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Verbrugghe et al.

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[54] PHOTOGRAPHIC SILVER HALIDE COLOR MATERIAL UTILIZING BENZOYLACETAMIDE COLOR COUPLERS

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[52] **U.S. Cl.** **96/55,** 96/74, 96/100, 96/56.2, 96/56.3

[51] **Int. Cl.** **G03c 7/00,** G03c 1/40

[58] **Field of Search** 96/55, 100

[56] **References Cited**

UNITED STATES PATENTS

2,895,826	7/1959	Salminen et al.	96/100
3,056,675	10/1962	Hoffstadt	96/100
3,393,040	7/1968	Verbrugghe et al.	96/100

Primary Examiner—J. Travis Brown

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[57] **ABSTRACT**

Photographic materials are described comprising a light-sensitive silver halide emulsion layer and a benzoylacetamide color coupler capable of forming a yellow azomethine dye by reaction with an oxidized aromatic primary amino developing agent in which the benzoyl part of the color coupler contains at least one substituent of the formula:

$$RCG_2Q-$$

wherein:

R is hydrogen, fluorine or polyhaloalkyl, and

Q is oxygen, sulphur or sulphonyl.

These color couplers in light-sensitive silver halide emulsions provide photographic materials having improved light stability.

8 Claims, No Drawings

PHOTOGRAPHIC SILVER HALIDE COLOR MATERIAL UTILIZING BENZOYLACETAMIDE COLOR COUPLERS

This invention relates to the production of photographic color images, to yellow forming color couplers used therein and to photographic materials containing such color couplers.

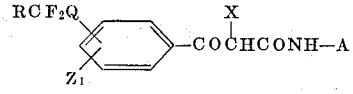
It is known that for the production of a photographic color image in a light-sensitive silver halide layer, the exposed silver halide is developed to a silver image by means of an aromatic primary amino compound in the presence of a color coupler which reacts with the oxidized developing substance to form a dyestuff on the areas corresponding to the silver image.

In the subtractive three-color photography a light-sensitive photographic color material is used containing a red-sensitized, a green-sensitized and a blue-sensitive silver halide emulsion layer wherein on color development, by the use of appropriate color couplers, a cyan, magenta and yellow dyestuff image are formed respectively.

One of the basic difficulties confronting color photography concerns the stability of the dyes making up the colored photographic images against light, heat and humidity. Although color photography has undergone much improvement since the appearance of the use of coupler compounds for the formation of colored images, greater dye stability is still needed and sought after.

According to the present invention there are provided novel benzoylacetamide color couplers comprising in the benzoyl part at least one substituent corresponding to the formula RCF_2Q- wherein Q stands for oxygen, sulphur, or sulphonyl and R stands for hydrogen, fluorine or poly-halo-alkyl such as $-CHF_2$, -CHFCl, -CHFBr, $-CFCl_2$, $-CCl_3$, -CHF-CF_3, etc.

More particularly, in accordance with the present invention there are provided novel yellow forming color couplers corresponding to the following general formula :



wherein :

Q and R have the same significance as above,

X stands for a hydrogen atom or a substituent that exhibits two equivalent character on color development e.g. a halogen atom, a $-S-R_1$ group wherein R_1 stands for alkyl including substituted alkyl, aryl including substituted aryl or a heterocycle including a substituted heterocycle; etc. or an $O-R_2$ group wherein R_2 stands for alkyl including substituted alkyl, aryl including substituted aryl, or acyl including substituted acyl such as acetyl and benzoyl,

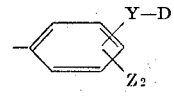
Z_1 stands for hydrogen, the group RCF_2Q- wherein R and Q have the same significance as above or a substituent e.g. alkyl such as methyl, alkoxy such as methoxy, halogen such as chlorine, and dialkylamino such as dimethylamino, and

A represents an aromatic nucleus such as phenyl and naphthyl including a substituted aromatic nucleus or a heterocyclic nucleus such as thiazole and pyridine, including a substituted heterocyclic nucleus, said color couplers preferably being fast to diffusion in photographic colloid layers by the presence in the amide part of the molecule of a radical, which is directly linked to the group A or through a substituent thereof, rendering the compound fast to diffusion and corresponding to the formula —Y—D wherein D stands for an acyclic aliphatic hydrocarbon residue with from 5 to 20 carbon atoms and Y stands for a chemical bond, oxygen, sulphur, sulphonyl, —N—(alkyl)—, —CONH—, —NHCO—, $-N(R_3)SO_2-$ or $-SO_2N(R_3)-$ with R_3 = H or alkyl.

The aryl or heterocyclic group represented by A comprising a ballasting group rendering the color couplers less liable to diffuse from a photographic colloid layer in which it is incorporated may be any of those customarily present in the amide part of the benzoyl-acetamide color couplers. Numerous examples of color couplers carrying such aryl and heterocyclic groups, some of which comprise in addition to the said ballasting group substituents favorably influencing the physical,

spectral and/or sensitometric properties of the color couplers and the dyes formed therewith, can be found in the literature; see, for example, U.S. Pat. Nos. 3,138,604, 3,369,899, 3,393,040 and 3,393,041.

