Improvements relating to Sensitive Photographic Elements

We, KODAK LIMITED, a British Company, of Kodak House, Kingsway, London, W.C.2, do hereby declare the nature of this invention 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.

It has now been found that certain dyes which are ordinarily water-soluble and wander rather readily can be modified by the introduction into the molecule of a group or groups adapted to bring about chemical combination or complex formation with the gelatine or other colloid of the layer in which they are incorporated. Thus, by the introduction of an aldehyde group, into a dyestuff, more especially in an aromatic nucleus thereof, a combination takes place between the dye and gelatine, particularly under alkaline conditions. This eliminates or greatly reduces the tendency of the dye to wander out of the gelatine layer.

Examples of suitable yellow screening dyes are:

\[
\begin{align*}
1. & \quad \text{2-Hydroxy-5-phenylazobenzaldehyde} \\
& \quad \text{CHO} \\
& \quad \text{N=N-} \\
& \quad \text{OH} \\
\end{align*}
\]

\[
\begin{align*}
2. & \quad \text{2:4-Dihydroxy-5-phenylazobenzaldehyde} \\
& \quad \text{CHO} \\
& \quad \text{N=N-} \\
& \quad \text{OH} \\
& \quad \text{OH} \\
\end{align*}
\]

Such dyes may be incorporated in a photographic emulsion or a filter or other layer by simple mixing with the ingredients thereof. Instead of being directly added they may be heated with gelatine made slightly alkaline. A concentrated solution in gelatine so prepared can then be shredded and washed and afterwards diluted with plain gelatine or gelatinsilver halide emulsion for coating.

These dyes may be decolourised and removed from the gelatine by certain acid oxidising processing baths—e.g. acid permanganate bleach, or quinone-alcohol bleach.

Dated this 24th day of September, 1934.

W. P. THOMPSON & Co.,
12, Church Street, Liverpool, 1.

COMPLETE SPECIFICATION

Improvements relating to Sensitive Photographic Elements

We, KODAK LIMITED, a British Company, 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 organized under the Laws of the State of New York, United States of America, of 843, 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 sensitive photographic elements. More particularly it relates to a coloured coating material for use as a screening layer with sensitive photographic elements which include films or plates having one or more layers of light sensitive emulsion coated on a support such as glass, cellloid or paper.

It is known that the glass 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. The colloid, such as gelatine, serves as the carrier for the dye. Most frequently it is necessary to use a yellow dye in view of the sensitivity of gelatine-silver 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 colours other than blue e.g. 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 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 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 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 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 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 desensitize the emulsion to 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 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 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 during the coating operations and until the layers are thoroughly dry. Certain colloidal dyes wander less but are particularly liable to desensitize emulsion layers particularly cyanine-sensitized gelatine-silver halide emulsion layers into which they wander even though the quantity of diffusing dye be small.

It has now been found that while certain colouring matters are ordinarily water-soluble and wander rather readily, corresponding compounds which differ from them only by the presence of an aldehyde group or aldehyde groups (—C=O) in the molecule exhibit very much less tendency to wander from the layers in which they are incorporated and very much less tendency to desensitize the emulsions in adjacent layers. This reduction in tendency to desensitize exhibited by colouring matters containing the aldehyde group may be due to their having less desensitizing effect or may be wholly or in part a consequence of their having less tendency to wander. Whatever may be the reason, however, colouring matters containing one or more aldehyde groups show definite advantages over other colouring matters when used as screening colours.

For convenience, such a colouring matter or dye containing a free aldehyde group is referred to hereinafter as an aldehyde dye.

It appears possible that the presence of the aldehyde group in the colouring matter brings about chemical combination or complex formation with the gelatine or other protein which is used as the carrier for the aldehyde dye, but we do not desire our invention to be limited by this or any other theory since it can be practised without regard to such theory. The invention is not limited to the use of gelatine as a carrier.
According to one feature of the present invention a sensitive photographic element has a coloured screening layer comprising an aldehyde dye, preferably one of high molecular weight, as hereinbefore defined and a carrier therefor. Other features of the invention will be apparent from the following description and the appended claims.

