

## PATENT SPECIFICATION



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### COMPLETE SPECIFICATION

#### Process of Colour Photography

We, KODAK LIMITED, a Company registered under the laws of Great Britain, of Kodak House, Kingsway, London, W.C.2 (Assignees of KARL SCHINZEL, of 5 Ottendorfergasse No. 12, Troppau (Silesia), Czechoslovakia, (formerly residing in Vienna, Austria), a Citizen of the Republic of Czechoslovakia), do hereby declare the nature of this invention 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 improvements in processes of colour photography and in particular to production of dye images from photographic silver salt images.

It is known that coloured photographic images may be formed by using a developer which forms a coloured compound on development.

In the production of three-colour photographs using elements having three differentially colour sensitive silver halide layers on a single support, there is often employed a process of colour development in which a coupling component combines with the oxidation product of an aromatic amino developing agent. It has now been found that in three-colour reversal development and three-colour redevelopment (i.e. development of silver salt images obtained from developed silver images) the most favourable results are obtained with simple direct colour developers which are oxidised to insoluble or at least non-diffusing dyes by silver halide which has been exposed or rendered developable in any other manner, e.g. by treatment with fogging agents.

According to the present invention, in a process of three-colour photography in which three colour component silver salt images on a single support are processed to different colours, a colour component silver salt image is converted into a dye image with a developer consisting of an alkaline solution or suspension of a leuco vat dye, the silver being subsequently removed without removing the dye associated therewith. Two or more com-

ponent images may be so converted. Leuco vat dyes are to be distinguished from compounds in which two molecules of the developer combine on oxidation to form the dyes. The leuco forms of dyes used in a present invention are transformed into the final component dye image by simple oxidation.

The leuco-indophenols, leuco-indamines and leuco-azomethines are not to be considered as leuco vat dyes within the meaning of the present invention, since, although they are sufficiently stable in alkaline solution to serve as developers and have been proposed for this purpose, the finished dyes from these compounds are, however, rather easily decomposed by acids. Nor are reduced lignone dyes to be regarded as leuco vat dyes within the meaning of the present invention.

The leuco-forms of the vat dye used in the vat dyeing of textiles are very easily reoxidised in alkaline solution. Pure dry thioindigo white and seleno-indigo white can, however, be preserved for a long time. Indigo white is less stable. Among the indigoid and analogous vat dyes there are much more stable leuco-derivatives, such as amino-thio-indigo white, and certain highly-halogenated thioindigos, if they are reduced in the presence of a small quantity of alkali. Those which form difficultly soluble alkali salts also give stable leuco derivatives, as for example dinaphthacridonequinone (Chemisches Zentralblatt, 1932, Vol. 2, p. 3402), anthraquinonethioxanthenes and other anthraquinone dyes,  $\beta$ -tetra-hydroflavanthrene and its red dimethoxy, as well as its green acylamino derivatives, dihydrophenanthridine yellow (51 Berichte, Vol. 1, p. 443) and dihydropyranthrene, and its golden-yellow dimethyl derivatives. Especially stable are thionyl indigo white which, like 2:2'-diphenyl-thioindigo white, does not oxidise to the dye with air but requires hydrogen peroxide and alkali, NN'-diphenyl-indigo white, NN'-dimethyl indigo white, 2:2'-dibenzoyl-thioindigo white, leuco- $\delta$ -pyrindigo (58 Berichte, Vol. 2, p. 1726), the lemon-

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yellow di-isobarbituric acid from 5-amino-uracil, diamino-dinaphthylene dioxide (which has an almost insoluble sodium salt), the completely or partially reduced dibenzothianthrene diquinone (55 Berichte, Vol. 2, p. 2557). Many amino-anthraquinones, also acylated ones or those with heterocyclic rings attached, or substituted by alkoxy- or arylhydroxy- or acylhydroxy-groups, are reduced by a great variety of reducing agents or by catalytic hydrogenation to their anthranol or anthrone-form. It was found that not only the derivatives of anthrahydroquinone, but also those of the anthranol form are capable of developing the latent image. If the reduced dye is in its anthrone form it is converted into the alkaline salt of the anthranol form by warming with caustic alkali, if necessary with addition of alcohol, and the anthranol form is used for development. Images of the lemon-yellow dianthrone are obtained with the salt of dianthrone. Tetrahydro-helianthrone is produced very similarly and goes to tetrahydroxy-helianthrone. The leuco-forms of the condensation products from two molecules of, for example, indoxyl, thio-indoxyl, hydroxy-selenonaphthene, with one molecule of a saturated or unsaturated aliphatic, or aromatic dialdehyde are somewhat stabler than those of the simple indigo dyes.

It has been questioned whether indigo white, or any of the leuco-vat dyes, have developing power at all. Liesegang in 1895 stated that indigo white (or its sulphonic acid) is capable of producing a strong black image, and Aribat also confirmed this later, but Lumiere and Seyewetz found that it was probably ascribable to an impurity of hydrosulphite or ferrous sulphate. Neither of these authors has investigated whether an indigo image is also formed.