The group A comprising a radical rendering the yellow-forming color coupler fast to diffusion is preferably one having the general formula :



wherein :

Y-D has the same significance as above, and

Z_2 stands for a hydrogen atom or any substituent that favorably influences the physical, spectral or sensitometric properties of the molecule e.g. alkyl including substituted alkyl such as carboxyalkyl, sulphoalkyl, aryl including substituted aryl, halogen such as chlorine, a water-solubilizing group such as sulpho or carboxyl in acid or salt form, a fluorosulfphonyl group, an alkoxy-carbonyl group such as carbethoxy, a sulphamoyl group including a substituted sulphamoyl group such as diethylsulphamoyl, phenylsulphamoyl, an alkylsuphonyl group such as methylsulphonyl, an alkoxy group such as methoxy, an alkylthio group such as methylthio, an aryloxy group including a substituted aryloxy group, an arylthio group including a substituted arylthio group, or the group



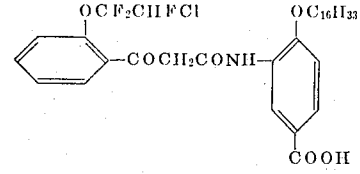
wherein each of R_4 and R_5 stands for alkyl, aryl, aralkyl or together represent the atoms necessary to form a mopholine nucleus or piperidine nucleus.

The color couplers of the present invention are distinguished from all known benzoylacetamide color couplers by having attached to the benzoyl group at least one substituent of the formula RCF_2Q- wherein R and Q have the significance given above. The color couplers of the present invention have useful properties not shared by couplers of the same structure except that they do not contain said RCF_2Q- group in the benzoyl part of the molecule. One such useful property is that the dyes produced from the color couplers of the present invention have a markedly improved light-stability as compared with dyes similarly produced from the known benzoylacetamide color couplers.

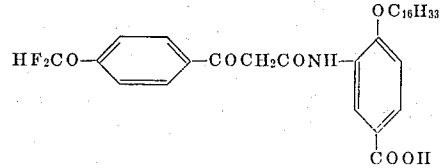
Apart from manifesting a high stability against light, the dyes formed on color development from the color couplers of the present invention possess favorable spectral properties and a high degree of resistance under conditions of high humidity and heat.

The following compounds are representative color couplers of the present invention. However, it is to be understood that the invention is not limited to these specific couplers.

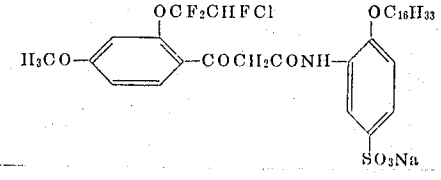
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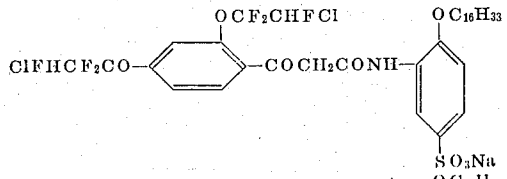
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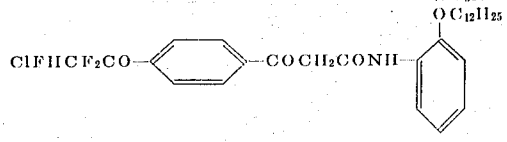
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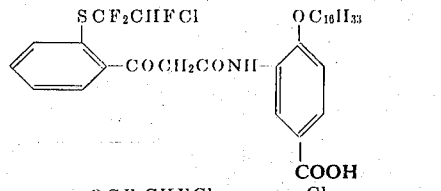
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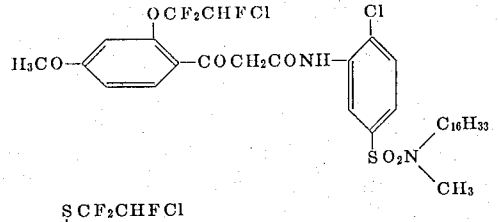
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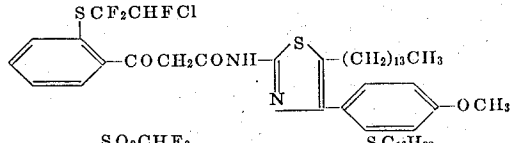
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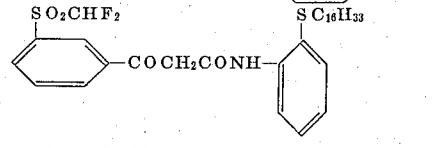
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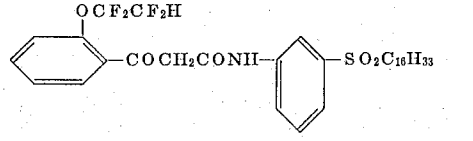
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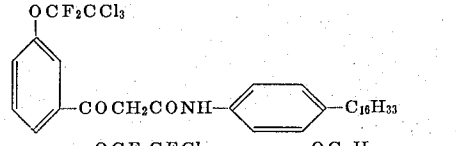
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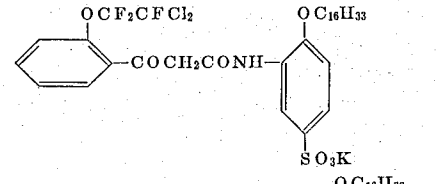
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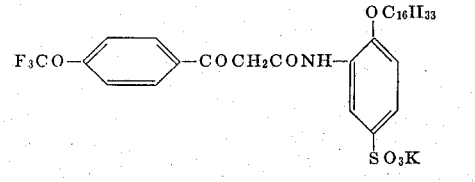
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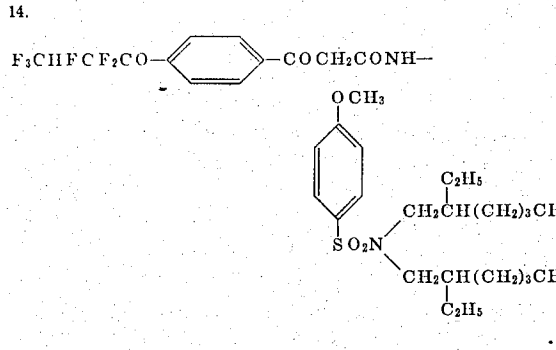
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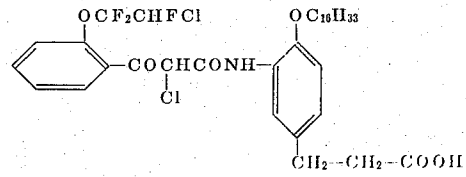
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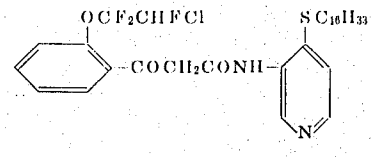
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As will be illustrated in the preparation hereinafter the yellow-forming benzoylacetamide color couplers according to the present invention can be prepared according to the methods known in the art of preparing benzoyl-acetamide color couplers by condensing the appropriately substituted benzoylacetic acid esters with aromatic or heterocyclic amines containing a diffusion-fast making group.

