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(*Under International Convention.*)

Date claimed for Patent under Patents and Designs Act, 1907, being date of first Foreign Application (in Germany), 6th Feb., 1912

Date of Application (in the United Kingdom), 31st Jan., 1913

At the expiration of twelve months from the date of the first Foreign Application, the provision of Section 91 (3) (a) of the Patents and Designs Act, 1907, as to inspection of Specification, became operative

Accepted, 2nd Feb., 1914

COMPLETE SPECIFICATION.

Improvements in and relating to Colour Photography.

I, Doctor RUDOLF FISCHER, of 20, Beymestrasse, Berlin-Steglitz, in the Empire of Germany, 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:—

The subject-matter of my invention is an improved process of making photographic pictures.

The development of photographic halogen-silver films leads, in general, to a black picture substantially composed of silver. Individual cases are, however, well known in which coloured pictures can be obtained directly when developing. Thus, developing with pyrogallol yields a yellowish-brown picture, with indoxyl a blue, and with thioindoxyl a red picture. Also, the other customary photographic developers yield, under suitable conditions *e.g.* absence of sodium sulphite and similar bodies, more or less coloured pictures. The colours thus obtained are, however, either not very decided or, as in the case of the developers from the indigo group, not readily obtainable.

Now I have found that exceedingly highly coloured pictures can be very readily obtained by not using the oxydisation products of the developers alone, but by adding to the developers substances which become coupled with those oxydisation products of the developer which are formed whilst developing and form coloured bodies soluble with difficulty. According to the developers or coupling bodies which are employed I obtain representatives of various classes of colouring materials or dyes, of which the following are given as examples:—

p-amidophenols	+	phenols: idophenols,
p-phenylenediamines	+	phenols: indoanilines and oxazines,
p-phenylenediamines	+	amines: indamines,
p-phenylenediamines	+	thiophenols: indothiophenols,
p-amidophenols *p*-phenylenediamines	+	combinations containing acid methylene groups: azomethine.

The bodies soluble with most difficulty are obtained with *p*-phenylenediamine

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as developer and phenols or compounds with acid methylene groups as coupling bodies.

The *p*-phenylenediamines comprise the side chain homologues and nucleus homologues, also the substitution products of *p*-phenylenediamine in one amido group or in the nucleus the other being free.

EXAMPLES:—

p-phenylenediamine, *p*-toluylenediamine, amido-*p*-phenylenediamine, chlor-*p*-phenylenediamine, monoethyl-*p*-phenylenediamine, dimethyl-*p*-phenylenediamine.

Further, one amido group may be included in a ring system: *p*-aminophenylene-piperidine.

By phenols, likewise, the side chain and nucleus homologues and the substitution products are to be understood.

EXAMPLE:—

Phenols, cresols, α-naphthol, *o*-amidophenol, trichlor-naphthol, resorcin-methyl-ether, α-naphthol-sulphonic acids.

The acid methylene compounds may be both of an aliphatic and also of an aromatic nature.

EXAMPLES:—

Ethyl-aceto-acetate, malono-nitrile, chloracetophenone, diketohydrindene, nitrobenzyl-cyanide, thioindoxyl.

Further, the methylene group may be substituted when the substituting group is split off during the reaction.

EXAMPLES:—

Chlor-ethyl-aceto-acetate, thioindoxyl-carboxylic acid. The colouring matter or dye produced in these processes of development can be reduced to leuco compounds which likewise possess developing properties and likewise yield colored pictures directly during the developing process when the oxydation products are soluble with difficulty. Here also it is found that the above specially mentioned classes of coloring materials yield the best results. The developing properties of a part of these classes are already known; for example, the developer pyramidol N.B. dioxydiphenylamine is a leuco-indophenol. Nevertheless, only black pictures were obtained, and it was not observed that colored oxydation products soluble with such difficulty could be obtained and that colored pictures were obtained. It is preferable to omit the admixture of sodium sulphite or similar bodies. The employment of the leuco bodies is, however, not very preferable because they change readily, whilst the first described separate form of employment has the advantage that the components can be preserved separately and need be mixed only immediately before the development or when developing.

