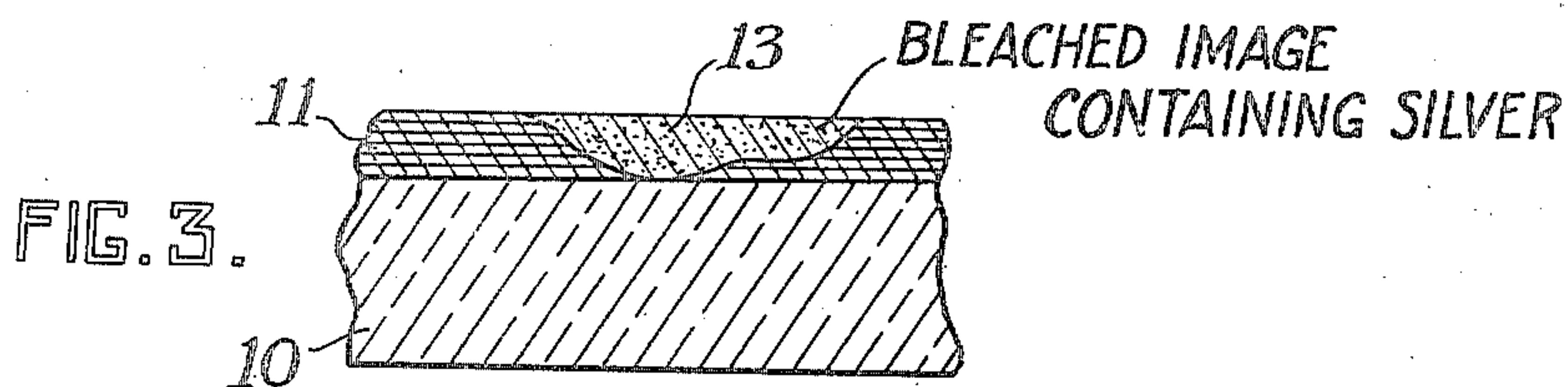
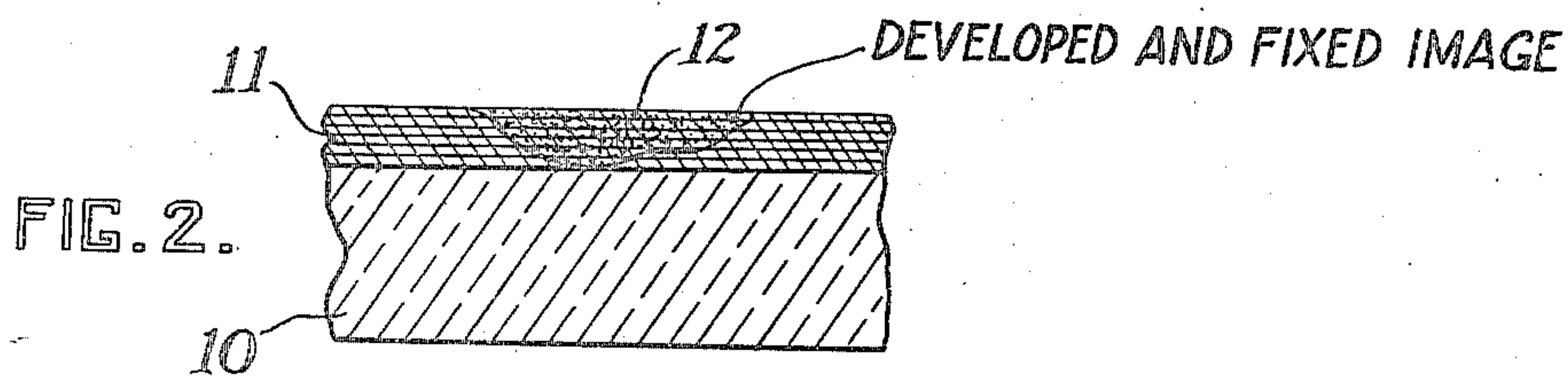
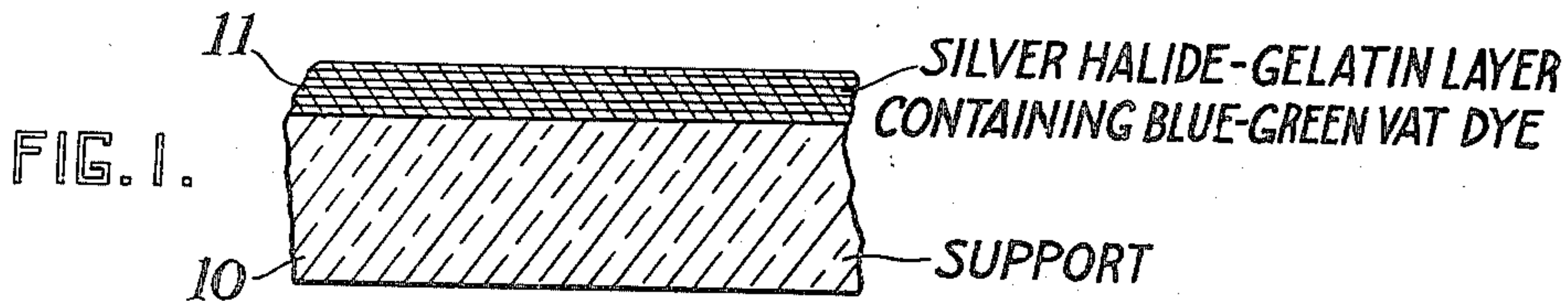
Dec. 19, 1939.

