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COLOR PHOTOGRAPHY

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8 Claims. (Cl. 95—6)

This invention relates to photography and more particularly to photographic elements bearing emulsions which develop to form metallic silver and dyes in admixture with each other.

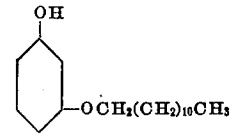
A principal object of this invention is to provide water insoluble dye-forming bodies, hereinafter termed "color-formers", which yield dyes by coupling with the oxidation products of photographic developing agents. A further object of the invention is to prepare multilayer photographic films containing color-formers which do not migrate from layer to layer or from the film into the processing baths. Another object of the invention is to prepare photographic emulsions containing dispersed therein such color-formers. A further object is to prepare colored photographs by employing such emulsions on either opaque or transparent supports. Additional and more specific objects will plainly appear from the detailed specification and claims presented herein in exemplification and not in limitation of the present invention.

It has already been proposed to incorporate with photographic emulsions color-formers which, in the presence of the oxidation products of certain photographic developing agents, form more or less insoluble dyes in situ with the metallic silver image. In subtractive multicolor photography it is also known to coat multiple layers of emulsions, having different color sensitivities, as monopack films. It has also been proposed to incorporate in the individual emulsion layers of such monopacks dye-forming components which couple with the oxidation products of certain photographic developing agents to form more or less insoluble dyes.

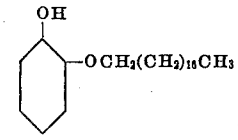
Prior to the present invention it has been highly desirable that both the dye-forming components themselves, and the dyes thus formed, remain within the layer in which the dye-component was originally incorporated and that at any stage in the life of the film, that they do not migrate or diffuse to another layer.

The above requirements are effectively obtained in the present novel invention as will hereinafter be described.

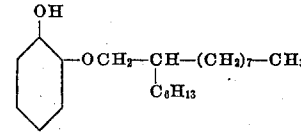
It has now been discovered that certain phenolic bodies are particularly suited for the above purposes. They are generically the alkoxy monohydric and preferably mononuclear phenols in which the paraposition to phenolic hydroxyl is unoccupied, and in which the alkoxy group has at least eight carbon atoms. The latter group may be saturated or unsaturated, straight or branched chain, and primary, secondary, or tertiary. Specific ethers that may be used are resorcinol mono-n-dodecyl ether of the formula



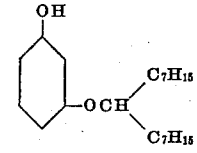
pyrocatechol-n-octadecyl ether of the formula



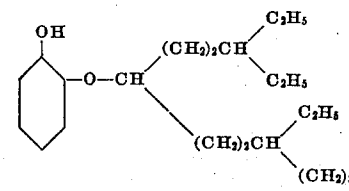
resorcinol mono-n-octyl ether, resorcinol mono-n-decyl ether, resorcinol mono-myricyl ether, pyrocatechol mono-n-dodecyl ether, resorcinol mono-n-octadecyl ether, pyrocatechol mono-2-hexyldecyl ether, of the formula



resorcinol mono-8-n-pentadecyl ether of the formula



resorcinol mono-n-9,10-octadecenyl ether, and pyrocatechol mono-6-(3,9-diethyl) tridecyl ether of the formula



The alkoxy phenols of the above type may be prepared in any convenient manner, as, for example, by condensing an ortho or meta dihydric phenol with the appropriate alkyl halide. Resorcinol mono-n-dodecyl ether may for example be prepared as follows, parts given being by weight: Nine and five-tenths (9.5) parts of potassium hydroxide and 20 parts of dry n-butyl alcohol are gently heated to boiling under reflux.

Twenty-one and five-tenths (21.5) parts of resorcinol dissolved in 48 parts of dry n-butyl alcohol are added slowly with continued boiling, followed by 41.0 parts of n-dodecyl bromide, and 0.8 part of solid potassium iodide. The reaction is allowed to continue with gentle refluxing for twenty hours. The reaction vessel is then cooled; water is added; and the butyl alcohol is distilled off. After cooling, a waxy solid layer appears, and the aqueous layer is decanted off. After washing and boiling with hot water until the solution shows a negative test for resorcinol, the solid mass is heated with a solution of 10 parts of sodium hydroxide in 200 parts of water and 80 parts of ethyl alcohol. The mono ether passes into this solution leaving the diether as an oil. After separation and acidification of the aqueous layer with hydrochloric acid, the free resorcinol mono-n-dodecyl ether is obtained as a semi-solid mass. The crude product thus obtained is dissolved in diethyl ether, repeatedly washed with water and the diethyl ether allowed to evaporate off, whereupon the pure mono-n-dodecyl ether of resorcinol is obtained by vacuum distillation (B. P. 247° C. at 20 mm.).