The sensitive photographic element may have at least one light sensitive emulsion on a support and over said emulsion a light screening layer containing aldehyde dye. 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 a light screening layer containing aldehyde dye 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 sensitive 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 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 aldehyde dye between said blue sensitive layer and the other sensitive layer or layers.

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 screening layers containing aldehyde 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 valuable properties of aldehyde 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 light absorbent layer containing aldehyde 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 coloured yellow or coated with a yellow filter layer.

As already indicated a yellow screening layer is generally desired. Preferably the aldehyde dyes employed with the present invention are azo dyes, among which many yellow dyes may be found. Preferably the aldehyde group is a substituent in an aromatic nucleus.

Aldehyde dyes which are suitable for use in the present invention are aldehyde substitution products of benzene and naphthalene-azo-phenol and their derivatives. So far as we are aware these aldehyde dyes have not heretofore been made. Dyes of the azo class corresponding to which dyes containing the aldehyde group may be made are benzene-azo-phenol, benzene-azo-resorcinol, benzene-azo-creosol and Diamond Yellow G. Diamond Yellow G is formed by coupling diazotized 2-amino-benzoic acid and salicylic acid. Its Rowe Colour Index number is 218. 110

Aldehyde dyes corresponding to azo dyes having a greater number of azo groups may also be used, but in general these dyes have a deeper shade and, while suitable for filter dyes do not always give the proper screening effect to restrict the passage of blue light. The following specific aldehyde dyes, whose probable constitutions are as given by the formula, have been found suitable:

Example 1.

\[ \text{2-hydroxy-5-phenylazo-benzaldehyde} \]

\[
\text{CHO} \quad \text{N} = \text{N} \quad - \text{OH}
\]

One molecular proportion of aniline is diazotized in the usual manner and the resulting benzene-diazonium chloride
solution is added slowly to a 2 per cent sodium hydroxide solution in which one molecular proportion of salicylaldehyde has been dissolved. The dye precipitates as a buff coloured solid which dissolves in 2 per cent caustic soda yielding an orange solution.

Example 2.

\[ \begin{array}{c}
  \text{CHO} \\
  \text{N} = \text{N} \\
  \text{OH} \\
  \text{OH}
\end{array} \]

One molecular proportion of aniline is diazotized using slightly more than the minimum amount of hydrochloric acid. The benzene diazonium chloride solution is added to a cold 70 per cent alcoholic solution of resorcyaldehyde. Upon addition of three molecular proportions of sodium acetate the dye is formed and separates out of solution. The dye is soluble in 5 per cent sodium carbonate solution.

Example 3.

\[ \begin{array}{c}
  \text{CHO} \\
  \text{N} = \text{N} \\
  \text{OH} \\
  \text{OH}
\end{array} \]

One molecular proportion of \( m \)-nitrobenzaldehyde is added to a cold solution of three molecular proportions of stannous chloride in seven molecular proportions of concentrated hydrochloric acid. The temperature of the reaction is maintained below 25° C. After standing for two hours a solution of sodium sulphide prepared from 7 to 8 molecular proportions of fused sodium sulphide in twice their weight of water is added slowly. After standing for several hours the tin sulphide is filtered off and the filtrate diazotized by adding two molecular proportions of hydrochloric acid followed by one molecular proportion of sodium nitrite in the form of a 20 per cent caustic solution containing one molecular 45 proportion of resorcinol. The crude dye is purified by recrystallizing from dilute alcohol.

