PATENT SPECIFICATION

Application Date: June 29, 1936. No. 18020/36. **477,524**
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Specification Accepted: Dec. 29, 1937.

PROVISIONAL SPECIFICATION
No. 18020 A.D. 1936.

Improvements in and relating to Colour Photography

We, KODAK LIMITED, a Company registered under the Laws of Great Britain, of Kodak House, Kingsway, London, W.C.2, do hereby declare the nature of this invention which has been communicated to us by Eastman Kodak Company, a Company organised under the Laws of the State of New Jersey, United States of America, of 343, State Street, Rochester, New York, United States of America, to be as follows:—

This invention relates to a new or improved colour photographic process and to a new or improved multi-layer colour photographic element, especially for the production of pictures in natural colours.

It has already been proposed to produce coloured images in one or more layers of a photographic element by introducing into a gelatino-silver halide layer or layers colouring matters adapted to be decolourised and/or removed either where the silver image develops or where the silver images does not develop. Dyestuffs particularly suggested for this purpose were azo dyestuffs which are readily reducible by means of bleaching agents such as sodium hydrosulphite or stannous chloride or even weaker reducing agents. Azo dyestuffs, and especially polyazo dyes, tend to de-sensitize colour sensitized gelatino-silver halide layers in which they may be incorporated. Vat dyestuffs show much less tendency to de-sensitize colour sensitized gelatino-silver halide layers in which they may be incorporated but their reduction products are difficult to remove from selected regions of the emulsion, because of the readiness with which the leuco bodies are re-oxidised and because the strong reducing agents usually employed for reducing vat dyes, e.g. hydrosulphite or stannous chloride, have a detrimental effect upon the gelatine and do not differentiate sufficiently in their action between those respective areas in which the silver image is and is not present.

It has now been found, and this forms the basis of the present invention, that if a vat dyestuff is incorporated in a gelatino-silver halide emulsion, which may be sensitized with a sensitizer to any desired region of the spectrum, such dyestuff can be reduced in and removed from the areas in which the silver image is developed with the aid of stannous chloride used in conjunction with alkali. Stannous chloride is usually employed for reduction purposes in an acidified form in which form it is a very powerful reducing agent. We have found, however, that in conjunction with alkali the reducing action is less powerful enabling the catalytic action of the silver to produce a differential effect. Further, the alkali present facilitates the removal of the leuco compound produced by reduction. The reduction of the vat dye is approximately proportional to the amount of metallic silver due to the catalytic effect which appears to be exerted by the silver so that in those areas in which the silver image has not developed little or no reduction and removal of the vat dye is effected and in those areas in which the metallic silver is present the dyestuff image corresponds in density to the silver image. After treatment with stannous chloride in conjunction with alkali and washing if necessary, the silver may be removed leaving clear transparent reversed dye images.

The effective reducing agent is probably sodium stannite and it is preferable therefore to employ a quantity of alkali slightly in excess of that theoretically necessary to form this body. Even when using this reducing agent, some difficulty may still be encountered in removing the leuco compound sufficiently from the emulsion and it has been further found that such removal is facilitated by the addition to the alkaline stannous chloride bath of a strong organic base such as ethanolamine. This may serve as a solvent for the leuco compound or may form a soluble complex therewith or may simply serve to increase the alkalinity of the bath without unduly softening the gelatine. Whatever may be the reason, and we do not wish to commit ourselves to any theory, much improved results are obtained by the inclusion in the alkaline stannous chloride bleaching bath of a strong organic base.

We have also found that the selectivity of the bleaching and the removal of the bleached dye are favourably influenced by the inclusion in the bleaching bath of a small proportion of anthraquinone or anthrahydroquinone (either of which appears to form a soluble compound or complex with the leuco compound whether the bath also contains an organic base such as triethanolamine or not.

Examples of suitable bleach baths for indigo are:—

1.	Stannous chloride $SnCl_2 2H_2O$ - - - -	8 gms.
	Water - - - - - - - - -	100 cc.
	Sodium Hydroxide solution (100 gms. per litre)	100 cc.
2.	Stannous chloride $SnCl_2 2H_2O$ - - - -	8 gms.
	Water - - - - - - - - -	100 cc.
	Sodium Hydroxide solution (100 gms. per litre)	100 cc.
	Triethanolamine - - - - - - -	10 cc.
	Anthraquinone - - - - - - -	0.0025 gms.