M. W. SEYMOUR

2,184,022

COLOR PHOTOGRAPHY

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## UNITED STATES PATENT OFFICE

2,184,022

## COLOR PHOTOGRAPHY

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## 10 Claims. (Cl. 95-8)

This invention relates to color photography and particularly to a method for producing natural color pictures.

It is known that colored images may be formed in gelatin layers sensitized with silver salts and colored with dyes which may be reduced to colorless compounds in the presence of a silver image. A process of this type is described in the U. S. patent to Christensen, No. 1,517,049, granted November 25, 1924. After formation of a silver image by exposure, development, and fixation, the layer is treated with a reducing agent such as sodium hydrosulfite or stannous chloride which decolorizes the dye at the places where a silver image was formed. The dye remaining in the other portions of the gelatin layer thereby forms a colored image.

According to one form of the Christensen process for producing pictures in natural colors, a support is coated with three superimposed emulsion layers. Each layer is sensitized for one of the primary colors of white light, and is dyed the complementary color. That is, the image-forming dye in each layer absorbs light of the color for which the same layer is sensitized. This is the only relation of color and sensitivity which permits making a picture in natural colors by exposure directly to a colored subject or to another picture in natural colors followed by the processing method described by Christensen. It has therefore been called the "natural order" of color and sensitivity. The only coloring dyes disclosed in the Christensen patent are water-soluble polyazo dyes (dianil dyes). In the use of soluble azo dyes with the natural order of sensitivity, certain difficulties are encountered in practice. Although the magnitude of these difficulties varies with the particular dye employed, the amount of dye present in the emulsion layer per unit of area, and the type of sensitizing dye employed, the difficulties appear to result largely from the lowering of photographic sensitivity in the spectral region absorbed by the image-forming dye. This, of course, is precisely the region which each layer is intended to record.

Films such as that disclosed in Gaspar U. S. Patent 1,985,344, can be used to make natural color pictures by printing with suitably colored lights from black and white or colored component images, but they cannot be used to make naturally color pictures by direct exposure to an original subject or another naturally colored picture. Hence it is of considerable advantage to retain the natural order of sensitivity described by Christensen.

According to the present invention, I have been able to retain the natural order of sensitivity, and, at the same time, to overcome the difficulties encountered in the use of azo dyes of color complementary to those for which the

layers are sensitized. This improvement has been attained by using colloidal dispersions of vat dyes together with certain alkaline bleaching solutions which reduce the vat dyes most rapidly in the regions of the developed silver images. The improvement which I have achieved by the use of vat dyes depends at least partly on the fact that these dyes reduce the photographic sensitivity of the layers on which they are coated to a considerably less extent than the polyazo dyes hitherto employed, especially as respects the sensitivity to light of the spectral regions closely approaching the maximum absorption of the dye in the same layer.

By the term "vat dye" I refer to a dye which is insoluble in water and which may be reduced to a compound which is more soluble than the dye and which may be oxidized to form the original dye.

