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2,768,894

PHOTOGRAPHIC ELEMENT WITH EMULSION LAYER CONTAINING COLOR FORMER AND WETTING AGENT

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10 Claims. (Cl. 95-6)

This invention relates to color photography and more particularly to color forming gelatino silver halide emulsions and emulsion layers containing non-ionic wetting agents derived from branched-chain aliphatic alcohols. It relates further to photographic elements and multilayer color materials containing such emulsion layers.

Conventional subtractive multilayer materials are composed of separate emulsion layers sensitized to the primary colors of the spectrum, namely, blue, green and red, and contain color formers fast to diffusion which, upon development with primary aromatic amino developing agents, yield azomethine, indoaniline or phenazonium (azine) dye images. It is customary to separate these emulsion layers by intermediate gelatin layers which serve as separating layers and if colored by the addition of a dye, act also as filter layers. These separating layers prevent color falsification which occurs otherwise as the result of the migration of silver halide grains and color formers of two adjoining emulsion layers. The top layer of the multilayer element is overcoated with a gelatin layer which serves primarily as an antiabrasion layer but may contain an ultraviolet absorbing substance. Generally, these intermediate or surface gelatin layers are coated immediately as soon as the emulsion layer which it is supposed to cover has been coated and chilled and it is not necessary to dry the emulsion layer before it is overcoated.

It is necessary to add saponin or synthetic surface active agents to the emulsion and clear gelatin layers to permit the even wetting of the support or of the layer coated onto the support. The surface active agents are also needed in order to avoid the formation of repellency spots which may vary in size from those barely visible, to those several inches in diameter.

Among the most useful color formers available to the photographic industry are those which contain a benzimidazole nucleus which is further substituted by a long chain alkyl group attached to one of the nitrogen atoms, and a sulfonic or carboxylic acid group. However, gelatino silver halide emulsion layers containing this type of color former suffer from the serious shortcoming that they cannot be overcoated in the chilled state with plain gelatin layers in the conventional manner. For some reason, air bubbles are formed when the chilled emulsion containing the benzimidazole color former is overcoated with a warm gelatin solution. The gelatin layers become streaky and are of uneven thickness. This deficiency in surface regularity is translated to the next emulsion layer which, in turn, becomes also uneven and streaky. Furthermore, air bubbles are formed which are large enough to be seen without magnification but become particularly disturbing when the finished color film is used for projection. This shortcoming is not alleviated by the use of conventional surface active agents such as saponin or the conventional synthetic surfactants.

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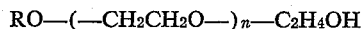
In order to avoid these unacceptable defects, it has been necessary up to now to dry completely the emulsions containing the benzimidazole substituted color former before overcoating them with the warm gelatin solution of the separating layer. This intermediate drying involved a serious loss of time, tied up the coating machinery and resulted in a serious reduction in output.

It is, therefore, an object of the present invention to provide for the overcoating of photographic emulsions containing a color former with a benzimidazole nucleus with warm gelatin solution without necessitating the intermediate drying of the emulsions.

Other objects will be apparent from the following description of the invention.

I have found that a photographic emulsion containing a color former in which the color forming portion of the molecule is linked directly to the carbon atom in the 2-position of a benzimidazole nucleus, and in which the benzimidazole nucleus is further substituted by a long aliphatic hydrocarbon chain attached to the nitrogen atom in the 1-position and by a water solubilizing group such as a sulfonic or carboxylic acid group which is attached to the benzene ring, can be overcoated immediately after chilling and without intermediate drying by adding to this emulsion, a non-ionic wetting agent which is the reaction product of a branched-chain monohydric alcohol with ethylene oxide.