Similar baths may be used for other vat dyes.

An element suitable for processing according to this invention is one having three gelatino-silver halide layers inseparably coated on a single support and preferably on the same side thereof sensitized to colours covering substantially the whole of the visible spectrum and containing respectively dispersions of vat dyes complementary to the colours to which the layers are sensitive. Preferably the upper layer is sensitive to blue, the middle layer sensitive to green and the lower layer sensitive to red. The emulsion layers should be thin to give transparency and rapid emulsions should be used. Known sensitizers are incorporated in the red and green sensitized layers.

By way of example the element may consist

1. of a film as follows:—

Layer	Sensitivity	Dye	Thickness.
Top	Blue	Algosol Golden Yellow I.G.K.	3.3
Middle	Green	Algol Pink B.B.K.	3.3
Bottom	Red	Indigo	5.3
		Total	11.9

ten thousandths of an inch

2. or of a paper as follows:—

Layer	Sensitivity	Dye	Thickness.
Top	Blue	Algosol Golden Yellow I.G.K.	2.8
Clear	Intermediate	nil	3.6
Middle	Green	Algol Pink B.B.K.	1.8
Clear	Intermediate	nil	3.0
Bottom	Red	Indigo	1.8
		Total	13.0

ten thousandths of an inch

The vat dyestuff may be incorporated in the emulsions by the method described in Specification No. 446,234.

Dated this 25th day of June, 1936.
W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

PROVISIONAL SPECIFICATION

No. 28514 A.D. 1936.

Improvements in or relating to Colour Photography

We, KODAK LIMITED, a Company registered under the Laws of Great Britain, of Kodak House, Kingsway, London, W.C.2, do hereby declare the nature of this invention which has been communicated to us by Eastman Kodak Company, a Company organised under the Laws of the State of New Jersey, United States of America, of 343, State Street, Rochester, New York, United States of America, to be as follows:—

This invention relates to a new or improved colour photographic process and to a new or improved multi-layer colour photographic element, especially for the production of pictures in natural colours.

It has already been proposed to produce coloured images in one or more layers of a photograhphic element by introducing into a gelatine-silver halide layer or layers colouring matters adapted to be decolourised and/or removed either where the silver image develops or where the silver image does not develop. Dyestuffs particularly suggested for this purpose were azo dyestuffs which are readily reducible by means of bleaching agents such as sodium hydrosulphite or stannous chloride or even weaker reducing agents. Azo dyestuffs, and especially polyazo dyes, tend to de-sensitize colour sensitized gelatine-silver halide layers in which they may be incorporated. Vat dyestuffs show much less tendency to de-sensitize colour sensitized gelatine-silver halide layers in which they may be incorporated but their reduction products are difficult to remove from selected regions of the emulsion because of the readiness with which the leuco bodies are re-oxidised and the strong reducing agents usually employed for reducing vat dyes, e.g. hydrosulphite, do not seem to differentiate sufficiently in their action between those respective areas in which the silver image is and is not present. Stannous chloride does not appear to accomplish the reduction to a sufficient extent at all.

It has now been found, and this forms the basis of the present invention, that if a vat dyestuff is incorporated in a light sensitive gelatine-silver halide emulsion, which may be sensitized with a sensitizer to any desired region of the spectrum, or in a gelatine layer containing a developed silver image, such dyestuff can be reduced in and removed from the areas in which the silver image is developed with the aid of an alkaline reducing agent. In our co-pending application No. 18020/36 (Serial No. 477,524) we have described the use of stannous chloride in conjunction with alkali. We have now found that, in general, the use of alkali in conjunction with any reducing agent for vat dye facilitates the removal of the leuco compound produced by reduction. In some cases the choice of a suitable reducing agent has to be determined by the ease of reduction of the vat dye.

