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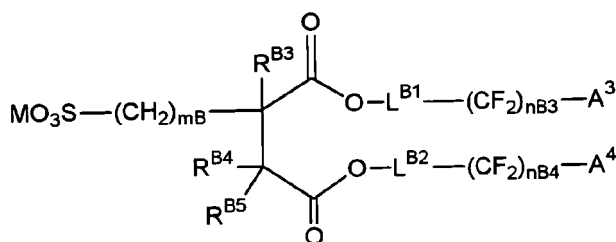
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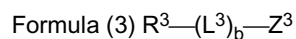
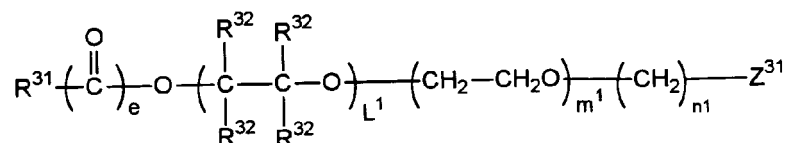
(54) **Silver halide photosensitive material and packaged body containing the same**

(57) The present invention provides a silver halide photosensitive material having, on at least one side of a transparent support, at least one photosensitive silver halide emulsion layer, and including an anionic fluorocarbon compound represented by the following formula (1), an anionic hydrocarbon compound represented by the following formula (2), and at least one of an anionic hydrocarbon compound represented by the following formula (3) or an anionic hydrocarbon compound represented by the following formula (4):

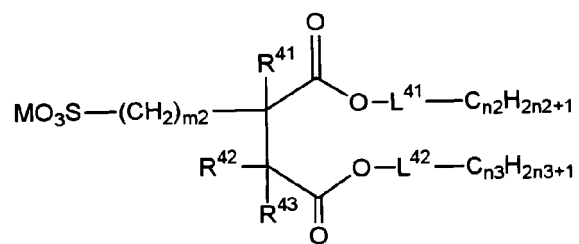
**Formula (1)**



**Formula (2)**



Formula (4)



A silver halide photosensitive material excellent in coated surface state and antistatic property, and a packaged body containing the silver halide photosensitive material are provided.

**Description**

## BACKGROUND OF THE INVENTION

## 5 Field of the Invention

**[0001]** The present invention relates to a silver halide photosensitive material excellent in coated surface state and antistatic property, as well as a packaged body containing the same.

## 10 Description of the Related Art

**[0002]** Compounds having a fluoroalkyl chain have been known as surfactants. Such surfactants can provide various surface modifications due to the inherent nature of the fluoroalkyl chain (for example, water repellency, oil repellency, lubricity, antistatic property, or the like) and have been used for general surface finishing for base materials such as fibers, cloths, carpets, resins, and the like. Further, in the case of adding surfactants having a fluoroalkyl chain (hereinafter referred to as fluorocarbon surfactants) to solutions of aqueous mediums having various compositions, not only is it possible to form uniform coated films with no repellency but also to form an adsorption layer of the surfactant on the surface of the substrate upon forming a coated film, thereby bringing inherent properties of the fluoroalkyl chains to the surfaces of coated films.

**[0003]** In photosensitive materials as well, various surfactants are used and play an important role. A photosensitive material is usually prepared by coating a plurality of coating solutions including an aqueous solution of a hydrophilic colloidal binder (for example, gelatin) individually on a support to thereby form a plurality of layers. Also, simultaneous multilayer coating of a plurality of hydrophilic colloidal layers has also been frequently conducted. The layers include an antistatic layer, an undercoat layer, an antihalation layer, a silver halide emulsion layer, an intermediate layer, a filter layer, a protective layer, and the like, to each of which various materials are added for providing various functions. Further, polymer latex is sometimes incorporated in the hydrophilic colloidal layers for improving physical properties of the film. Further, for incorporating functional compounds, which are slightly soluble in water, such as a color coupler, an ultraviolet absorber, a fluorescent whitening agent, a lubricant, or the like in a hydrophilic colloidal layer, the materials are dispersed under emulsification as they are or in a state of being dissolved in an organic solvent having a high boiling point, such as a phosphate ester compound or a phthalate ester compound, in a hydrophilic colloidal solution and used for the preparation of a coating solution. As described above, a photosensitive material comprises various hydrophilic colloidal layers, and it is required for their manufacture that a coating solution containing various materials is coated uniformly and at a high speed with no defects such as repellency or coating unevenness. In order to satisfy such a demand, addition of a surfactant as a coating aid to coating solutions has often been conducted.

**[0004]** On the other hand, photosensitive materials are in contact with various substances during manufacture thereof, photographing, and development treatment. For example, during the manufacturing step, in a case where the photosensitive material is in a rolled state, a back layer formed on the backside of the support is sometimes in contact with a surface layer. Further, photosensitive materials for direct use are sometimes in contact with a screen or human hands. Further, in the case of transporting a photosensitive material during a processing step, the photosensitive material is sometimes brought into contact with a stainless steel material, a rubber roller comprising various compositions, or the like. Upon contact with the materials described above, certain kinds of compounds of surfactant oriented on the surface of the photosensitive material are sometimes transferred to the materials. In addition, upon contact with various members, since the surface of the photosensitive material (gelatin layer) tends to be charged positively and causes unnecessary electric discharge depending on the case, undesired exposure marks (referred to as static marks) remain on the photosensitive material. Chargeability of gelatin is decreased, for example, by preventing charge (decreasing the amount of charge), facilitating leakage of accumulated charge, or the like. For preventing charge, a compound having a fluorine atom is effective, and a fluorocarbon surfactant is often added. Further, as a means for facilitating leakage of accumulated charge, addition of a surfactant containing a polyoxyethylene group to thereby lower the surface resistance value of the photosensitive material has often been adopted as disclosed in Japanese Patent Application Laid-Open (JP-A) No. 61-47948. All patents, patent publications, and non-patent literature cited in this specification are hereby expressly incorporated by reference herein. From the viewpoints of preventing charge and facilitating leakage of charge, a nonionic hydrocarbon surfactant, a nonionic fluorocarbon surfactant, and an anionic fluorocarbon surfactant are often used in combination in a delicate balance to provide resistance to static charge in silver halide photosensitive materials, particularly in silver halide photosensitive materials sensitive to X-ray irradiation (X-ray photosensitive materials), as disclosed in JP-A Nos. 62-109044 and 7-159929.

**[0005]** Further, while JP-A No. 2005-03888 discloses a silver halide photosensitive material excellent in resistance to static charge and antistatic property due to the use of a nonionic fluorocarbon compound and an anionic fluorocarbon compound in combination, this cannot cope with the demands upon high-speed coating in view of surface state per-

formance.

[0006] Generally, the silver halide photosensitive materials described above are cut into sheets, and a laminate is formed by stacking a plurality of sheets and a non-photosensitive plate material usually referred to as protection cardboard, and then the laminate is packaged with a moisture-proof packaging material and distributed as a sealed packaged body on the market. Further, upon use, it is loaded in this packaged body as it is in an image recording apparatus, the package is opened in the apparatus, and the silver halide photosensitive materials are taken out one by one and subjected to imagewise exposure and development treatment. Therefore, in a case where the silver halide photosensitive material loaded in the lowermost portion is in contact with the protection cardboard for a long time in a press contact state, the silver halide emulsion surface is directly influenced by the packaging material. For example, in a case where the protection cardboard generates dust, the silver halide photosensitive material rubs against the protection cardboard and receives scratches on the surface due to vibration generated during transportation or upon loading to the image recording apparatus. Further, in the case of undergoing a relatively intensive impact, the protection cardboard is sometimes torn or peeled, resulting in trouble.

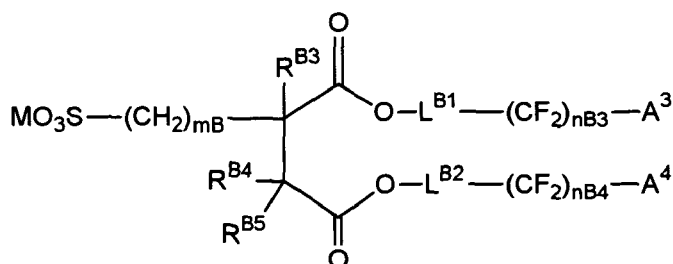
[0007] Accordingly, for favorably maintaining and providing overall performance of the silver halide photosensitive material, it is also an important task to improve the constituent elements not only of the silver halide photosensitive material but also of the packaged body including the protection cardboard.

## SUMMARY OF THE INVENTION

[0008] The present invention has been made in view of the above circumstances and provides a silver halide photosensitive material and a packaged body with the following aspects.