The above described higher alkoxy phenols are incorporated in photographic emulsions, for example, as follows:—

To 100 cc. of 2% by weight aqueous gelatin solution is added a solution consisting of 8 ccs. ethyl alcohol and 0.4 gram of the alkoxy phenol, e. g. the mono-n-dodecyl ether of resorcinol. The total weight of the combined solutions is then brought to 150 grams with water, after which the mixture is added to 100 grams of a silver halide-gelatino emulsion (which may or may not contain sensitizers) and mixed thoroughly. The latter emulsion is coated upon a suitable photographic support such as paper or a cellulose derivative base, or upon another photographic emulsion layer which may or may not contain another color-forming dye component. Alternatively, the silver halide emulsion may be coated on a plain or colored separating layer as one sensitive layer of a series of such layers on a monopack, multi-layered film for use in color photography.

After exposure directly in a camera or by printing through appropriate color records, the above film comprising at least one sensitive layer containing a higher alkoxy phenol is developed by means of an alkaline solution of p-phenylenediamine or its alkyl substituted derivatives such as p-amino-dimethyl- or diethyl-aniline, whereupon the exposed silver halides are reduced to metallic silver and insuluble blue-green dyes are formed in situ with the reduced silver due to the coupling of the oxidation products of the p-phenylene diamine developer, or its alkyl substituted derivative, with the dihydric phenolic ether. Other p-phenylenediamines whose oxidation products couple with the alkoxyphenol to form insoluble dyes may be used to develop the exposed silver halide. It is necessary that one of the amino groups be primary; the other may be primary but should preferably be secondary or tertiary.

Besides the above use, these higher alkoxy phenols may also be applied in color photography processes where a uniformly-dyed layer containing a silver image is differentially bleached with respect to the amount of silver present. In such a case, either before or after the formation of the silver image with a developer whose oxidation products are non-coupling with the color-forming dihydric phenolic ether, an overall blue-green dye is formed in the emulsion layer by treating it with a solution of the direct oxidation product of the p-phenylene-diamine type of developer such as p-nitroso-aniline, p-nitroso-dimethyl-aniline, p-nitroso-diethyl-aniline, etc. After the layer of dye is formed, it is differentially bleached by treatment with a solution of stannous chloride and potassium bromide according to the process of Christensen.

The above described higher alkoxy phenols may also be incorporated in gelatin layers and sensitized by treatment with potassium or ammonium bichromate. After appropriate exposure through a color separation record, the film may be developed in a p-phenylene-diamine type of developer whereupon the chromium oxides formed by the exposure oxidize the developing agent and cause coupling with the alkoxy phenol to form blue-green dye images which need only washing to complete the colored picture. Another method is to "develop" the exposed bichromated colloid layer containing the alkoxy phenol with hot water to remove the soluble colloid wherever it was not exposed and then to form a blue-green image by treatment with p-nitroso-aniline or an alkylated p-nitroso-aniline derivative solution.

Among the characteristic advantages of the high-mono-alkyl ethers of dihydric phenols herein described are:

A. When incorporated in a given photographic layer they do not migrate or diffuse either in their dry state or when the film is subjected to bathing in water or alkaline solutions.

B. These compounds will react with the oxidation product of a p-phenylenediamine developer, as produced in the reduction of silver halides, to form blue-green dyes of such color-absorption and transmission characteristics as to make them particularly useful in multicolor photography processes for the production of colored images.

C. The dyes thus produced do not tend to migrate nor diffuse after their formation.

Inasmuch as the novel color-formers herein described are insoluble in water and in the ordinary photographic processing baths, the excess color-forming bodies which have not entered into the dye-formation process therefore remain in the photographic layer in such a fine state of division that they have not the slightest effect on quality of the finished product. However, their presence in the finished color picture may be readily detected by suitable tests.

While the foregoing specification sets forth preferred exemplifications of the present invention it is intended to include all variations and modifications within the spirit and scope of the appended claims.

We claim:

1. A photographic emulsion comprising an alkoxy monohydric phenol in which the alkoxy group contains at least eight carbon atoms, and in which the para position to phenolic hydroxyl is unoccupied.

2. A color-forming photographic layer comprising a gelatino-silver halide emulsion and an alkoxy monohydric phenol in which the alkoxy group contains at least eight carbon atoms and in which the para position to the phenolic hydroxyl is unoccupied.

3. A color-forming photographic emulsion containing an alkoxy mononuclear monohydric phenol in which the alkoxy group contains at least eight carbon atoms and in which the para position to the phenolic hydroxyl is unoccupied.

4. A color-forming photographic emulsion con-

taining a mono alkyl ether of resorcinol in which the alkyl radical contains at least eight carbon atoms.

5. A color-forming photographic emulsion comprising a gelatino-silver halide emulsion containing a mono-n-alkyl ether of resorcinol in which the alkyl radical contains at least 8 carbon atoms.

6. A color-forming photographic emulsion containing a mono-n-dodecyl ether of resorcinol.

7. A color-forming photographic emulsion containing a mono-n-octadecyl ether of resorcinol.

8. A color-forming photographic emulsion containing a mono-n-9, 10-octadecenyl ether of resorcinol.

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