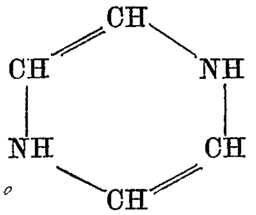
It is necessary in all cases, that the reduction be accomplished with the catalytic assistance of the silver so that the reduction of the vat dye is approximately proportional to the amount of metallic silver and so that, accordingly in those areas in which the silver image has not developed little or no reduction and removal of the vat dye is effected and in those areas in which the metallic silver is present the density of the dyestuff image is in inverse proportion to the density to the silver image. After treatment with the reducing agent in conjunction with alkali and washing if necessary, the silver may be removed leaving clear transparent reversed dye images.

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 colour or other light shade but most of the anthraquinone vat dyes form deeply coloured compounds upon reduction. In referring to " vat dyes " it is understood that we intend to include the dyes generally included in this class.

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 Farbstofftabellen No. 1344), Brilliant Indigo BASF/G (Schultz Farbstofftabellen No. 1318), Brilliant Indigo BASF/4G Schultz Farbstofftabellen 1319), and 7—7^1 dimethyl indigo (Schultz Farbstofftabellen No. 1320). All of these dyes are coloured blue or greenish blue with the exception of thioindigo, which is of a magenta colour.

Another type of dye which may be used in our invention is the anthraquinone type. The first class of this type is the class of acylaminoanthraquinones. These include Idanthrene Yellow GK (Schultz Farbstofftabellen No. 1220), which is a yellow dye, and Algol Pink BBK (Schultz Farbstofftabellen No.

1221), which is 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 coloured 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 Idanthrene 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 carbocylic 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 Idanthrene Golden Yellow GK, 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, 1286 C) 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 Idanthrene Red-Violet RRK (Schultz, Farbstofftabellen No. 1260).

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

Among the dyes of the vat dye class there may be found a few which are not so desirable as others 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 gelatine after reduction and oxidize back to the coloured 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 coloured 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 sufficiently intense colour 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, auxiliary solvents may be placed in the bleach bath to aid in removing the reduced leuco forms of the dyes from the gelatine 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, decolourize 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 gelatine, at the time of oxidation in the method of making the dye preparations hereafter described.

In practising the present invention a dispersion of the vat dye is formed in a protective colloid such as gelatine. 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 photographic element is developed, washed and fixed in plain or acid hypo solutions. The element is then washed again and bleached in a solution which decolourizes 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 element is then again washed and dried. A pure vat dye image is thereby left in the element. This process may be carried out in a similar manner upon an element 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 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. A bleaching solution may be employed which acts not only on the dye but also removes the silver image.

The present invention may be employed for the colour processing of a photographic element comprising a support coated with three superimposed emulsion layers each of which is sensitized for one of the primary colours of white light and is dyed the complementary colour. That is, the image-forming dye in each layer absorbs light of the colour for which the same layer is sensitized. This is the only relation of colour and sensitivity which permits making a picture in natural colours by exposure directly to a coloured subject or to another picture in natural colours followed by removal of colour from the areas in which silver has been developed. It has therefore been called the "natural order" of colour and sensitivity.

The present invention, however, is also suitable for producing a coloured image in one of a plurality of emulsion layers superimposed on a single support. Thus a three layer element may have the lowest layer or the two lower layers coloured with a vat dye and the upper two layers or the uppermost layer uncoloured. The images in the uncoloured layers can afterwards be coloured by colour development or that in the uppermost layer may be coloured according to the present invention by introducing a vat dye after development. The present invention may therefore be employed in processing colour photographic elements according to the methods described in applications Nos. 27765/35 (Serial No. 468,560) and 5227/36 (Serial No. 475,786).

An element particularly suitable for processing according to this invention is one having three gelatine-silver halide layers inseparably coated on a single support and preferably on the same side thereof sensitized to colours covering substantially the whole of the visible spectrum and containing respectively dispersions of vat dyes complementary to the colours to which the layers are sensitive. Preferably the upper layer is sensitive to blue, the middle layer sensitive to green and the lower layer sensitive to red. The emulsion layers should be thin to give transparency and/or to enable clean high lights to be obtained. Rapid emulsions should be used in elements for exposure in a camera. Known sensitizers are incorporated in the red and green sensitized layers. Suitable dyes for incorporation in the layers are, indigo for the blue-green (red sensitized) layer, Algol Pink BBK (Schultz Farbstofftabellen No. 1221) for the magenta (green sensitized) layer and Algosol Golden Yellow IGK or Indanthrene Golden Yellow GK (Schultz Farbstofftabellen No. 1286C) for the yellow blue sensitive layer. Clear gelatine layers may be present between the emulsion layers. These clear gelatine 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.