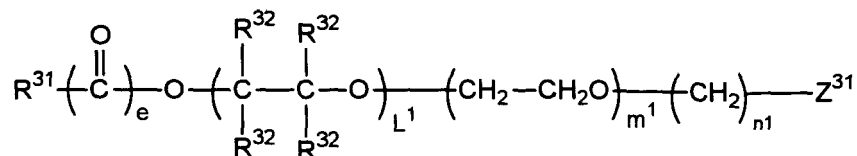
[0009] A first aspect of the invention is to provide a silver halide photosensitive material comprising, on at least one side of a transparent support, at least one photosensitive silver halide emulsion layer, and containing an anionic fluorocarbon compound represented by the following formula (1), an anionic hydrocarbon compound represented by the following formula (2), and at least one of an anionic hydrocarbon compound represented by the following formula (3) or an anionic hydrocarbon compound represented by the following formula (4):

### Formula (1)



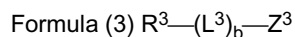
wherein  $\text{R}^{\text{B}3}$ ,  $\text{R}^{\text{B}4}$ , and  $\text{R}^{\text{B}5}$  each independently represent a hydrogen atom or a substituent;  $\text{A}^3$  and  $\text{A}^4$  each independently represent a fluorine atom or a hydrogen atom;  $n\text{B}3$  and  $n\text{B}4$  each independently represent an integer of from 4 to 8;  $\text{L}^{\text{B}1}$  and  $\text{L}^{\text{B}2}$  each independently represent an alkylene group, an alkyleneoxy group, or a divalent linking group formed by combining groups selected from among these groups;  $m\text{B}$  represents 0 or 1; and  $\text{M}$  represents a cation;

### Formula (2)



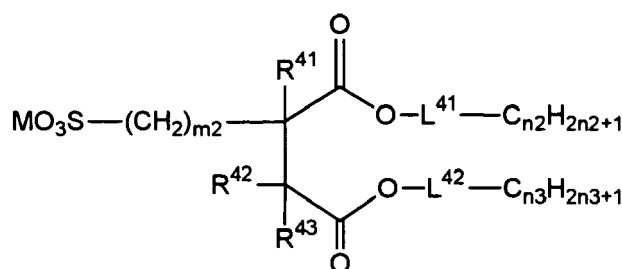
wherein  $\text{R}^{31}$  represents an alkyl group or alkenyl group having 6 to 25 carbon atoms;  $\text{R}^{32}$ s may be identical or different from one another and each represent a hydrogen atom, an alkyl group having 1 to 14 carbon atoms, an alkenyl group having 1 to 14 carbon atoms, an aralkyl group having 7 to 20 carbon atoms, or an aryl group having 6 to 18 carbon

atoms;  $L^1$  represents an integer of from 0 to 10;  $m^1$  represents an integer of from 0 to 30;  $n^1$  represents an integer of from 0 to 4;  $L^1$  and  $m^1$  do not simultaneously represent 0;  $e$  represents 0 or 1;  $Z^{31}$  represents an  $OSO_3M$  group or an  $SO_3M$  group; and  $M$  represents a cation;



wherein  $R^3$  represents an alkyl group, alkylene group, or aralkyl group having 6 to 24 carbon atoms;  $L^3$  represents an alkylene group having a hydroxy group and 3 to 5 carbon atoms, a vinylene group, a vinylenealkylene group, or a divalent linking group formed by combining groups selected from among these groups;  $b$  represents 0 or 1;  $Z^3$  represents an  $OSO_3M$  group or an  $SO_3M$  group; and  $M$  represents a cation; and

Formula (4)



wherein  $R^{41}$ ,  $R^{42}$ , and  $R^{43}$  each independently represent a hydrogen atom or a substituent;  $n^2$  and  $n^3$  each independently represent an integer of from 1 to 5;  $L^{41}$  and  $L^{42}$  each independently represent an alkylene group having no fluorine atoms, an alkyleneoxy group, or a divalent linking group formed by combining groups selected from among these groups;  $m^2$  represents 0 or 1; and  $M$  represents a cation.

**[0010]** A second aspect of the invention is to provide a packaged body in which a laminate formed by stacking a sheet of the silver halide photosensitive material according to the first aspect and a non-photosensitive plate material having a layer coated with an organic material on the surface thereof is packed and sealed with a light shielding sack-shaped material.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0011]** An object of the present invention is to provide a silver halide photosensitive material excellent in coated surface state and antistatic property, and a packaged body including the same.

**[0012]** In the invention, each group includes any of embodiments including a case where the group is unsubstituted and a case where the group has a substituent, unless otherwise specified.

**[0013]** Conventionally, surfactants, particularly fluorocarbon surfactants, have been used as materials having both functions of a coating aid for providing homogeneity to a coated film, and an agent for providing antistatic property to photosensitive materials.

**[0014]** However, such materials do not always have satisfactory performance with respect to the recent demands for increasing the sensitivity of photographic materials and for coating at a higher speed, and further technical improvement has been demanded for the surfactants.

**[0015]** In the course of the present inventors' earnest efforts to improve the technology of the surfactant in order to attain the above object, it has been found that even compounds which satisfy the demands for increase in sensitivity and increase in coating speed as described above have often failed to reach practical use because of poor storability in the packaged embodiment, and that it is a significant task to attain both of these performances and storage stability.

**[0016]** As a result of further efforts, the inventors found that high-speed coating adaptability can be satisfied by incorporating a specified anionic surfactant into a surfactant containing a fluoroalkyl group, and thereby arrived at the present invention. Further, it has been found that, by constituting a packaged body using a protection cardboard material whose surface is coated, the aforementioned performances and storage stability can be made compatible, whereby the present invention according to the second aspect was achieved.

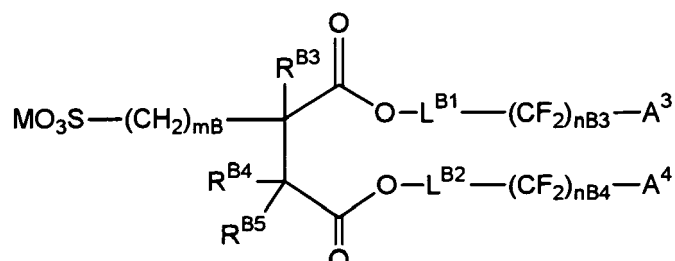
**[0017]** The present invention provides a silver halide photosensitive material excellent in coated surface state and antistatic property, and a packaged body containing the same.

**[0018]** The present invention is described in detail below.

1. Compound represented by formula (1) to (5)

**[0019]** First, the compound represented by formula (1) is described in detail.

Formula (1)



**[0020]** In formula (1), R<sup>B3</sup>, R<sup>B4</sup>, and R<sup>B5</sup> each independently represent a hydrogen atom or a substituent. A<sup>3</sup> and A<sup>4</sup> each independently represent a fluorine atom or a hydrogen atom. nB3 and nB4 each independently represent an integer of from 4 to 8. L<sup>B1</sup> and L<sup>B2</sup> each independently represent a substituted or unsubstituted alkylene group, a substituted or unsubstituted alkyleneoxy group, or a divalent linking group formed by combining groups selected from among these groups. mB represents 0 or 1. M represents a cation.

**[0021]** In formula (1),  $R^{B3}$ ,  $R^{B4}$ , and  $R^{B4}$  each independently represent a hydrogen atom or a substituent. As the substituent, substituent T described below can be applied.

**[0022]** R<sup>B3</sup>, R<sup>B4</sup>, and R<sup>B5</sup> are preferably an alkyl group or a hydrogen atom, more preferably an alkyl group having 1 to 12 carbon atoms or a hydrogen atom, even more preferably a methyl group or a hydrogen atom, and particularly preferably a hydrogen atom.

**[0023]** In formula (1), A<sup>3</sup> and A<sup>4</sup> each independently represent a fluorine atom or a hydrogen atom. A<sup>3</sup> and A<sup>4</sup> may be the same or different from each other. As A<sup>3</sup> and A<sup>4</sup>, it is preferred that both of A<sup>3</sup> and A<sup>4</sup> are simultaneously a fluorine atom or a hydrogen atom, and it is more preferred that both of A<sup>3</sup> and A<sup>4</sup> are a fluorine atom.

**[0024]** nB3 and nB4 each independently represent an integer of from 4 to 8. nB3 and nB4 may be the same or different from each other as far as nB3 and nB4 are an integer of from 4 to 8. nB3 and nB4 are preferably an integer of from 4 to 6 and nB3 is equal to nB4. More preferably, nB3 and nB4 are 4 or 6 and nB3 is equal to nB4. Even more preferably, both of nB3 and nB4 are 4.

**[0025]** mB represents 0 or 1, and both are similarly preferable.

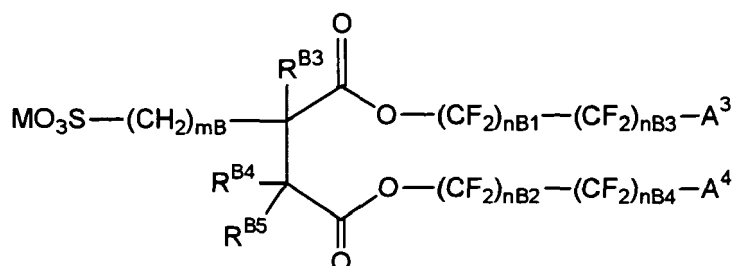
**[0026]** L<sup>B1</sup> and L<sup>B2</sup> each independently represent a substituted or unsubstituted alkylene group, a substituted or unsubstituted alkyleneoxy group, or a divalent linking group formed by combining groups selected from among these groups. As the substituent, substituent T described below can be applied. L<sup>B1</sup> and L<sup>B2</sup> each have preferably 6 or less carbon atoms, and preferably, L<sup>B1</sup> and L<sup>B2</sup> are an unsubstituted alkylene group.

