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COMPLETE SPECIFICATION.

Method of Colour Processing a Colour Photographic Element.

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 Ottendorfergasse No. 12, Troppau (Silesia), Czechoslovakia, formerly residing in Vienna, Austria, a Citizen of the Republic of Austria), 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 the method of colour processing a colour photographic element.

It is known that thio-glycollic acid anilide and thio-glycollic- β -naphthalide give, with silver salts, precipitates which are much less soluble than silver chloride. There are even mercaptans, such as the so-called thiocarbonyl, which will convert silver iodide into an orange-coloured silver mercaptide. It has also been proposed to tone a silver halide photographic print by treating it with a solution of *p*-dimethylaminobenzylidenerhodanine, more specifically to print on bromide paper a green colour separation record from a colour photograph, bleach the image and tone it magenta with a weak ammoniacal solution of *p*-dimethylaminobenzylidenerhodanine, the thus toned separation record being afterwards superimposed with the toned red separation record on the toned blue separation record.

It has now been found that the coloured mercaptides formed by reaction between metallic salts, especially silver salts, and organic mercaptans or their alkali metal or ammonium salts are suitable for the production of coloured images useful in the colour processing of a multi-layer colour photographic element of the kind having three differentially colour sensitized silver halide emulsions inseparably coated on a single support.

When the emulsions form three superimposed layers, the upper layer is generally blue-violet sensitive, the middle layer yellow and green sensitive and the lower layer red sensitive. The order of the three

layers may be changed, if a very sharp blue image is desired, by having the upper emulsion sensitive to blue-violet, the middle emulsion to red and orange, (or infra-red for printing) and the lower emulsion to yellow and green. The three layers may be coated on the same side of the support or the red or yellow-green sensitive emulsion can be situated alone on the back of the support and the two others on the front.

In the case of a three-layer colour photographic element of kind defined above, the not specifically colour sensitized layer is one of the outer layers and the formation of the middle, purple or blue-green, component image offers the greatest difficulty. The present invention is particularly suitable for the image in this layer since it does not require the exposure of the silver halide to light.

According to the present invention there is provided a method of colour processing a multi-layer colour photographic element of the kind defined above in which a silver salt image in one of the layers is converted into a coloured mercaptide of silver or other metal by reaction with an organic mercaptan or its ammonium or alkali metal salt. Such silver salt image may be the remaining (reversed) image after removal of a developed silver image or may be a silver salt image produced from a silver image. The conversion to coloured mercaptide of the residual silver halide in the middle layer of a three-layer element is particularly easy if the middle layer consists of silver chloride whose residual component can be converted into a coloured mercaptide directly or after previous conversion to silver ferrocyanide. Silver bromide is less reactive. It is, therefore, advisable if the middle layer consists of silver bromide to remove all the metallic silver after completion of the two other component colour images, to reduce the silver bromide of the middle emulsion and to convert into silver ferrocyanide by means of potassium ferrocyanide, or a mixture of silver ferrocyanide and lead ferrocyanide by means of one of the known lead intensifiers which

is best weakly acidified with acetic acid. The same procedure could be followed in the case of images obtained by rehalogenising developed and fixed silver images; it is, however, simpler to convert the metallic silver formed during general black development directly into silver chloride or silver ferrocyanide or also lead ferrocyanide, after fixing of the residual silver bromide.

The present invention may also be employed for the treatment of a colour component composed of silver chloride, or of silver ferrocyanide or of lead ferrocyanide, image in the upper layer of a three layer element.

Many of the silver mercaptides are yellow to red but it is possible to synthesise purple-red and blue-green mercaptans which will form mercaptides of the same colour with silver salts.

Conversion of silver bromide into silver mercaptide by reaction with mercaptans or their alkali metal or ammonium salts is often possible in the presence of a small percentage of thiourea in the solution. Suitable coloured organic mercaptans can be obtained by various methods known in themselves. In general, it is a matter of introducing a mercaptan group or a radical containing a mercaptan group into a dyestuff or colouring matter and methods of doing this are well known.

Thus, suitable organic mercaptans can be obtained by taking aromatic compounds of high molecular weight, which may be dyes such as vat dyes and which contain a diazotisable amino group, diazotizing and treating the diazonium salt with a xanthogenate (i.e. a mixture of carbon bisulphide and alkali), whereby the sulphhydryl group is produced by saponification. Known anthraquinone or vat dye intermediates containing a thiophenol group are suitable mercaptans, e.g. the intermediate products employed in the synthesis of thiazole derivatives of anthraquinone. The thioglycollic acid residue (which contains the sulphhydryl group) may also be introduced into such amino compounds, or into organic compounds containing a hydroxyl group, by treatment with chloracetyl chloride to give the chloracetyl derivative, if necessary in the presence of tertiary organic bases, and then condensing two molecules of this chloracetyl derivative with sodium disulphide or polysulphide to give a disulphide which yields a mercaptan on reduction.

Derivatives of dyes such as thioindigo containing the thiophenol group can be obtained by reacting the carboxylic acid chlorides or sulphonic acid chlorides of such dyes, with phenol-*o*-disulphide or phenol-*p*-disulphide or dithio-*m*-toluidine

and the resulting disulphides reduced to thiophenols by mild reducing agents. The disulphides obtained by oxidising mercapto aldehydes (whereby two molecules are linked together) can be condensed to anils with amino derivatives of dyes and then reduced to mercaptans (the disulphide group being split again). Disulphides of aromatic sulphochlorides can be reacted with amino derivatives of dyes whereby two molecules of such amino derivatives are linked together through the disulphide group; reduction splits the disulphide group giving thiophenol derivatives. In many cases the sulphochlorides of dyestuffs can themselves be easily reduced direct to the corresponding thiophenols. Dithiosalicic acid dichloride (Ber. 31, 1670, 59, 1077) can be reacted with dyestuffs containing amino, hydroxyl, and even sulphhydryl groups in the presence of tertiary organic bases, the resulting disulphide derivative of the dyestuff being finally reduced to the mercaptan as described in other cases above.

Other suitable compounds for use in the present invention are the thiophenols of quinoline yellow, of dithioanthraruffine, of thiazoles and of oxazines.

The insoluble silver and lead salts of thiophenols are very stable, and are therefore quite suitable.

By way of example, a yellow image can be readily obtained by treating a silver chloride image with an aqueous solution of the β -naphthalide of thioglycollic acid. In the case of a silver bromide image, it is best to add thiourea to the solution (which is soluble to the extent of about 1%). A red image can be obtained from a silver halide image by treatment with an aqueous solution of thiocarbonyl.

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. The method of colour processing a colour photographic element having three differentially colour sensitized silver halide emulsions inseparably coated on a single support in which a silver salt image in one of the layers is converted into a coloured mercaptide by reaction with an organic mercaptan or its ammonium or alkali metal salt.

2. The method as claimed in Claim 1, in which the silver salt image consists of silver chloride, initially present in the element or produced therein from a silver image or silver bromide image.

3. The method as claimed in Claim 1 or 2, in which the silver salt image is converted into silver ferrocyanide or lead ferrocyanide or a mixture thereof before

reaction with the organic mercaptan or its ammonium or alkali metal salt.

4. The method as claimed in any of the preceding Claims, in which the organic mercaptan is a derivative of a vat dye.
5. The method as claimed in any of the preceding Claims, in which the organic mercaptan is a derivative of a diazotizable amino compound.
6. A photographic element of the kind

defined containing a coloured image composed of a silver or other metal mercaptide.

7. The method of forming coloured photographic images substantially as herein described.

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Dated this 22nd day of October, 1938.

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