The dispersion of the vat dye in the sensitive emulsions may be effected as described in the following examples 1 to 4.

EXAMPLE 1.

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

Indigo, powdered - -	1.6	grams
Sodium hydrosulphite - -	3.2	,,
Potassium hydroxide solution, 100 grams per liter -	25	cc.

(De-ashed gelatine is a known product consisting of gelatine so purified as to leave substantially no ash upon ignition). 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 gelatine in 75 ccs. of water. With the solution kept below

100° F. 3.2 grams of potassium persulphate 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 gelatine 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 gelatine. This solution was then coated on a cellulose acetate support and dried.

EXAMPLE 2.

A. Durindone Red B Powder (thioindigo, (Schultz Farbstofftabellen No. 1344)	30	grams
Sodium hydrosulphite	30	,,
Sodium hydroxide (100 gm./liter)	300	cc.
Water	550	cc.
B. Gelatine (25% solution)	250	cc.
C. Ammonium persulphate	40	grams

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 added, and the mixture vigorously stirred. This mixture turns a deep magenta colour, 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	50	grams
Sodium hydrosulphite	48	,,
Sodium hydroxide (100 gm/liter)	415	cc.
Distilled water	800	cc.
B. Gelatine (25% solution)	1300	grams
C. Ammonium persulphate	59	grams

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 added 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 gelatine the dye may be employed in the form of a salt of the sulphuric 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 gelatine 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 gelatine. To this dispersion there were added 200 ccs. of a 15% gelatine 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 coloured dispersion was then remelted, mixed with an approximately equal volume of an ordinary blue sensitive 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).

Typical methods of forming an image

in the sensitive layer containing the vat dye will now be described. 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 thiosulphate fixing bath to remove the unexposed silver halide. The film is washed again and bleached for about ten minutes in the following:—

Commercial potassium sulphide, fused	2.5 grams
Sodium hydroxide, 10% solution	25. ccs.
Water to	100. ccs.

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 gelatine layer. The Film is then again washed with water and treated for several minutes in a 4% solution of potassium cyanide to remove the silver sulphide image which has been formed. The film is there again washed in water and dried.

In the place of the alkaline potassium sulphide 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	5 grams
Pyridine	5 cc.
Water to	100 cc.

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 the preferred 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 ($SnCl_2,2H_2O$)	8 grams
Sodium hydroxide, 10% solution	100 ccs.
Triethanolamine	10 ccs.
Anthraquinone	0.0025 grams
Water	100 ccs.

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% solution 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 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 colour 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 contains 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 colour 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.

We have described the three-layer film above as having the layer sensitized for the colour complementary to the colour of the vat dye used in the layer. It should be understood, however, that the photographic emulsion mixed with dyed gelatine may be sensitized for any colour, or no colour at all, aside from the blue or violet to which it is naturally sensitive, or may be panchromatic, regardless of the colour of the gelatine. In the preferred form of the invention, the emulsion as described above, is sensitized for the colour complementary to the colour of the gelatine 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 colour subject or to a picture in natural colours, the layers may also be exposed to one or more three-colour 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-colour component images will usually be made through tricolour 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 on to a red-sensitized or panchromatic emulsion layer containing colloidally dispersed indigo, a positive printed from a negative taken through a green filter may be used for printing through a green filter on to a green-sensitized emulsion layer containing colloidally 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 on to a blue-sensitive emulsion layer containing the colloidally dispersed dye prepared by oxidizing Algosol Golden Yellow IGK.

Even in making exposures to a colour subject or to a naturally coloured picture, it is frequently desirable to employ colour 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 colour 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 colour 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).

The use of an alkaline solution of stannous chloride as a bleaching bath for the vat dye is particularly important. The leuco compounds of the vat dyes are much more readily soluble in alkaline solutions than in neutral solutions and it has been 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, we do not wish to be limited to this explanation of the solution.

