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(54) ANIONIC SURFACE ACTIVE COMPOUNDS, PHOTOGRAPHIC ELEMENTS CONTAINING THEM AND PROCESSES FOR PREPARING THE ELEMENTS.

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DE-A-2 610 485
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US-A-3 470 258

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Description

The present invention relates to anionic compounds comprising fluorocarbons and polyglycidyl groups. These compounds are particularly useful surface active agents and can be used as coating aids in coating photographic elements. The invention further relates to photographic elements containing such anionic compounds and to processes for preparing such elements.

In the preparation of photographic elements a support is often coated with one or more layers comprising an aqueous solution of gelatin or other hydrophilic binder. For multilayer elements, layers are generally coated simultaneously on conventional photographic supports as described in US—A—2,761,791.

A critical commercial step in preparing photographic elements is the coating of a photographic emulsion (a dispersion of silver halide crystals in an aqueous binder) onto the support. The coating process is generally carried out on a continuously operating machine wherein a single layer or a plurality of layers are simultaneously applied to the support.

In the simultaneous coating operation, it is important that the coating compositions used lie on the surface of the support so as to form a distinct layer of uniform thickness. The layers once formed should be stable to deformation from spreading, chilling, drying or other common coating treatments.

Many of the possible imperfections and non-uniformities resulting from the coating operation can be controlled by the addition of surface active agents to the coating composition.

A wide variety of surface active agents, such as alkyl aryl polyether sulphonates, have been suggested for use as coating aids to control and enhance coating uniformity, to reduce certain types of layer thickness non-uniformities and to impart certain physical properties to the surface of the coated product.

Surfactants are also added to eliminate coating problems such as formation of cross-roll patterns due to poor static or dynamic wettability of the support. Other problems involve edge withdrawal and layer inversion in simultaneous multilayer applications, repellency spots and poor wetting of the coating application apparatus.

As some of these coating problems are sensitive to the speed at which the layer is applied to the support, the lowering of the coating speed may at least partially solve these particular problems. However, the use of coating machines at low coating speeds is highly uneconomical.

It has been found that in the use of the surfactants as coating aids many conventional surfactants interact or coagulate with the hydrophilic colloid to form insoluble materials, interfere with the photographic properties of silver halide by increasing fog or desensitizing, interfere with other additives imparting an easily wettable surface to the dry coating or adversely alter the triboelectric charging of the dry coating.

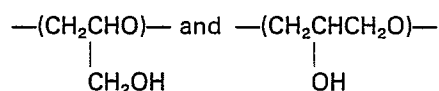
Thus, a surfactant which controls the surface properties of the coating and additionally has the proper solubility characteristics to avoid the above problems is much sought after. The surfactants generally should reduce the surface tension of aqueous solutions to low values, contribute to favourable wettability properties of the uppermost surface of the dried product, and be effective in allowing the manufacture of uniform coatings which are free of repellency spots.

Among the many types of surfactants previously proposed are the non-ionic compounds containing fluorinated hydrocarbon and polyglycidyl groups, as described in British Specification 1,524,631. Unfortunately such nonionic compounds provide highly variable results when they are used as coating aids as illustrated in Example 3 below.

FR—A—2,260,812 discloses the addition of an organic fluoro compound to the surface layer of a photographic light-sensitive material as a means of improving its adhesion resistance.

The present invention provides a novel class of fluorocarbon surfactants which because of the presence of an anionic group, allow the surfactants to be water-soluble while keeping the molecule size to a minimum. In addition to the present surfactants performing excellently in photographic coating compositions in general it is believed that those of relatively small molecular size will be especially useful in high speed coating applications where the dynamic rheological properties become increasingly significant.

According to the present invention there is provided a water-soluble surface active compound consisting of a terminal fluorocarbon group linked by a linking group to a polyglycidyl chain comprising a random mixture of groups of the formula



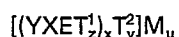
having attached thereto at least one anion, the or each anion having an associated cation.

The present surfactants provide desirable surface properties to coatings resulting in coated products which are uniform and free of adverse photographic and sensitometric problems.

Preferably the anion is sulphate. The polyglycidyl group may be linked to the fluorocarbon group by a hydrocarbon group, e.g. CH₂.

