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3,623,877
**SILVER HALIDE COLOR PHOTOGRAPHIC
MATERIALS CONTAINING ALKALINE
EARTH METAL SALTS OF COLOR
COUPLERS**

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4 Claims

ABSTRACT OF THE DISCLOSURE

This application describes a process for the incorporation into a gelatino silver halide emulsion of a color coupler containing a carboxylic acid group which is characterised in that it comprises reacting an alkali metal salt of the color coupler with a water-soluble alkaline earth metal salt or magnesium salt in the presence of gelatin or a colloid medium compatible with gelatin to form a dispersion of the color coupler in the colloid medium and incorporating the said dispersion in the gelatino silver halide emulsion.

This invention relates to color photographic materials and their production.

Well known forms of color photography make use of color photographic materials which comprise photographic silver halide emulsions containing color couplers. These color couplers are destined to react with the oxidation products of aromatic amino color developing agents, such as N,N-dialkyl paraphenylenediamines and like compounds, formed during developing of the silver image, to form a colored dye image, usually an image in an indophenol or azomethine dye.

Considerable problems exist when making the addition of color coupler to the silver halide emulsion layer, the colloid medium of which is usually gelatin. One well known method is to employ a color coupler which has an acidic solubilising group and to dissolve the said color coupler in a solution of alkali metal hydroxide and add the resulting solution of the emulsion. A difficulty which arises is that there is frequently a tendency for reaction to occur between the acid group of the color coupler and the gelatin of the emulsion, giving rise to an increase in viscosity, with attendant difficulties in coating the resulting emulsion.

It is an object of the present invention to provide an improved process for the introduction of a color coupler into a gelatino silver halide emulsion, effective where the color coupler used contains a carboxylic acid group.

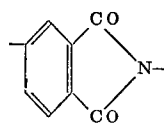
According to the present invention there is provided a process for the incorporation into a gelatino silver halide emulsion of a color coupler containing a carboxylic acid group which comprises reacting on alkali metal salt of the color coupler with a water-soluble alkaline earth metal salt or magnesium salt in the presence of gelatin or a colloid medium compatible with gelatin to form a dispersion of the color coupler in the colloid medium and incorporating the said dispersion in the gelatino silver halide emulsion.

By reacting a said color coupler with an alkaline earth metal or magnesium salt, e.g. calcium chloride, in the presence of gelatin or a colloid medium compatible therewith the calcium salt of the color coupler is obtained as a fine dispersion. This dispersion is of viscosity comparable with that of aqueous gelatin of the same concentration, i.e. is less than than the viscosity achieved

by the direct addition of the color coupler which comprises the free carboxylic acid or the alkali metal salt thereof to the gelatin.

It has been found that the effect is achieved with any of the alkaline earth metal salts, i.e. calcium, barium or strontium, and with the magnesium salts but the control of viscosity is best achieved with the aid of the calcium salts.

Whilst the method of the invention may be employed in association with any color coupler which has one or more free carboxylic acid groups or is capable of easily yielding a free carboxylic acid group and is thus able to form an alkali metal salt, it is of particular value in connection with color couplers which contain a phthalimide ring



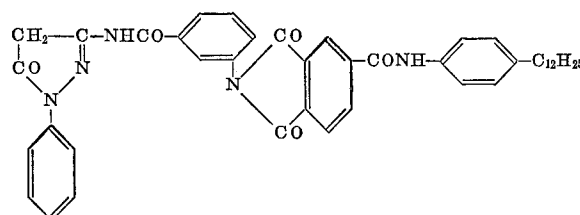
or a succinimide ring, and other analogous color couplers of which fission of the ring leads to compounds with free carboxylic acid groups, as described in British patent specification Nos. 944,838, 949,944, 1,004,075, 1,039,452 and 1,069,061.