It has already been stated above that difficulty is sometimes encountered in removing the reduced or leuco form of the vat dye from the gelatine 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 ccs. or less per liter of bleach bath to 200 ccs. 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 gelatine 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 the good shadow densities are retained with the treatment necessary to clear the highlights. The anthraquinone in this bath is probably reduced to anthrahydroquinone; at all events the same results may be obtained by the addition of this latter compound to the bleach bath. An example of the bleach bath to which anthraquinone and triethanolamine have been added, is as follows:—

Stannous chloride	8 grams
Sodium hydroxide, 10% solution	100 ccs.
Triethanolamine	10 ccs.
Anthraquinone	0.0025 grams
Water	100 ccs.

The use of vat dyes and alkaline stannous chloride and other alkaline reducing bleach baths to form colour images will be seen to possess numerous advantages over the prior art methods. The vat dyes have far less detrimental effect on the colour 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-colour pictures in natural colours can be produced.

The support of the emulsion layers may be a transparent material such as glass or cellulose ester or an opaque material, such as paper. The total thickness of the coatings will not, as a rule, exceed the normal thickness of a single coating.

Dated this 17th day of October, 1936.
W. P. THOMPSON & CO.,
12, Church Street, Liverpool,
Chartered Patent Agents.

COMPLETE SPECIFICATION

Improvements in and relating to Colour Photography

We, Kodak Limited, a Company registered under the Laws of Great Britain, of Kodak House, Kingsway, London, W.C.2, do hereby declare the nature of this invention which has been communicated to us by Eastman Kodak Company, a Company organised under the Laws of the State of New Jersey, United States of America, of 343, State Street, Rochester, New York, United States of America, 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 new or improved colour photographic process, especially for the production of pictures in natural colours.

It has already been proposed to produce coloured images in one or more layers of a photographic element by introducing into a gelatino-silver halide layer or layers colouring matters adapted to be decolourised and/or removed either where the silver image develops or where the silver image does not develop. Azo dyestuffs have been most suggested for this purpose since these are readily reducible by means of bleaching agents such as sodium hydrosulphite or stannous chloride or even weaker reducing agents. Azo dyestuffs, and especially polyazo dyes, tend to de-sensitize colour sensitized gelatino-silver halide layers in which they may be incorporated. Vat dyestuffs have also been proposed. Vat dyestuffs show much less tendency to de-sensitize colour sensitized gelatino-silver halide layers in which they may be incorporated but their reduction products are difficult to remove from selected regions of the emulsion because of the readiness with which the leuco bodies are re-oxidised; moreover the strong reducing agents usually employed for reducing vat dyes, e.g. sodium hydrosulphite, do not seem to differentiate sufficiently in their action between those respective areas in which the silver image is and is not present. Stannous chloride does not appear to accomplish the reduction to a sufficient extent at all.

It has now been found, and this forms the basis of the present invention, that if a vat dyestuff is incorporated in a light sensitive gelatino-silver halide emulsion, which may be sensitized with a colour sensitizer to any desired region of the spectrum, or in a gelatine layer containing a developed silver image, such dyestuff can be reduced in and removed from the areas in which the silver image is developed with the aid of alkaline stannous chloride. Instead of alkaline stannous chloride, alkaline alkali sulphide or alkaline alkali cyanide may be used. The use of alkali in conjunction with these reducing agents facilitates the removal of the leuco compound produced by reduction. In some cases the choice of the reducing agent has to be determined by the ease of reduction of the vat dye. The alkali and the reducing agent may be applied separately provided that they are allowed to act in conjunction with one another.