Most of the vat dyes fall into two general classes: those derived from indigo and those derived from anthraquinone. Some of the indigo vat dyes on reduction form compounds of a yellow color or other light shade but most of the anthraquinone vat dyes form deeply colored compounds upon reduction. In referring to "vat dyes" it is understood that we intend to include the dyes generally included in this class.

As stated above, I have found that colloidal dispersions of the dyes known as "vat dyes" may be used to color a gelatin layer and may be bleached at the points of the silver image to form a colored image. The vat dyes in general are very insoluble in water and are relatively inert as far as their effect on photographic sensitivity is concerned. The vat dyes also have other advantages over polyazo dyes, as will be apparent from the following description of my invention.

I have also found that a solution of stannous chloride is valuable as a bleaching agent for the vat dyes if the solution is made strongly alkaline.

In the accompanying drawing Fig. 1 is a sectional view of a film having a single gelatin layer colored with a blue-green vat dye.

Fig. 2 shows the layer with a developed and fixed image.

Fig. 3 shows the layer after bleaching, containing the silver image.

Fig. 4 shows the layer containing the bleached image with the silver removed.

Fig. 5 is a sectional view of a three-layer film having differently sensitized layers colored with vat dyes.

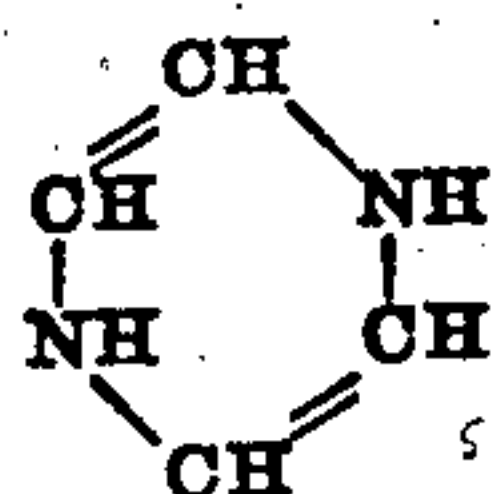
Fig. 6 is a sectional view of a three-layer film having clear gelatin layers between the colored layers.

Among the dyes which may be used according to our invention are indigo and its derivatives, known as the indigoid dyes. These include, in addition to indigo, thioindigo (Schultz Farbstoff-



tabellen No. 1344), Brilliant Indigo BASF/G (Schultz Farbstofftabellen No. 1318), Brilliant Indigo BASF/4G (Schultz Farbstofftabellen No. 1319), and 7-7<sup>1</sup> dimethyl indigo (Schultz Farbstofftabellen No. 1320). All of these dyes are colored blue or greenish blue with the exception of thioindigo, which is of a magenta color.

Another type of dye which may be used according to our invention is the anthraquinone type. The first class of this type is the class of acylaminoanthraquinones. These include Indanthrene Yellow GK (Schultz Farbstofftabellen No. 1220), which is a yellow dye, and Algol Pink BBK (Schultz Farbstofftabellen No. 1221), which is a magenta dye. The second class of anthraquinone dyes is that of the polyanthraquinonylamines. These dyes are secondary amines containing two or more anthraquinone residues linked by NH groups. An example of this class of dye is Algol Red BTK (Schultz Farbstofftabellen No. 1261). This dye is colored magenta. The third class of the anthraquinone dyes is that of the hydroazines. These dyes contain the ring



connecting to anthraquinone nuclei. Dyes of this class are Indanthrene Blue 5G (Schultz Farbstofftabellen No. 1238) and Caledon Blue 3G (Schultz, Farbstofftabellen No. 1232), both of which are greenish blue dyes. Another class of anthraquinone dyes is that of the complex carbocyclic quinones. These dyes contain at least two quinonoid CO groups connected by a conjugated chain of alternate single and double bonds, and also contain either the pyrene or perylene ring systems in the molecule. Dyes of this class are Indanthrene Golden Yellow GKA, which is variously said to be 3:4:8:9-dibenzpyrene-5:10-quinone, ("The Synthetic Dyestuffs," Cain and Thorpe, 7th ed., 1934, p. 240) or a halogen derivative of 4.5.8.9-dibenzpyrene-3:10-quinone (Schultz, Farbstofftabellen, 1286C) and the dye prepared by the oxidation of Algosol Golden Yellow IGK (manufactured by the I. G. F. A., Germany). Still another class is that of the anthraquinone acridones. A dye of this type is Indanthrene Red-Violet RRK (Schultz Farbstofftabellen No. 1260).