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A preferred class of surfactants according to this invention have the formula:



- 5 wherein Y is a fluorocarbon group;
 X represents a linking group comprising a hydrocarbon group having 1 to 6 carbon atoms, an ether, ester, amine, amido or sulphonamido group or a combination thereof;
 E is a polyglycidyl chain;
 T¹ and T² are independently an anionic group attached to E;
 10 M is a monovalent cation associated with T¹ or T²;
 z is 0 or an integer from 1 up to the maximum number of sites on E to which an anionic group can be attached;
 y is 0 or 1 provided that z+y is at least equal to 1;
 x is 1 or 2; and
 15 u is the number of cations required to neutralize the anionic groups present.
 The preferred fluorocarbon groups have the formula A(CF₂)_a where A is hydrogen or fluorine and a is 4 to 8, preferably 6 to 8. Preferably x = 1 and y = 0.
 The preferred linking group X has the formula:

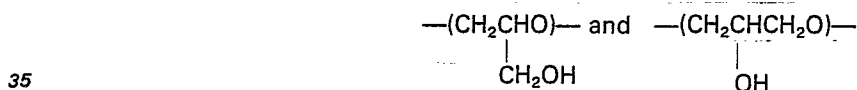


wherein Z is an ether, ester, amine, amido or sulphonamido linking group; and D is an ether or amine linking group; c is 0 or 1; m is 0 or 1; and b is 0 or 1 provided that where b is 0, c+m is 1 and when b is 1, m is 0 and c is 0 or 1.

- 25 Examples of groups which Z and D may represent are —O—, —O—CO—, —CO—O—, —NR—, —CONH—, —NHCO, —SO₂NH— and —NH—SO₂— wherein R is alkyl or aryl.

Examples of linking groups X are alkylene preferably containing from 1 to 6 carbon atoms such as methylene, isopropylene; or arylene such as phenylene. The preferred linking group is CH₂.

- 30 Polyglycidyl groups are well-known and described, for example, in US—A—3,514,293. These groups are optionally named poly(hydroxypropylene ethers) and have the formula C₃H₆O₂. They are believed to comprise a random mixture of groups of the formula

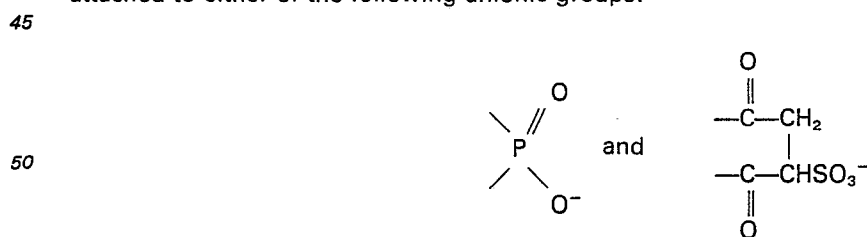


The polyglycidyl chains are formed in known manner by condensing glycidol to form a linear or branched chain linked by ether bonds.

- 40 T¹ and T² are each independently anionic groups attached to E. They preferably comprise anions derived from an organic or inorganic acid.

Examples of anionic groups represented by T¹ include sulphosuccinate, sulphonate, sulphate and phosphate.

The anionic group T² links together two or more (YXET_z¹) units. For example, two such units may be attached to either of the following anionic groups:



- 55 to form the appropriate double ester.

When the surfactant of the invention contains more than one anionic group it is possible for them to comprise more than one type of anionic group. The maximum number of anionic groups present may equal the number of sites in E to which the anionic group are attachable.

- 60 Examples of monovalent cations M are Li⁺, Na⁺, K⁺ and $\overset{+}{N}R'_4$ wherein each R' independently represents hydrogen or alkyl, preferably containing 1 to 3 carbon atoms such as methyl and propyl.

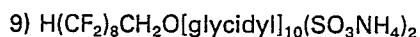
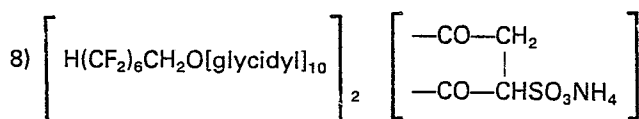
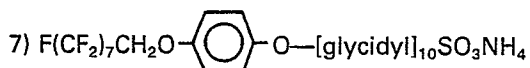
A preferred class of surfactants have the formula:



wherein T¹ is an anionic group, M is a cationic group, A is H or F and f is from 4 to 8, preferably 6 to 8 and d is from 2 to 30, often 4 to 30 and preferably 2 to 10.