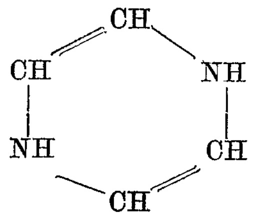
It is necessary in all cases, that the reduction be accomplished with the catalytic assistance of the silver so that the reduction of the vat dye is approximately proportional to the amount of metallic silver and so that, accordingly, in those areas in which the silver image has not developed little or no reduction and removal of the vat dye is effected and in those areas in which the metallic silver is present the density of the dyestuff image is in inverse proportion to the density to the silver image. Stannous chloride is usually employed for reduction purposes in an acidified form but in this form it does not satisfactory accomplish this differential reduction of vat dyes. Indeed, in experiments we performed little or no reduction was obtained at all. We have found, however, that when stannous chloride is used in conjunction with alkali reduction of vat dyes is accomplished under the catalytic action of the silver enabling a satisfactory differential effect to be obtained. Further the alkali present facilitates the removal of the leuco compound produced by reduction. Alkaline stannous chloride is the preferred reducing agent in the practice of the present invention.

After treatment with the reducing agent in conjunction with alkali and washing if necessary, the silver may be removed leaving clear transparent reversed dye images.

In referring to " vat dyes " it is understood that we intend to include any of the dyes generally included in this class.

Among the dyes which may be used are indigo and its derivatives, known as the indigoid dyes. These include, in addition to indigo, thioindigo (Schultz Farbstofftabellen No. 1344), Brilliant indigo BASF/G (Schultz Farbstofftabellen No. 1318), Brilliant Indigo BASF/4G (Schultz Farbstofftabellen No. 1319), and 7-7^1 dimethyl indigo (Schultz Farbstofftabellen No. 1320). All of these dyes are coloured blue or greenish blue with the exception of thioindigo, which is of a magenta colour. The reduction products are generally yellow or other light shade.

Other dyes which may be used are those of 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 coloured 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 GK, which 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 GC, which is said to be formed by the action of Hydrogen sulphide on dibenzoyl - 2:6 - diamino anthraquinone (Schultz Farbstofftabellen, No. 1274*a*).

Most of the anthraquinone dyes, as is known, form deeply coloured products on reduction. Some vat dyes are not so desirable as others for use in the present invention. For example, some vat dyes, although readily reduced in the regions of the silver image, remain in the gelatine after reduction and oxidize back to the coloured 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 coloured layer, as if no reduction had occurred. Some vat dyes are so easily reduced in some bleaches that reduction takes place throughout the entire layer and not only where there is a silver image. The leuco compounds of some vat dyes have a low solubility which makes it difficult to prepare dyed layers of sufficiently intense colour for use in the dye bleaching process. Some vat dyes tend to precipitate in fine crystals of visible size upon oxidation of the leuco compound making the preparation of colloidal dispersions rather difficult.

Although certain vat dyes, as indicated 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, auxiliary solvents may be placed in the bleach bath to aid in removing the reduced leuco forms of the dyes from the gelatine 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, decolourize 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 gelatine at the time of oxidation in the method of making the dye preparations hereafter described.

In practising the present invention a dispersion of the vat dye is formed in a protective colloid such as gelatine. This dispersion may then be mixed with a sensitive silver halide emulsion and coated on a suitable support. After exposure of the layer to form a latent image, the photographic element is developed, washed and fixed in plain or acid hypo solutions. The element is then washed again and bleached in a solution which decolourizes 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 element is then again washed and dried. A pure vat dye image (reversed) is thereby left in the element. This process may be carried out in a similar manner upon an element having two or more superposed sensitive layers. The layer in which the vat dye is incorporated may be sensitized for any desired band of the spectrum or may be a panchromatic emulsion.

Another method of carrying out the process, which is applicable to a single emulsion layer, or to the topmost of two or more superimposed 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. A bleaching solution may be employed which acts not only on the dye but also removes the silver image.

The present invention may be employed for the colour processing of a photographic element comprising a support coated with three superimposed emulsion layers each of which is sensitized for one of the primary colours of white light and is dyed the complementary colour to one of the primary colours.

The present invention, however, is also suitable for producing a coloured image in one of a plurality of emulsion layers superimposed on a single support. Thus a three layer element may have the lowest layer or the two lower layers coloured with a vat dye and the upper two layers or the uppermost layer uncoloured. The images in the uncoloured layers can afterwards be coloured by colour development or that in the uppermost layer may be coloured according to the present invention by introducing a vat dye after development. The present invention may therefore be employed in processing colour photographic elements according to the method described in applications Nos. 468,560, 475,786 and 475,784.