The preparation of the amino compounds containing a diffusion-fast-making group can be prepared analogously to the preparation technique illustrated hereinafter. A detailed description of the preparation of all aromatic and heterocyclic amino compounds suitable for being condensed with the benzoylacetic acid esters is not deemed necessary since the preparation will not cause difficulties to those skilled in the art of preparative organic chemistry. A whole series of aromatic and heterocyclic amines which comprise a group rendering the molecule non-migratory and which are suitable for being condensed with the benzoyl acetic acid esters substituted with the group RCF_2Q-, Q and R having the same significance as above, in order to form color couplers according to the present invention can be found in U. K. Pat. Nos. 939,030, 983,648, 1,099,418 and 1,104,729 and in U.S. Pat. Nos. 3,138,604, 3,369,899, 3,393,040 and 3,393,041.

Examples of benzoylacetic acid esters suitable for being condensed with aromatic or heterocyclic amines to form color couplers according to the present invention are :

o- and p-(1,1,2-trifluoro-2-chloroethoxy)-benzoylacetic acid ethyl ester,

o-(1,1,2-trifluoro-2-chloroethylthio)-benzoylacetic acid ethyl ester,

p-difluoromethyloxybenzoylacetic acid ethyl ester, 2,2-di(1,1,2-trifluoro-2-chloroethoxy)-benzoylacetic acid ethyl ester,

2-(1,1,2-trifluoro-2-chloroethoxy)-4-methoxy-benzoyl acetic acid ethyl ester,

m-difluoromethylsulphonylbenzoylacetic acid ethyl ester, o- and m-(1,1,-difluoro-2,2,2-trichloroethoxy)-benzoyl-acetic acid ethyl ester,

o-(1,1,2,2-tetrafluoroethoxy)-benzoylacetic acid ethyl ester,

p-trifluoromethoxybenzoylacetic acid ethyl ester, p-(1,1,2-trifluoro-2-bromoethoxy)-benzoylacetic acid ethyl ester,

o-(1,1,2-trifluoro-2,2-dichloroethoxy)-benzoylacetic acid ethyl ester, and

p-(1,1,2,3,3,3,-hexafluoropropoxy)-benzoylacetic acid ethyl ester.

PREPARATION 1

a. o-(1,1,2-trifluoro-2-chloroethoxy)-benzoylacetic acid ethyl ester.

