United States Patent [19]

Van Poucke et al.

[11] **3,892,576**

[45] **July 1, 1975**

[54] **PHOTOGRAPHIC WATER-INSOLUBLE COMPOUNDS HAVING A HYDROPHOBIC DIFFUSION-FAST SUBSTITUENT**

[75] Inventors: **Raphaël Karel Van Poucke,** Berchem; **Arthur Henri De Cat,** Mortsel, both of Belgium

[73] Assignee: **Agfa-Gevaert N.V.,** Mortsel, Belgium

[22] Filed: **Feb. 8, 1971**

[21] Appl. No.: **113,646**

[30] **Foreign Application Priority Data**

Feb. 24, 1970 United Kingdom 8840/70

[52] **U.S. Cl.** **96/100;** 96/109; 96/55

[51] **Int. Cl.** **G03c 1/40**

[58] **Field of Search** 96/55, 100, 95

[56] **References Cited**

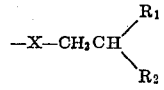
UNITED STATES PATENTS

3,005,709	10/1961	Coles	96/100
3,409,439	11/1968	Yoshida	96/100
3,658,545	4/1972	Iwama	96/100
3,676,141	7/1972	Hara	96/100
3,692,527	11/1972	Konig	96/100

Primary Examiner—Norman G. Torchin
Assistant Examiner—John L. Goodrow
Attorney, Agent, or Firm—A. W. Breiner

[57] **ABSTRACT**

Photographic materials are described which comprise in a light-sensitive silver halide emulsion layer or in another water-permeable colloid layer a non-diffusing water-insoluble photographic component containing a hydrophobic diffusion-fast making group of the formula



wherein X is an ether group, a thioether group, a sulphonyl group, CONH, NHCO or SO_2NH and each of R_1 and R_2 is a branched-chain C_4—C_{12} alkyl group. The described materials comprise the said component in the form of a finely divided dispersion which shows no crystallization tendency.

12 Claims, No Drawings

PHOTOGRAPHIC WATER-INSOLUBLE COMPOUNDS HAVING A HYDROPHOBIC DIFFUSION-FAST SUBSTITUENT

This invention relates to water-insoluble photographic components containing branched-chain hydrophobic groups rendering said components fast to diffusion in photographic hydrophilic colloid media and to photographic elements containing such components.

In the preparation of photographic silver halide emulsion layers and other hydrophilic colloid layers of a photographic silver halide material it is often necessary to incorporate therein components such as colour couplers, mask-formers, competing couplers, U.V.-absorbers, etc. that are non-diffusible in these hydrophilic colloid media so that they do not wander from their original site. For this purpose the said components are usually provided in their molecule with one or more ballast groups e.g. a long chain aliphatic group such as an alkyl group containing from 5 to 20 C-atoms in straight line. This ballast group imparts to the molecule a hydrophobic character and holds the component firmly in the original hydrophilic colloid layer.

The methods according to which these non-diffusing components are incorporated into the photographic hydrophilic colloid layers present numerous problems and much effort has been directed to solve these problems.

A method commonly employed to incorporate these non-diffusing components into hydrophilic colloid compositions such as a gelatino silver halide emulsion is to provide in the molecule of said components one or more salt-forming groups i.e. carboxy and/or sulpho groups so that they can be dissolved in the hydrophilic colloid composition in the form of their soluble alkali metal salts.

The incorporation of these non-diffusible components containing salt-forming groups into aqueous hydrophilic colloid compositions frequently poses a number of difficulties. Indeed, many of these components carrying sulpho and/or carboxyl groups are not soluble enough, i.e. in the concentration desired, in said alkaline solutions while others crystallize after some time in said solutions or give rise to flocculation when incorporating the ingredient solution in the aqueous hydrophilic colloid medium. Moreover, some compounds are soluble only in highly alkaline solutions which are too basic for use as such in conventional light-sensitive silver halide material, where approximately neutral solutions are most desirable; when highly alkaline solutions are used the hydrophilic colloid composition should be reacidified afterwards whereby flocculation might occur and whereby inorganic salts are formed. Another problem accompanying the use of these components is due to the presence of the water-solubilizing groups, especially the sulpho groups. Indeed, these groups have a marked influence on the viscosity of the hydrophilic colloid medium e.g. it is difficult to obtain, under the same circumstances, reproducible viscosity values for hydrophilic colloid compositions comprising suchlike components and on storing such compositions the viscosity undergoes further changes.

Alternate processes of incorporating non-diffusing components in photographic colloids make use of dispersion techniques.

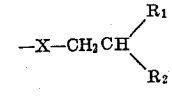
According to one such method, e.g. as described in German Patent Specification No. 1,127,714, water-insoluble colour couplers are dissolved in low-boiling substantially water-immiscible solvents such as ethyl acetate, methylene chloride, chloroform, etc. whereupon the solution formed is dispersed in extremely fine droplets in the presence of a wetting or dispersing agent into the hydrophilic colloid medium after which the solvent is removed by evaporation, leaving behind a dispersion of colour coupler distributed throughout the hydrophilic colloid composition.