The reaction products of ethylene oxide and branched-chain aliphatic alcohols are prepared in accordance with the procedure given in U. S. Patent 1,970,578 with the exception that branched-chain alcohols are used in place of the normal (straight-chain) alcohols disclosed in this patent. In general, the reaction products of this invention are prepared by reacting one molar equivalent of the branched-chain monohydric alcohol with from 5 to 20 molar equivalents of ethylene oxide. The reaction is carried out at elevated temperatures and under pressure in the presence of suitable catalysts or in aqueous alkaline or acid solutions as described in U. S. Patent 1,970,578. The reaction products obtained have at room temperature, the consistency of wax, sirup or honey and are soluble in water and in the lower alcohols such as methanol, ethanol, n-propanol, isopropanol or mixtures of these alcohols with water. The reaction products are characterized by the following general formula:



wherein R is a branched-chain alkyl group having from 8 to 18 carbon atoms and n represents an integer from 4 to 19.

The following alcohols are illustrative of the branched-chain monohydric alcohols which can be reacted with ethylene oxide to yield the surfactants utilized in accordance with this invention.

- 2-ethylhexanol-1
- 1,1-dimethyldecanol-1
- 2-n-butyloctanol-1
- 4-n-butyloctanol-1
- 2,5,8-trimethylnonan-5
- 2,6,8-trimethylnonan-4
- 2-ethyldecanol-1
- 2-n-propylnonan-1
- 2,2-dimethyldecanol-1
- 2,6-dimethyldecanol-6
- 4-methyl-4-propyloctanol-5
- 2-methyldodecanol-1
- 3-methyldodecanol-3
- 2-methyldodecanol-2
- 2-butylnonanol-1
- 2,5,9-trimethyldecanol-5
- 3-ethylundecanol-3

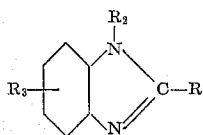
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3-methyldodecanol-3
 2,8-dimethyl-5-ethylnonan-5
 3,3,5-triethylheptanol-4
 2,3,3,5,5,6-hexamethylheptanol-4
 2-methyltridecanol-3
 3-n-butyldecanol-1
 2,8-dimethyl-5-propylnonan-5
 2-n-pentylnonan-1
 7-ethyl-2-methylundecan-4
 2,8-dimethyl-5-isobutylnonan-5
 3,7,11-trimethyldodecanol-1
 3,3,5,5-tetraethylheptanol-4
 2,4-dimethyltridecanol-4
 7-methylpentadecan-9
 2,6,7,11-tetramethyldodecanol-6
 2,8-dimethyl-5-isoamylnonan-5
 3,9-diethyltridecanol-6
 2,6,10-trimethylpentadecan-2

The amounts of the reaction product employed range from 0.005% to 2.0% based on the weight of dry gelatin used in the preparation of the liquid emulsion containing the benzimidazole substituted color former. The reaction products of the branched-chain monohydric alcohol and ethylene oxide are compatible in these emulsions with saponin; the combined use of these two surfactants has the added advantage of spreading the emulsion coating more evenly.

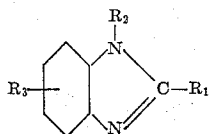
It has already been proposed to use various non-ionic wetting agents in photographic color emulsions for a variety of purposes including the prevention of static and fog, and improved dispersion of the color formers in the emulsion. However, the surfactants recommended by the prior art are incapable of accomplishing the immediate overcoating of a chilled emulsion containing a benzimidazole substituted color former with a warm gelatin solution and necessitate the intermediate drying of the emulsion.

The color formers used contain, in their molecule, a benzimidazole nucleus which is substituted on the nitrogen atom in the 1-position by an alkyl chain of at least 10 carbon atoms and substituted in the 5-position by a water solubilizing group, and in which the benzimidazole nucleus is connected through its carbon atom in the 2-position to the residue of a color forming residue which is reactive with the oxidation products of a primary amino developing agent and contains a reactive methylene or ethenol or phenolic hydroxyl group. These color formers are characterized by the following general formula:



wherein R is a radical containing a reactive methylene, ethenol or phenolic hydroxyl group capable of reacting with the oxidation products of an aromatic amino developing agent to form an azomethine, indoaniline or phenazonium dyestuff, R₂ is an alkyl chain containing at least 10 carbon atoms, e. g., decyl, undecyl, dodecyl, tetradecyl, pentadecyl, hexadecyl, octadecyl and the like, and R₃ is a water solubilizing group such as sulfo, carboxy and the like.