**[0027]** M represents a cation, and as the cation represented by M, for example, an alkaline metal ion (a lithium ion, a sodium ion, a potassium ion, or the like), an alkaline earth metal ion (a barium ion, a calcium ion, or the like), an ammonium ion, or the like are preferably applied.

**[0028]** M is preferably a lithium ion, a sodium ion, a potassium ion, or an ammonium ion; more preferably a lithium ion, a sodium ion, or a potassium ion; and even more preferably a sodium ion.

[0029] As formula (1), the following formula (1-A) is preferable.

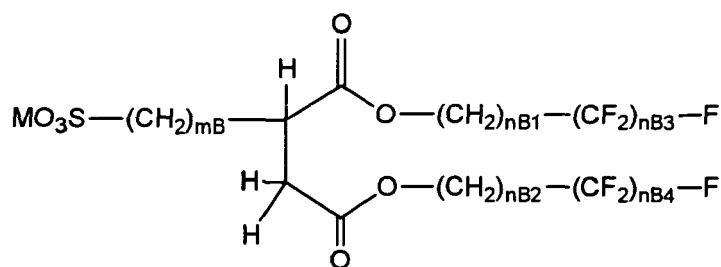
## Formula (1-A)



**[0030]** In the formula,  $\text{A}^3$ ,  $\text{A}^4$ ,  $\text{R}^{B3}$ ,  $\text{R}^{B4}$ ,  $\text{R}^{B5}$ ,  $nB3$ ,  $nB4$ ,  $mB$ , and  $M$  each have the same meaning as in formula (1), and preferable ranges are similar to those in formula (1).  $nB1$  and  $nB2$  each independently represent an integer of from 1 to 6.  $nB1$  and  $nB2$  may be the same or different from each other as far as these are an integer of from 1 to 6.  $nB1$  and  $nB2$  are preferably an integer of 1 to 6 and  $nB1$  is equal to  $nB2$ . More preferably,  $nB1$  and  $nB2$  are an integer of from 1 to 3 and  $nB1$  is equal to  $nB2$ . Even more preferably,  $nB1$  and  $nB2$  are 2 or 3 and  $nB1$  is equal to  $nB2$ . Particularly preferably, both of  $nB1$  and  $nB2$  are 2.

**[0031]** As formula (1), the following formula (1-B) is preferable.

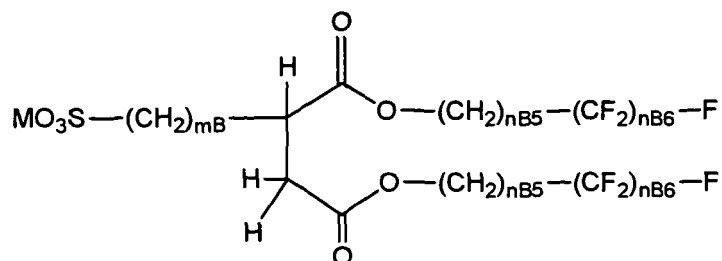
## Formula (1-B)



**[0032]** In the formula,  $nB1$ ,  $nB2$ ,  $nB3$ ,  $nB4$ ,  $mB$ , and  $M$  each have the same meaning as in formula (1-A) described above, and preferable ranges are similar to those in formula (1-A).

**[0033]** As formula (1) described above, more preferred is the following formula (1-C).

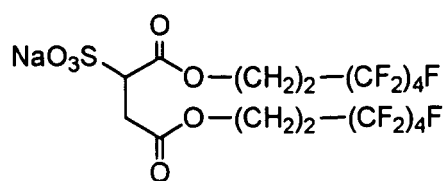
## Formula (1-C)



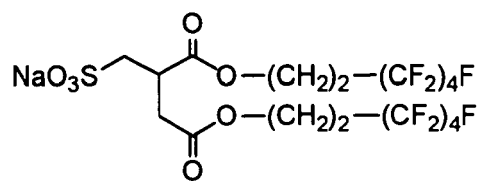
**[0034]** In the formula,  $nB5$  represents 2 or 3.  $nB6$  represents an integer of from 4 to 6.  $mB$  represents 0 or 1, and both are similarly preferable.  $M$  has the same meaning as in formula (1) described above, and preferable range is also similar to that in formula (1).

**[0035]** Specific examples of the compound represented by the above formula (1-B) are shown below, but the present invention is not limited in these.