Another process for dispersing non-diffusing components in photographic hydrophilic colloid compositions is described in U.S. Pat. No. 2,322,027. According to this method a colour coupler is dissolved in a high-boiling oily solvent such as tricresyl phosphate and di-n-butyl phthalate whereupon the resulting solution is dispersed in the form of extremely fine droplets in the hydrophilic colloid composition, the oily solvent being left in the said composition.

One of the advantages of these dispersion techniques is that components may be used which contain no salt-forming groups. However, these processes also pose difficulties. Indeed, components that are intended to be incorporated into photographic colloid media from solutions in low-boiling or high-boiling organic solvents should have a sufficient solubility in said solvents and be homogeneously distributed through the said colloid media before as well as after coating to form a hydrophilic colloid layer of a photographic material so that no crystallization of the component occurs.

This condition limits the number of components suitable for such applications. Various components having one or more ballast groups of hydrophobic character are not sufficiently soluble in said organic low or high boiling solvents or give rise to crystallization of the component either when dispersing the organic solution into the hydrophilic colloid medium, or when coating the hydrophilic colloid medium to form a layer of a photographic material or when processing the photographic material. In this way the degree of dispersion is markedly decreased and as a consequence has a disadvantageous effect on the sensitometric characteristics of the photographic material.

It has now been found that photographic water-insoluble components, such as colour couplers, mask-formers, competing couplers, U.V.-absorbers, etc., not containing a hydrophilic group and comprising as diffusion-fast making hydrophobic group a group of the formula



wherein X stands for O, S, SO_2, CONH, NHCO or SO_2NH and each of R_1 and R_2 stands for a branched-chain C_4—C_{12} alkyl group, are particularly suitable for being dispersed into hydrophilic colloid media with the aid of high-boiling and/or low-boiling water-immiscible or sparingly water-miscible solvents in that their solubility in the said solvents is superior than the solubility of the corresponding components having straight-chain ballasting alkyl groups and that as compared with the latter components they do not give rise to the above disadvantageous effects of crystallization. The above diffusion fast making group should be hydrolytically stable in the processing solutions for the photographic

material and therefor not ester linked to the molecule of the photographic component.

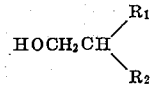
By colour coupler is meant any compound which in silver halide photography couples with an oxidized aromatic primary amino colour developing agent to form a dye image. Examples of such colour developing agents are p-phenylene diamine and derivatives thereof for example N,N-dialkyl-p-phenylene diamines 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, 2-amino-5-diethylamino-toluene, etc.

By mask-forming component there is meant a compound which oxidatively couplers with a colour coupler in an oxidizing bleaching bath as for example described in United Kingdom Patent Specification Nos. 880,862 and 975,932 to form a coloured mask image.

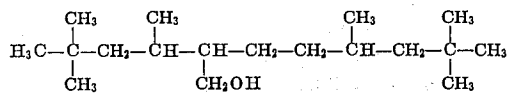
Competing couplers are compounds which are used in conjunction with colour couplers in silver halide colour photography and which couple with the oxidized aromatic primary amino colour development agent to form colourless coupling products e.g. as described in United Kingdom Patent Specification No. 861,138.

In the preparation of the photographic components according to the present invention inexpensive and easily available primary branched-chain alcohols comprising at least 10 carbon atoms can be used as starting materials for introducing the diffusion fast making group in the photographic component molecule.

Examples of branched-chain alcohols that can be used are the widely known branched-chain primary oxo-alcohols having at least 10 C-atoms and which can be represented by the formula



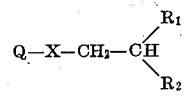
wherein R_1 and R_2 have the same significance as above, such as isodecylalcohol, isotridecylalcohol, isohexadecylalcohol and isooctadecylalcohol. Isodecylalcohol is a commercial material prepared from C_9-olefins (tripropylene) by means of the oxo-synthesis (cf. H. Rompp - Chemie Lexikon - Franck'sche Verlag - Stuttgart, W. Germany) and is a mixture of primary branched-chain C_{10}-alcohols. Isotridecylalcohol is a commercial material prepared from C_{12}-olefins (triisobutylene, tetrapropylene or di(2-methyl-1 pentene) by means of the oxo-reaction and is a mixture of primary branched-chain C_{13}-alcohols. Isohexadecylalcohol and isooctadecylalcohol are commercial materials prepared by aldol-condensation of C_8- or C_9 aldehydes formed by oxo-synthesis, isohexadecylalcohol is a mixture of branched-chain primary C_{16}-alcohols mainly consisting of alcohols as represented by the above formula wherein R_1 = dimethylbutyl and R_2 = dimethylhexyl whereas isooctadecylalcohol is a branched-chain alcohol for which the following formula is given:



More details regarding the composition, the preparation and the properties of branched-chain oxo-alcohols can be found in Fortsch.Chem.Forsch. Bd 11/1 p. 121–134.

Other branched-chain alcohols which can be used as starting materials are the branched-chain alcohols prepared by alkaline condensation, using catalytic amounts of alkali such as potassium hydroxide at temperatures comprised between 200° and 300°C, (known as Guerbet-reaction — see e.g. Fette-Seifen-Anstrichmittel, 71, no. 3, p. 215–218 (1969)) of a branched-chain alcohol with the same or other branched-chain alcohol.