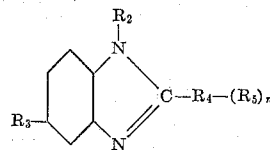
More particularly, color formers containing a benzimidazole nucleus as part of the molecule and capable of forming dye images upon development with a dialkylaminoaniline developing agent are illustrated by the following structural formulae:



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and

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wherein R₁ is a hydroxy aromatic radical, such as substituted or unsubstituted hydroxynaphthyl, hydroxyphenyl and the like, the hydroxy group being nuclear attached, and said radical being linked to the benzimidazole radical in ortho-position to said hydroxy group, R₄ is a phenyl radical, R₅ is the grouping —NH—COCH₂A in which A is an alkyl radical, e. g., acetyl, propionyl, butyryl and the like, an aroyl radical, e. g., benzoyl, naphthoyl and the like, a cyano or carbethoxy group and R₂ and R₃ have the same values as above. Suitable examples of color formers embraced by these general formulae are disclosed in U. S. Patents 2,545,687 and 2,547,307 in which their method of preparation is also described.

Color formers substituted by a benzimidazole nucleus and capable of forming magenta phenazonium (azine) dye images upon development with either the triamino-benzene developers described in U. S. Patent 2,486,440 or with N,N-dialkylphenylenediamine developers are disclosed in L. C. Hensley's copending application Serial No. 293,643, filed June 14, 1952, now United States Patent 2,701,766, entitled "Developers for and Method of Producing Phenazonium Dyestuff Images with p-Di-alkylaminoaniline Developing Agents." They are characterized by the following general formula:

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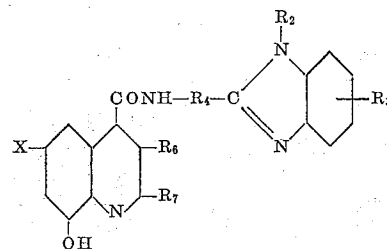
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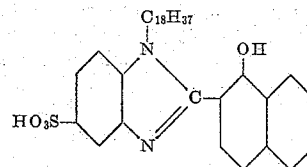


wherein R₂, R₃ and R₄ have the same values as above, R₆ is hydrogen, a carboxyalkyl, allyl or lower alkyl group, R₇ is an allyl, lower alkyl, aryl or heterocyclic group.

The invention is further illustrated by the following examples but it is to be understood that the invention is not restricted thereto. The parts and percentages are by weight unless otherwise stated.

Example 1

To 1 kilogram of a liquid gelatino silver halide emulsion sensitized to red light and containing about 80 grams of gelatin, 50 grams of silver bromo iodide and 5 grams of 1-octadecyl-2-[2'-(1'-hydroxynaphthyl)]benzimidazole-5-sulfonic acid as a color former which is characterized by the following structural formula:



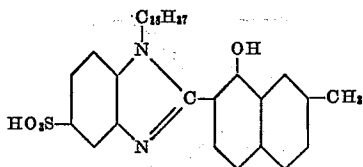
there was added 1.25 grams of saponin and 100 milligrams of the reaction product of 1 molar equivalent of 2,6,8-trimethylnonan-4 and 12 molar equivalents of ethylene oxide prepared in analogy to the procedure described in Example 19 of U. S. Patent 1,970,578. This emulsion was coated upon a cellulose acetate film base, chilled and immediately overcoated with a warm aqueous solution of gelatin having a temperature of 40° C. and

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containing 20 grams of gelatin and 1 gram of saponin per liter. The coating was dried, exposed in a sensitometer and developed to a cyan image with a color developer containing a p-dialkylaminoaniline as the developing agent. After shortstopping, bleaching, fixing and washing, the color developed film was dried. It was completely free of air bubbles, whereas a comparison sample which had been prepared in an analogous manner except that the condensation product of 2,4,6-trimethylnonan-4 and ethylene oxide had been omitted showed a large number of air bubbles which were visible to the naked eye and became more pronounced upon projection.