Another dye which may be used is Algol Yellow GCA, which is said to be formed by the action of Hydrogen sulphide on dibenzoyl-2:6-diamino anthraquinone (Schultz, Farbstofftabellen, No. 1274a).

I have found that dyes of the vat dye class are not uniformly desirable for use in the dye bleaching process herein described. For example, some of the dyes which are readily reduced in the regions of the silver image remain in the gelatin after reduction and oxidize back to the colored compound in the wash water or the bath used to remove the residual silver image. This gives the effect of a more or less uniform colored layer, as if no reduction had occurred. Another feature possessed by some of the dyes, is their extreme ease of reduction in some bleaches which results in their reduction throughout the entire layer and not only where there is a silver image. Still another feature possessed by some vat dyes is the relatively low solubility of their leuco compounds, which makes it difficult to prepare dyed layers of suf-

ficiently intense color for use in the dye bleaching process. Moreover, the tendency of some of the dyes to precipitate in fine crystals of visible size upon oxidation of the leuco compound makes difficult the preparation of colloidal dispersions.

Although certain of the vat dyes described above possess some properties which are undesirable in our process, there are ways in which these undesirable properties may be partially or entirely overcome. For example, certain solvents placed in the bleach bath aid in removing the reduced leuco forms of the dyes from the gelatin so that they cannot remain and be oxidized back to the dye in the locations of the silver image. Dyes which reduce too easily and, therefore, decolorize throughout the layer may be used with a milder or more dilute bleaching bath or a bleaching agent of different character so that their reduction is of consequence only where there is a silver image. For example, it was found that, although thioindigo bleached throughout the film in the alkaline potassium sulphide bleach bath which gave good images with indigo, it was possible by means of an alkaline stannous chloride bleaching solution to form images with both thioindigo and indigo. The tendency of dyes to separate out in visible crystals is modified by the dilution of the vat and by the presence and concentration of certain dispersing agents, for example of the gelatin, at the time of oxidation in the method of making the dye preparations hereafter described.

According to my process, a dispersion of the vat dye is formed in a protective colloid such as gelatin. This dispersion may then be mixed with a sensitive halide emulsion and coated on a suitable support. After exposure of the layer to form a latent image, the film is developed, washed and fixed in plain or acid hypo solution. The film is then washed again and bleached in a solution which decolorizes the dye in the region of the silver image. After a further washing, the silver image is removed by treatment with oxidizing and fixing agents which may be applied successively or combined in the same solution. The film is then again washed and dried. A pure vat dye image is thereby left in the film. This process may be carried out in a similar manner for a film having two or more superposed sensitive layers.

Another method of carrying out the process, which is applicable to a single emulsion layer, or to the topmost of two or more superimposed emulsion layers is the following: The emulsion coating does not contain the dye at the time of exposure. After exposure to light, development and fixation, the film is bathed in a solution of the leuco compound of the dye. This is allowed to oxidize as by the action of the air, whereupon the film is washed and then submitted to the bleaching solution. The silver image is then removed, leaving a reversed dye image in the layer.

My invention will now be described with particular reference to the accompanying drawing. In Fig. 1 I have shown a sectional view of a film comprising a support 10 of transparent material which may be a cellulosic material, such as cellulose acetate or cellulose acetate propionate or which may be composed of a synthetic resin. This support 10 has coated on it a sensitive layer 11 comprising gelatin sensitized with silver halide and containing a blue-green vat dye. After exposure, development and fixation there results a silver image 12 in the colored layer 11 as shown in Fig. 2. The film is then treated in a



suitable bleach bath which decolorizes the dye at the points of the silver image and leaves a bleached or decolorized image 13 containing silver in the otherwise colored layer 11. The silver is then removed with suitable reagents and there remains a clear image portion 14, as shown in Fig. 4.