The components according to the present invention can be represented by the following general formula:



wherein:

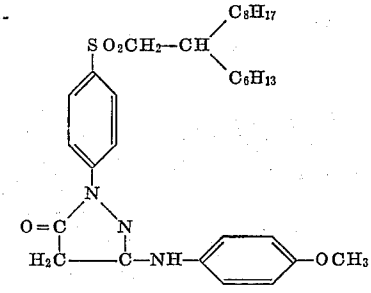
X, R_1 and R_2 have the same significance given above, and

Q stands for the residue of a photographic component that is to be incorporated in photographic hydrophilic colloid media in a form fast to diffusion, for example a colour coupler residue capable of forming a dye image on coupling with an oxidized aromatic primary amino colour developing agent such as a residue of a cyan-forming colour coupler of the phenol or naphthol type, of a magenta-forming colour coupler of the pyrazolone or indazolone type or of a yellow forming colour coupler of the acylacetamide especially the benzoylacetanilide type, a mask-former residue, a U.V.-absorber residue and a competing coupler residue.

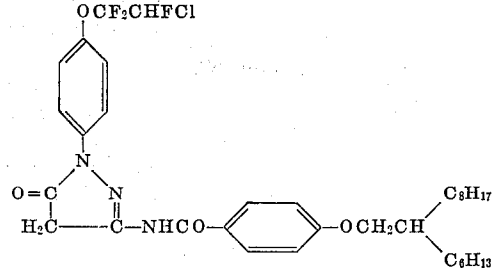
In accordance with the present invention there is provided a photographic silver halide material comprising in a silver halide emulsion layer or in a hydrophilic colloid layer of said material a water-insoluble photographic component comprising in its molecule a group rendering said component fast to diffusion in hydrophilic colloid media wherein said group is a group of the above formula.

The following are representative examples of photographic components having a branched-chain diffusion-fast making group as defined above in accordance with the invention.

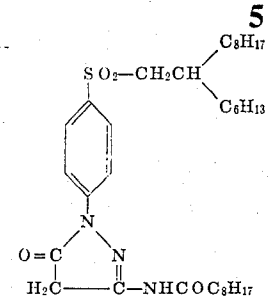
1---



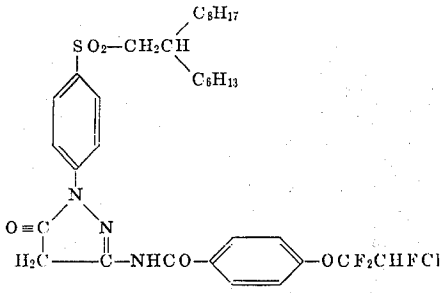
2---



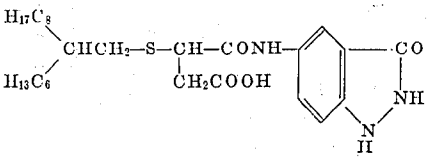
3.



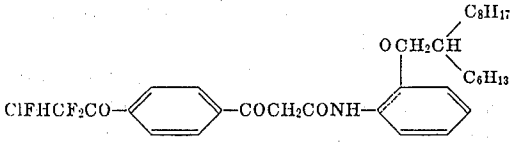
4.



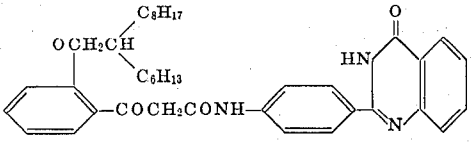
5.



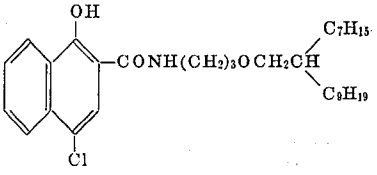
6.



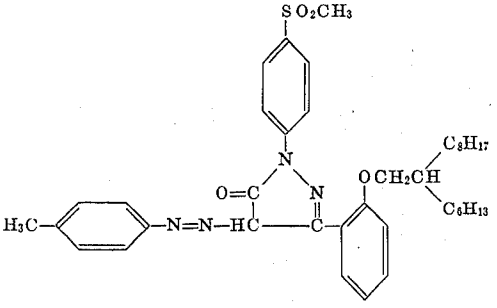
7.



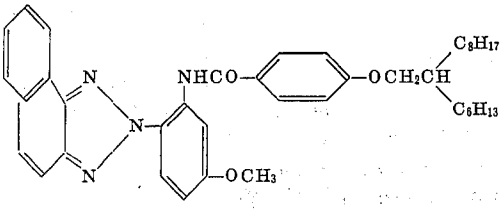
8.



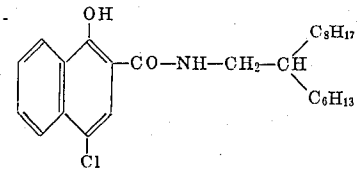
9.