Example II

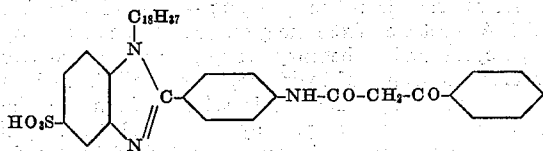
To one kilogram of a gelatino silver halide emulsion as described in Example I, there was added as a cyan color former, 6 grams of 1-octadecyl-2'-[2'-(1'-hydroxy-7'-methyl)naphthyl]benzimidazole-5-sulfonic acid having the following structural formula:



and 50 milligrams of the reaction product of 1 molar equivalent of 7-ethyl-2-methylundecanol-4 and 15 molar equivalents of ethylene oxide. The emulsion was coated onto a cellulose acetate-butyrate filmbase, chilled and overcoated with a warm 2.5% gelatin solution containing 0.5 gram of saponin per liter. The material was dried, exposed and processed to a color image which was free from air bubbles, whereas a comparison sample containing 1.0 gram of saponin but no ethylene oxide reaction product was full of air bubbles.

Example III

One gram of saponin, 0.175 gram of the reaction product of 1 molar equivalent of 2,6,8-trimethylnonan-4, 12 molar equivalents of ethylene oxide and five grams of the yellow color former of 2-(4'-benzoylacetaminophenyl)-1-octadecylbenzimidazole-5-sulfonic acid having the following structural formula:



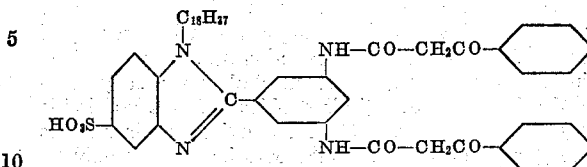
were added to a blue sensitive gelatino silver halide emulsion. This emulsion was coated onto a cellulose acetate filmbase, chilled and immediately overcoated with a warm 2% gelatin solution containing 1.0 gram of saponin per liter. The material was dried, exposed through a transparency, developed in a black and white developer, shortstopped, color developed in a developer containing N,N-di-(β-hydroxyethyl)phenylenediamine as the color developing agent, shortstopped, bleached, fixed, washed and dried. A positive yellow azomethine dye image was obtained which was completely free from air bubbles, whereas a comparison sample which had been prepared in an identical manner except that the condensation product of 2,6,8-trimethylnonan-4 and ethylene oxide had been omitted was streaky and marred by large air bubbles.

Example IV

Example III was repeated with the exception that the 5 grams of 2-(4'-benzoylacetaminophenyl)-1-octadecylbenzimidazole-5-sulfonic acid were replaced by 7 grams

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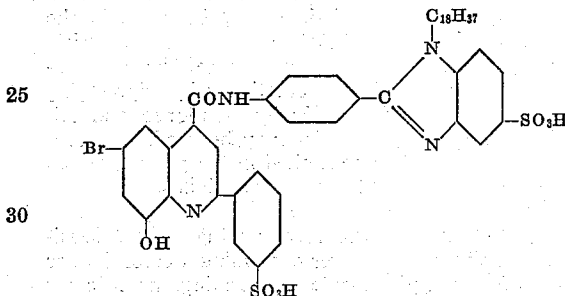
of 2[(3',5'-dibenzoyl-acetamino)phenyl]-1-octadecylbenzimidazole-5-sulfonic acid having the following structural formula:



The yellow picture obtained after reversal development did not show any air bubbles, whereas the type material which had been prepared without the use of the ethylene oxide addition product was streaky and full of air bubbles.