The color developers can also be employed in such a form that they are incorporated in the film or the film-carrier, or a separate layer is applied to the layer or film sensitive to light. Either the leuco compounds, the separate components, or only one of the two may be so incorporated or used. The coloring-material picture can be isolated by removing silver by means of one of one of the well-known agents.

EXAMPLES:—

1. 2 g. trichlor α-naphthol dissolved in 20 cms. acetone and added to the following solution:—

2 g. hydrochloride of *p*-phenylenediamine, 30 g. soda, 1000 cms. water. A greenish-blue picture is obtained.

2. 2 g. thymol dissolved in 20 cms. acetone are added to the following solution:—

Hydrochloride of *p*-amidophenylenepiperidine, 40 g. soda, 100 cms. water. Blue picture.

3. 2 g. α-naphthol dissolved in 20 cms. acetone are added to the following solution:—

2 g. hydrochloride of dimethylparaphenylenediamine, 30 g. soda, 1000 cms. water. Blue picture.

4. 2 g. thioindoxyl-carboxylic acid dissolved in 40 cms. acetone are added to the following solution and shaken well:—

2 g. hydrochloride of monoethylparaphenylenediamine, 40 g. potash, 1000 cms. water. Red picture.

5. 2 g. *O*-nitrobenzylcyanide in 20 cms. acetone are added to a solution of 2 g. hydrochloride of dimethyl paraphenylenediamine, 30 g. soda, 1000 cms. water. Brownish-red picture.

6. 2 g. α-chlor-ethyl-aceto-acetate in 20 cms. acetone are added to 2 g. diethyl-paraphenylenediamine 40 g. potash, 1000 cms. water. Yellow picture.

7. 2 g. *p*-nitrobenzylcyanide in 20 cms. acetone are added to 1 g. *p*-amido-phenol, 40 g. potash, 1000 cms. water. Brown picture.

8. 2 g. 4 oxy-2 amido-4¹diethylamido-diphenylamine, 50 g. potash, 1000 cms. water. Blue picture.

9. 2 g. 4-dimethylamidophenyl-u-cyan-azomethine-phenyl. 100 g. potash, 100 cms. water. Orange-colored picture.

I am aware that it has previously been proposed, in the production of colour photographs, to use leuco compounds to obtain the colour images, and also for developing bichromated images for obtaining colour photographs to use a mixture of compounds capable of being converted into colouring matters by the action of chromium dioxide.

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

1. A process of making colored photographic pictures, consisting in latent pictures obtained in halogen-silver films being developed with such developers as contain, besides the developing substance, a body which couples itself with the oxydisation product of the developer to form a colored body soluble with difficulty.

2. A process for developing exposed halogen silver emulsions characterised by the use for developing of the leuco compounds of the groups of colouring matters produced by the compounds associated together in Claim 1 substantially as described.

3. A process according to Claims 1 and 2, characterised by the developing substance giving the color, or the developer and the coupling body, or only one of the two, being put into the film to be developed, into the film carrier, or into a separate layer on the film to be developed.

4. A process according to Claim 1, characterized by *p*-phenylenediamine with α-naphthol and its derivatives being used, or by using as developing agents the side chain homologues and nucleus homologues of *p*-phenylenediamine and their derivatives substituted in the nucleus or in the one amido group, the amido group being able to be contained in a ring system, and by using as a coupling body phenol, its side chain homologues and nucleus homologues, its and their halogen derivatives, sulpho-acid derivatives, hydroxyl-derivatives and their ethers.

5. A process according to Claim 1, characterized by *p*-amidophenol, its side chain homologues and nucleus homologues, its and their nucleus substitution products, and *p*-phenylenediamine, its side chain and nucleus homologues, its and their derivatives substituted in the nucleus and in one amido group being employed as developers, one amido group being able to be contained in a ring system, and by aliphatic and aromatic compounds containing methylene groups of an acid character being employed as coupling bodies.

6. A process according to Claim 2, characterized by the leuco compounds of the colouring matters produced from the compounds mentioned in 4 and 5 being employed for developing.

Dated this 31st day of January, 1913.

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