An element particularly suitable for processing according to this invention is one having three gelatino-silver halide layers inseparably coated on a single support and preferably on the same side thereof sensitized to colours covering substantially the whole of the visible spectrum and containing respectively dispersions of vat dyes complementary to the colours to which the layers are sensitive. That is, the image-forming dye in each layer absorbs light of the colour for which the same layer is sensitized. This is the only relation to colour and sensitivity which permits making a picture in natural colours by exposure directly to a coloured subject or to another from the areas in which silver has been developed. It has therefore been called the " natural order " of colour and sensitivity.

Preferably the upper layer is sensitive to blue, the middle layer sensitive to green and the lower layer sensitive to red. The emulsion layer should be thin to give transparency and/or to enable clean high lights to be obtained. Rapid emulsions should be used in elements for exposure in a camera. Known sensitizers are incorporated in the red and green sensitized layers. Suitable dyes for incorporation in the layers are, indigo for the blue-green (red sensitized) layer, Algol Pink BBK (Schultz Farbstofftabellen No. 1221) for the magenta (green sensitized) layer and Algosol Golden Yellow IGK or Indanthrene Golden Yellow GK (Schultz Farbstofftabellen No. 1286C) for the yellow (blue sensitive) layer. Clear gelatine layers may be present between the emulsion layers. These clear gelatine 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.

The dispersion of the vat dye in the sensitive emulsions may be effected as described in specification No. 446,234 or in the following examples 1 to 4.

EXAMPLE 1.

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

Indigo, powdered	1.6	grams
Sodium hydrosulphite	3.2	,,
Potassium hydroxide solution, 100 grams per litre	26	cc.

(De-ashed gelatine is a known product consisting of gelatine so purified as to leave substantially no ash upon ignition.)

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 might have been reformed 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 gelatine in 75 ccs. of water. With the solution kept below 100° F., 3.2 grams of potassium persulphate 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 gelatine 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 gelatine. This solution was then coated on a cellulose acetate support and dried.

EXAMPLE 2.

A. Durindone Red B Powder (thioindigo, (Schultz Farbstofftabellen No. 1344)	30	grams
Sodium hydrosulphite	30	,,
Sodium hydroxide (100 gm./litre)	300	cc.
Water	550	cc.
B. Gelatine (25% solution	250	cc.
C. Ammonium persulphate	40	grams

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 added, and the mixture vigorously stirred. This mixture turns a deep magenta colour, 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 - -	50 grams
Sodium hydrosulphite -	48 ,,
Sodium hydroxide (100 gm/litre - - -	415 cc.
Distilled water - -	800 cc.

B. Gelatine (25% solution)	1300 grams
C. Ammonium persulphate -	59 grams

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 added 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 gelatine the dye may be employed in the form of a salt of the sulphuric 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 gelatine 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 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 gelatine. To this dispersion there were added 200 ccs. of a 15% gelatine 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 coloured dispersion was then remelted, mixed with an approximately equal volume of an ordinary blue sensitive 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).

Typical methods of forming an image in the sensitive layer containing the vat dye will now be described. 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 thiosulphate fixing bath to remove the unexposed silver halide. The film is washed again and bleached for about ten minutes in the following:—

Commercial potassium sulphide, fused - - -	2.5 grams
Sodium hydroxide, 10% solution - - - -	25. ccs.
Water to - - - -	100. ccs.

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 sulphide image which has been formed. The film is then again washed in water and dried.

In the place of the alkaline potassium sulphide 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	5 grams
Pyridine	5 cc.
Water to	100 cc.

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 the preferred 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 ($SnCl_2,2H_2O$)	8 grams
Sodium hydroxide, 10% solution	100 ccs.
Triethanolamine	10 ccs.
Anthraquinone	0.0025 grams
Water	100 ccs.

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% solution 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 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. These may serve as solvents for the leuco bodies or may form soluble complexes therewith or may simply serve to increase the alkalinity of the bath. Whatever may be the reason, and we do not commit ourselves to any theory, the presence of an alkylolamine in the bath is beneficial. The amount of sodium hydroxide should, however, be sufficient to keep the stannous compounds in solution. The effective reducing agent may possibly be sodium stannite and it is preferable therefore to employ a quantity of alkali slightly in excess of that theoretically necessary to form this body.