Examples of preferred fluorosurfactants include

- 1) H(CF₂)₆CH₂O[glycidyl]₄SO₃NH₄
- 2) H(CF₂)₆CH₂O[glycidyl]₁₀SO₃NH₄
- 3) H(CF₂)₈CH₂O[glycidyl]₂₀SO₃NH₄
- 4) H(CF₂)₆CH₂O[glycidyl]₄PO₃(NH₄)₂
- 5) H(CF₂)₆CH₂O[glycidyl]₄SO₃N(C₂H₅)₄
- 6) F(CH₂)₇CH₂O[glycidyl]₁₀SO₃NH₄



The fluorosurfactants of the present invention are useful alone or in combination with conventional anionic and non-ionic surfactants to achieve improved surface properties.

It is recognised that the number of polyglycidyl groups (d) represents an average value with a distribution of molecular weight around this value.

The surface active agents of the present invention are prepared by methods in themselves known from a suitable fluorocarbon starting material. Suitable fluorocarbon starting compounds have a labile functional group or atom such as iodide or a carboxylic acid, sulphonic acid, amine, alcohol or ethylenically unsaturated group. Examples of fluorocarbon materials useful for this purpose include H(CF₂)₈COOH, C₇F₁₅—SO₃H, H(CF₂)₆CH₂OH, H(CF)₈CH₂OH, C₇H₁₅CH₂OH and C₅F₁₁CF = CF₂. These compounds can be reacted directly with glycidol or first with a bifunctional compound to form any desired link.

To prepare compounds containing linking groups, Z, —CH₂— and D, the fluorocarbon is reacted with a bifunctional hydrocarbon compound in which the functional groups are both hydroxyl groups such as ethylene glycol; both amine groups such as ethylenediamine; or containing one hydroxyl group and one amino group such as ethanolamine. The functional group of the fluorocarbon starting compound may be a carboxylic acid chloride to yield the amide or ester link, or sulphonyl chloride to yield the sulphonamide link. An ethylenically unsaturated fluorocarbon material such as C₅H₁₁CF = CF₂ may be used to provide an ether or amine link. In the latter case, a vinyl fluorine atom is attacked by a hydroxyl or amino group of the bifunctional hydrocarbon compound. Linking group D is formed by reaction of the remaining free functional group of the hydrocarbon with glycidyl.

The anionic groups are attached to the polyglycidol chain by conventional techniques such as sulphation and phosphation. The cation is added by neutralizing to the salt.

The invention also provides a photographic element comprising a support having thereon at least one layer containing a hydrophilic colloid and a surfactant characterised in that the surfactant is one according to the present invention.

A coating composition which is particularly useful in preparing photographic elements comprises an aqueous hydrophilic colloid and the surfactant as described above. The hydrophilic colloid is preferably gelatin. Other hydrophilic colloids useful herein include modified gelatin, colloidal albumin, cellulose derivatives, polyvinyl alcohol, water-soluble polyacrylates, polyacrylamide and copolymers thereof.

A process of preparing a photographic element comprises coating a support such as film base such as poly(ethylene terephthalate), paper, glass or aluminium foil with at least one layer of a coating composition comprising a hydrophilic colloid and a surfactant according to the present invention. Preferably the support is coated with a silver halide emulsion layer or layers and the layers of the coatings described above as well as any other layers useful therein simultaneously with a multicoating apparatus such as a bead coating apparatus.

The fluorosurfactants of the present invention are particularly useful in coatings for photographic elements because they have the ability to lower the surface tension of an aqueous solution of gelatin to a value of less than 30 mN/m measured under static conditions at concentrations generally used for photographic products. Examples of such concentrations are from 0.03 to 0.5 weight/volume percent. This prevents non-uniformities in thickness of freshly coated layers caused by localized surface tension gradients.

The measurement of the surface tension (static) of an aqueous solution of gelatin (5% weight/volume) containing the surfactant over a concentration range, including the critical micelle concentration (CMC), is made with a Wilhelmy Blade surface Tensiometer.

5 The ability to provide a dried down gelatin layer into which it is incorporated in an amount equal to the critical micelle concentration with a highly wettable surface to aqueous processing solutions or other liquids applied to the surface during use may be assessed by measurement of contact angle. The wettability of the surface may be defined in terms of an advancing contact angle, θ_A . It may be advantageous for the surface active agent to provide $\theta_A \leq 45^\circ$ in respect of the surface when spread with pure water.

