

PATENT SPECIFICATION



Application Date: Sept. 24, 1934. No. 26382/35.
(Divided out of Application No. 27418/34.)
Complete Specification Left: Sept. 24, 1935.
Complete Specification Accepted: April 24, 1936.

446,234

PROVISIONAL SPECIFICATION

Improvements relating to Sensitive Photographic Elements

ERRATUM

SPECIFICATION No. 446,234.

Page 4, line 35, for "ferrocyanide" read
"ferricyanide"

THE PATENT OFFICE,
June 30th, 1936.

ing of dye from layer to layer during or after coating.

More particularly, where it is desired to incorporate a gelatine or other colloid layer containing colouring matter in a photographic element containing one or more light-sensitive layers adjacent to the coloured layer, it is essential that the colouring matter should remain in the layer originally containing it throughout coating operations and any other treatment prior to light exposure. As most aniline dyes tend to wander freely from layer to layer until such layers are thoroughly dry, they are not generally suited to this purpose. Certain colloidal dyes are more suitable. These wander relatively slightly, but are liable to desensitize photographic emulsion layers into which they wander even though the quantity of diffusing dye be small.

Dyes which are non-diffusing and lend themselves to decolourization in photographic processing baths may be incorporated in a gelatine or other colloid layer by bringing about their production in insoluble form within the gelatine by the coupling of water-soluble components or the action of a water-soluble reagent such as an oxidising agent upon a water-soluble component or water-soluble components or by a combination of these methods.

graphic exposure and if necessary, after development and fixation, the dye may be bleached and removed by reduction or oxidation, depending on the nature of the dye. Suitable reducing agents are, for example, sodium hydrosulphite in acid, neutral, or alkaline solution, or sodium bisulphite. Suitable oxidising agents are chromic acid, potassium permanganate (acid yield) or other common photographic bleaching agents for dissolving a silver image or converting it to a salt. When the bleached dye is rather difficultly soluble in the bleach bath or in water, alcohol or another solvent may be added to the bleach bath or the wash water to remove the bleached dye more easily.

The dyes may be formed as described in the following examples in all of which a solution of gelatine of about 10% strength is used. The alkali may be sodium or ammonium hydroxide and serves also as the solvent.

EXAMPLE 1.
Magenta colour. 2 mols. of thioindoxyllic acid were dissolved in alkali and gelatine and oxidised by the addition of potassium ferricyanide solution, forming 1 mol. of thioindigo.

EXAMPLE 2.
Magenta colour. 1 mol. of thioindoxyllic acid together with 1 mol. of

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PROVISIONAL SPECIFICATION

Improvements relating to Sensitive Photographic Elements

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 York, United States of America, of 343, State Street, Rochester, New York, United States of America, to be as follows:—

This invention relates to the production of coloured colloid layers especially for photographic purposes, and more particularly to the production of coloured gelatine layers.

When it is desirable to coat a dye-containing layer of emulsion or gelatine contiguously with another layer which is to contain either a different dye or no dye at all, it is essential that there be no wandering of dye from layer to layer during or after coating.

More particularly, where it is desired to incorporate a gelatine or other colloid layer containing colouring matter in a photographic element containing one or more light-sensitive layers adjacent to the coloured layer, it is essential that the colouring matter should remain in the layer originally containing it throughout coating operations and any other treatment prior to light exposure. As most aniline dyes tend to wander freely from layer to layer until such layers are thoroughly dry, they are not generally suited to this purpose. Certain colloidal dyes are more suitable. These wander relatively slightly, but are liable to desensitize photographic emulsion layers into which they wander even though the quantity of diffusing dye be small.

Dyes which are non-diffusing and lend themselves to decolourization in photographic processing baths may be incorporated in a gelatine or other colloid layer by bringing about their production in insoluble form within the gelatine by the coupling of water-soluble components or the action of a water-soluble reagent such as an oxidising agent upon a water-soluble component or water-soluble components or by a combination of these methods.