27.3 g. of o-(1,1,2-trifluoro-2-chloroethoxy)-benzoyl chloride (Bull.Soc.Chim.Fr. 1957, 821) were added with stirring to a suspension of 30.4 g. of the sodium salt of ethylacetoacetate in 50 ml. of dichloromethane. After having

been stirred for three hours the mixture was acidified with hydrochloric acid. The dichloromethane layer was separated, washed with water until acid free and concentrated by evaporation. The remainting oily residue was added to a solution of 4 g. of a sodium hydroxide, 4 ml of ammonium hydroxide and 13.3 g. of ammonium chloride in 60 ml. of water. The mixture was stirred for three hours at 40° C. whereupon the solution was extracted with dichloromethane. The extract was washed with water, dried and concentrated by evaporation. The residue was distilled yielding a colorless oil with boiling point : 135°–136° C./1 mm.

b. 3-nitro-4-hexadecyloxybenzoic acid

39.4 g. of 3-nitro-4-hydroxy-benzoic acid methyl ester, 13.2 g. of potassium hydroxide and 61 g. of hexadecylbromide where refluxed for five hours. The ester group was hydrolized by boiling with 20 g. of potassium hydroxide in 100 ml. of water. The reaction mixture was poured into diluted acid yielding a light-brown grainy product. This product was recrystallized from ethanol.

Melting point : 96°–98° C.

c. 3-amino-4-hexadecyloxybenzoic acid

40.7 g. of 3-nitro-4-hexadecyloxybenzoic acid in 170 ml. of ethylene glycol monomethyl ether were hydro-genated at 80° C. using Raney Nickel as catalyst and a hydrogen pressure of 1,500 p.s.i. A crystalline product varying from white to light-brown was obtained.

Melting point : 99°–100° C.

d. o-(1,1,2-trifluoro-2-chloroethoxy)-benzoyl-(2'-hexadecyloxy-5'-carboxy) acetanilide

32.5 g. of the above β-ketoester and 37.7 g. of the above amino compound were refluxed in 100 ml. of xylene. The mixture of xylene and ethanol formed was gradually distilled off in about 1 h. Upon cooling a crystalline precipitate formed which was filtered off and washed with hexane.

Melting point : 140° C.

PREPARATION 2

a. p-difluoromethoxybenzoic acid.

31.6 g. of p-tolyl difluoromethyl ether (Miller, Thanassi, J.Org.Chem. 25, 1960, p. 2010) were oxidized by means of 158 g. of potassium permanganate in 1,000 ml. of water at boiling temperature.

Melting point : 171° C.

b. p-difluoromethoxybenzoyl chloride.

37.5 g. of p-difluoromethoxybenzoic acid prepared as described above were boiled with 45 ml. of thionyl chloride. The excess of thionyl chloride was distilled off yielding a colorless liquid with boiling point : 72° C./5 mm.

c. p-difluoromethoxybenzoylacetic acid ethyl ester.

This compound was prepared according to the method described in preparation 1.a) starting from 20.65 g. of p-difluoromethoxy-benzoyl chloride. A light yellow oil with boiling point 146° C /1 mm was obtained. d. p-difluoromethoxybenzoyl-(2'-hexadecyloxy-5'-carboxy)-acetanilide

This compound was prepared in an analogous way as the compound of preparation 1.d) from 25.8 g. of the above α-ketoester and 37.7 g. of the amino compound of preparation 1.c). The crude product was recrystallized from isopropanol.

Melting point : 155° C.

PREPARATION 3

a. o-(1,1,2-trifluoro-2-chloroethoxy)-p-methoxybenzoic acid methyl ester

o-(1,1,2-trifluoro-2-chloroethoxy)-p-methoxybenzoic acid methyl ester was prepared according to the method of Lichtenberger (Bull.Soc.Chim.Fr. 1962, p. 259) starting from 72.8 g. of 2-hydroxy-4-methoxybenzoic acid methyl ester (Herzig : Monatsh.f.Chem. 24 (1903) p. 1887). A colorless oil was obtained having a boiling point of 136°–140°C/1.5 mm.

b. o-(1,1,2-trifluoro-2-chloroethoxy)-p-methoxybenzoic acid

60 g. of the foregoing compound were hydrolized by boiling with 80 ml. of 5 N sodium hydroxide in 150 ml. of methanol. The reaction mixture was poured into diluted acid. A white crystalline product with melting point 110° C. was obtained.

c. o-(1,1,2-trifluoro-2-chloroethoxy)-p-methoxybenzoyl chloride.

This compound was prepared according to the method described in preparation 2.b) starting from 56.9 g. of the corresponding acid. A colorless oil with boiling point 176° C./18 mm. was obtained. d. o-(1,1,2-trifluoro-2-chloroethoxy)-p-methoxybenzoyl-acetic acid ethyl ester.

This compound was prepared according to the method described in preparation 1.a) starting from 30.3 g. of the acid chloride. A light yellow liquid with boiling point 180° C./0.7 mm. was obtained. e. o-(1,1,2-trifluoro-2-chloroethoxy)-p-methoxybenzoyl-(2'-hexadecyloxy-5'-fluorosulphonyl)-acetanilide.