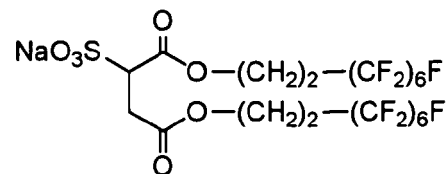
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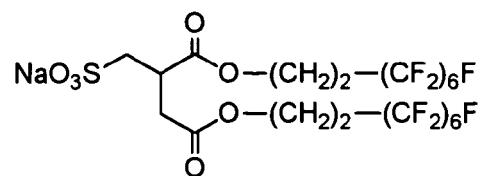
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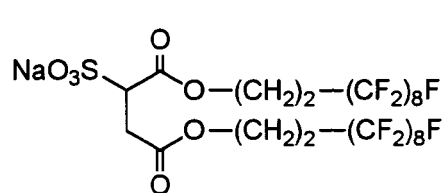
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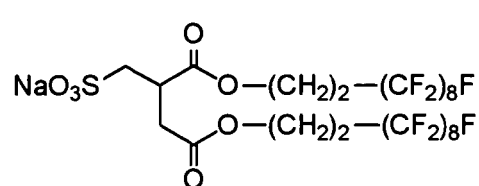
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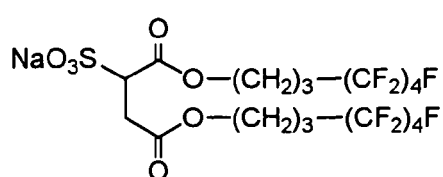
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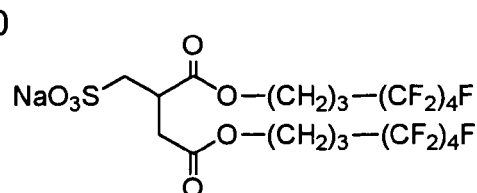
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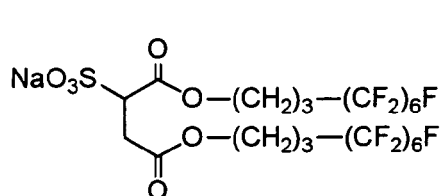
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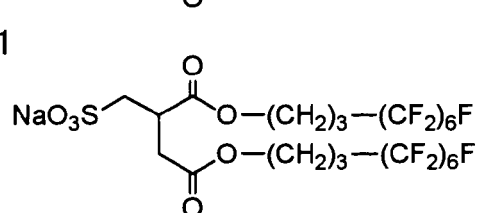
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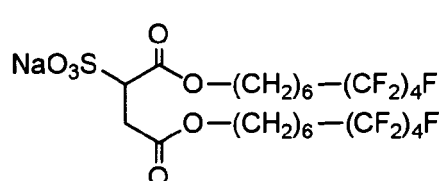
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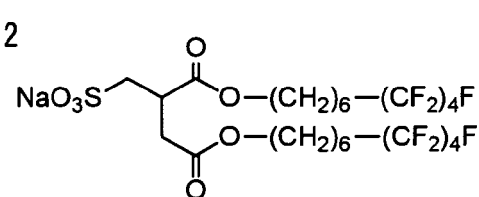
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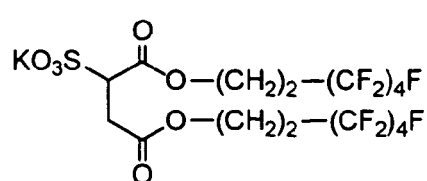
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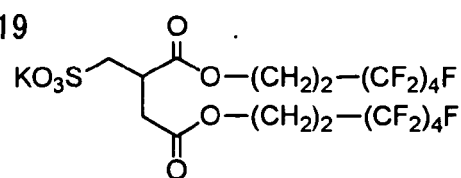
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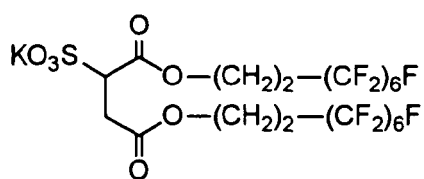
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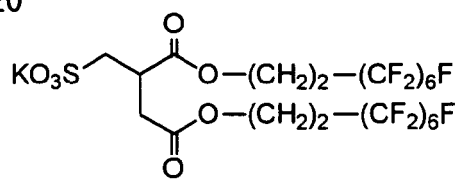
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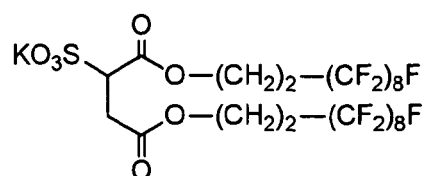
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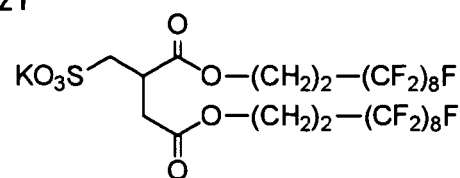
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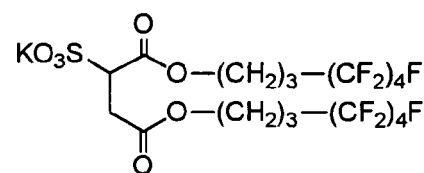
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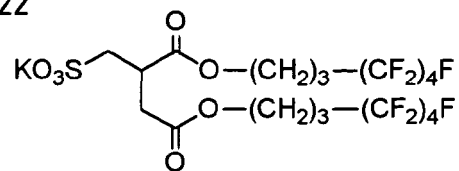
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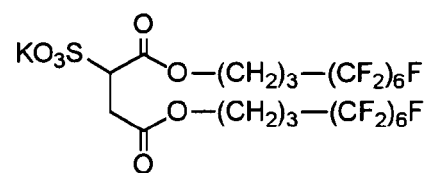
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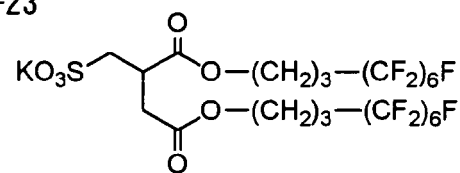
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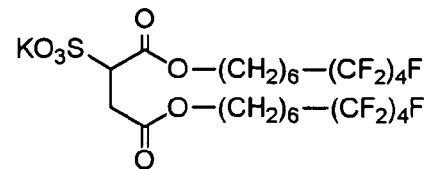
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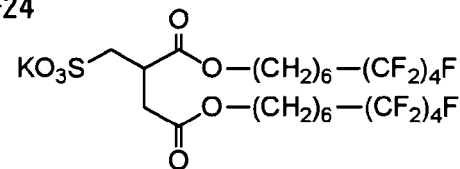
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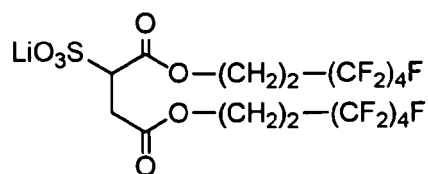
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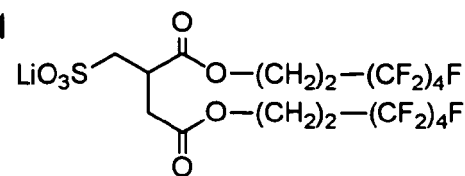
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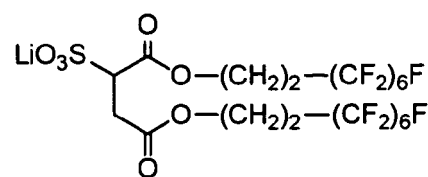
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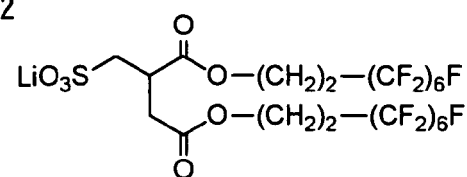
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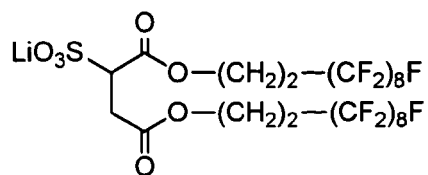
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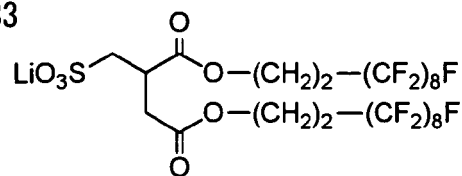
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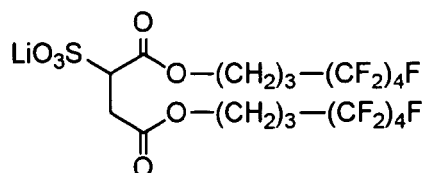
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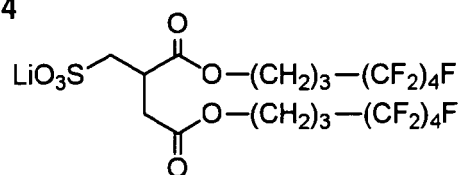
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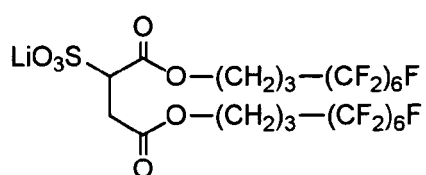
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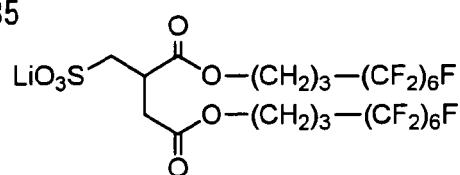
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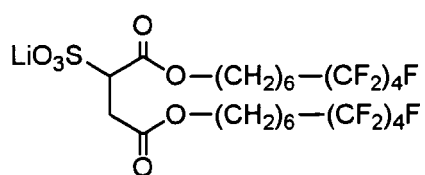
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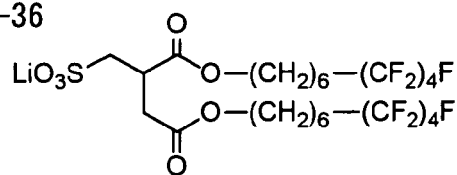
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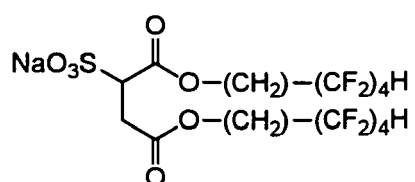
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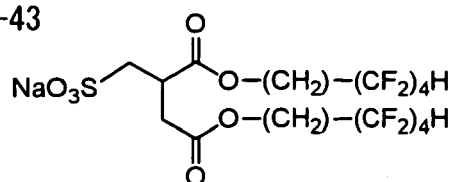
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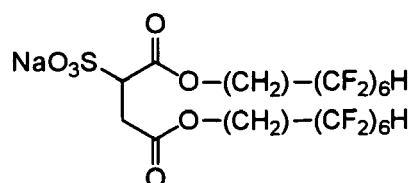
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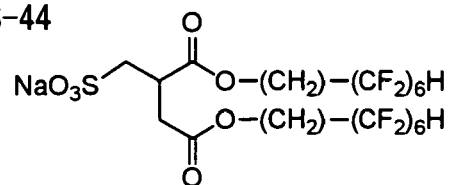
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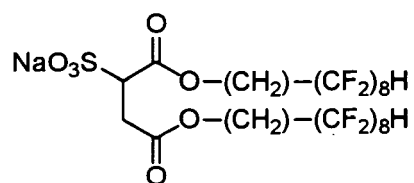
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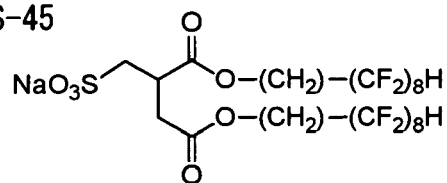
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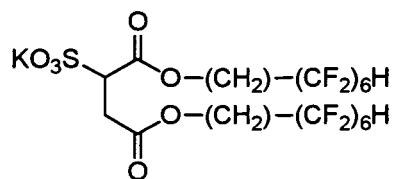
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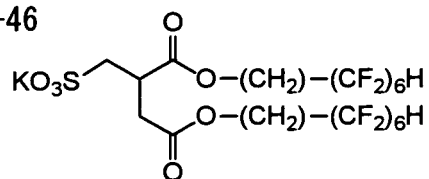
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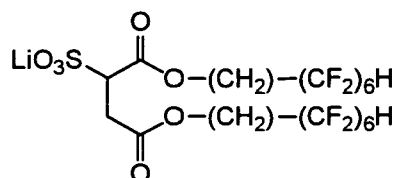
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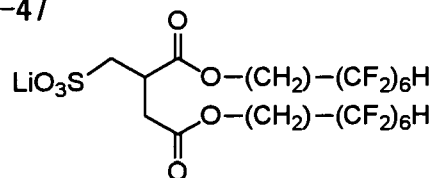
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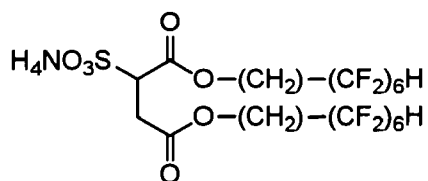
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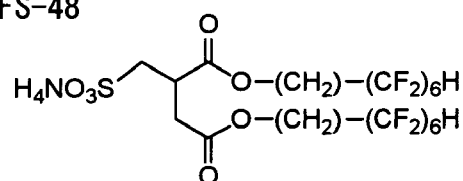
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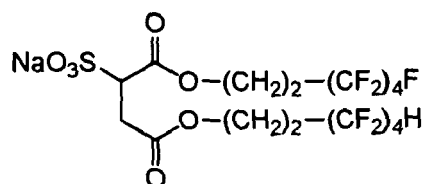
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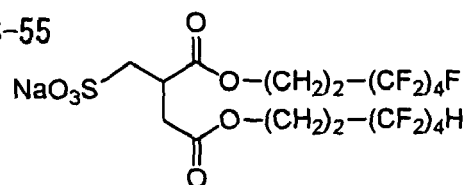
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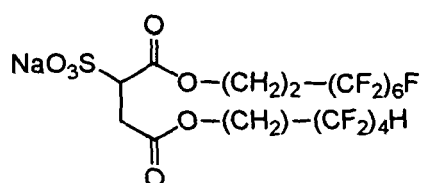
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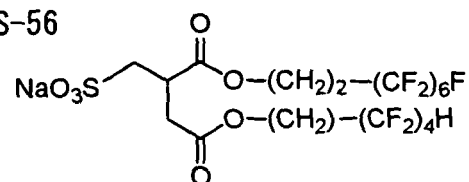
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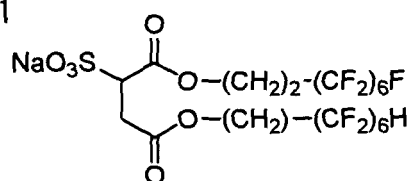
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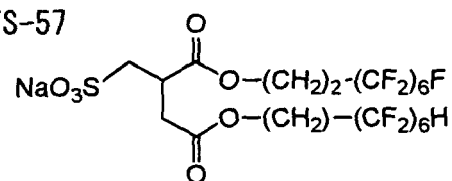
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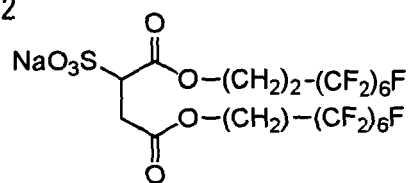
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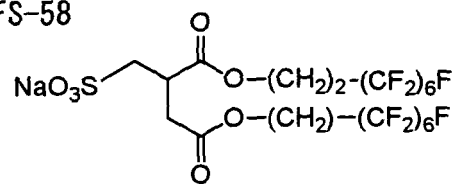
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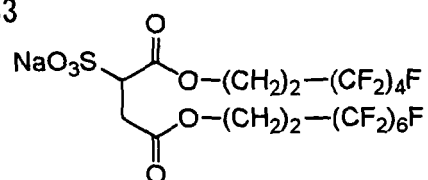
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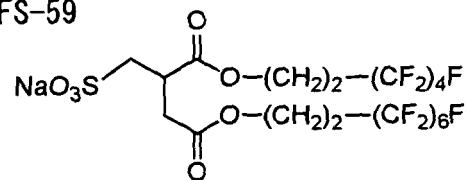
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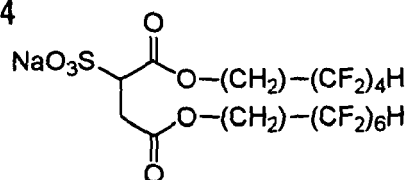
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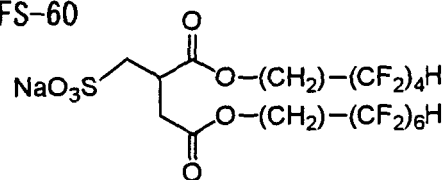
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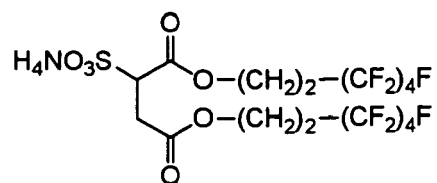
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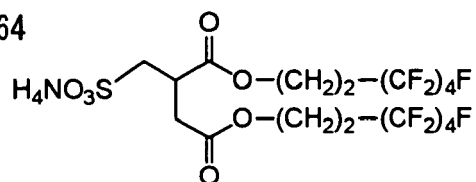
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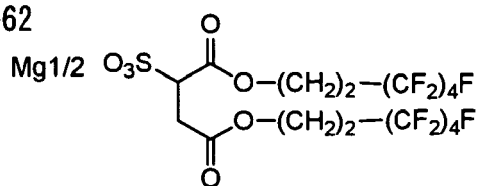
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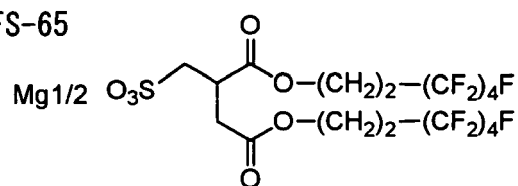
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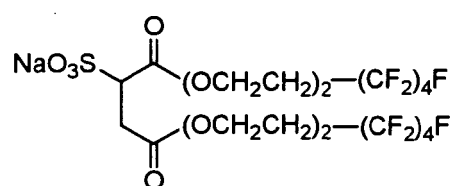
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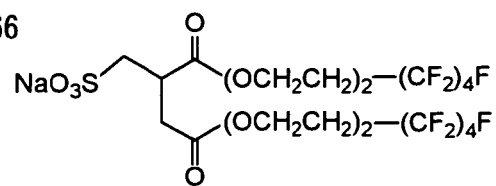
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FS-63