Thus a leuco vat dyestuff may be mixed with the gelatine or other colloid and oxidised in situ with a water-soluble oxidising agent such as potassium ferricyanide. For example, the component or components of the dye to be formed can be added in alkaline solution and then an oxidising agent in aqueous solution can be added to effect the coupling or to oxidise the leuco compound. The dye is formed in fine colloidal suspension in the gelatine, substantially transparent in any layer of practical thickness. The gelatine is then set, shredded, and washed to remove soluble salts or other reaction products, after which it may be melted and coated on or under an emulsion, or between two emulsions. Such a coating might also constitute a substratum, an anti-halation backing or, conceivably, the support itself of a photographic element. After photographic exposure and if necessary, after development and fixation, the dye may be bleached and removed by reduction or oxidation, depending on the nature of the dye. Suitable reducing agents are, for example, sodium hydrosulphite in acid, neutral, or alkaline solution, or sodium bisulphite. Suitable oxidising agents are chromic acid, potassium permanganate (acid yield) or other common photographic bleaching agents for dissolving a silver image or converting it to a salt. When the bleached dye is rather difficultly soluble in the bleach bath or in water, alcohol or another solvent may be added to the bleach bath or the wash water to remove the bleached dye more easily.

The dyes may be formed as described in the following examples in all of which a solution of gelatine of about 10% strength is used. The alkali may be sodium or ammonium hydroxide and serves also as the solvent.

EXAMPLE 1.

Magenta colour. 2 mols. of thioindoxyllic acid were dissolved in alkali and gelatine and oxidised by the addition of potassium ferricyanide solution, forming 1 mol. of thioindigo.

EXAMPLE 2.

Magenta colour. 1 mol. of thioindoxyllic acid together with 1 mol. of

diethyl *p*-phenylene diamine (HCl) were dissolved in alkali and gelatine. Addition of potassium ferricyanide solution effected oxidation and coupling.

5 EXAMPLE 3.
1 1 mol. of paranitrophenyl acetonitrile (or 2:4 dinitrophenyl acetonitrile) together with 1 mol. of diethyl *p*-phenylene diamine (HCl) was dissolved in acetone
10 (or alcohol) and water and gelatine. Alkali was then added and the mixture treated with a solution of potassium ferricyanide. A magenta colour resulted.

 EXAMPLE 4.
15 1 mol. of acetoacetanilide together with

1 mol. of diethyl *p*-phenylene diamine (HCl) was dissolved and coupled as indicated in Example 2. A yellow colour resulted.

 EXAMPLE 5. 20
To obtain a magenta colour thioindigo white was oxidised to thioindigo as in Example 1.

Dated this 23rd day of September, 1935.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.

COMPLETE SPECIFICATION

Improvements relating to Sensitive Photographic Elements

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
30 Company, a Company organised under the Laws of the State of New York, United States of America, of 343, State Street, Rochester, New York, United States of America, and in what manner
35 the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to sensitive photographic elements. More particularly it relates to a coloured coating material for use as a screening layer with sensitive photographic elements and is an improvement in or modification of the invention described and claimed in
45 specification No. 390,093.

It is known that the light which reaches a sensitive layer in a photographic element may be reduced in amount or restricted in colour by the use of a light screening layer coated over the sensitive layer and composed of a colloid such as gelatine coloured with a dye. Most frequently it is necessary to use a yellow dye in view of the sensitivity of gelatino-silver
50 halide emulsions to blue light; such sensitivity to blue light makes it desirable or necessary to employ a yellow screening layer over an emulsion layer or layers sensitized to colour other than blue e.g.
60 red or green.

It may also, however, be desirable or necessary to use screening layers of other colours e.g. a red layer over a red-sensitized emulsion or a green layer over
65 a green-sensitized emulsion. It is also sometimes desirable or necessary to incorporate a screening dye in a light sensitive

emulsion layer itself to reduce the quantity or restrict the colour of the light falling on an under layer.