Example V

Six grams of the magenta color former 2-[4-(6-bromo-8-hydroxy-2-(2'-sulfophenyl)-cinchoninoyl)-aminophenyl]-1-octadecyl-5-sulfobenzimidazole having the following structural formula:



were added together with 0.2 gram of the reaction product of 2,6,8-trimethylnonan-4 and ethyleneoxide and 0.8 gram of saponin to a green sensitive emulsion which was coated onto the cellulose acetate film base, chilled and immediately overcoated with an aqueous gelatin solution containing 22 grams of gelatin and 1.2 grams of saponin per liter and having a temperature of 40° C. The material is dried, exposed with green light through a black and white transparency, developed in a color developer containing 4-(di-β-hydroxyethyl)-aminoaniline as the color developing agent, shortstopped, hardened, bleached, fixed, washed and dried. The finished magenta positive was free from air bubbles, whereas a comparison sample from which the reaction product of 2,6,8-trimethylnonan-4 and ethylene oxide had been omitted was unusable because it contained a great number of large air bubbles.

Example VI

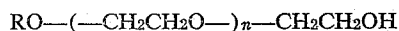
A cellulose acetate butyrate film base was coated with a red sensitive emulsion containing 5 grams of 1-octadecyl-2-[2'-(1'-hydroxynaphthyl)]-benzimidazole-5-sulfonic acid, 1.25 grams of saponin, 0.15 gram of the reaction product of ethylene oxide and 2,6,8-nonan-4 as described in Example I. The red sensitive emulsion was chilled and immediately overcoated with a warm 2% gelatin solution which contained .5 gram of saponin per liter. This gelatin layer was chilled and overcoated with a green sensitive silver halide emulsion containing, per kilogram, 15 grams of 1-(4'-phenoxy-3'-sulfophenyl)-3-stearyl-5-pyrazole and .5 gram of saponin. The green sensitive emulsion was chilled after coating and overcoated with a 2% clear gelatin containing 0.5 gram of saponin per liter. The gelatin layer was chilled and overcoated with a blue sensitive emulsion containing 2-(4'-benzoylacetaminophenyl)-1-octadecylbenzimidazole-5-sulfonic acid, 0.175 gram of the reaction product of ethylene oxide and 2,6,8-trimethylnonan-4, and 1.0 gram of saponin as described in Example III. This blue sensitive emulsion was chilled and overcoated with a clear gelatin antiabrasion layer which contained 0.5 gram of saponin per liter.

The finished multilayer color film was dried, exposed through a multicolor transparency and processed by reversal development to a duplicate color transparency. The color developed material was completely free of air bubbles. A comparison sample which had been prepared without the use of the reaction product of ethylene oxide and the branched-chain alcohol was streaky, contained a large number of air bubbles and was unsuitable for projection purposes. The formation of air bubbles in another comparison sample could be avoided only by drying the red sensitive and the blue sensitive emulsion layers containing the benzimidazole substituted color formers before overcoating them with the gelatin separation and anti-abrasion gelatin coatings. However, this intermediate drying had the disadvantage of extending the time needed for the coating operation and thus reducing the potential output of the coating equipment.

While the present invention has been described with reference to certain preferred procedures, materials and uses, it is understood that the invention is not limited thereto, that numerous variations may be made in the procedures herein described and that equivalent materials may be substituted. For example, benzimidazole substituted color formers and aromatic amino developing agents other than those specifically mentioned and utilized in the foregoing examples may be used. Accordingly, I do not intend to be limited in the patent granted except as necessitated by the appended claims.