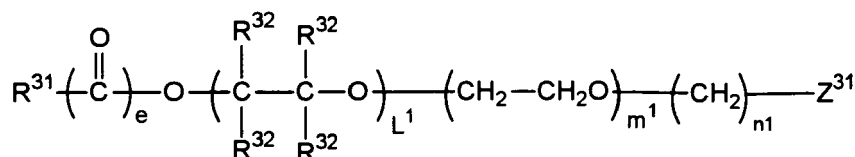
FS-66



**[0036]** The coating amount of the compound represented by formula (1) is preferably in a range of from 0.01 mg/m<sup>2</sup> to 100 mg/m<sup>2</sup>, more preferably from 0.1 mg/m<sup>2</sup> to 50 mg/m<sup>2</sup>, and even more preferably from 0.3 mg/m<sup>2</sup> to 10 mg/m<sup>2</sup>.

**[0037]** Next, the compound represented by the following formula (2) used in the present invention is explained in detail.

**Formula (2)**



**[0038]** In the formula, R<sup>31</sup> represents an alkyl group or alkenyl group having 6 to 25 carbon atoms. R<sup>32</sup>s may be identical or different from one another and each represent a hydrogen atom, an alkyl group having 1 to 14 carbon atoms, an alkenyl group having 1 to 14 carbon atoms, an aralkyl group having 7 to 20 carbon atoms, or an aryl group having 6 to 18 carbon atoms. L<sup>1</sup> represents an integer of from 0 to 10. m<sup>1</sup> represents an integer of from 0 to 30. However, L<sup>1</sup> and m<sup>1</sup> do not simultaneously represent 0. n1 represents an integer of from 0 to 4. e represents 0 or 1. Z<sup>31</sup> represents an OSO<sub>3</sub>M group or an SO<sub>3</sub>M group, and M represents a cation.

**[0039]** In formula (2) described above, R<sup>31</sup> represents an alkyl group or alkenyl group having 6 to 25 carbon atoms. R<sup>31</sup> has preferably 6 to 22 carbon atoms, more preferably 6 to 20 carbon atoms, and particularly preferably 8 to 18 carbon atoms. Although the alkyl group and the alkenyl group may have a cyclic structure, a linear alkyl group and a linear alkenyl group are more preferable. The alkyl group and the alkenyl group may have a substituent; however, an unsubstituted alkyl group and alkenyl group are preferable. The linear alkyl group and the linear alkenyl group may be branched. The position of the double bond of the alkenyl group is not particularly limited. An alkyl group is more preferable than an alkenyl group.

**[0040]** In formula (2) described above, R<sup>32</sup>s each represent a hydrogen atom, an alkyl group having 1 to 14 carbon atoms, an alkenyl group having 1 to 14 carbon atoms, an aralkyl group having 7 to 20 carbon atoms, or an aryl group having 6 to 18 carbon atoms. The alkyl group and the alkenyl group preferably have 1 to 8 carbon atoms, more preferably 1 to 6 carbon atoms, and particularly preferably 1 to 4 carbon atoms. The aralkyl group preferably has 7 to 13 carbon atoms, and particularly preferably 7 to 10 carbon atoms. The aryl group preferably has 6 to 12 carbon atoms, and particularly preferably 6 to 10 carbon atoms.

**[0041]** R<sup>32</sup>s, in formula (2) described above, may bond to each other to have a cyclic structure. Further, R<sup>32</sup>s may have a substituent and examples of the preferable substituent are shown below.

**[0042]** As examples of the preferable substituent, a halogen atom (for example, a fluorine atom, a chlorine atom, or a bromine atom), an alkyl group (for example, methyl, ethyl, isopropyl, n-propyl, or t-butyl), an alkenyl group (for example, allyl or 2-butenyl), an alkynyl group (for example, propargyl), an aralkyl group (for example, benzyl), an aryl group (for example, phenyl or naphthyl), a hydroxy group, an alkoxy group (for example, methoxy, ethoxy, butoxy, or ethoxyethoxy), an aryloxy group (for example, phenoxy or 2-naphthyloxy), and the like are described.

**[0043]** R<sup>32</sup>s each preferably represent a hydrogen atom or an alkyl group having 1 to 8 carbon atoms, more preferably a hydrogen atom or an alkyl group having 1 to 6 carbon atoms, even more preferably a hydrogen atom or an alkyl group having 1 to 4 carbon atoms, and particularly preferably a hydrogen atom, a methyl group, or a hydroxymethyl group.