Example 4.

\[ \begin{array}{c}
  \text{CHO} \\
  \text{N} = \text{N} \\
  \text{OH} \\
  \text{OH}
\end{array} \]

One molecular proportion of \( a \)-napthylamine is dissolved in 3 molecular proportions of hot dilute hydrochloric acid and then chilled to \(-2 \)° C. The amine is diazotized by the slow addition of 1.1 molecular proportion of sodium nitrite dissolved in 3 times its weight of water. A molecular proportion of salicylaldehyde is dissolved in a 5 per cent caustic solution and chilled to 0° C. With good stirring, the above diazonium salt is added in a slow steady stream to the cold salicylaldehyde solution when the 2-hydroxy-5-\( a \)-napthylazo- benzaldehyde separates. The crude dye may be purified by dissolving in 5 per cent caustic soda, filtering, and reprecipitating with dilute hydrochloric acid. This product may be recrystallized from hot benzene, if a very pure product is desired.

Example 5.

\[ \begin{array}{c}
  \text{CHO} \\
  \text{N} = \text{N} \\
  \text{OH} \\
  \text{OH}
\end{array} \]

One molecular proportion of benzidine is dissolved in 1\( \frac{1}{2} \) molecular proportions of 30 per cent hydrochloric acid diluted to 5 times its volume with hot water. The solution is cooled to 10-12° and an additional 1\( \frac{1}{2} \) molecular proportions of 30\% hydrochloric acid are added. A solution of 2 molecular proportions of sodium nitrite in twice their weight of water is added rapidly to the suspension of benzidine dihydrochloride and allowed to stand for ten minutes keeping the temperature between 10-15° C. The diazotized solution should not be acid to congo paper and, if it is, sodium acetate is added until no test is given. One molecular proportion of phenol is dissolved in 8 times its weight of 60 per cent alcohol and added slowly to the diazonium salt solution. Simultaneously, two molecular proportions of sodium acetate are added with good stirring. After 3 hour one molecular proportion of salicylaldehyde is added to the diazonium salt solution, followed by two molecular proportions of sodium carbonate, keeping
the temperature between 15–20° C. After one-half hour, the thick brown paste which is the crude dye is filtered off.

This is made by following the procedure of Example 5 but employing two molecular proportions of salicyaldehyde instead of one of phenol and one of salicyaldehyde.

One molecular proportion of benzidine disulphonic acid is treated with 12 molecular proportions of concentrated hydrochloric acid diluted with twice their volume of water and warmed to 70° C. The resulting suspension is then cooled to 0–5° C. and an equal amount of ice added. A 20 per cent solution of sodium nitrite (containing 2.2 molecular proportions) is added rapidly to the cold suspension with stirring and the resulting mixture allowed to stand for 20 minutes. Meanwhile 2.2 molecular proportions of salicyaldehyde are dissolved in 50–60 times their volume of water containing 6 molecular proportions of sodium carbonate. The diazonium salt solution is added slowly to the well stirred salicyaldehyde solution which is kept between 16–20° C.

After one hour, the resulting clear orange liquid is treated with a saturated salt solution which throws out the dye.

This is made by following the procedure of example 5 but employing one molecular proportion of salicyaldehyde instead of one molecular proportion of phenol. Other aldehyde dyes, not of the azo class, which we may use, are the hydroxy benzaldehydes, such as nitro or dinitro hydroxy benzaldehyde. The formula for nitro hydroxy benzaldehyde is:

![Diagram of nitro hydroxy benzaldehyde]

We may also use aldehyde dyes of the indophenol type, such as the dyes formed by coupling nitroso dialkyl-anilines with hydroxy benzaldehydes.

Aldehyde dyes of the fluorescein class are suitable.

It is most convenient to use the aldehyde dyes in the salt form by dissolving them in a slightly alkaline solution of sodium hydroxide. For example, when using 2-hydroxy-5-phenylazo-benzaldehyde, one gram of dye is dissolved in five cc. of water and 5 cc. of acetone containing 5 cc. of a 10 per cent solution of sodium hydroxide. This solution may be mixed directly with a sensitive emulsion or with plain gelatine. Another suitable method which may be used instead of direct addition of the dye solution to the emulsion is to heat the dye with a gelatine solution made slightly alkaline. The concentrated gelatine solution thus formed is then chilled and washed, afterwards diluted with plain gelatine or mixed with a sensitive emulsion for coating on the film support. Such a concentrated gelatine-dye solution may be made in the following manner:

A gelatine solution containing the dye is made up containing the following:

- Gelatine - 10 g.
- Dye (2-hydroxy 5-phenylazo-benzaldehyde) - - 1 g.
- Water - - - 5 cc.
- Acetone - - - 5 cc.
- Sodium hydroxide (10% solution) - - 5 cc.
- Water to - - - 100 cc.