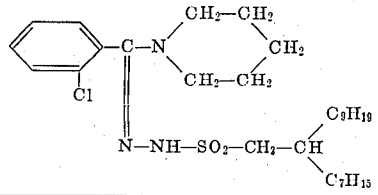
10.



11.



12.



The following preparations illustrate how these compounds can be prepared.

PREPARATION 1: COMPOUND 1

a. p-isohexadecylthio-chlorobenzene

14.5 g of p-chlorothiophenol and 4 g of sodium hydroxide were dissolved in 200 ml of methanol, whereupon 30.5 g of isohexadecyl bromide prepared as known by those skilled in the art of organic synthesis from isohexadecyl alcohol (commercially available from Esso Belgium N.V., Antwerp, Belgium), and hydrobromic acid, were added and the whole was refluxed for 5 hours. The reaction mixture was poured into 1 l of water and the oil formed was extracted with methylene chloride. After drying, over magnesium sulphate and distillation under reduced pressure, 28 g of p-isohexadecylthio-chlorobenzene were obtained.

Boiling point: 160°–165°C/0.15 mm.

b. p-isohexadecylsulphonyl-chlorobenzene

A mixture of 36.9 g of p-isohexadecylthio-chlorobenzene, 180 ml of acetic acid and 80 ml of dioxan was heated to 90°C whereupon 41 ml of 50% aqueous hydrogen peroxide were added in 1 hour. The mixture was stirred for 1 h on a boiling water bath and then cooled to room temperature. The oil formed upon pouring into 400 ml of water was separated and the aqueous layer extracted with ether. The ether layer was washed with a 10% solution of sodium bisulphite, dried and concentrated.

Yield: 37 g.

c. p-isohexadecylsulphonylphenylhydrazine

40 g of p-isohexadecylsulphonyl-chlorobenzene in 70 ml of ethylene glycol monomethyl ether and 41.6 ml of anhydrous hydrazine were refluxed for 60 hours. Upon pouring the reaction mixture into 800 ml of water and extracting with benzene, 36 g of an oil comprising 92% of p-isohexadecylsulphonyl-phenylhydrazine were obtained.

d. 1-p-isohexadecylsulphonylphenyl-3-amino-2-pyrazolin-5-on

36 g of the above hydrazine, 20 g of β-amino-β-ethoxyacrylic acid ethyl ester, 0.6 ml of acetic acid and 25 ml of acetonitril were heated for 2 hours at 60°C.

The acetonitrile was removed by evaporation and the residue was treated with a solution of 4.6 g of sodium in 100 ml of methanol. The mixture was kept for 3 hours at 40°–45°C whereupon 100 ml of water was added and the mixture was acidified to pH 3 by means of 5 N hydrochloric acid. The precipitate formed was filtered off and recrystalized, after drying, from methanol.

Yield: 20 g.
Melting point: 147°C.
e. Compound 1
46 g of the above 2-pyrazolin-5-on and 20 g of anisidine hydrochloride were refluxed for 90 minutes in 80 ml of acetic acid. The mixture was poured into 800 ml of water whereupon the oil formed was purified by dissolving in boiling acetonitrile.
Yield: 30 g.
Melting point: 40°C.

PREPARATION 2: COMPOUND 2

a. p-isohexadecyloxy-benzoic acid
57.5 g of sodium were dissolved in 2800 ml of ethylene glycol monomethyl ether whereupon 380 g of p-hydroxy-benzoic acid methyl ester were added followed by 762 g of isohexadecyl bromide. The reaction mixture was refluxed for 20 hours and then treated with 380 g of sodium hydroxide in 1 l of water whereupon the mixture was again refluxed for 2 hours. One litre of concentrated hydrochloric acid was added and the mixture poured into 10 l of water. The oil formed was separated and the aqueous layer extracted with methylene chloride. The organic layer and the methylene chloride extract were put together and washed with water. The mixture was dried and the solvent removed.
Yield: 694 g of an oil comprising 98% of p-isohexadecyloxybenzoic acid.
b. p-isohexadecyloxy-benzoyl chloride
36.2 g of p-isohexadecyloxy-benzoic acid and 35.7 g of thionyl chloride were refluxed for 5 hours on a water bath whereupon the excess of thionyl chloride was removed by evaporation. The residue was distilled at a reduced pressure of 0.1 mm.
Yield: 33.5 g
Boiling point: 180°C.
c. Compound 2
26.7 g of anhydrous aluminium chloride were dissolved in 200 ml of pyridine. Once the exothermic reaction had come to an end, 30.7 g of 1-p-(1,1,2-trifluoro-2-chloroethoxy)phenyl-3-amino-2-pyrazolin-5-on prepared as described in Belgian Patent Specification 736,252 were added as well as 38 g of p-isohexadecyloxy-benzoylchloride. The mixture was stirred for 4 hours at 80°C whereupon it was concentrated by evaporation and the residue dissolved in 400 ml of ethylene glycol monomethyl ether. The mixture was poured into 280 ml of concentrated hydrochloric acid and 800 g of ice. The precipitate formed was filtered and washed with water, whereupon it was recrystallized from 400 ml of ethanol.
Yield: 35.5 g.
Melting point: 173°C.