10 The surfactants of the present invention also have the ability to produce a uniform coating without repellency spots. By "repellency" is meant the round-shaped unevenness or hole in a coated layer which is produced by a small globule of surface active insoluble liquid in contact with the liquid-air interface during coating of the layer.

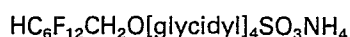
15 The control of coating uniformity is assessed by coating a pair of layers, the upper of which contains the surface active agent under test, onto a polyethylene terephthalate film base suitably subbed to give good adhesion to gelatin. The bottom layer consists of a 4% solution of a bone gelatin in water coated at 85.4 millilitres/m² and the top layer consists of 7% bone gelatin with colloidal silver added to give a grey coloration (the gelatin being chosen as one containing natural fats or small droplets of liquids known to cause repellency spots) to which is added the surface active agent in an amount at or above the critical micelle concentration. The coverage of the top layer is 14.2 millilitres/m². Both layers are applied 20 simultaneously at a temperature of 40°C using a conventional double slide hopper with applied suction and at a linear coating speed of 30 m/min.

25 Preferably, the surface active agent is sufficiently soluble in an aqueous solution of gelatin (5% weight/volume) for it not to remain as a separate phase in the solution. If the solubility of the surface active agent is insufficient to meet this requirement, the presence of a separate phase could result in the coating having a mottled appearance i.e. a non-uniform coating. The greater the insolubility of the surface active agent, the more non-uniform the coating becomes. In this case, the limiting concentration of the surface active agent is reached either very near to the critical micelle concentration or without micelle formation at all.

30 Preferably, the surface active agent is not so soluble in the bulk aqueous phase that adsorption at the liquid-air interface takes place only with difficulty and then at high concentrations. Although the surface active agent works at high concentration, its use at high concentrations is both uneconomical and undesirable. Preferably, the critical micelle concentration of the surface active agent occurs at a value of up to 0.5 g of the dry surface active agent per 100 ml of water.

35 The invention is illustrated by the following examples.

Example 1



40 The starting material for the preparation of the compound above was $\text{HC}_6\text{F}_{12}\text{CH}_2\text{OH}$ which was commercially available.

6.77 g of glycidol was added dropwise over 40 minutes to a mixture of 8 g of 1—H, 1—H, 7—H, dodecafluoro heptanol and 0.33 ml of triethylamine under a stream of nitrogen maintaining the 45 temperature at 115—125°C. The mixture was stirred for 2.5 hours at this temperature. The cooled gum represented the product. The yield was 14.13 g.

Eleven grams of the above compound was dissolved in dimethyl formamide (10 cm³ dry) and ethylene chloride (30 cm³ dry). The solution was treated with one mole of a dioxane-sulphur trioxide (1:1) complex at 0°C. The resulting sulphated mixture was converted with gaseous ammonia at 0°C to its corresponding 50 ammonium salt.

The solvent was removed under reduced pressure and the residue was tested in the following manner.

The above structure was confirmed using NMR and Mass Spectroscopy measurements.

55 The surface tension (static) of an aqueous solution of this surface active agent was measured as a function of bulk concentration with a Wilhelmy Blade surface Tensiometer. It was found that the surface tension was lowered to about 22mN/m at or above the critical micelle concentration (CMC).

The wettability was estimated from contact angle measurements on the dried down gelatin containing the surfactant. It was found that when the concentration of the surface active agent exceeded the critical micelle concentration the surface was wettable with both water and tetrachloroethylene (a liquid 60 commonly applied to the surface during printing by the wet-gate-method).

A test coating of the surface active agent was carried out with the surface active agent added at concentrations of 0.02 and 0.2% weight/volume to the top layer of the two layer coating. At the higher concentration, repellency spots were completely suppressed, no other coating imperfections were produced and a uniform coating resulted.

65 The surface active agent was added to a radiation-sensitive photographic emulsion, i.e. a gelatino photographic silver bromiodide emulsion, and was tested for changes in sensitometric response from

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that of the coating without the surface active agent. The test indicated that the surface active agent was photographically inert.