It has further been found that the reaction between the alkaline metal salts of the color coupler of these types and the magnesium or alkaline earth metal salt is accelerated by the presence in the reaction mixture of a proportion of phenol. Exemplary of such color couplers are 4-(4-dodecylphenylaminocarbonyl)-N-(1-phenyl-5-pyrazonyl-3-)phthalimide, 4-(4-dodecylphenylaminocarbonyl)-N-[4-(4-methoxybenzoyl acetamide)phenyl]phthalimide, 4-(n-octadecylaminocarbonyl)-N-[β-(1-hydroxy-2-naphthamido)-ethyl]phthalimide, 1-phenyl-3-[α-(N-n-octadecylsuccinido)acetyl-amido]-5-pyrazolone.

Examples of other color couplers of use in the process of the present invention are 1-phenyl-3-(β-[N-(p-n-dodecylphenyl)-acetyl-amino]-β-carboxyl-n-propionyl-amino)-5-pyrazolone, 2-(β-[N-(p-n-dodecylphenyl)isobutyl-tyramino]-β-carboxy-n-propionyl-amino)-4-chloro-5-methylphenol, 4'-methoxybenzoylacet-5-(β-n-hexadecylsulphonylamino-β-carboxy-n-propionyl-amino)-2-methoxyanilide, 1-phenyl-3-[α-[N-n-hexadecylacetyl-amino]-β-carboxy-n-propionyl-amino]-5-pyrazolone.

In order to form the alkali metal salt of the color coupler the color coupler is dissolved in an alkali metal hydroxide solution e.g. caustic soda solution.

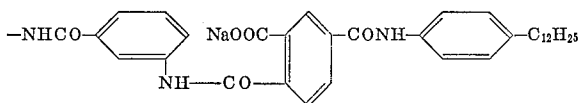
A color coupler of use in the present invention (referred to in Example 1 which follows as color coupler (A) has the formula:



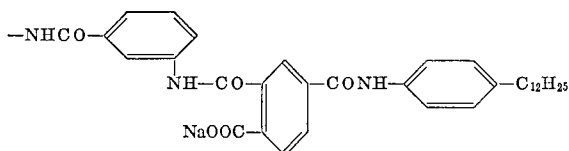
When this color coupled is dissolved in alkali, e.g. caustic soda, the imide ring opens to yield the sodium salt

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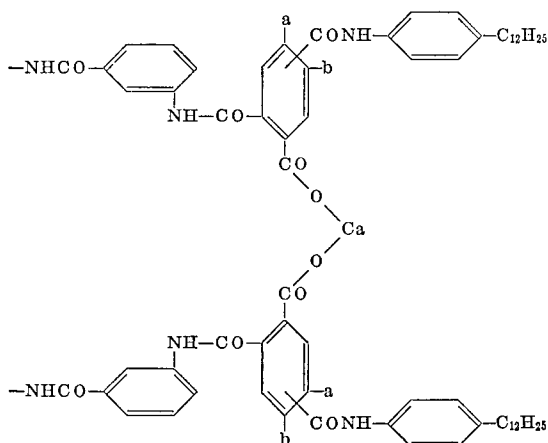
of the color coupler. The imide ring may open in one of two senses thus:



or



Thus when the sodium salt of the color coupler is reacted with an alkaline earth or magnesium salt in the presence of an aqueous colloid medium the resultant salt (calcium salt shown) may be shown thus:



The long chain alkyl ballasting group being substituted in either the *a* or *b* position in the phenyl ring depending on how the imide ring broke when forming the alkali metal salt of the colour coupler.

The following examples will serve to illustrate the invention.

EXAMPLE 1

Solution I

To a dispersion of 270 g. of gelatin in 2450 ml. of distilled water, add 1280 ml. of 0.1 molar calcium chloride solution and 118 ml. of 25% (w./v.) solution of phenol in methylated spirit.

Solution II

Dissolve 160 g. of color coupler A (see above) in 240 ml. of 2 N potassium hydroxide solution and dilute with distilled water to 1600 ml.