35.5 g. of the above α-ketoester and 41.5 g. of 3-amino-4-hexadecyloxybenzene sulphofluoride (prepared as described in United Kingdom Patent Specification 983,648) were allowed to react according to the method described in preparation 1.d). A white crystalline product with melting point 85° C. was obtained after recrystallization from acetonitrile. f. o-(1,1,2-trifluoro-2-chloroethoxy)-p-methoxybenzoyl-(2'-hexadecyloxy-5'-sulpho)-acetanilide potassium salt.

7.23 g. of the above sulphofluoride in 40 **ml of acetone were refluxed while stirring with** 6 ml of 5 N potassium hydroxide. After having been refluxed for 30 minutes the reaction mixture was acidified with acetic acid. Upon cooling a white crystalline precipitate formed.

PREPARATION 4 a. o,p-di(1,1,2-trifluoro-2-chloroethoxy)benzoic acid methyl ester

o,p-di(1,1,2-trifluoro-2-chloroethoxy)-benzoic acid methyl ester was prepared according to the method described in preparation 3.a) starting from 67.2 g. of dihydroxy benzoic acid methyl ester. A colorless oil with boiling point 161°–162 °C/5 mm was obtained. b. o,p-di(1,1,2-trifluoro-2-chloroethoxy)benzoic acid was prepared as described in preparation 3.b) starting from 80 g of the above methyl ester. A white crystalline product with melting point 70° C. was obtained. c. o,p-di(1,1,2-trifluoro-2-chloroethoxy)benzoyl chloride was prepared as described in preparation 2.b) starting from 77.4 g of the corresponding acid. A light yellow oil with boiling point 175°C/19 mm was obtained. d. o,p-di(1,1,2-trifluoro-2-chloroethoxy)benzoylacetic acid ethyl ester was prepared as described in preparation 1.a) starting from 40.6 of the corresponding acid chloride. A yellow oil with boiling point 182° C./0.4 mm was obtained. e. o,p-di(1,1,2-trifluoro-2-chloroethoxy(benzoyl-(2'-hexadecyloxy-5'-fluorosulphonylacetanilide 45.7 g. of the above β-ketoester and 41.5 g of 3-amino-4-hexadecyloxy-benzene sulphofluoride were allowed to react according to the method described in preparation 1.d). A white crystalline product with melting point 122° C. was obtained. f. o,p-di(1,1,2-trifluoro-2-chloroethoxy)benzoyl-(2'-hexadecyloxy-5'-sulpho)acetanilide potassium salt was prepared according to the method described in preparation 3.f) starting from 8.26 g. of the sulphofluoride compound. After recrystallization from a mixture of water and methanol a white crystalline product was obtained.

PREPARATION 5

a. p-(1,1,2-trifluoro-2-chloroethoxy)benzoylacetic acid ethyl ester

This compound was prepared according to the method described in preparation 1.a) starting from 27.3 g. of p-(1,1,2-trifluoro-2-chloroethoxy)benzoyl chloride (Lichtenberger Bull.Soc.Chim.Fr. 1957, p. 821). A light yellow oil with boiling point 158° C./0.25 mm. was obtained.

b. o-dodecyloxyaniline was prepared as described in United Kingdom Patent Specification 1,099,418. c. p-(1,1,2-trifluoro-2-chloroethoxy)benzoyl-(2'-dodecyloxy)-acetanilide.

This compound was prepared according to the method described in preparation 1.d) starting from 32.5 g. of the above β-ketoester and 27.7 g. of o-dodecyloxyaniline. A white crystalline product with melting point 116° C. was obtained after recrystallization from methanol.

PREPARATION 6 a. o-(1,1,1-trifluoro-2-chloroethylthio)benzoylacetic acid ethyl ester.

This compound was prepared according to the method described in preparation 3.b), c) and d) starting from 57 g. of o-(1,1,2-trifluoro-2-chloroethylthio)benzoic acid methyl ester (Lichtenberger, Bull.Soc.Chim.Fr. 1962, p. 258). A light yellow oil with boiling point 182° C./0.4 mm. was obtained.

b. o-(1,1,2-trifluoro-2-chloroethylthio)benzoyl-(2'-hexadecyloxy-5'-carboxy)-acetanilide.

This compound was prepared according to the method described in preparation 1.d) starting from 34 g. of the β-ketoester described in step a) and 37.6 g. of 3-amino-4-hexadecyloxybenzoic acid. A white crystalline product with melting point 165° C. was obtained.

PREPARATION 7

o-(1,1,2-trifluoro-2-chloroethoxy)-p-methoxybenzoyl-[2'-chloro-5'-(N-methyl-N-hexadecylsulphamoyl)]acetanilide was prepared according to the method described in preparation 1.d) starting from 35.5 g. of o-(1,1,2-trifluoro-2-chloroethoxy)-p-methoxybenzoylacetic acid ethyl ester and 44.5 g. of 2-chloro-5-N-methyl-N-hexadecylsulphamoyl) aniline (prepared as described in U.K. Pat. specification No. 1,104,729). A white crystalline product with melting point 86°C was obtained.