PREPARATION 3: COMPOUND 3

27 g of anhydrous aluminium chloride were dissolved in 200 ml of pyridine. To the solution formed were added 46.3 g of 1-p-isohexadecylsulphonylphenyl-3-amino-2-pyrazolin-5-on and 17.6 g of isononane carboxylic acid chloride prepared in the usual way from the corresponding carboxylic acid marketed by Novadel, Ltd., London. The mixture was stirred for 1 hour on a water bath whereupon it was concentrated by evaporation under reduced pressure and the residue formed was dissolved in boiling methanol. The mixture was acidified with 280 ml of concentrated hydrochloric acid and the precipitate formed was recrystallized, after having been washed with water, from 300 ml of ethanol.
Yield: 32 g.
Melting point: 126°C.

PREPARATION 4: COMPOUND 4

This compound was prepared in an analogous way as compound 3 starting from 27.3 g of p-(1,1,2-trifluoro-2-chloroethoxy)-benzoyl chloride (Bull.Soc.Chim.Fr. 1957, 821). After recrystallization from ethanol, 40 g of colour coupler were obtained.
Melting point: 160°C.

PREPARATION 5: COMPOUND 5

a. Isohexadecylthio-succinic anhydride
This compound was prepared by addition of isohexadecylmercaptan to maleinic anhydride in the presence of triethylene diamine according to the method described in Journal Organic Chemistry 27; 3140–3146 (1962). When starting from 130 g of isohexadecylmercaptan 100 g of a reddish brown oil were obtained.
Boiling point: 200°C/0.5 mm.
b. Compound 5
2.2 g of 5-amino-indazolone were dissolved with heating in 10 ml of acetic acid. 5.1 g of isohexadecylthio-succinic anhydride were added whereupon the white precipitate formed was recrystallized from acetonitrile.
Melting point: 162°C.

PREPARATION 6: COMPOUND 6

a. o-isohexadecyloxy-nitrobenzene
260 g of o-nitrophenol were dissolved in 1200 ml of dimethylformamide whereupon 123 g of potassium hydroxide were added. 600 g of 95% isohexadecyl bromide were added whereupon the mixture was refluxed for 90 minutes. The mixture was poured into water and the oil formed extracted with methylene chloride, whereupon the residue was distilled under a reduced pressure of 0.2 mm and a temperature of 180°C.
Yield: 800 g.
b. o-isohexadecyloxyaniline
497 g of the above nitro compound were dissolved in 3 l of methanol and then reduced by catalytic hydrogenation using Raney-nickel as catalyst at 80°C and a hydrogen pressure of 1800 psi. The Raney nickel was filtered off and the methanol removed by evaporation whereupon the residue was distilled under a reduced pressure of 0.2 mm at 155°–160°C.
Yield: 400 g.
c. Compound 6
22.7 g of p-(1,1,2-trifluoro-2-chloro-ethoxy)-benzoylacetic acid ethyl ester prepared as described in Belgian Patent Specification 736,253 were condensed with 24 g of o-isohexadecyloxyaniline in a medium of 53 ml of xylene, by removing during 1 hour the alcohol formed during the condensation by distillation. The oil formed was treated, after removal of the xylene, with 70 ml of water and 7 g of copper acetate. The copper chelate formed was filtered off and washed with acetonitrile. The mixture was taken up in methylene chloride whereupon 100 ml of 5N hydrochloric acid were added and then the organic layer was washed till neutral. After removal of the solvent, 34 g of an oil were obtained. According to thin layer chromatography this oil did not comprise impurities. The content of active methylene groups in the product obtained was deter-

mined by titration with potassium methylate in dimethyl formamide as solvent and was found to be 100%.

PREPARATION 7: COMPOUND 7

a. o-isohexadecyloxy-acetophenone

600 g of o-hydroxyacetophenone in 3 l of dimethyl formamide were treated with 252 g of sodium methylate. The methanol formed was removed by evaporation on a boiling water bath at a reduced pressure of 20 mm. Then 1345 g of isohexadecyl bromide were added and the mixture stirred for 6 hours on a boiling water bath. The reaction mixture was poured into 10 l of water, the organic layer was separated and the aqueous layer extracted with methylene chloride. After removal of the solvent by evaporation, the oil was treated in a thin film evaporator at 155°C and a reduced pressure of 0.45 mm Hg to remove the low boiling fractions.

Yield: 845 g.

b. o-isohexadecyloxybenzoic acid

3.6 l of 5N sodium hydroxide were cooled to 10°C whereupon 846 g of bromine were added dropwise in about 30 minutes. The mixture was cooled to 5°C whereupon 640 g of o-isohexadecyloxyacetophenone in 4 l of dioxan were added in 1 hour. The exothermic reaction was kept between 0° and 5°C by external cooling with ice. The mixture was then stirred for 1 hour at 30°C whereupon it was refluxed for 90 minutes. The bromoform formed as well as the dioxan were removed by evaporation whereupon the mixture was acidified with hydrochloric acid. The oil-layer formed was extracted with methylene chloride and then concentrated after drying. The volatile substances were removed by treatment in a thin film evaporator at 195°C and a reduced pressure of 0.3 mm.