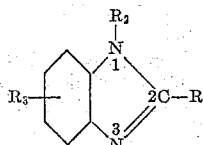
I claim:

1. A photographic element comprising a light sensitive gelatino silver halide layer containing a color former fast to diffusion and capable of forming, upon color development with a primary aromatic amino developing agent, a dye image selected from the glass consisting of azomethine, indoaniline and phenazonium dye images, said color former containing a benzimidazole nucleus connected through its carbon atoms in the 2-position to the residue of the color forming molecule which is reactive with the oxidation product of a primary developing agent and contains a reactive group selected from the class consisting of a reactive methylene, ethenol and phenolic hydroxy group, said benzimidazole nucleus being substituted on one of the nitrogen atoms by a long chain aliphatic group and substituted in the benzene portion by a water solubilizing group, said emulsion containing as a surface active agent, the non-ionic reaction product of a branched-chain monohydric alcohol and ethylene oxide characterized by the following general formula:



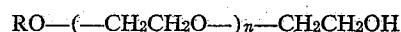
wherein R is a branched chain alkyl group having from 8 to 18 carbon atoms, and n is an integer from 4 to 19.

2. A photographic element comprising a support bearing a photographic gelatino silver halide emulsion layer containing a color former fast to diffusion which is reactive with the oxidation products of a primary amino developing agent to yield, upon exposure and development with a primary amino developing agent, a dye image selected from the group consisting of azomethine, indoaniline and phenazonium dyes, said color former containing a benzimidazole radical characterized by the following general formula:



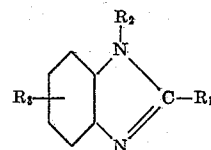
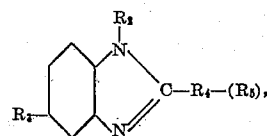
wherein R is the residue of the color forming molecule and contains a group selected from the class consisting of methylene, ethenol and phenolic hydroxy groups capable of reacting with the oxidation products of the pri-

mary amino developing agent, R2 is an aliphatic hydrocarbon radical containing at least 10 carbon atoms, R3 is a water solubilizing group and the carbon in the 2-position is linked to the residue of the color forming molecule which contains a reactive group selected from the group consisting of methylene, ethenol and phenolic hydroxy groups, said emulsion containing a non-ionic surfactant characterized by the following general formula:

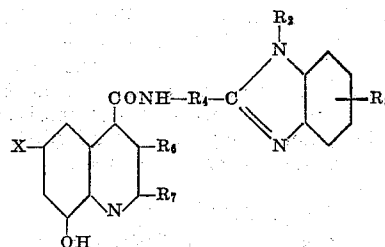


wherein R is a branched-chain alkyl group having from 8 to 18 carbon atoms and n is an integer from 4 to 19.

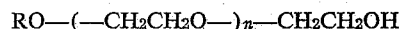
3. A photographic element comprising a support bearing a photographic silver halide emulsion layer containing, in addition to a benzimidazole substituted color former selected from the class corresponding to the following formulae:



and



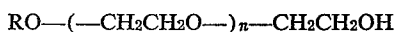
wherein R1 is a hydroxy aromatic radical, the hydroxy group being nuclear attached, and said radical being linked to the benzimidazole nucleus in ortho position to said hydroxy group, R2 is an alkyl chain of at least 10 carbon atoms, R3 is a water solubilizing group, R4 is a phenyl radical, R5 is the grouping $-NH-COCH_2A$ in which A is selected from the group consisting of alkyl, aryl, cyano and carbethoxy groups, R6 is selected from the class consisting of hydrogen, carboxyalkyl, allyl and lower alkyl groups, and R7 is selected from the class consisting of lower alkyl, allyl, aryl and heterocyclic groups; a non-ionic surfactant characterized by the following general formula:



wherein R is a branched-chain alkyl group having from 8 to 18 carbon atoms and n is an integer from 4 to 19.