PREPARATION 8

2-[o-(1,1,2-trifluoro-2-chloroethylthio)benzoyl-acetamido]-4-p-methoxyphenyl-5-tetradecylthiazole was prepared according to the method described in preparation 1.d) starting from 34 g. of o-(1,1,2-trifluoro-2-chloroethylthio)benzoylacetic acid ethyl ester and 40.2 g. of 2-amino-4-p-methoxyphenyl-5-tetradecylthiazole (prepared as described in U.S. Pat. specification No. 3,393,041). The reaction mixture was taken up in acetonitrile and the solution was cooled to room temperature whereby a light yellow oil separated.

The yellow color formers according to the present invention are of the non-diffusible type i.e., they comprise in their molecule an organic radical sufficiently large for preventing the color coupler of wandering from the colloid layer, in which the coupler is incorporated, to another colloid layer.

For preparing a usable photographic multilayer color material the non-diffusing color couplers for each color separation image are usually incorporated into the coating compositions of the differently sensitized silver halide emulsion layers. However, the non-diffusing color couplers may also be added to the coating compositions of non-light-sensitive colloid layers which are in water-permeable relationship with the light-sensitive silver halide emulsion layers.

During the preparation of the light-sensitive color material the non-migratory yellow forming color couplers according to the above general formulae can be incorporated in the coating composition of the silver halide emulsion layers or other colloid layers in water-permeable relationship therewith according to any technique known by those skilled in the art for incorporating photographic ingredients, more particularly color couplers, into colloid compositions. For instance, the water-soluble color couplers i.e., those containing one or more water-solubilizing groups such as sulpho or carboxyl groups (in acid or salt form) can be incorporated into the coating composition of the layer in question from an aqueous solution and the water-insoluble or insufficiently water-soluble color couplers from a solution in the appropriate water-miscible or water-immiscible high-boiling or low-boiling organic solvents or mixtures thereof whereupon the solution obtained is dispersed, occasionally in the presence of a wetting or dispersing agent, in a hydrophilic colloid composition forming or forming part of the binding agent of the colloid layer. The hydrophilic colloid composition may of course comprise in addition to the colloid carrier all other sorts of ingredients. The water-insoluble color couplers carrying fluorosulphonyl groups or carboxylic acid ester groups such as ethoxycarbonyl groups can also be converted by alkaline hydrolysis (e.g., as described in U.K. Pat. specification No. 939,030) in the corresponding sulphonic acids or carboxylic acids respectively which in their turn can be incorporated in hydrophilic colloid compositions in the form of their alkali salts from aqueous solutions.

The solution of said color coupler need not necessarily be dispersed or dissolved directly in the coating composition of the silver halide emulsion layer or other water-permeable layer. Said solution may advantageously be first dispersed or dissolved in an aqueous non-light-sensitive hydrophilic colloid solution whereupon the resultant mixture, after the occasional removal of the organic solvents employed, is intimately mixed with the said coating composition of the light-sensitive silver halide emulsion layer or other water-permeable layer just before coating. For more details about particularly suitable dispersing techniques that can be employed for incorporating the color couplers of the invention into a hydrophilic colloid layer of a photographic material there can be referred to U.K. Pat. specification Nos. 791,219, 1,098,594, 1,099,414, 1,099,415, 1,099,416 and 1,099,417, French Pat. specification Nos. 1,555,663, Belgian Pat. specification No. 722,026 and to U.S. Pat. No. 2,304,940.

The couplers according to the invention may be used in conjunction with various kinds of photographic emulsions. Various silver salts may be used as the sensitive salt such as silver bromide, silver iodide, silver chloride or mixed silver halides such as silver chlorobromide, silver bromoiodide and silver chlorobromoiodide. The couplers can be used in emulsions of the mixed packet type as described in U.S. Pat. No. 2,698,794 or emulsions of the mixed grain type as described in U.S. Pat. No. 2,592,243. The color couplers can be used with emulsions wherein latent images are formed predominantly on the surface of the silver halide crystal; or with emulsions wherein latent images are formed predominantly inside the silver halide crystal.

The hydrophilic colloid used as the vehicle for the silver halide may be, for example, gelatin, colloidal albumin, zein, casein, a cellulose derivative, a synthetic hydrophilic colloid such as polyvinyl alcohol, poly-N-vinyl pyrrolidone, etc. If desired, compatible mixtures of two or more of these colloids may be employed for dispersing the silver halide.

The light-sensitive silver halide emulsions of use in the preparation of a photographic material according to the present invention may be chemically as well as optically sensitized. They may be chemically sensitized by effecting the ripening in the presence of small amounts of sulphur containing compounds such as allyl thiocyanate, allyl thiourea, sodium thiosulphate, etc. The emulsions may also be sensitized by means of reductors for instance tin compounds as described in French Pat. No. 1,146,955 and in Belgian Pat. No. 568,687, imino-amino methane sulphinic acid compounds as described in U.K. Pat. No. 789,823 and small amounts of noble metal compounds such as gold, platinum, palladium, iridium, ruthenium and rhodium compounds. They may be optically sensitized by means of cyanine and merocyanine dyes.