Where the film support 10 carries three superposed layers, as shown in Fig. 5, these layers may be sensitized to the red, green and blue regions of the spectrum and each layer usually contains a vat dye of a complementary color. As shown in this figure the layer 15 is red sensitive and contains a blue-green vat dye, the layer 16 is green sensitive and contains a magenta vat dye, and the layer 17, blue sensitive and contains a yellow vat dye. Suitable dyes for this purpose are, indigo for the blue-green layer, Algol Pink BBK (Schultz Farbstofftabellen No. 1221) for the magenta layer and Algosol Golden Yellow IGK or Indanthrene Golden Yellow GK (Schultz Farbstofftabellen No. 1286C) for the yellow layer. This film is exposed and an image formed as described above. A further modification of this form is shown in Fig. 6, in which clear gelatin layers 18 are used between layers 15, 16, and 17. These clear gelatin layers help to prevent wandering of the sensitizing dyes, fusion of the successive emulsion layers at the interface, and, possibly, spreading of the bleaching action beyond the desired layers.

I will now refer to the specific ways of dispersing the vat dye in the sensitive emulsion and of forming the image or images according to my invention.

#### Example 1

A dispersion of indigo was prepared as follows: there was added to 75 ccs. of water, 0.4 grams of de-ashed gelatin and to this solution there was added the following:

Indigo, powdered	grams	1.6
Sodium hydrosulfite	do	3.2
Potassium hydroxide solution, 100 grams per liter	cc	25

This solution was placed in an air-tight container, warmed and agitated occasionally until the indigo was reduced and converted into the leuco form which gave a deep yellow solution. This solution was then filtered into a second container. This container was closed and again agitated until any of the indigo which may have been formed by oxidization during the filtering was again reduced to a clear yellow solution. This solution was then mixed with a warm solution of 25 grams of de-ashed gelatin in 75 ccs. of water. With the solution kept below 100° F., 3.2 grams of potassium persulfate were added to oxidize the leuco indigo back to the dye and the solution was stirred for ten minutes. The yellow solution of leuco indigo turned rapidly to a transparent blue colloidal dispersion of indigo. Ammonium persulphate or hydrogen peroxide or other oxidizing agents may also be employed in place of potassium persulphate. The gelatin was set, shredded and thoroughly washed in cold water. The noodles thus formed were drained and re-melted. This solution was then mixed with an approximately equal volume of a red sensitive photographic emulsion, preferably of comparatively fine grain and high ratio of silver salts to gelatin. This solution was then coated on a cellulose acetate support and dried.

#### Example 2

A. Durindone Red B Powder	grams	30
Sodium hydrosulfite	do	30
Sodium hydroxide (100 gm/liter)	cc	300
Water	cc	550
B. Gelatin (25% solution)	cc	250
C. Ammonium persulfate	grams	40

A is warmed in a stoppered bottle until complete solution is obtained. Then B is added in a small stream while the bottle is agitated to secure mixing of the solutions. A greenish coagulum is formed together with a supernatant yellowish liquid. The mixture is then cooled to a temperature of about 36° C. Then C is dumped in, and the mixture vigorously stirred. This mixture turns a deep magenta color, and the coagulum is redissolved. The solution is preferably filtered and then set to a gel by chilling. The gel is shredded and thoroughly washed in cold running water. The drained and remelted gel may be mixed with a photographic emulsion, preferably one which has been sensitized to green light.

#### Example 3

A. Algol Pink BBK	grams	50
Sodium hydrosulfite	do	48
Sodium hydroxide (100 gm./liter)	cc	415
Distilled water	cc	800
B. Gelatin (25% solution)	grams	1300
C. Ammonium persulfate	do	59

A is placed in a stoppered bottle and kept at room temperature with frequent shaking for about thirty minutes. In this time complete reduction of the dye to its leuco compound takes place. B is then added in hot solution in portions of 100-200 cc., the bottle being stoppered and shaken after the addition of each portion. With the temperature of the mixture at about 38-40° C., C is dumped in and the mixture is vigorously shaken. A clear Algol Pink BBK colloidal suspension is thus produced. The solution is filtered, set, shredded, washed, and finally mixed with a photographic emulsion as already described.