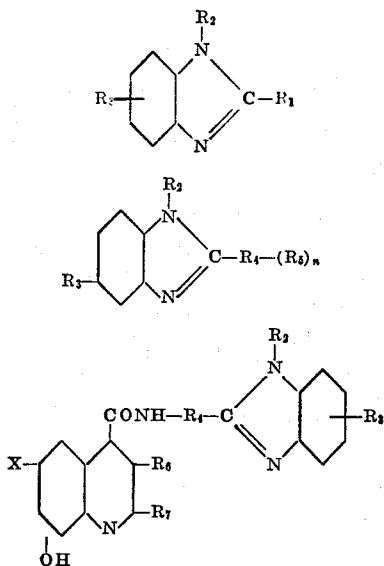
4. A multilayer photographic color film comprising a support bearing superimposed red, green and blue sensitive gelatino silver halide emulsions containing color formers capable of yielding, upon development with a primary amino developing agent, a dye image selected from the group consisting of azomethine, indoaniline and phenazonium dye images, the emulsion layers being in contact with gelatin layers free from silver halide and at least one of the photographic gelatin silver halide emulsion layers containing a color former having a benzimidazole nucleus which is connected through its carbon atom in the 2-position to the residue of the color forming molecule which is reactive with the oxidation products of the primary amino developing agent and containing a reactive group selected from the class consisting of reactive methylene, ethenol and phenolic hydroxy

groups, said benzimidazole nucleus being substituted on one of the nitrogen atoms by an alkyl radical containing at least 10 carbon atoms, and in the benzene portion by a water-solubilizing group, said emulsion containing as a surfactant, the non-ionic reaction product of a branched-chain monohydric alcohol and ethylene oxide characterized by the following general formula:

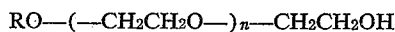


wherein R is a branched-chain alkyl group having from 8 to 18 carbon atoms and n is an integer from 4 to 19.

5. A multilayer photographic color film having a support bearing in the following order, a red sensitive gelatino silver halide emulsion layer containing a color former, a separating gelatin layer, a green sensitive gelatino silver halide emulsion layer containing a color former, a separating gelatin layer, a blue sensitive emulsion layer and a gelatin surface coat, said color formers being fast to diffusion and capable of forming, upon development with a primary amino developing agent, a dye image selected from the group consisting of azomethine, indoaniline and phenazonium dyestuffs complementary in color to the sensitivity of the layer in which the color former is incorporated, at least one of the silver halide emulsion layers containing as the color former, a compound selected from the class corresponding to the following formulae:



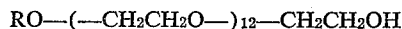
wherein R₁ is a hydroxy aromatic radical, the hydroxy group being nuclear attached, and said radical being linked to the benzimidazole nucleus in ortho position to said hydroxy group, R₂ is an alkyl chain of at least 10 carbon atoms, R₃ is a water solubilizing group, R₄ is a phenyl radical, R₅ is the grouping $\text{---NH---COCH}_2\text{A}$ in which A is selected from the group consisting of alkyloyl, aroyl, cyano, and carbethoxy groups, R₆ is selected from the class consisting of hydrogen, carboxyalkyl, allyl and lower alkyl groups and R₇ is selected from the class consisting of lower alkyl, allyl, aryl and heterocyclic groups; said emulsion containing a benzimidazole substituted color former containing as a surfactant, the reaction product of said branched-chain monohydric alcohol and ethylene oxide characterized by the following general formula:



wherein R is a branched-chain alkyl group of from 8 to 18 carbons and n is an integer from 4 to 19.

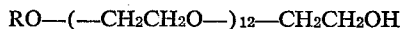
6. A photographic element according to claim 1 wherein said branched chain alcohol is 2,6,8-trimethylnonanol-4.

7. A photographic element according to claim 2 wherein said surfactant is characterized by the following formula:



wherein R is a 2,6,8-trimethylnonanol-4 group.

8. A photographic element according to claim 3 wherein said surfactant is characterized by the following formula:



wherein R is a 2,6,8-trimethylnonanol-4 group.

9. A multilayer photographic color film according to claim 4 wherein said branched chain alcohol is 2,6,8-trimethylnonanol-4.

10. A multilayer photographic color film according to claim 5 wherein said branched chain alcohol is 2,6,8-trimethylnonanol-4.

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