Example 2

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The starting material and the preparation of the compound above were in accordance with the method described in Example 1 except that the amount of glycidol used was increased by an amount to provide the longer glycidyl chain length.

10 The surface tension (static) of an aqueous solution of the surface active agent was measured in accordance with Experiment 1 above and was found to be between 22 and 26mN/m at or above the CMC.

The wettability of a dried down layer of gelatin containing the surface active agent was measured and was found to be satisfactory.

15 A test coating of the surface active agent at a concentration of 0.3% weight/volume was carried out and the resultant coating was completely free from repellency spots and was uniform in appearance.

Example 3

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The starting material for the preparation of the compound above was $\text{H}(\text{CF}_2)_8\text{CH}_2\text{OH}$. The preparation was carried out in accordance with the method described in Example 1 except that the amount of glycidol used was increased by an amount to provide the longer glycidyl chain length.

25 The surface tension (static) of an aqueous solution of the surface active agent was measured and was found to be approximately 26mN/m at or above the CMC.

The wettability of a dried down layer of gelatin containing the surface active agent was measured and was found to be satisfactory.

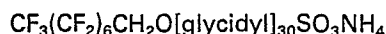
30 A test coating of the surface active agent at a concentration of 0.1% weight/volume was carried out and the coating was completely free from repellency spots and was uniform in appearance.

As previously indicated, non-ionic surfactants containing fluorocarbon and polyglycidyl groups as described in GB—A—1,524,631 give highly variable results when they are used as coating aids. The substitution of $\text{H}(\text{CF}_2)_8\text{CH}_2\text{O}[\text{glycidyl}]_{20}\text{SO}_3\text{NH}_4$ by either $\text{H}(\text{CF}_2)_3\text{CH}_2\text{O}[\text{glycidyl}]_4\text{OH}$ or $\text{H}(\text{CF}_2)_{10}\text{CH}_2\text{O}[\text{glycidyl}]_{20}\text{OH}$ in the test coating procedure of this Example provided coatings that were mottled and highly non-uniform. In contrast, the substitution of $\text{H}(\text{CF}_2)_8\text{CH}_2\text{O}[\text{glycidyl}]_{19}\text{OH}$ in this coating procedure provided a coating having uniformity comparable to that obtained with $\text{H}(\text{CF}_2)_8\text{CH}_2\text{O}[\text{glycidyl}]_{20}\text{SO}_3\text{NH}_4$.

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Example 4

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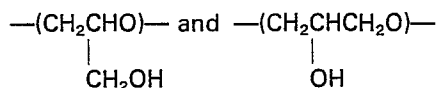
The compound above was prepared by a method analogous to that used in Example 1. It was tested and was found to possess properties similar to those found in Examples 1—3 and providing a figure of 18mN/m for surface tension.

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Claims

1. A water-soluble surface active compound consisting of a terminal fluorocarbon group linked by a linking group to a polyglycidyl chain comprising a random mixture of groups of the formula

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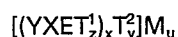
having attached thereto at least one anion, the or each anion having an associated cation.

2. A compound as claimed in Claim 1 wherein the terminal fluorocarbon group is directly linked to the polyglycidyl chain with a hydrocarbon linking group.

3. A compound as claimed in Claim 1 or 2 in which the anion is sulphate.

60

4. A compound as claimed in Claim 1 having the formula:



65 wherein Y is a fluorocarbon group;

X represents a linking group comprising a hydrocarbon group having 1 to 6 carbon atoms, an ether, ester, amine, amido or sulphonamido group or a combination thereof;

E is a polyglycidyl chain;

T¹ and T² are independently an anionic group attached to E;

5 M is a monovalent cation associated with T¹ or T²

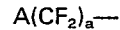
z is 0 or an integer from 1 up to the maximum number of sites on E to which an anionic group may be attached;

y is 0 or 1 provided that z+y is at least equal to 1;

x is 1 or 2; and

10 u is the number of cations required to neutralize the anionic groups present.

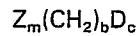
5. A compound as claimed in any of Claims 1—4 wherein the fluorocarbon group has the formula:



15 wherein A is H or F and a is 4 to 8, preferably 6 to 8.