#### Example 4

According to another method of dispersing the dye in gelatin the dye may be employed in the form of a salt of the sulfuric acid half ester of the leuco compound commonly known as the "indigosol" or "Algosol" form. Some of the advantages of this method are that the indigosols can be dissolved more quickly than the vat dyes which require an alkaline reducing solution for dissolving the dye, and that better dispersions are obtained from the indigosols in the case of certain dyes. According to this method 10 grams of Algosol Golden Yellow IGK, 50 grams of gelatin and 2.6 grams of sodium nitrite were dissolved in 750 ccs. of water. The mixture was then acidified with 4 ccs. of concentrated hydrochloric acid and diluted with 50 ccs. of water. The acid was added slowly with constant stirring. By this treatment the Algosol derivative was hydrolyzed and oxidized to the dye in dispersion in the gelatin. To this dispersion there were added 200 ccs. of a 15% gelatin solution which had been acidified to a pH of approximately 3. After mixing, any tendency of the dye to coagulate may be eliminated by making the solution faintly alkaline with ammonia. The mixture was then chilled and set, cut into shreds and washed thoroughly to eliminate by-products of the reaction and excess of reagents. This colored dispersion was then remelted, mixed with an approximately



equal volume of an ordinary blue sensitive silver halide emulsion, coated on a transparent support and dried.

A similar method may be used to prepare a colloidal dispersion of indigo from Indigosol O (Schultz, Farbstofftabellen, 1303).

I will now describe methods of forming an image in the sensitive layer containing the vat dye. The photographic emulsion which contains a colloidal dispersion of indigo and which has preferably been previously sensitized for red light is exposed, preferably by red light, to an original subject or to a positive image. It is then developed in the usual way, washed in water and fixed in an ordinary sodium thiosulfate fixing bath to remove the unexposed silver halide. The film is washed again and bleached for about ten minutes in the following:

Commercial potassium sulfide, fused	grams--	2.5
Sodium hydroxide, 10% solution	cc--	25
Water to	cc--	100

The treatment in this bath is sufficient to reduce the indigo to its leuco compound in the presence of the silver image and to substantially remove the reduced compound from the gelatin layer. The film is then again washed in water and treated for several minutes in a 4% solution of potassium cyanide to remove the silver sulfide image which has been formed. The film is then again washed in water and dried.

In the place of the alkaline potassium sulfide solution, a solution of potassium cyanide or other alkali cyanide may be employed for reducing the dye. The action of such a cyanide solution is accelerated by the addition of a small amount of pyridine. For example, the following solution is used as a bleach after the development and fixing of the film:

Potassium cyanide	grams--	5
Pyridine	cc--	5
Water to	cc--	100

If this solution is allowed to act for a sufficiently long time, it not only forms a bleached dye image, but also removes the silver image completely from the film so that no other treatment except washing is necessary. This process may require several hours. Where treatment for this length of time is undesirable, the bleaching may be interrupted whenever the reduction of the dye has proceeded to the required extent, and the remaining silver may be removed by reagents such as cupric chloride followed by hypo. This bleaching solution works rather well with indigo, although it does not bleach some of the other vat dyes as completely as desirable.

According to my preferred modification of the method of forming the dye image, the sensitive element containing the vat dye dispersed in the layer, after development and fixing, is bleached for about ten minutes at 60° F. in the following solution:

Stannous chloride (SnCl <sub>2</sub> , 2H <sub>2</sub> O)	grams--	8
Sodium hydroxide, 10% solution	cc--	100
Triethanolamine	cc--	10
Anthraquinone	grams--	0.0025
Water	cc--	100

After bleaching in this solution the film is washed and treated for a few minutes in a 5% cupric chloride solution to convert the silver image to silver chloride. The film is then washed, fixed in an ordinary hypo fixing bath or in a 3% solu-

tion of potassium cyanide to remove the residual silver salt, and again washed and dried. It should be understood that the relative proportions of the ingredients in the alkaline stannous chloride solution may be varied considerably and that the triethanolamine and anthraquinone may be omitted or replaced by similar substances. For example, in place of triethanolamine, mono- or di-ethanolamine may be employed. The amount of sodium hydroxide should, however, be sufficient to keep the stannous compounds in solution.