Yield: 400 g of product comprising 90% of free carboxyl groups.

c. o-isohexadecyloxybenzoyl chloride

400 g of the above carboxylic acid were heated on a boiling water bath for 3 hours together with 280 ml of thionyl chloride. After removal of the excess of thionyl chloride the residue was distilled in a rotating film evaporator at 190°C and 0.3 mm Hg.

Yield: 341 g.

d. o-isohexadecyloxy-benzoyl acetic acid methyl ester

237 g of sodium ethyl acetoacetate suspended in 380 ml of methylene chloride were treated with 267 g of o-isohexadecyloxybenzoyl chloride. The mixture was left standing overnight at room temperature and then acidified with 525 ml of 2N hydrochloric acid. The methylene chloride was separated from the mixture whereupon the mixture was washed 3 times with a 5% solution of sodium chloride. The organic layer was separated and the methylene chloride removed by evaporation. The residual oil was treated with 38 g of sodium methylate in 1300 ml of methanol, refluxed for 1 hour and then left standing overnight at room temperature. After removal of the methanol by evaporation, the residue was taken up in methylene chloride and washed three times with water. The solvent was removed by evaporation yielding 258 g of an oil having a content of active methylene groups of 95%.

e. Compound 7

46 g of o-isohexadecyloxybenzoylacetic acid methyl ester and 24 g of 2-(p-aminophenyl)-quinazolone were condensed by boiling in 75 ml of xylene and 90 ml of dimethyl formamide, the alcohol formed being removed from the reaction mixture. After having been cooled, the reaction mixture was poured into 800 ml of acetonitrile.

Yield: 32 g.

Melting point: 141°C.

PREPARATION 8: COMPOUND 8

a. β-isooctadecyloxy-propionitrile

135 g of isooctadecyl alcohol commercially available from Farbwerke Hoechst A.G., Frankfurt (M) - Hoechst, W. Germany and 1 g of sodium methylate were stirred whereupon 30 g of freshly distilled acrylonitrile were added dropwise at 20°C. The mixture was kept for 1 hour at 30°C, yielding 149 g of an oil comprising at most 1 % of alcohol acccording to thin layer chromatography.

b. β-isooctadecyloxy-propylamine

0.46 mole of the above nitrile was hydrogenated at 60°–65°C in a solution of absolute ethanol saturated with ammonia, using a hydrogen pressure of 1500 psi and 10 g of Raney nickel as catalyst. After 2 hours the theoretical amount of hydrogen was taken up and the catalyst was filtered off. The mixture was concentrated by evaporation and 126 g of an oil having an amine content of 96% was obtained. No secondary amine was present.

c. Compound 8

60 g of 1-hydroxy-4-chloronaphthoic acid phenyl ester and 66 g of β-isooctadecyloxypropylamine were heated for 1 hour on an oil bath of 150°C. The mixture was then heated under reduced pressure and the phenol formed removed by distillation. The oil formed was boiled twice with 280 ml of acetonitrile and the oil that separated, after cooling was isolated. According to thin layer chromatography no amine was present anymore.

PREPARATION 9: COMPOUND 9

a. 1-p-methylsulphonylphenyl-3-o-isohexadecyloxyphenyl-2-pyrazolin-5-one

42 g of o-isohexadecyloxybenzoylacetic acid methyl ester and 19 g of p-methylsulphonylphenylhydrazine were refluxed for 2 hours in 100 ml of acetic acid. The acetic acid was removed in a rotating film evaporator and the residue was treated with decolourizing carbon. The product was recrystallized from 180 ml of methanol.

Yield: 20 g.

Melting point: 95°C.

b. Compound 9

4.7 g of diazotised p-anisidine were added to 16.7 g of the above pyrazolin-5-one compound dissolved in 30 ml of 2N sodium hydroxide and 15 ml of ethylene glycol monomethyl ether. The mixture was acidified with acetic acid and the precipitate formed was filtered off. After having been taken up in n-hexane and dried, 20 g were obtained.

Melting point: 85°C.

PREPARATION 10: COMPOUND 10

2.9 g of 2-(2'-amino-4'-methoxyphenyl)-2H-naphtho[1,2-d]triazole and 3.8 g of p-isohexadecyloxybenzoyl chloride in 30 ml of dioxan and 0.8 ml of pyridine were heated for 4 hours at 60°C. The mixture was poured into water and the oily precipi-

tate was extracted with chloroform. After washing with water and drying, 6.3 g of residue were obtained, which after treatment with acetonitrile yielded 5 g of product having a melting point of 80°C.

PREPARATION 11: COMPOUND 11

a. Isohexadecylamine

1 kg of isohexadecylbromide and 2 litres of liquid ammonia were agitated in an autoclave for 24 hours at 60°C. The residue was then treated with 4 litres of 40percent acetic acid. Two layers formed and the aqueous layer was separated and treated with 10 N sodium hydroxide. The oil formed was extracted with isopropylether, concentrated by evaporation and distilled under reduced pressure.