**[0044]** In formula (2) described above, L<sup>1</sup> represents an integer of from 0 to 10. L<sup>1</sup> is preferably an integer of from 0 to 8, more preferably an integer of from 0 to 6, even more preferably an integer of from 0 to 4, and particularly preferably 0.

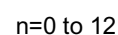
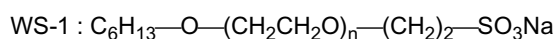
**[0045]** In formula (2) described above, m<sup>1</sup> represents an integer of from 0 to 30. m<sup>1</sup> is preferably an integer of from 0 to 25, more preferably an integer of from 0 to 20, and particularly preferably an integer of from 0 to 15.

**[0046]** In formula (2) described above, n1 represents an integer of from 0 to 4. Particularly preferably, n1 is an integer of from 2 to 4.

**[0047]** In formula (2) described above, Z<sup>31</sup> represents an OSO<sub>3</sub>M group or an SO<sub>3</sub>M group, and M represents a cation. As the cation represented by M, for example, an alkaline metal ion (a lithium ion, a sodium ion, a potassium ion, or the like), an alkaline earth metal ion (a barium ion, a calcium ion, or the like), an ammonium ion, or the like is applied preferably. Among these, a lithium ion, a sodium ion, a potassium ion, and an ammonium ion are particularly preferable.

**[0048]** In formula (2) described above, e represents 0 or 1, and e is preferably 0.

**[0049]** Specific examples of the compound represented by formula (2) described above are shown below, but the present invention is not restricted to these specific examples.



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(continued)

	WS-2 : $C_6H_{13}-O-(CH_2CH_2O)_n-(CH_2)_3-SO_3Na$	n=0 to 12
	WS-3 : $C_6H_{13}-O-(CH_2CH_2O)_n-(CH_2)_4-SO_3Na$	n=0 to 12
5	WS-4 : $C_8H_{17}-O-(CH_2CH_2O)_n-(CH_2)_2-SO_3Na$	n=0 to 12
	WS-5 : $C_8H_{17}-O-(CH_2CH_2O)_n-(CH_2)_3-SO_3Na$	n=0 to 12
	WS-6 : $C_8H_{17}-O-(CH_2CH_2O)_n-(CH_2)_4-SO_3Na$	n=0 to 12
	WS-7 : $C_{10}H_{21}-O-(CH_2CH_2O)_n-(CH_2)_2-SO_3Na$	n=0 to 12
10	WS-8 : $C_{10}H_{21}-O-(CH_2CH_2O)_n-(CH_2)_3-SO_3Na$	n=0 to 12
	WS-9 : $C_{10}H_{21}-O-(CH_2CH_2O)_n-(CH_2)_4-SO_3Na$	n=0 to 12
	WS-10 : $C_{10}H_{21}-O-(CH_2CH_2O)_n-(CH_2)_4-SO_3K$	n=0 to 12
	WS-11 : $C_{10}H_{21}-O-(CH_2CH_2O)_n-(CH_2)_4-SO_3NH_3$	n=0 to 12
15	WS-12 : $C_{11}H_{23}-O-(CH_2CH_2O)_n-(CH_2)_2-SO_3Na$	n=0 to 12
	WS-13 : $C_{11}H_{23}-O-(CH_2CH_2O)_n-(CH_2)_3-SO_3Na$	n=0 to 12
	WS-14 : $C_{11}H_{23}-O-(CH_2CH_2O)_n-(CH_2)_4-SO_3Na$	n=0 to 12
	WS-15 : $C_{12}H_{25}-O-(CH_2CH_2O)_n-(CH_2)_2-SO_3Na$	n=0 to 20
20	WS-16 : $C_{12}H_{25}-O-(CH_2CH_2O)_n-(CH_2)_3-SO_3Na$	n=0 to 20
	WS-17 : $C_{12}H_{25}-O-(CH_2CH_2O)_n-(CH_2)_4-SO_3Na$	n=0 to 20
	WS-18 : $C_{14}H_{29}-O-(CH_2CH_2O)_n-(CH_2)_2-SO_3Na$	n=0 to 25
	WS-19 : $C_{14}H_{29}-O-(CH_2CH_2O)_n-(CH_2)_3-SO_3Na$	n=0 to 25
	WS-20 : $C_{14}H_{29}-O-(CH_2CH_2O)_n-(CH_2)_4-SO_3Na$	n=0 to 25
25	WS-21 : $C_{16}H_{33}-O-(CH_2CH_2O)_n-(CH_2)_3-SO_3NH_3$	n=0 to 30
	WS-22 : $C_{16}H_{33}-O-(CH_2CH_2O)_n-(CH_2)_4-SO_3Na$	n=0 to 30
	WS-23 : $C_{18}H_{37}-O-(CH_2CH_2O)_n-(CH_2)_3-SO_3Na$	n=0 to 30
30	WS-24 : $C_{18}H_{37}-O-(CH_2CH_2O)_n-(CH_2)_4-SO_3Na$	n=0 to 30
	WS-25 : $C_{20}H_{41}-O-(CH_2CH_2O)_n-(CH_2)_4-SO_3Na$	n=0 to 30
	WS-26 : $C_8H_{17}CH=C_8H_{15}-O-(CH_2CH_2O)_n-(CH_2)_3-SO_3Na$	n=0 to 30
	WS-27 : $C_{22}H_{45}-O-(CH_2CH_2O)_n-(CH_2)_2-SO_3Na$	n=0 to 30
	WS-28 : $C_{24}H_{49}-O-(CH_2CH_2O)_n-(CH_2)_2-SO_3Na$	n=0 to 30
35	WS-29 : $C_{24}H_{49}-O-(CH_2CH_2O)_n-(CH_2)_2-SO_3Li$	n=0 to 30
	WS-30 : $C_6H_{13}-O-(CH_2CH_2O)_n-OSO_3Na$	n=0 to 12
	WS-31 : $C_8H_{17}-O-(CH_2CH_2O)_n-SO_3Na$	n=0 to 12
	WS-32 : $C_9H_{19}-O-(CH_2CH_2O)_n-SO_3Na$	n=0 to 12
40	WS-33 : $C_{10}H_{21}-O-(CH_2CH_2O)_n-SO_3Na$	n=0 to 12
	WS-34 : $C_{11}H_{23}-O-(CH_2CH_2O)_n-SO_3Na$	n=0 to 12
	WS-35 : $C_{12}H_{25}-O-(CH_2CH_2O)_n-SO_3Na$	n=0 to 12
	WS-36 : $C_{14}H_{29}-O-(CH_2CH_2O)_n-SO_3Na$	n=0 to 20
	WS-37 : $C_{16}H_{33}-O-(CH_2CH_2O)_n-SO_3Na$	n=0 to 25
45	WS-38 : $C_{18}H_{37}-O-(CH_2CH_2O)_n-SO_3Na$	n=0 to 30
	WS-39 : $C_{18}H_{37}-O-(CH_2CH_2O)_n-SO_3K$	n=0 to 30
	WS-40 : $C_{18}H_{37}-O-(CH_2CH_2O)_n-SO_3Li$	n=0 to 30
	WS-41 : $C_7H_{15}C(=O)O-(CH_2CH_2O)_2-(CH_2)_2-SO_3Na$	
50	WS-42 : $C_9H_{19}C(=O)O-(CH_2CH_2O)_4-(CH_2)_2-SO_3Na$	
	WS-43 : $C_9H_{19}C(=O)O-(CH_2CH_2O)_6-(CH_2)_3-SO_3Na$	
	WS-44 : $C_9H_{19}C(=O)O-(CH_2CH_2O)_8-(CH_2)_4-SO_3Na$	
	WS-45 : $C_{11}H_{23}C(=O)O-(CH_2CH_2O)_{15}-(CH_2)_n-SO_3Na$	
	WS-46 : $C_8H_{17}CH=C_7H_{13}C(=O)O-(CH_2CH_2O)_{15}-(CH_2)_3-SO_3Na$	
55	WS-47 : $C_{21}H_{43}C(=O)O-(CH_2CH_2O)_{20}-(CH_2)_2-SO_3Na$	

**[0050]** The compound represented by formula (2) described above can be synthesized by the known methods described in JP-A No. 2001-3263, J. Amer. Chem. Soc., vol. 65, page 2196, (1943), J Phys. Chem., vol. 90, page 2413,

(1986), J. Dispersion Sci. and Tech., vol. 4, page 361, (1983), U.S. Patent (USP) No. 5,602,087, and the like.

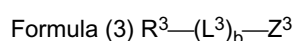
**[0051]** The substituent T is explained in detail below.