When it is desired to form a natural color picture by exposing a film consisting of two or more superposed layers, the treatment of the film is carried out in a similar manner. For example, a three layer film may have the top layer sensitive to blue only and contain a dispersion of the vat dye made from Algosol Golden Yellow IGK. The middle layer may be sensitized for green and contain a colloidal dispersion of Algol Pink BBK and the bottom layer may be sensitized for red and contain a colloidal dispersion of indigo. The film may be exposed from the coated side of the support to form simultaneously an image in each of the layers. The film may then be treated as described above to bleach the dyes in the regions of the silver images and a natural color picture obtained in this way. If desired, the order of coating the layers may be reversed, the yellow-dyed blue sensitive layer being placed next to the support. In this event, the exposure is preferably made through the support.

I have described the three-layer film above as having the layer sensitized for the color complementary to the color of the vat dye used in the layer. It should be understood, however, that the photographic emulsion mixed with dyed gelatin may be sensitized for any color, or no color at all, aside from the blue or violet to which it is naturally sensitive, or may be panchromatic, regardless of the color of the gelatin. In the preferred form of my invention, the emulsion, as described above, is sensitized for the color complementary to the color of the gelatin with which it is mixed.

In place of coating all three layers on the same side of the support, two layers may be coated in superposition on the one side, and the third layer on the opposite side. The layers may be suitably arranged for exposing all three from the same side of the film, either one or two layers being exposed through the film support as well as through one or two of the other layers. Also, they may be suitably arranged for exposing one or two of the layers from the one side, and, either simultaneously or successively, one or two layers from the opposite side.

Instead of exposing emulsion layers containing vat dyes directly to a color subject or to a picture in natural colors, the layers may also be exposed to one or more three-color component positives or negatives. These component positives or negatives may consist of images which are of themselves black and white or they may consist of dye or pigment images. Exposures to three-color component images will usually be made through tri-color or other suitable filters, simultaneously or successively. For example, a positive printed from a negative taken through a red filter may be used for printing through a red filter onto a red-sensitized or panchromatic emulsion layer containing colloiddally dispersed indigo, a positive printed from a negative taken through a green filter may be used for printing



through a green filter onto a green-sensitized emulsion layer containing colloiddally dispersed Algol Pink BBK, and a positive printed from a negative taken through a blue filter may be used for printing through a blue filter onto a blue-sensitive emulsion layer containing the colloiddally dispersed dye prepared by oxidizing Algosol Golden Yellow IGK.

Even in making exposures to a color subject or to a naturally colored picture, it is frequently desirable to employ color filters in the light beam so that exposures are made simultaneously or successively with three narrow spectral bands. The positions of these three bands in the spectrum are chosen with consideration of the spectral sensitivity and absorption of the photographic emulsion layers described in this specification and, in the case of exposures to a color picture, also for the spectral absorption of the dyes or pigments comprising this picture, the object being to secure as complete analysis and as pure a rendering of color as is possible or as may be desired. Ordinarily these filters will be red, green, and blue with narrow transmission bands, such as Wratten Filters 29, 61, and 50, or 70, 62, and 50 (See "Wratten Light Filters," Eastman Kodak Co., 1934).

One of the important features of my invention is the use of an alkaline solution of stannous chloride as a bleaching bath for the vat dye. The leuco compounds of the vat dyes are much more readily soluble in alkaline solutions than in neutral solutions and I have found that an alkaline solution of stannous chloride is especially effective in bleaching the vat dye to its leuco compound in the presence of the silver image. This solution also aids in removing the leuco compound of the dye from the gelatin layer so that clear highlights result. Stannous chloride in alkaline solution is commonly said to form an alkali stannite, such as sodium stannite in sodium hydroxide solution. However, I do not wish to be limited to this explanation of the solution.

I have stated above that difficulty is sometimes encountered in removing the reduced or leuco form of the vat dye from the gelatin layer after bleaching. In this event, when the layer is washed or treated in the bath which oxidizes the silver image and removes it from the layer, the leuco compound of the vat dye remaining in the emulsion layer is oxidized back to the dye. This results in reducing the transparency of the highlights and these then vary from slightly veiled highlights to very dense dye images, depending upon the dyes employed.

These effects may be overcome with many dyes by the addition of a solvent such as triethanolamine to the sodium stannite or alkaline stannous chloride bleach bath or to other suitable alkaline reducing solutions. The amount of triethanolamine may vary from 50 cc. or less per liter of bleach bath to 200 cc. or more per liter, depending on the requirements of the particular type of dye or dyes. By the use of triethanolamine in this way many dyes can be made to yield acceptable dye images that otherwise yield only very dense images. Even with dyes that furnish quite satisfactory images, the clarity of the highlights is frequently improved.