This gelatine solution is set, shredded, and washed, and the water drained off. When coated as a plain layer, this 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.

5 These aldehyde dyes may be
decolourized and removed from the
gelatine by acid oxidising baths, e.g. an
acid-permanganate or a quinone-bromide-
algohol bleach bath.

10 In our copending application No.
440,032 we have described a method for
directly processing a photographic
element to a natural colour photograph
and have there described a method in
which the latent images in the layers are
developed to silver and the silver then
bleached out with an acid permanganate
solution of the following composition:

Potassium permanganate 4%

20 solution - 1 cc.
Sulphuric acid 20% solution 1 cc.
Water - - 20 cc.

Such a bleach out bath will sufficiently
decolorize and remove any aldehyde dye
present in a light screening layer. In
another stage of the process the following
in the aforesaid application No. 440,032 and in
the process for the production of a
negative in minus colours described in our

copending application No. 447,092 we
have described a method in which the
images in all the layers are colour
developed to one colour and then the
image in the upper layers only is bleached
and decolourised by a quinone bromide
bleach bath having the following

composition:

glycyrine - 500 cc.
isopropyl alcohol - 1000 cc.
water - - 75 cc.
quinone - 5 g.
hydrobromic acid
(conc.) - 20 g.

Such a bath will also decolourize and
remove aldehyde dye from a light
screening layer.

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 our 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. A sensitive photographic element
having a coloured screening layer compriseing
an aldehyde dye and a carrier
therefor.

2. A sensitive photographic element
having a coloured screening layer compriseing
gelatine dyed with an aldehyde
dye.

3. A sensitive photographic element
having, adjacent to a light sensitive
layer, a coloured screening layer
comprising gelatine and an aldehyde dye.

4. A sensitive photographic element as
claimed in Claim 3, wherein the screening
layer is over the sensitive layer and serves
as a filter for the light falling thereon.

5. A sensitive photographic element
having at least two emulsion layers
sensitive to light in different regions of
the spectrum and a light screening layer
containing aldehyde dye over one of said
emulsion layers.

6. A sensitive photographic element
having one side of a single support at
least two emulsion layers sensitive to
light in different regions of the spectrum
and a light screening layer containing
aldehyde dye over one of said emulsion
layers.

7. A sensitive photographic element as
claimed in Claim 5 or 6 in which one of
the light sensitive layers 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 con
taining yellow aldehyde dye between said
blue sensitive layer and the other sensitive
layer or layers.

8. A sensitive photographic element
as claimed in any of Claims 5 to 7 which
have three or more inseparable differen
tially sensitised layers of emulsion on the
same side of a single support and in which the
light screening layer is between the
layer farthest from the support and the
other layers.

9. A sensitive photographic element
as claimed in any of Claims 5 to 8 in which
the gelatine is employed as the carrier for
the aldehyde dye in the light screening layer.

10. A sensitive photographic element
as claimed in any of the preceding claims in
which the aldehyde dye is an azo-dye.

11. A sensitive photographic element as
claimed in any of the preceding claims in
which the aldehyde dye contains one or
more hydroxy groups.

12. A sensitive photographic element as
claimed in any of the preceding claims in
which the aldehyde dye is one of high
molecular weight.

13. A light sensitive photographic
element as claimed in any of the
preceding Claims in which the aldehyde dye has an aldehyde group in an aromatic nucleus.

14. in a sensitive photographic element, a light screening layer containing aldehyde dye, substantially as described, with reference to the examples.

Dated this 23rd day of September, 1935.

W. P. THOMPSON & Co.,
12, Church Street, Liverpool, 1,

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