The said emulsions may also comprise compounds which sensitize the emulsions by development acceleration for example compounds of the polyoxyalkylene type such as alkylene oxide condensation products as described among others U.S. Pat. Nos. 2,531,832, 2,533,990, 3,210,191 and 3,158,484, in U.K. Pat. Nos. 920,637 and 991,608 and in Belgian Pat. Nos. 648,710 and onium derivatives of amino-N-oxides as described in U.K. Pat. No. 1,121,696.

Further, the emulsions may comprise stabilizers e.g., heterocyclic nitrogen-containing thioxo compounds such as benzothiazoline-2-thione and 1-phenyl-2-tetrazoline-5thione

and compounds of the hydroxytriazolopyrimidine type. They can also be stabilized with mercury compounds such as the mercury compounds described in Belgian Pat. Nos. 524,121, 677,337 and 707,386 and in U.S. Pat. No. 3,179,520.

The light-sensitive emulsions may also comprise all other kinds of ingredients such as plasticizers, hardening agents, wetting agents, etc.

The non-diffusing yellow color formers described in the present invention are usually incorporated into a blue-sensitive silver halide emulsion for forming one of the differently sensitized silver halide emulsion layers of a photographic multilayer color material. Such photographic multilayer color material usually comprises a support, a red-sensitized silver halide emulsion layer with a cyan color former, a green-sensitized silver halide emulsion layer with a magenta color former and a blue-sensitive silver halide emulsion layer with a yellow color former.

The emulsions can be coated on a wide variety of photographic emulsion supports. Typical supports include cellulose ester film, polyvinylacetal film, polystyrene film, polyethylene terephthalate film and related films or resinous materials, as well as paper and glass.

For the production of photographic color images according to the present invention an exposed silver halide emulsion layer is developed with an aromatic primary amino developing substance in the presence of a color coupler according to the present invention. All color developing agents capable of forming azomethine dyes can be utilized as developers. Suitable developing agents are aromatic compounds such as p-phenylene diamine and derivatives for example N,N-dialkyl-p-phenylene diamines such as N,N-diethyl-p-phenylene diamine, N,N-dialkyl-N'-sulphomethyl-p-phenylene diamines, and N,N-dialkyl-N'-carboxymethyl-p-phenylene diamines.

The following examples illustrates the present invention.

EXAMPLE 1

117 g. of a blue-sensitive silver bromoiodide emulsion (2.3 mole percent of iodide) which comprises per kg 73.4 g. of gelatin and an amount of silver halide equivalent to 47 g. of silver nitrate, are diluted with 192.5 g. of a 7.5 percent aqueous solution of gelatin and 100 g. of distilled water. To the emulsion obtained is added a solution of color coupler 1 of the above list of color couplers prepared by dissolving at 55° C. 0.006 mole of the color coupler in 54 ml of distilled water, 6 ml. of 2 N sodium hydroxide and 18 ml. of ethanol. After neutralization and addition of the common additives such as stabilizers, wetting agents, and hardeners the necessary amount of distilled water to obtain 575 g. of emulsion is added whereupon the emulsion is coated on a cellulose triacetate support pro rata of 150 g. per sq.m. The emulsion layer is dried and overcoated with a gelatin antistress layer.

After drying, the material formed is exposed for 1/20 sec. through a continuous wedge with constant 0.30 and then developed for 8 min. at 20° C. in a developing bath of the following composition:

N:N-diethyl-p-phenylene diamine sulphate	2.75 g
hydroxylamine sulphate	1.2 g
sodium hexametaphosphate	4 g
anhydrous sodium sulphite	2 g
anhydrous potassium carbonate	75 g
potassium bromide	2.5 g
water to make	1 liter

The developed material is treated for 2 min. at 18°–20°C in an intermediate bath comprising 30 g. of sodium sulphate in 1 liter of water.

The material is rinsed for 15 min. with water and treated in a bleach bath of the following composition:

borax	20 g
anhydrous potassium bromide	15 g
anhydrous sodium bisulphate	4.2 g
potassium hexacyanoferrate(III)	100 g
water to make	1 liter

After bleaching, the material is rinsed with water for 5 min. and fixed in an aqueous solution of 200 g. of sodium thiosulphate per liter.

After a final rinsing for 15 min. the material is dried.

A yellow colored wedge image is obtained having an absorption maximum of 436 mm.

EXAMPLES 2 and 3

Example 1 is repeated with the difference that color coupler 1 is replaced by 0.006 mole of color couplers 3 and 6.

Yellow colored wedge images are obtained both having absorption maxima of 432 nm.