6. A compound as claimed in Claim 4 or 5 wherein the linking group X is CH₂.

7. A compound as claimed in Claim 4 or 5 wherein X has the formula:

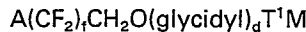


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wherein Z is an ether, ester, amine, amido or sulphonamido linking group; and D is an ether or amine linking group; c is 0 or 1; m is 0 or 1; and b is 0 or 1 provided that where b is 0, c+m is 1 and when b is 1, m is 0 and c is 0 or 1.

8. A compound as claimed in any of Claims 1—7 having the formula:

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wherein T¹ is an anionic group, M is a cationic group, A is H or F, f is from 4 to 8 and d is from 2 to 30.

30 9. A photographic element comprising a support having thereon at least one layer containing a hydrophilic colloid and a surfactant characterised in that the surfactant is one according to any of Claims 1 to 8.

10. A photographic element as claimed in Claim 9, in which the support has at least one photographic silver halide emulsion layer thereon.

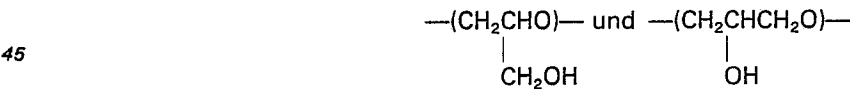
35 11. A process for preparing a photographic element comprising coating a support with a composition comprising a hydrophilic colloid and a surfactant according to any of Claims 1 to 8.

12. A process as claimed in Claim 11, in which the support is coated with a photographic silver halide emulsion layer.

Patentansprüche

40

1. Wasserlösliche oberflächenaktive Verbindung mit einer endständigen Fluorkohlenstoffgruppe, die über ein Bindeglied an eine Polyglycidylkette mit einer willkürlichen Mischung von Gruppen der Formeln



gebunden ist und an die mindestens ein Anion gebunden ist, dem oder denen jeweils ein Kation zugeordnet ist.

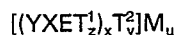
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2. Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß die endständige Fluorkohlenstoffgruppe direkt über ein Kohlenwasserstoffbindeglied an die Polyglycidylkette gebunden ist.

3. Verbindung nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Anion ein Sulfatanion ist.

4. Verbindung nach Anspruch 1, dadurch gekennzeichnet, daß sie der folgenden Formel entspricht

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in der bedeuten:

Y eine Fluorkohlenstoffgruppe,

60 X ein Bindeglied aus einer Kohlenwasserstoffgruppe mit 1 bis 6 Kohlenstoffatomen, einer Ether-, Ester-, Amino-, Amido- oder Sulfonamidogruppe oder einer Kombination hiervon;

E eine Polyglycidylkette;

T¹ und T² unabhängig voneinander an E gebundene anionische Gruppen;

M ein monovalentes Kation, das T¹ oder T² zugeordnet ist;

65 z gleich 0 oder eine Zahl von 1 bis zur maximalen Anzahl von Positionen an E, an die anionische Gruppen gebunden sein können;

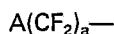
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y gleich 0 oder 1, wobei gilt, daß z und y mindestens gleich 1 ist;

x gleich 1 oder 2 und

u die Anzahl von Kationen, die erforderlich ist, um die vorhandenen anionischen Gruppen zu neutralisieren.

- 5 5. Verbindung nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß die Fluorkohlenstoffgruppe der folgenden Formel entspricht:

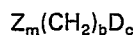


10 in der A gleich H oder F ist und a für 4 bis 8, vorzugsweise 6 bis 8 steht.

6. Verbindung nach Anspruch 4 oder 5, dadurch gekennzeichnet, daß das Bindeglied X eine $-\text{CH}_2-$ Gruppe ist.

7. Verbindung nach Anspruch 4 oder 5, dadurch gekennzeichnet, daß X der folgenden Formel entspricht:

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in der bedeuten: Z ein Ether-, Ester-, Amino-, Amido-, oder Sulfonamidbindeglied; D ein Ether- oder Aminobindeglied; c gleich 0 oder 1; m gleich 0 oder 1 und b gleich 0 oder 1, vorausgesetzt, daß, wenn b gleich 0 ist, c+m gleich 1 ist und wenn b gleich 1 ist, m gleich 0 und c gleich 0 oder 1 ist.

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8. Verbindung nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß sie der folgenden Formel entspricht:



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in der T^1 eine anionische Gruppe und M eine kationische Gruppe darstellen, A gleich H oder F ist und f für eine Zahl von 4 bis 8 und d für eine Zahl von 2 bis 30 steht.