A further difficulty encountered in the bleaching of certain vat dyes in gelatin layers is the general or overall bleaching of the dye compound which occurs due to the time of treatment or concentration of the bleaching solution necessary

to clear the highlights and which causes poor images to be formed.

It has been found that the bleaching of the dyes in the highlights can be considerably promoted by adding anthraquinone to the bleach bath with the result that good shadow densities are retained with the treatment necessary to clear the highlights. Since the anthraquinone in this bath is probably reduced to anthrahydroquinone the same results may be obtained by the addition of this latter compound to the bleach bath. An example of a bleach bath to which anthraquinone and triethanolamine have been added, is as follows:

Stannous chloride-----grams--	8	15
Sodium hydroxide, 10% solution-----cc--	100	
Triethanolamine -----cc--	10	
Anthraquinone -----grams--	0.0025	
Water -----cc--	100	20

The use of vat dyes and alkaline stannous chloride and other alkaline reducing bleach baths to form color images will be seen to possess numerous advantages over the prior art methods. The vat dyes have far less detrimental effect on the color sensitizing of photographic emulsions than dyes previously used. Clean highlights may be formed by the use of our bleach baths and in the case of the three-layer film distinct and clear three-color pictures in natural colors are produced.

I intend to include as my invention all modifications and equivalents coming within the scope of the appended claims.

What I claim is:

1. The process of producing a colored photographic image in a gelatin layer, which comprises forming a silver image in a gelatin layer containing a vat dye, bleaching the dye in an alkaline stannous chloride solution in the region of the silver image, and removing the silver from the layer.

2. The process of producing a colored photographic image in a gelatin layer, which comprises forming a visible silver image in a gelatin layer containing a vat dye, bleaching the dye in an alkaline stannous chloride solution in the region of the silver image, and removing the silver from the layer.

3. The process of producing a colored photographic image in a gelatin layer, which comprises forming a silver image in a gelatino-silver halide emulsion layer, fixing out the unexposed silver halide, treating the layer containing the silver image with a solution of a leuco compound of a vat dye, causing the leuco compound to oxidize to the colored form of the dye, and bleaching the vat dye in an alkaline stannous chloride solution in the region of the silver image.

4. In the process of forming a colored photographic image in gelatin, the step of bleaching a vat dye in the region of a silver image with an alkaline stannous chloride bath.

5. The method of producing a colored photographic image in a gelatino-silver halide layer colored with a vat dye and sensitized to the color absorbed by the dye, which comprises exposing the sensitive layer to light of the color absorbed by the vat dye, developing and fixing to form a silver image, and bleaching the dye in an alkaline stannous chloride solution only in the region of the silver image.

6. The method of producing a colored photographic image in a gelatino-silver halide layer



colored with a vat dye and sensitized to the color absorbed by the dye, which comprises exposing the sensitive layer to light of the color absorbed by the vat dye, developing and fixing to form a silver image, bleaching the dye in an alkaline stannous chloride solution only in the region of the silver image, and removing the silver from the layer.

7. The method of producing a colored photographic image in a gelatin layer colored with a vat dye and containing a silver image, which comprises bleaching the dye in the region of the silver image in a bleach bath comprising an alkaline solution of stannous chloride and triethanolamine.

8. A bleach bath for producing a colored image in a gelatin layer uniformly colored with a vat dye and containing a silver image, comprising an

alkaline solution of stannous chloride and triethanolamine.

9. The process of producing a colored photographic image in a gelatin layer, which comprises forming a developed and fixed silver image and a uniform colloidal dispersion of a vat dye in the same gelatin layer, bleaching the vat dye in the region of the silver image in an alkaline stannous chloride solution and removing the silver from the layer.

10. The process of producing a colored photographic image in a gelatin layer, which comprises forming a silver image in a gelatin layer containing a vat dye uniformly dispersed therein, bleaching the dye with stannous chloride and an alkali in solution in the region of the silver image, and removing the silver from the layer.

MERRILL W. SEYMOUR.