EXAMPLE 4

117 g. of a blue-sensitive silver bromo-iodide emulsion (2.3 mole percent of iodide) containing per kg 73.4 g. of gelatin and an amount of silver halide equivalent to 47 g. of silver nitrate are melted and diluted with 192.5 g. of a 7.5 percent aqueous solution of gelatin and 100 g. of distilled water. To the emulsion obtained is added a gelatin gel comprising a dispersion of color coupler 5 prepared by admixing by means of an ultrasonic wave generator a solution of 0.006 mole of said color coupler in a mixture of 14 ml. of ethyl acetate, 1.5 ml. of tricresyl-phosphate and 0.75 ml. of dibutylphthalate with 100 ml. of a 5 percent solution of gelatin and removing the ethyl acetate by evaporation under reduced pressure. After neutralization and addition of the usual additives such as hardeners, wetting agents, and stabilizers the necessary amount of distilled water to obtain 575 g. of emulsion is added whereupon the emulsion is coated on a cellulose triacetate support pro rata of 150 g. per sq.m. The emulsion layer is dried and overcoated with a gelatin antistress layer.

Exposure and processing occurs as described in Example 1.

A yellow colored wedge image having an absorption maximum of 440 nm. is obtained.

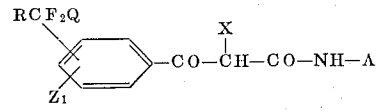
EXAMPLES 5 and 6

Example 4 is repeated with the difference that color coupler 5 is replaced by 0.006 mole of color couplers 7 and 8.

Yellow colored wedge images are obtained having absorption maxima of 452 nm. and 470 nm. respectively.

WE CLAIM:

1. Photographic material comprising a light-sensitive silver halide emulsion layer and a benzoylacetamide color coupler capable of forming a yellow azomethine dye by reaction with an oxidized aromatic primary amino developing agent, wherein said color coupler corresponds to the following general formula:



wherein:

R stands for hydrogen, fluorine or polyhaloalkyl,

Q stands for oxygen, sulphur or sulphonyl,

X stands for hydrogen or a substituent that exhibits two-equivalent character on color development selected from the group consisting of a halogen atom, a -S-R_1 group wherein R_1 stands for alkyl, aryl, and a heterocycle; or an O-R_2 group wherein R_2 stands for alkyl, aryl, and acyl,

A stands for a member selected from the group consisting of a 6-carbon mononuclear aryl group, a 10-carbon dinuclear aryl group, a thiazolyl group, and pyridyl group, and

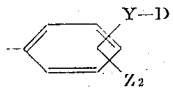
Z_1 stands for hydrogen, the group RCF_2O- wherein R and Q have the same significance as above, alkyl, alkoxy, halogen, or dialkylamino.

2. A photographic material according to claim 1, wherein said color coupler is fast to diffusion in photographic colloid layers by the presence in the amide part of its molecule of a group, which is directly linked to the group A or through a

substituent thereof, rendering the molecule fast to diffusion and corresponding to the formula -Y-D wherein D stands for an acyclic aliphatic hydrocarbon residue with from 5 to 20 carbon atoms and Y stands for a chemical bond, oxygen, sulphur, sulphonyl, -N(alkyl)-, -CONH-, -NHCO-, $-N(R_3)SO_2-$ and $-SO_2N(R_3)-$ wherein R_3=H or alkyl.

3. A photographic material according to claim 2, wherein A stands for a phenyl nucleus, a thiazolyl nucleus or a pyridyl nucleus.

4. A photographic material according to claim 2, wherein A stands for the group corresponding to the formula :

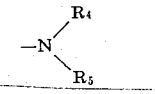


wherein :

Y stands for a chemical bond, oxygen, sulphur, sulphonyl, -N(alkyl)-, -CONH-, -NHCO-, $-N(R_3)SO_2-$ and $-SO_2N(R_3)-$ wherein R_3=H or alkyl,

D stands for an acyclic aliphatic hydrocarbon residue with from 5 to 20 carbon atoms,

Z_2 stands for hydrogen, an alkyl group, an aryl group, a halogen atom, a sulpho or carboxyl group in acid or salt form, a fluorosulphonyl group, an alkoxycarbonyl group, a sulphamoyl group, an alkylsulphonyl group, an alkoxy group, an alkylthio group, an aryloxy group, an arylthio group or the group



wherein each of R_4 and R_5 stands for alkyl, aryl or aralkyl or together represent the atoms necessary to form a morpholine or piperidine nucleus.

5. Photographic multilayer color material comprising in one of the light-sensitive silver halide emulsion layers or in a non-light-sensitive water-permeable colloid layer in water-permeable relationship with the light-sensitive silver halide emulsion layer a color coupler according to claim 1.

6. Photographic multilayer color material according to claim 5, comprising three silver halide emulsion layers which are differently optically sensitized, wherein the blue-sensitive silver halide emulsion layer or a non-light-sensitive colloid layer in water-permeable relationship therewith incorporates the said color coupler.

7. Process for the production of a photographic color image by development of a photographic element containing image-wise exposed silver halide with the aid of an aromatic primary amino developing agent, which by reduction of the exposed silver halide is converted into its oxidized form and as such forms a yellow azomethine dye by reaction with a color coupler according to claim 1.

8. Process according to claim 7, wherein said color coupler is present in a blue-sensitive silver halide emulsion layer or other colloid layer in water-permeable relationship therewith of the said photographic element.

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