Boiling Point: 108°C/8 mm.

b. Compound 11

60 g of 1-hydroxy-4-chloronaphthoic acid phenyl ester and 48.2 g of isohexadecylamine were heated for 1 hour on an oil bath of 140°C under a reduced pressure of 1 mm. The phenol formed was removed by distillation and the residue was boiled twice with acetonitrile. The oil layer formed was separated from the layer of acetonitrile. Acccording to thin layer chromatography neither phenol nor starting products were present anymore.

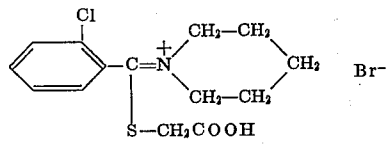
PREPARATION 12: COMPOUND 12

a. isooctadecylsulphonylhydrazide

A solution of 36 g of isooctadecylsulphochloride (obtained by treatment of sodium isooctadecyl sulphonate prepared as described in United Kingdom Patent Application No. 27,080/70 with thionylchloride) in 80 ml of dioxan was added dropwise at room temperature to 25 ml of hydrazine hydrate in 25 ml of dioxan. The mixture was stirred for 15 min. and then poured into ice-water. After extraction with methylene chloride and concentration by evaporation, 35 g of oil having a sulphonylhydrazide content of 95% were obtained.

b. Compound 12

38 g of 2-chloro-N-piperidyl-s-carboxymethyl-benzoisothioamide corresponding to the formula:



and 35 g of isooctadecylsulphonylhydrazide were heated for 12 hours in 300 ml of pyridine at 80°C.

The mixture was poured into water and the sticky precipitate was extracted with methylene chloride whereupon it was washed with 1N hydrochloric acid and then with water until neutral. The residue was dried over magnesium chloride and concentrated by evaporation.

Yield: 47 g of an oil having a content of 96% of active mask forming compound.

The compounds of the invention are preferably incorporated into hydrophilic colloid media from solutions in high-boiling sparingly water-miscible solvents such as di-n-butyl phthalate and tricresyl phosphate or in low-boiling sparingly water-miscible solvents such as ethyl acetate, methylene chloride, chloroform, etc. or mixtures thereof in that they have a high solubility therein and very fine dispersions in hydrophilic colloid compositions of the compounds of the invention can be obtained by means of these solvents. For this purpose these solutions are dispersed in extremely fine droplets, preferably in the presence of a wetting or dispersing agent into the hydrophilic colloid medium the low-boiling sparingly water-miscible solvent then being removed by evaporation.

Of course, the compounds of the invention can also be incorporated into the hydrophilic colloid composition in other ways. For instance, when the compound can be liquefied by slight heating (when it has a low melting point) or when it is liquid at room temperature the liquid can be dispersed as such in the hydrophilic colloid composition.

The hydrophilic colloid composition into which the compounds of the invention are dispersed need not necessarily be the coating composition itself of the hydrophilic colloid layer such as a silver halide emulsion layer into which the compounds are intended to be present. Especially in the case of photographic emulsion components that are intended to be incorporated into light-sensitive silver halide emulsions, it may be advantageous to first disperse the components into non-light-sensitive hydrophilic colloid compositions which are then in their turn admixed with the colloid coating composition, such as a silver halide emulsion, from which the hydrophilic colloid layer will be coated.

For more details about suitable dispersing techniques that may be employed for incorporating the compounds of the invention into a hydrophilic colloid layer of a photographic material there can be referred to e.g. U.S. Pat. Nos. 2,269,158, 2,284,887, 2,304,939, **2,304,940** and 2,322,027, United Kingdom Patent Specification No. 791,219, French Patent Specification No. 1,555,663, German Patent Specification No. 1,127,714 and to Belgian Patent Specification No. 747,589.

Since the components containing branched-chain diffusion-fast making groups in accordance with the invention have a higher solubility in the high-boiling or low-boiling water-immiscible solvents or mixtures thereof than the corresponding components with straight-chain diffusion-fast making groups a larger amount of component can be dispersed in the hydrophilic colloid which is of particular importance in the case of colour couplers since the coupling activity is increased which favours the dye density obtained. The colour couplers yield dyes of excellent stability and spectral characteristics.

By the increased solubility in sparingly water-miscible organic solvents of the components of the invention they have a high reistance to crystallization. Further, as compared with the corresponding components having a straight-chain diffusion-fast making group the components according to the invention generally have a lower melting point and some of them are even liquid at room temperature.

In the following table the solubility in ethyl acetate is given in percentages by weight measured at 40°C, of colour couplers according to the present invention having a branched-chain diffusion-fast making group as defined above, as compared with structurally isomeric colour couplers having instead of the branched-chain diffusion-fast making group a straight-chain diffusion-fast making group with the same number of carbon atoms.

Table

Compound of the invention	Solubility of the compound of the invention	Solubility of the structurally isomeric compound
1	30 %	8 %
2	50 %	<5 %
3	50 %	20 %(*)
4	50 %	8 %
6	<50 %	25 %
7	30 %	<5 %

(*) In the structurally isomeric colour coupler the hexadecylsulphonyl group is a straight-chain group but the octyl group in the 3-position of the 2-pyrazolin-5-one ring is still a branched-chain group.