Numerous screening dyes have been proposed among which are Tartrazine, Naphthol Yellow and Quinoline Yellow. Most if not all of the known screening dyes have undesirable qualities. They
70 have the property of desensitizing cyanine-sensitized emulsions and are therefore unsuitable for incorporation in emulsions which have been colour sensitized by cyanine dyes since the colour sensitivity is
75 thereby impaired and in some cases wholly destroyed. They also have the property of diffusing or wandering out of the layer in which they are incorporated. When it is desired to coat a layer of
80 sensitive emulsion or plain gelatine containing a dye adjacent to another layer which is to contain either a definite dye or no dye at all, it is essential that there should be as little wandering as possible
85 of the dye from layer to layer during or after coating; and when the layer in which the dye is incorporated is light-sensitive, it is further essential that the dye does not de-sensitize the emulsion to
90 any serious extent. Again, when it is desired to coat a light screening layer on a layer of sensitive emulsion or a layer of sensitive emulsion on a light screening layer, it is important that there shall be
95 as little wandering as possible of the dye from the light screening layer to the emulsion and it is also desirable that if any dye does wander its nature or amount should be such as not seriously to impair
100 the sensitivity of the emulsion.

It has been found particularly difficult to find yellow dyes which fulfil these requirements. Most aniline dyes tend to wander quite freely from layer to layer
110 during the coating operations and until

the layers are thoroughly dry. Certain colloidal dyes wander less but are particularly liable to de-sensitize emulsion layers particularly cyanine-sensitized gelatino-silver halide emulsion layers

5 into which they wander even though the quantity of diffusing dye be small.

The prior specification was concerned with a coloured screening layer comprising a protective colloid medium containing a colloidal suspension of an indo-phenol dye.

10 It has now been found that other vat dyes which lend themselves to decolorization in photographic processing may be incorporated in carriers for use as screening layers by bringing about their production in insoluble form by oxidation within the carrier. The production of vat dyes in insoluble form within a body of gelatine or other colloid can be brought about by the oxidation of the leuco compound which may also be formed in situ in some cases by the coupling of water soluble components or by the action of a water soluble reagent upon a water soluble component or water soluble components or by a combination of these methods. The gelatine or other colloid containing the insoluble vat dye can then be employed as a light absorbent layer in a sensitive photographic element.

15 The sensitive photographic element may have at least one light sensitive emulsion on a support and over said emulsion a light screening layer containing the vat dye produced in situ in the colloid medium by oxidation. Preferably the sensitive photographic element has at least two emulsion layers sensitive to light in different regions of the spectrum either on one side of a single support or distributed between the two sides of a single support and the light screening layer is placed over one of said emulsion layers. The word "over" is used in this connection in an optical sense as meaning that the light screening layer is placed so that the incident light is constrained to pass through the screening layer before falling upon the screened emulsion. Thus where the light passes through the support before impinging upon the sensitive emulsion the light screening layer lies either between the emulsion and the support or on the side of the support remote from the emulsion to be screened. However, where it is desired to screen one sensitive layer and not another the screening layer may be placed between the two sensitive layers. The present invention may therefore be utilised in the construction of the sensitive elements described and claimed in our co-pending application

65 No. 26523/34 (Serial No. 444,198). The

invention therefore includes a sensitive photographic element having at least two emulsion layers on a single support, one of which is sensitive to blue light but insensitive to light to which the other layer or layers is or are sensitive, and having a light screening layer containing yellow vat dye, produced within the colloid medium of the screening layer by oxidation, between said blue sensitive layer and the other sensitive layer or layers.

70 In the production of light absorbent layers in sensitive photographic elements it is most convenient to use gelatine as the carrier. The invention is not limited to the use of gelatine as a carrier. Other colloids which may be used in some cases are gum arabic and starch although gelatine is of more general applicability. For the colouration of the gelatine the leuco compound of the vat dyestuff may be mixed therewith and oxidised in situ with a water-soluble oxidising agent such as potassium ferricyanide; or the components of a vat dye can be added in alkaline solution and then an oxidising agent in aqueous solution can be added to effect the coupling and oxidise the leuco compound. The dye is formed in fine colloidal suspension in the gelatine, substantially transparent in any layer of practical thickness. The gelatine is then set, shredded, and washed to remove soluble salts or other reaction products, after which it may be melted and coated on or under an emulsion, or between two emulsions. Such a coating might also constitute a substratum, an anti-halation backing or, conceivably, the support itself of a photographic exposure and if necessary, after development and fixation, the dye may be bleached and removed by reduction. Suitable reducing agents, are, for example, sodium hydrosulphite in acid, neutral, or alkaline solution, or sodium bisulphite. When the bleached dye is rather difficultly soluble in the bleach bath or in water, alcohol or other solvent for the bleached dye may be added to the bleach bath or the wash water to remove the bleached dye more easily.