Adjust the temperature of both I and II to 50° C. and add I to II with stirring. Adjust the pH of the mixture to 9.0. Hold at 50° C. for 90 minutes.

EXAMPLE 2

Solution I

Dissolve 240 g. of the color coupler 4'-methoxybenzoyl-acet-2-methoxy-5-[β-carboxy-β(N-p-dodecylphenylacetyl-amino)propionyl-amino]anilide in 384 ml. of methanol, 240 ml. of 2 N potassium hydroxide solution and 1400 ml. of distilled water, and dilute to 2400 ml. with distilled water.

Solution II

Disperse 120 g. of gelatin in 1080 ml. of distilled water and add to this 300 ml. of 10% w./v. aqueous poly (vinyl alcohol) solution, 360 ml. of 4% w./v. aqueous

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Manoxol O.T. solution (dispersing agent) and 120 ml. of N acetic acid.

Add Solution II to Solution I and raise the temperature of the mixture to 65° C. Add, with stirring, 140 ml. of 1.0 molar magnesium chloride solution, also at 65° C., and 60 ml. of N acetic acid.

EXAMPLE 3

Dissolve 210 g. of the color coupler.

5'-[3-carboxy-3(N-octadecylisobutyramido)propionamido]-2'-methoxy-α-(4-methoxybenzoyl)acetanilide in 336 ml. of methanol, 168 ml. of 2 N potassium hydroxide solution and 1250 ml. of distilled water, and dilute to 2100 ml. with distilled water. To this mixture add 250 ml. of 10% w./v. aqueous poly (vinyl alcohol) solution and 107 g. of gelatin dispersed in 1500 ml. of distilled water. Raise the temperature to 60° C. and add, with stirring, 700 ml. of 0.2 molar calcium chloride solution, also at 60° C. Cool to 45° C. and add 400 ml. of 4% w./v. aqueous solution of Manoxol O.T. (dispersing agent).

The procedures described in Examples 1-3 yield dispersions in the form of particles smaller than 1μ in diameter. The viscosities of the formulations when measured showed little difference to those of gelatin solutions of equivalent concentrations.

The dispersions were added to gelatino silver halide photographic emulsions and coated as a green sensitive layer in the case of Example 1 and as blue sensitive layers in the cases of Examples 2 and 3 in standard reversal color material. No significant sensitometric differences were observed when compared with control coatings containing the same color couplers added by the conventional technique.

We claim as our invention:

1. A process for the production of a photographic gelatino silver halide emulsion comprising a color coupler, uniformly dispersed therein, which comprises incorporating into a gelatino silver halide emulsion a color coupler which contains a carboxylic acid group of which a calcium, barium or strontium salt is water-insoluble, by forming a dispersion of a said water-insoluble salt of the color coupler in an aqueous medium comprising gelatin or a colloid compatible with gelatin by reaction between an alkali metal salt of the color coupler and a water-soluble calcium, barium or strontium salt, in the presence of aqueous gelatin or an aqueous solution of a said compatible colloid, and incorporating said dispersion in the gelatino silver halide emulsion.

2. A process according to claim 1 wherein the color coupler is of the type which comprises a phthalimide or succinimide ring before conversion to the alkali metal salt thereof.

3. A process according to claim 2 wherein phenol is present in the reaction mixture.

4. A gelatino silver halide emulsion which comprises a color coupler containing a carboxylic acid group of which a calcium, barium or strontium salt is water-insoluble, which has been incorporated therein by a process which comprises reacting an alkali metal salt of the color coupler with a water-soluble calcium, barium or strontium salt in the presence of aqueous gelatin or an aqueous colloid medium compatible with gelatin to form a dispersion of the color coupler in the colloid medium and incorporating the said dispersion in the gelatino silver halide emulsion.

References Cited

UNITED STATES PATENTS

2,396,275	3/1946	Kirby	96-100
3,383,214	5/1968	Anderson	96-100

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