**[0052]** As substituent T, for example, an alkyl group (preferably an alkyl group having 1 to 20 carbon atoms, more preferably having 1 to 12 carbon atoms, and particularly preferably having 1 to 8 carbon atoms; and as examples, a methyl group, an ethyl group, an isopropyl group, a tert-butyl group, a n-octyl group, a n-decyl group, a n-hexadecyl group, a cyclopropyl group, a cyclopentyl group, a cyclohexyl group, and the like are described), an alkenyl group (preferably an alkenyl group having 2 to 20 carbon atoms, more preferably having 2 to 12 carbon atoms, and particularly preferably having 2 to 8 carbon atoms; and as examples, a vinyl group, an allyl group, a 2-butenyl group, a 3-pentenyl group, and the like are described), an alkynyl group (preferably an alkynyl group having 2 to 20 carbon atoms, more preferably having 2 to 12 carbon atoms, and particularly preferably having 2 to 8 carbon atoms; and as examples, a propargyl group, a 3-pentynyl group, and the like are described), an aryl group (preferably an aryl group having 6 to 30 carbon atoms, more preferably having 6 to 20 carbon atoms, and particularly preferably having 6 to 12 carbon atoms; and as examples, a phenyl group, a p-methylphenyl group, a naphthyl group, and the like are described), a substituted or unsubstituted amino group (preferably an amino group having 0 to 20 carbon atoms, more preferably having 0 to 10 carbon atoms, and particularly preferably having 0 to 6 carbon atoms; and as examples, an unsubstituted amino group, a methylamino group, a dimethylamino group, a diethylamino group, a benzylamino group, and the like are described), an alkoxy group (preferably an alkoxy group having 1 to 20 carbon atoms, more preferably having 1 to 12 carbon atoms, and particularly preferably having 1 to 8 carbon atoms; and as examples, a methoxy group, an ethoxy group, a butoxy group, and the like are described), an aryloxy group (preferably an aryloxy group having 6 to 20 carbon atoms, more preferably having 6 to 16 carbon atoms, and particularly preferably having 6 to 12 carbon atoms; and as examples, a phenyloxy group, a 2-naphthyloxy group, and the like are described), an acyl group (preferably an acyl group having 1 to 20 carbon atoms, more preferably having 1 to 16 carbon atoms, and particularly preferably having 1 to 12 carbon atoms; and as examples, an acetyl group, a benzoyl group, a formyl group, a pivaloyl group, and the like are described), an alkoxycarbonyl group (preferably an alkoxycarbonyl group having 2 to 20 carbon atoms, more preferably having 2 to 16 carbon atoms, and particularly preferably having 2 to 12 carbon atoms; and as examples, a methoxycarbonyl group, an ethoxycarbonyl group, and the like are described), an aryloxycarbonyl group (preferably an aryloxycarbonyl group having 7 to 20 carbon atoms, more preferably having 7 to 16 carbon atoms, and particularly preferably having 7 to 10 carbon atoms; and as examples, a phenyloxycarbonyl group and the like are described), an acyloxy group (preferably an acyloxy group having 2 to 20 carbon atoms, more preferably having 2 to 16 carbon atoms, and particularly preferably having 2 to 10 carbon atoms; and as examples, an acetoxyl group, a benzoyloxy group, and the like are described), an acylamino group (preferably an acylamino group having 2 to 20 carbon atoms, more preferably having 2 to 16 carbon atoms, and particularly preferably having 2 to 10 carbon atoms; and as examples, an acetylamino group, a benzoylamino group, and the like are described), an alkoxycarbonylamino group (preferably an alkoxycarbonylamino group having 2 to 20 carbon atoms, more preferably having 2 to 16 carbon atoms, and particularly preferably having 2 to 12 carbon atoms; and as examples, a methoxycarbonylamino group and the like are described), an aryloxycarbonylamino group (preferably an aryloxycarbonylamino group having 7 to 20 carbon atoms, more preferably having 7 to 16 carbon atoms, and particularly preferably having 7 to 12 carbon atoms; and as examples, a phenyloxycarbonylamino group and the like are described), a sulfonylamino group (preferably a sulfonylamino group having 1 to 20 carbon atoms, more preferably having 1 to 16 carbon atoms, and particularly preferably having 1 to 12 carbon atoms; and as examples, a methanesulfonylamino group, a benzenesulfonylamino group, and the like are described), a sulfamoyl group (preferably a sulfamoyl group having 0 to 20 carbon atoms, more preferably having 0 to 16 carbon atoms, and particularly preferably having 0 to 12 carbon atoms; and as examples, a sulfamoyl group, a methylsulfamoyl group, a dimethylsulfamoyl group, a phenylsulfamoyl group, and the like are described), a carbamoyl group (preferably a carbamoyl group having 1 to 20 carbon atoms, more preferably having 1 to 16 carbon atoms, and particularly preferably having 1 to 12 carbon atoms; and as examples, an unsubstituted carbamoyl group, a methylcarbamoyl group, a diethylcarbamoyl group, a phenylcarbamoyl group, and the like are described), an alkylthio group (preferably an alkylthio group having 1 to 20 carbon atoms, more preferably having 1 to 16 carbon atoms, and particularly preferably having 1 to 12 carbon atoms; and as examples, a methylthio group, an ethylthio group, and the like are described), an arylthio group (preferably an arylthio group having 6 to 20 carbon atoms, more preferably having 6 to 16 carbon atoms, and particularly preferably having 6 to 12 carbon atoms; and as examples, a phenylthio group and the like are described), a sulfonyl group (preferably a sulfonyl group having 1 to 20 carbon atoms, more preferably having 1 to 16 carbon atoms, and particularly preferably having 1 to 12 carbon atoms; and as examples, a mesyl group, a tosyl group, and the like are described), a sulfinyl group (preferably a sulfinyl group having 1 to 20 carbon atoms, more preferably having 1 to 16 carbon atoms, and particularly preferably having 1 to 12 carbon atoms; and as examples, a methanesulfinyl group, a benzenesulfinyl group, and the like are described), a ureido group (preferably a ureido group having 1 to 20 carbon atoms, more preferably having 1 to 16 carbon atoms, and particularly preferably having 1 to 12 carbon atoms; and as examples, an unsubstituted ureido group, a methylureido group, a phenylureido group, and the like are described), a phosphonoamido group (preferably a phosphonoamido group having 1 to 20 carbon atoms, more preferably having 1 to 16 carbon atoms, and particularly preferably

having 1 to 12 carbon atoms; and as examples, a diethylphosphonoamido group, a phenylphosphonoamido group, and the like are described), a hydroxy group, a mercapto group, a halogen atom (for example, a fluorine atom, a chlorine atom, a bromine atom, or an iodine atom), a cyano group, a sulfo group, a carboxy group, a nitro group, a hydroxamate group, a sulfinio group, a hydrazino group, an imino group, or a heterocyclic group (preferably a heterocyclic group having 1 to 30 carbon atoms, and more preferably having 1 to 12 carbon atoms; for example, a heterocyclic group having a hetero atom of a nitrogen atom, an oxygen atom, a sulfur atom, or the like; and as examples, an imidazolyl group, a pyridyl group, a quinolyl group, a furyl group, a piperidyl group, a morpholino group, a benzoxazolyl group, a benzimidazolyl group, a benzothiazolyl group, and the like are described), a silyl group (preferably a silyl group having 3 to 40 carbon atoms, more preferably having 3 to 30 carbon atoms, and particularly preferably having 3 to 24 carbon atoms; and as examples, a trimethylsilyl group, a triphenylsilyl group, and the like are described), and the like are described. These substituents may further have a substituent. And in the case where two or more substituents exist, these substituents may be the same or different from one another. And, when it is possible, these substituents may bond to each other to form a ring.

**[0053]** The coating amount of the compound represented by formula (2) is preferably in a range of from 0.1 mg/m<sup>2</sup> to 300 mg/m<sup>2</sup>, more preferably from 1 mg/m<sup>2</sup> to 150 mg/m<sup>2</sup>, and even more preferably from 5 mg/m<sup>2</sup> to 80 mg/m<sup>2</sup>.

**[0054]** Next, the compound represented by formula (3) is explained.



**[0055]** In the formula, R<sup>3</sup> may be branched or not, and represents an alkyl group, alkylene group, or aralkyl group having 6 to 24 carbon atoms. R<sup>3</sup> has preferably 8 to 10 carbon atoms, and more preferably 10 to 18 carbon atoms.

**[0056]** L<sup>3</sup> represents an alkylene group having a hydroxy group and 3 to 5 carbon atoms, a vinylene group, a vinylenealkylene group, or a divalent linking group formed by combining groups selected from among these groups. The number of the hydroxy group is not limited, however preferably 0 or 1. b represents 0 or 1. L<sup>3</sup> is preferably an alkylene group having a hydroxy group and 3 to 5 carbon atoms, a vinylenealkylene group, or a divalent linking group formed by combining the alkylene group and the vinylene group.

**[0057]** In formula (3) described above, Z<sup>3</sup> represents an OSO<sub>3</sub>M group or an SO<sub>3</sub>M group, and M represents a cation. As the cation represented by M, for example, an alkaline metal ion (a lithium ion, a sodium ion, a potassium ion, or the like), an alkaline earth metal ion (a barium ion, a calcium ion, or the like), an ammonium ion, or the like is preferably applied. Among these, a lithium ion, a sodium ion, a potassium ion, and an ammonium ion are particularly preferable.

**[0058]** Specific examples of the compound represented by formula (3) described above are shown below, but the present invention is not restricted to these specific examples.