Although the hydrophilic colloid media in which the compounds according to the invention are incorporated usually comprise gelatin as hydrophilic colloid, other water-soluble colloidal materials or mixtures of them can be used too e.g. colloidal albumin, zein, casein, a cellulose derivative such as carboxymethyl cellulose, a synthetic hydrophilic colloid such as polyvinyl alcohol, poly-N-vinyl pyrrolidone, etc.

The compounds of the invention may be used in photographic materials comprising various kinds of photographic emulsion layers. Various silver salts may be used as the sensitive salt such as silver bromide, silver iodide, silver chloride and mixed silver halides such as silver chlorobromide, silver bromoiodide and silver chlorobromoiodide.

The light-sensitive silver halide emulsions 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 Patent Specification No. 1,146,955 and in Belgian Patent Specification No. 568,687, imino-amino methane sulphinic acid compounds as described in United Kingdom Patent Specification 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 in U.S. Pat. Nos. 2,531,832, **2,533,990, 3,210,191** and 3,158,484, in United Kingdom Patent Specification Nos. 920,637 and 991,608 and in Belgian Patent Specification No. 648,710 and onium derivatives of amino-N-oxides as described in United Kingdom Patent Specification 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-5-thione and compounds of the hydroxytriazolopyrimidine type. They can also be stabilized with mercury compounds such as the mercury compounds described in Belgian Patent Specification 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 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 of resinous materials, as well as paper and glass.

The following examples illustrate the use of the compounds according to the present invention.

EXAMPLE 1

2 g of compound 1 were dissolved in 6 ml of ethyl acetate. The solution was added to 30 ml of a 7% aqueous gelatin solution comprising 0.1 g of sodium dodecylbenzenesulphonate whereupon the whole was mixed for 15 min. by means of a homogenizer.

The ethyl acetate was removed from the colloid composition by evaporation in a rotating film evaporator and then the composition was admixed with 100 g of green-sensitized light-sensitive emulsion comprising 5 g of silver bromide and 6 g of gelatin. The colour emulsion thus formed was coated on a support and dried.

After exposure, colour development using N,N-diethyl-p-phenylene diamine sulphate as colour developing agent, a treatment in a bleach bath and fixing bath a magenta image was obtained having an absorption maximum of 536 nm.

EXAMPLE 2

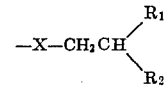
10 g of compound 6 were dissolved in 30 ml of ethyl acetate and the solution formed was dispersed by means of a homogenizer into 100 ml of water comprising 12.5 ml of a 10% aqueous solution of N-methyl-oleyltauride sodium salt.

The ethyl acetate was removed from the aqueous composition by evaporation under reduced pressure at 55°C and 200–400 mm Hg. In this way a stable dispersion in water of compound 6 was formed.

The aqueous dispersion was then admixed with a conventional blue-sensitive silver halide emulsion.

We claim:

1. Photographic material comprising a support, a light-sensitive silver halide emulsion layer on said support and a photographic water-insoluble component wherein said component is rendered fast to diffusion in hydrophilic colloid media by the presence in its molecule of a group corresponding to the formula:



wherein:

X represents an ether group, a thioether group, a sulphonyl group, a CONH group, an NHCO group, or an SO_2NH group, and

each of R_1 and R_2 represents a branched-chain C_4—C_{12} alkyl group.

2. A photographic material according to claim **1**, wherein R_1 is a branched-chain C_8-alkyl group and R_2 is a branched-chain C_6-alkyl group.

3. A photographic material according to claim **1**, wherein R_1 is a branched-chain C_7-alkyl group and R_2 is a branched-chain C_9 alkyl group.

4. A photographic material according to claim **1**, wherein said component is a cyan-forming colour coupler of the phenol or naphthol type.

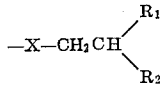
5. A photographic material according to claim 1, wherein said component is a magenta-forming colour coupler of the pyrazolon- or indazolon type.

6. A photographic material according to claim 1, wherein said component is a yellow-forming colour coupler of the acylacetamide type.

7. A photographic material according to claim 1, wherein said component is a mask-forming compound.

8. A photographic material according to claim 1, wherein said component is a U.V.-absorbing compound.

9. A photographic water-insoluble component comprising a group corresponding to the formula:



wherein:

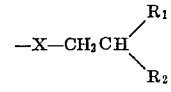
X represents an ether group, a thioether group, a sulphonyl group, a CONH group, an NHCO group or a SO_2NH group, and

each of R_1 and R_2 represents a branched-chain C_4—C_{12} alkyl group.

10. A photographic water-insoluble component according to claim 9, wherein R_1 is a branched-chain C_8-alkyl group and R_2 is a branched-chain C_6-alkyl group.

11. A photographic water-insoluble component according to claim 9, wherein R_1 is a branched-chain C_7-alkyl group and R_2 is a branched-chain C_9-alkyl group.

12. The photographic material according to claim 1 wherein said group



is bonded to Q wherein Q is the residue of a photographic component to be incorporated in a photographic hydrophilic colloid medium in a form fast to diffusion.

* * * * *