9. Photographisches Element mit einem Schichtträger, der mindestens eine Schicht aufweist, die ein hydrophiles Kolloid und eine oberflächenaktive Verbindung enthält, dadurch gekennzeichnet, daß die oberflächenaktive Verbindung eine solche nach einem der Ansprüche 1 bis 8 ist.

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10. Photographisches Element nach Anspruch 9, dadurch gekennzeichnet, daß auf den Träger mindestens eine photographische Silberhalogenidemulsionsschicht aufgetragen ist.

11. Verfahren zur Herstellung eines photographischen Elementes, bei dem man einen Schichtträger mit einer Beschichtungsmasse mit einem hydrophilen Kolloid und einer oberflächenaktiven Verbindung nach einem der Ansprüche 1 bis 8 beschichtet.

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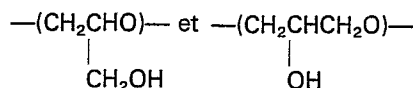
12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß man den Träger mit einer photographischen Silberhalogenidemulsionsschicht beschichtet.

Revendications

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1. Composé tensio-actif soluble dans l'eau consistant en un groupe terminal fluorocarboné lié par un groupe de liaison à une chaîne polyglycidyle comprenant un mélange aléatoire de groupes ayant pour formule:

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auxquels sont attachés au moins un anion, le ou chaque anion étant associé à un cation.

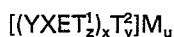
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2. Composé conforme à la revendication 1 dans lequel le groupe terminal fluorocarboné est lié directement à la chaîne polyglycidyle par un groupe de liaison hydrocarboné.

3. Composé conforme à la revendication 1 ou 2 dans lequel l'anion est le sulfate.

4. Composé conforme à la revendication 1 ayant pour formule:

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où

Y est un groupe fluorocarboné;

X représente un groupe de liaison comprenant un groupe hydrocarboné ayant de 1 à 6 atomes de carbone, un groupe éther, ester, amine, amido ou sulfonamido ou une combinaison de ces derniers;

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E est une chaîne polyglycidyle;

T^1 et T^2 sont indépendamment un groupe anionique attaché à E;

M est un cation monovalent associé avec T^1 ou T^2 ;

z est 0 ou un nombre entier de 1 au nombre maximum de sites sur E auxquels on peut attacher un

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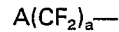
0 083 354

y est 0 ou 1 sachant que $z+y$ est au moins égal à 1;

x est 1 ou 2; et

u est le nombre de cations nécessaire pour neutraliser les groupes anioniques présents.

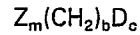
5 a pour formule: 5. Composé conforme à l'une quelconque des revendications 1 à 4 dans lequel le groupe fluorocarboné



où A est H ou F, et a est un nombre de 4 à 8, de préférence de 6 à 8.

10 6. Composé conforme à la revendication 4 ou 5 dans lequel le groupe de liaison X est CH_2 .

7. Composé conforme à la revendication 4 ou 5 dans lequel X a pour formule:



15 où Z est un groupe de liaison éther, ester, amine, amido ou sulfonamido; et D est un groupe de liaison éther ou amine; c est 0 ou 1; m est 0 ou 1; et b est 0 ou 1 sachant que si b est 0, $c+m$ est 1, et si b est 1, m est 0 et c est 0 ou 1.

8. Composé conforme à l'une quelconque des revendications 1 à 7 ayant pour formule:



où T^1 est un groupe anionique, M est un groupe cationique, A est H ou F, f est un nombre de 4 à 8 et d est un nombre de 2 à 30.

25 9. Produit photographique comprenant un support recouvert par au moins une couche contenant un colloïde hydrophile et un agent tensio-actif caractérisé en ce que l'agent tensio-actif est l'un de ceux conformes à l'une quelconque des revendications 1 à 8.

10. Produit photographique conforme à la revendication 9 dans lequel le support est recouvert par au moins une couche d'émulsion photographique aux halogénures d'argent.

30 11. Procédé pour préparer le produit photographique comprenant le couchage d'un support avec une composition comprenant un colloïde hydrophile et un agent tensio-actif conformément à l'une quelconque des revendications 1 à 8.

12. Procédé conforme à la revendication 11 dans lequel le support est recouvert d'une couche d'émulsion photographique aux halogénures d'argent.

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