The effect of a solvent such as triethanolamine in the alkaline reducing solution is to improve the transparency of the high lights. The amount of triethanolamine may vary from 50 ccs. or less per litre of bleach bath to 200 ccs. or more per litre, 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.

The effect of anthraquinone or anthrahydroquinone is to promote the bleaching of the dyes in the high lights without undue general or overall bleaching.

When it is desired to form a natural colour 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, the three layer film hereinbefore described, after exposure from the coated side of the support to form simultaneously an image in each of the layers, is treated as described above to bleach the dyes in the regions of the silver images and a natural colour 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 made through the support.

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 colour subject or to a picture in natural colours, the layers may also be exposed to one or more three-colour 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-colour component images will usually be made through tricolour 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 on to a red sensitized or panchromatic emulsion layer containing colloidally dispersed indigo, a positive printed from a negative taken through a green filter may be used for printing through a green filter on to a green-sensitized emulsion layer containing colloidally 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 on to a blue-sensitive emulsion layer containing the colloidally dispersed dye prepared by oxidizing Algosol Golden Yellow IGK.

Even in making exposures to a colour subject or to a naturally coloured picture, it is frequently desirable to employ colour 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 colour 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 colour 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).

The use of vat dyes and the alkaline reducing agents herein specified to form colour images will be seen to possess numerous advantages over the prior art methods. The vat dyes have far less detrimental effect on the colour 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-colour pictures in natural colours can be produced.

The support for the emulsion layers may be a transparent material such as glass or cellulose ester or an opaque material, such as paper. The total thickness of the coatings will not, as a rule, exceed the normal thickness of a single coating.

Having now particularly described and ascertained the nature of the said invention and in what manner the same is to be performed, as communicated to us by our foreign correspondents, we declare that what we claim is:—

1. The process of producing a colour photographic image in a gelatine layer diffusely dyed with a vat dye and containing a silver image which consists in reducing the vat dye in the regions of the silver image with the aid of alkaline stannous chloride.

2. The process of producing a coloured photographic image as claimed in claim 1 in which the vat dye is introduced diffusedly into a gelatine layer containing a silver image and the dye is thereafter reduced in the regions of the silver image with the aid of the alkaline stannous chloride.

3. The process as claimed in claim 2, in which the vat dye is introduced into the gelatine layer by treating the layer with a solution of the leuco dye and allowing the leuco dye to oxidize therein.

4. The process of producing a coloured photographic image in which a vat dye is colloidally dispersed in a gelatino-silver halide emulsion and a silver image is produced by exposure, development and fixing whereafter the vat dye is reduced in the regions where the silver has developed by treatment with alkaline stannous chloride.

5. A modification of the process claimed in any of the preceding claims in which, instead of alkaline stannous chloride, alkaline alkali sulphide or alkaline alkali cyanide is employed.

6. The process as claimed in either claim 1 or claim 4 in which the vat dye is contained in a gelatino-silver halide layer sensitized to a colour complementary to that of the dye.

7. The process as claimed in any of the preceding claims in which the silver is removed from the gelatine layer after reduction of the dye to leave a clear reversed coloured image.

8. The process as claimed in any of the preceding claims in which the alkaline reducing bath contains a solvent such as triethanolamine.

9. The process as claimed in any of the preceding claims in which the alkaline reducing bath contains anthraquinone or anthrahydroquinone.

10. The process as claimed in any of the preceding claims in which a photographic element having two or more layers containing different vat dyes is treated.

11. The process as claimed in any of the preceding claims in which an indigo dye is used.

12. The process as claimed in any of claims 1 to 10 in which an anthraquinone dye is employed.

13. The process as claimed in claim 10 applied to a photographic element having three superimposed gelatino-silver halide layers diffusely coloured with different vat dyes, one containing a silver image of the red component and diffusely dyed with indigo, the second containing a silver image of the green component and diffusely dyed with Algol Pink BBK and the third containing a silver image of the blue component and diffusely dyed with the dye obtained by oxidising Algosol Golden Yellow IGK.

14. The process of producing coloured photographic images substantially as described.

Dated this 28th day of July, 1937.
W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

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