It has now been found that indigo white, thio-indigo white and seleno-indigo white are really developers. It is, however, necessary to work with complete exclusion of atmospheric oxygen, since otherwise only a general blue fog results. Another condition is that an excess of potassium bromide, or alternatively at least 2% potassium iodide must be added to the developer, if moderately clear images are to be expected. The very finely divided indigo is reduced with aqueous alkaline sodium hydro-sulphite solution on which a layer of benzene or petroleum several centimeters deep is poured. The exposed film is covered by a protecting sheet to protect it from contact with the petroleum layer while passing there-through, otherwise hardly any development takes place. A developing method

of this nature is inconvenient for the amateur and the professional alike, but in motion-picture technique, where the film is developed by automatic machines, these difficulties are easily overcome allowing air-sensitive substances to be used for colour photography. The air in the developing apparatus is replaced by nitrogen or any other indifferent gas, also illuminating gas may be used in case of emergency, or preferably, the apparatus is installed in a room filled with such a gas and the operator must wear a gas mask with air supply.

It is understood that in colour development with leuco-vat dyes, and for washing, boiled or distilled water should be used, in order to avoid colour fog. The preparation of solutions of leuco-vat dyes is, of course, also done with the exclusion of atmospheric oxygen, after which they are filtered and placed in the developing machine. As little sodium hydrosulphite as possible should be used; the excess can be converted by addition of formaldehyde, or better still, non-tanning aldehyde into compounds which do not act as developers. This is not absolutely necessary, since even in the presence of sodium hydrosulphite, sufficiently "strong" colour images are formed.

Alkaline, or where possible, ammoniacal solutions of the leuco-vat dyes are usually best employed for the formation of the last, as a rule the middle, component image in a three-layer element, because most of them reduce unexposed silver halide also, unless very much potassium bromide, or a small percentage of potassium iodide is added to the developer. The principal method of making silver halide emulsions developable is, of course, by thiourea or other fogging agents by or reducing to silver ferrocyanide.

When using leuco-vat dyes it must be remembered that some of them in alkaline solutions have the ability to reduce an image forming dye already in the layers. Alkaline indigo white solutions if warm, for example, reduce halogenated indigo; thioindoxyl is even capable of reducing thioindigo to the leuco form. It is fortunate that colour development of the exposed silver halide usually takes place much more quickly than the action on the vat dye already present. This difficulty is entirely avoided, however, if a vat solution of weaker reduction potential is used last for development. The middle component image is formed with the vat solution of a highly-halogenated indigoid dye, which contains no excess of alkali, unless such excess is in the form of sodium carbonate. When the lower component image has been developed to indigo, or more

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greenish derivatives of the same, the middle image can be developed purple with the aid of the red-to red-violet leuco form of 6:6'-dihalogenated indigo.

5 Ammonia is recommended for use in the solution of the leuco-vat dye, because this attacks the gelatine much less, even when present in slight excess, than fixed alkali does. Alcohol or acetone to any desired amount may also be added to aqueous solution in addition to alkali or ammonia in the theoretically required amount, unless the film is harmed by it. Solutions of the leuco-vat dyes free from inorganic alkali can be used for development of the last emulsion in alcohol or acetone, with addition of aliphatic amines, ethylene diamine, piperidine or other organic base. If a three-layer element has the green or red sensitive emulsion on top, the green-blue or purple component image of this upper emulsion can also be produced by an aqueous suspension of indigo white or thioindigo white in which are dissolved small amounts containing boric acid; this is used after addition of potash or sodium carbonate. Working in this way, also the relatively stable, though not easily soluble, magnesium salts of leuco-vat dyes can be used for development as also the difficultly soluble alkali salts of the various highly halogenated indigo and thioindigo dyes, and many of the higher molecular vat dyes. Also aqueous suspensions or solutions of the leuco compounds in alcohol or acetone containing aromatic amines, reduce silver chloride made developable by exposure, by treatment with thiourea or other fogging agent, or even without exposure by prolonged action with absolute exclusion of atmospheric oxygen.

45 The fact that leuco-vat dyes will colour develop unexposed silver halide makes them particularly useful for the processing of the middle layer in a three-layer ele-

ment when this layer is treated last, especially in a reversal process. The leuco compound may for this purpose be in alkaline solution or in a solution containing alcohol or acetone.

55 Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. In a process of three-colour photography, in which three-colour component silver salt images on a single support are processed to different colours, the step which consists in converting a colour component silver salt image into a dye image with a developer consisting of an alkaline solution or suspension of a leuco-vat dye, the silver being subsequently removed without removing the dye associated therewith.

2. Process as claimed in claim 1, in which two or more colour component images are so converted into dye images.

3. Process as claimed in claim 1, in which the developing solution consists of an ammoniacal solution of the leuco-vat dye.

4. Process as claimed in claim 1, in which the silver salt image developed is in one of three gelatino silver halide emulsion layers on a single support wherein the images in the other layers have already been colour developed.

5. Process as claimed in claim 1, in which images in a multi-layer photographic element are successively developed with leuco-vat dyes and each developer has a lower reduction potential than the one used on a previously developed layer.

Dated this 1st day of December, 1938.

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