75 The use of a yellow screening layer between a layer sensitive to blue and layers sensitized to other colours, for example red and green, is particularly valuable since such red sensitized and green sensitized materials are always sensitive to blue light. The use of vat dyes for this purpose is particularly valuable since very much less wandering of the dyestuff occurs as compared with the dyes previously suggested and the sensitivity of the adjacent emulsions is much less seriously affected. Due to these valu-

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able properties of vat dyes it is quite practicable to have a light screening layer in a sensitive photographic element which has three or more inseparable differentially sensitized layers of emulsion on the same side of a single support. Such screening layer may be placed below the layer furthest from the support and above the other layers and, if desired, additional screening layers may be placed between the other layers. The present invention may, however, also be applied to the mixed grain type of emulsion which consists of several sets of sensitive silver halide grains, the grains of each set being sensitized to one colour. The grains in one or more of the sets may be coated with a colour screening layer containing vat dye. Thus if one set of grains is sensitized for the red, another set for the green and a third set for the blue, the grains of the first two sets can be coated with a yellow filter layer.

The dyes may be formed as described in the following examples in which a solution of gelatine of about 10% strength is used. The alkali may be sodium or ammonium hydroxide and serves also as the solvent.

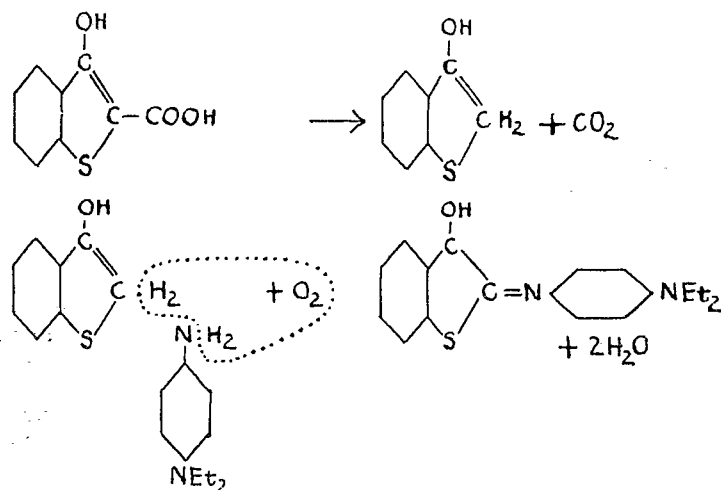
EXAMPLE 1.

Magenta colour. 2 mols. of thioindoxylic acid or 1 mol. of thioindigo white were dissolved in alkali and gelatine and oxidised by the addition of potassium ferrocyanide solution, forming 1 mol. of thioindigo.

EXAMPLE 2.

Magenta colour. 1 mol. of thioindoxylic acid together with 1 mol. of diethyl *p*-phenylene diamine (HCl) were dissolved in alkali and gelatine. Addition of potassium ferricyanide solution effected oxidation and coupling.

The formation of dyestuff probably takes place by the following reactions

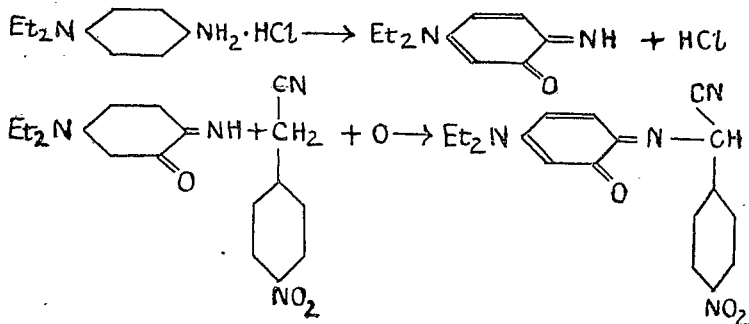


EXAMPLE 3.

