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PATENT SPECIFICATION



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COMPLETE SPECIFICATION

Process of Colour Photographic Development

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 Ottendorfgasse 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 photographic development.

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 layers on a single support there is often employed a process of coupling 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 the insoluble or at least non-diffusing dye 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 developing solution containing alkali, little or no sulphite and a developing agent consisting of a substituted hydroquinone of the benzene, naphthalene or anthracene series giving rise to an insoluble quinone dye on development, the silver being subse-

quent removed without removing the dye associated therewith. Two or more colour component images may be so converted. 55

The substituents may be aryl or heterocyclic groups. Thus a polyarylated hydroquinone or hydrogenated 1:4-anthraquinone may be used. A β -naphthohydroquinone may be used to give an *o*-naphthoquinone. 60

We are aware that some substituted hydroquinones and naphthohydroquinones have been proposed as photographic developers but so far as we are aware they have never been employed as colour developers for converting a colour component silver salt image in a three-colour photographic element into a dye image. 70

Many of the substituted hydroquinones and naphthohydroquinones give colours of a lemon-yellow shade suitable for three-colour photography. Those employed must give insoluble quinones on oxidation during development but must be soluble to some extent in water if they are to be used in alkali carbonate solution. 75

Examples of suitable yellow developers, according to the invention are: 80

1. 2:5-diphenyl-3:6-dibenzyl hydroquinone.
2. 2:5-dixylyl-hydroquinone.
3. 2:5-di-*p*-tolyl-hydroquinone.
4. 2:5-di-*p*-phenetyl-hydroquinone. 85
5. Octahydro - anthrahydroquinones especially the β -methyl derivative.
6. Hydrogenated 1:4-anthraquinone.

The effect of a β -stable amino group is to change the colours of the images produced with hydrogenated quinones to red. The amino group may be acylated to obtain images of the colour of the original unsubstituted quinone or of any other desired colour. 90 95

Partially hydrogenated higher quinones obtained by the combination of unsaturated hydrocarbons with naphthoquinones and anthraquinones may be used.

Other examples are: 100

7. 2:Phenyl- α -naphthol-hydroquinone and di-phenoxyhydroquinone which yield yellow images.
8. The hydroquinones of free and

- acylated, alkylated or arylated amino, hydroxy-, and mercapto-derivatives of benzoquinones and naphthoquinones or of higher quinones with or without heterocyclic substituents. Although the corresponding hydroquinones cannot as a rule be obtained by ordinary reduction, on account of their low stability, they can be successfully obtained in most cases by catalytic reduction in a suitable medium. The stated materials can be acylated, alkylated or arylated before reduction, or the finished quinones may be acylated, alkylated or arylated to prevent the simultaneous action of the hydroquinones upon the hydroxyl groups.
- The developing solutions should contain only the amount of alkali just necessary for solution, in order to prevent attacking of the gelatine. This sometimes makes it desirable to use ammonia.
- Whilst *o*-quinones of the benzene series can rarely be prepared easily, β -naphthoquinones can be formed during photographic development, if the 4-position of 1:2-dihydroxy-naphthalene is blocked e.g. by alkyl-, aryl-, acyl-, acylamino- or ketone groups, so that the great tendency to formation of 2-hydroxy α -naphthoquinone (hydroximidonaphthol) is stopped.
- The free, or alkylated or arylated, but not acylated, amino-hydroquinones, are not as a rule sufficiently stable to be used for development in solution containing sodium carbonate or alkali, unless atmospheric oxygen is excluded, and also the amino quinones formed are sometimes inclined to polymerize with formation of blackish products.
- Those aminonaphthohydroquinones in which the amino group is in the ring not containing the hydroxyl groups show very good stability.
- Examples of amino- and acylamino hydroquinones are:
9. phenyldiamino-hydroquinone.
 10. phenylmethyl-imidazol- β -naphthol-quinone.
 11. 4 - acetamino - 1:2 - dihydroxy-naphthalene.
 12. 2-acetamino-3-chlor-1:4-dihydroxy-naphthalene.
 13. 2:8-diacetamino - 1:4 - dihydroxy-naphthalene.
 14. 2:5-diacetaminohydroquinone.
- The brominated hydroquinones, such as *o*-bromhydroquinones also tri and tetrachloroquinone are most suitable starting materials for the synthetic preparation of substituted hydroquinones. They react with alkali phenolate, alkali naphtholate, sodium *p*-toluene sulphamide, in the presence of copper bronze; where the products are quinones they are reduced. In this manner, yellow or blue to purple substitution products can be obtained from halogenated thymoquinone.
- Further examples are the following:
15. The reduction product of α -naphthoquinone diphenylmethane (gives lemon-yellow).
 16. The reduction product of benzoquinone diphenylmethane.
 17. The product obtained by reduction of the condensation product of α -naphthoquinone with Michler's hydrol.
 18. The arylazo derivatives or arylhydrazones of 1:2-dihydroxynaphthalene give lemon-yellow).
 19. The aryl hydrazo derivatives of α -naphthol. (These can be prepared by reduction of arylazo derivatives of α -naphthol with hydrogen at ordinary temperature under elevated pressure using palladium as a catalyst).
- Substantially pure dyestuff images are left when the silver produced together with the colour during development, is removed by means of a silver solvent such as Farmer's solution.
- 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 developing solution containing alkali, little or no sulphite and a developing agent consisting of a substituted hydroquinone of the benzene, naphthalene or anthracene series giving rise to an insoluble quinone dye on development, 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 or 2 in which the developing agent consists of a poly-arylated hydroquinone.
 4. Process as claimed in claim 1 or 2 in which the developing agent is a hydrogenated 1:4-anthraquinone.
 5. Process as claimed in claim 1 or 2 in which the ring substituents are aryl or heterocyclic groups.
 6. Process as claimed in claim 1 or 2 in which a β -naphthohydroquinone is used as the developing agent.
 7. Process as claimed in claim 1, 2 or 6 in which the ring substituents are acylated amino groups.
 8. Process as claimed in claim 1, 2 or

6 in which the ring substituents are aryl-
azo groups or arylhydrazo groups.

9. Process for the production of a dye
image from a photographic silver salt
5 image, substantially as hereinbefore
described.

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