1 mol. of paranitrophenyl acetonitrile (or 2:4 dinitrophenyl acetonitrile) together with 1 mol. of diethyl *p*-phenylene diamine (HCl) was dissolved in acetone (or alcohol) and water and gelatine. Alkali

was then added and the mixture treated with a solution of potassium ferricyanide. A magenta colour resulted.

The formation of dyestuff probably takes place by the following reactions



EXAMPLE 4.

1 mol. of acetoacetanilide together with 1 mol. of diethyl *p*-phenylene diamine (HCl) was dissolved and coupled as indicated in Example 2. A yellow colour resulted.

While we have indicated in Examples 2 and 3 the probable course which the reactions take it will be understood that we do not desire to be limited by this theoretical explanation since the invention can be practised without its aid.

Other vat dyes which may be produced in situ in a protective colloid medium such as gelatine by oxidation of the leuco compound are:—

Schultz VII. No.	Dye
1301	Indigo
1343	Helindone Red B
1344	Durindone Red B (Thioindigo)
1260	Alizanthrene Red Violet 2 RN
1220	Vat Yellow R
1212	Indanthrene Yellow GK
1289	Benzoyl-1-aminoanthraquinone
1260	Naphthanthraquinone Carbathrene Red AFF
1221	Indanthrene Red Violet RRK
1261	Algol Pink BBK Indanthrene Golden Yellow GKA
1237	Algol Pink BTK
1238	Indanthrene Yellow 5 GK
1232	Duranthrene Blue CC
1319	Indanthrene Blue 5 G
1318	Caledon Blue 3 G
	Brilliant Indigo BASF/4G
	Brilliant Indigo BASF/4 G

The gelatine solution containing the insoluble vat dye prepared according to the example is set, shredded and washed and the water drawn off. For coating as a plain layer the solution is mixed with water in equal volume or a solution made so that the gelatine is present in the amount of about 5%. When added to a sensitive emulsion an amount may be used to give a dye strength corresponding to that in the plain gelatine or more or less may be used as desired.

Coloured screening layers, according to the present invention, may be coated over, or may form part of, a light sensitive layer or may be used as sub-coatings or

undercoatings and may serve either as a filter layer or as a non-halation backing on the rear face or support side of a photographic element. Coatings made according to our invention are particularly useful where it is important to restrict as far as possible the diffusion of the dye into another layer with which it is in contact, as in the case where two films are rolled together face to face and exposed together in the camera.

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. In combination with a sensitive photographic element, a coloured screening layer comprising a protective colloid medium containing a colloidal suspension of a vat dye, other than an indophenol, produced within said colloid medium by oxidation of soluble starting materials.

2. A photographic element comprising a support, a sensitive layer and a coloured screening layer as claimed in claim 1.

3. A photographic element as claimed in claim 2 wherein the screening layer is over the sensitized layer.

4. A photographic element as claimed in claim 2 wherein the screening layer and the sensitive layer are on opposite surfaces of the support.

5. A method of applying a screening dye coating to a sensitive photographic element by forming a colloidal suspension of a vat dye (other than an indophenol) by oxidation of soluble starting materials within the protective colloid and applying the suspension as a thin layer over the sensitive layer of the element or on the back surface of the support of the element.

6. A sensitive photographic element having at least two emulsion layers on a single support one of which is sensitive to blue light but insensitive to light which the other layer or layers is or are sensitive, and having a light screening layer containing yellow vat dye, produced in colloidal suspension within the colloid medium of the screening layer by oxidation of soluble starting materials, between said blue sensitive layer and the other sensitive layer or layers.

Dated this 23rd day of September, 1935.

W. P. THOMPSON & CO.,
12, Church Street, Liverpool, 1,
Chartered Patent Agents.