WH-1 : C<sub>3</sub>H<sub>7</sub>—CH=CH—CH<sub>2</sub>—SO<sub>3</sub>Na

WH-2 : C<sub>5</sub>H<sub>11</sub>—CH=CH—CH<sub>2</sub>—SO<sub>3</sub>Na

WH-3 : C<sub>7</sub>H<sub>15</sub>—CH=CH—CH<sub>2</sub>—SO<sub>3</sub>Na

WH-4 : C<sub>9</sub>H<sub>19</sub>—CH=CH—CH<sub>2</sub>—SO<sub>3</sub>Na

WH-5 : C<sub>11</sub>H<sub>23</sub>—CH=CH—CH<sub>2</sub>—SO<sub>3</sub>Na

WH-6 : C<sub>13</sub>H<sub>27</sub>—CH=CH—CH<sub>2</sub>—SO<sub>3</sub>Na

WH-7 : C<sub>15</sub>H<sub>31</sub>—CH=CH—CH<sub>2</sub>—SO<sub>3</sub>Na

WH-8 : C<sub>21</sub>H<sub>43</sub>—CH=CH—CH<sub>2</sub>—SO<sub>3</sub>Na

WH-9 : C<sub>21</sub>H<sub>43</sub>—CH=CH—CH(OH)CH<sub>2</sub>—CH<sub>2</sub>—SO<sub>3</sub>Na

WH-10 : C<sub>15</sub>H<sub>31</sub>—CH=CH—CH<sub>2</sub>—CH(OH)CH<sub>2</sub>—CH<sub>2</sub>—SO<sub>3</sub>Na

WH-11 : C<sub>6</sub>H<sub>13</sub>—CH(OH)CH<sub>2</sub>—CH<sub>2</sub>—SO<sub>3</sub>Na

WH-12 : C<sub>9</sub>H<sub>19</sub>—CH(OH)CH<sub>2</sub>—CH<sub>2</sub>—SO<sub>3</sub>Na

WH-13 : C<sub>11</sub>H<sub>23</sub>—CH(OH)CH<sub>2</sub>—CH<sub>2</sub>—SO<sub>3</sub>Na

WH-14 : C<sub>13</sub>H<sub>27</sub>—CH(OH)CH<sub>2</sub>—CH<sub>2</sub>—SO<sub>3</sub>Na

WH-15 : C<sub>15</sub>H<sub>31</sub>—CH(OH)CH<sub>2</sub>—CH<sub>2</sub>—SO<sub>3</sub>Na

WH-16 : C<sub>13</sub>H<sub>27</sub>—CH(OH)CH<sub>2</sub>—CH<sub>2</sub>—SO<sub>3</sub>Na

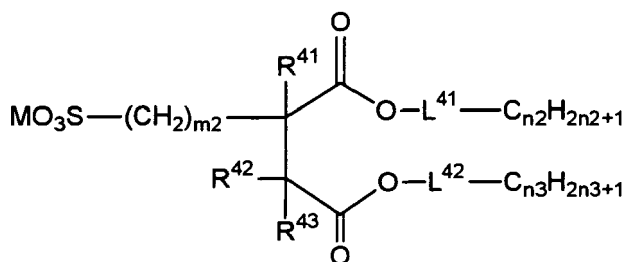
WH-17 : C<sub>21</sub>H<sub>43</sub>—CH(OH)CH<sub>2</sub>—CH<sub>2</sub>—SO<sub>3</sub>Na

WH-18 : C<sub>25</sub>H<sub>51</sub>—CH(OH)CH<sub>2</sub>—CH<sub>2</sub>—SO<sub>3</sub>Na

**[0059]** The coating amount of the compound represented by formula (3) is preferably in a range of from 0.01 mg/m<sup>2</sup> to 300 mg/m<sup>2</sup>, more preferably from 1 mg/m<sup>2</sup> to 100 mg/m<sup>2</sup>, and even more preferably from 3 mg/m<sup>2</sup> to 50 mg/m<sup>2</sup>.

**[0060]** Next, the compound represented by formula (4) is explained.

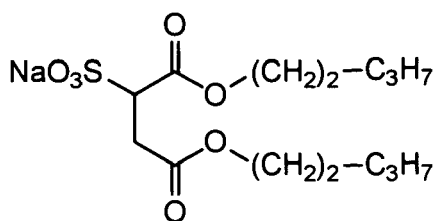
Formula (4)



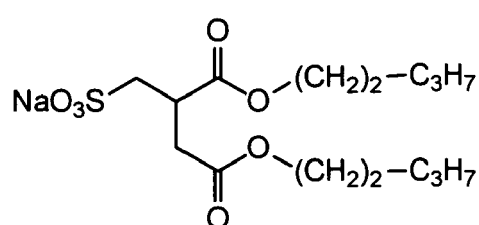
**[0061]** In the formula,  $\text{R}^{41}$ ,  $\text{R}^{42}$ , and  $\text{R}^{43}$  each independently represent a hydrogen atom or a substituent.  $n2$  and  $n3$  each independently represent an integer of from 1 to 5.  $\text{L}^{41}$  and  $\text{L}^{42}$  each independently represent an alkylene group substituted by a substituent other than a fluorine atom, an unsubstituted alkylene group, a substituted or unsubstituted alkyleneoxy group, or a divalent linking group formed by combining groups selected from among these groups.  $m2$  represents 0 or 1.  $M$  represents a cation.

**[0062]** Specific examples of the compound represented by formula (4) described above are shown below, but the present invention is not restricted to these specific examples.

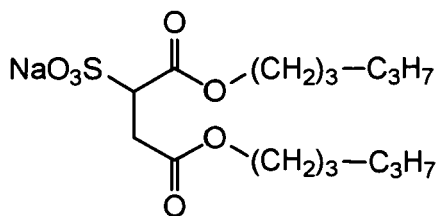
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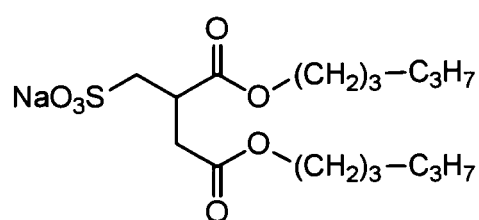
WT-2



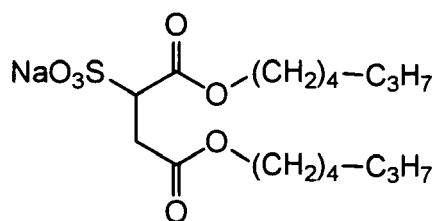
WT-3



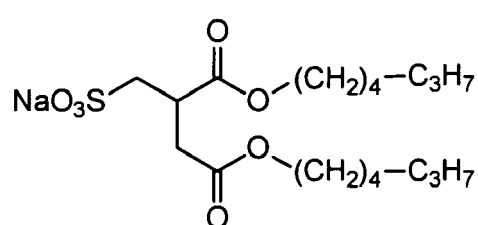
WT-4



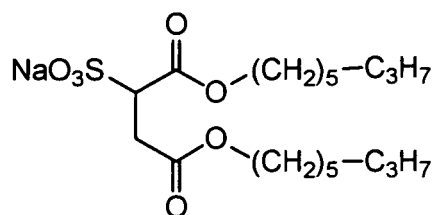
WT-5



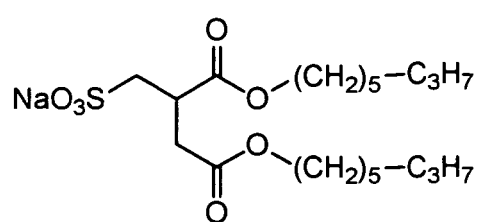
WT-6



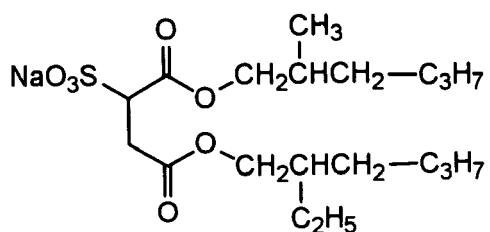
WT-7



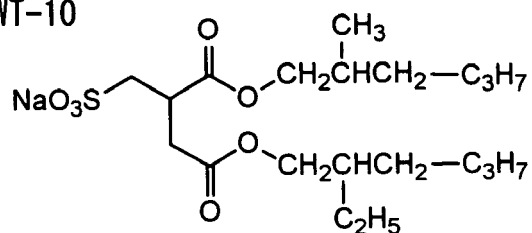
WT-8



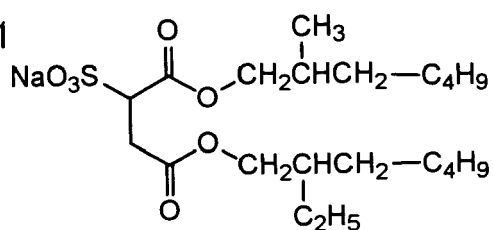
WT-9



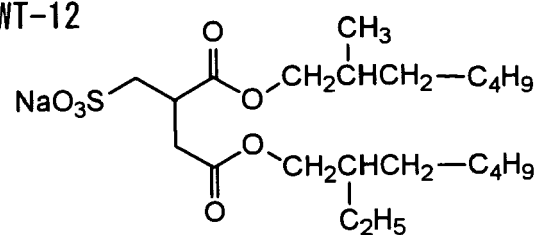
WT-10



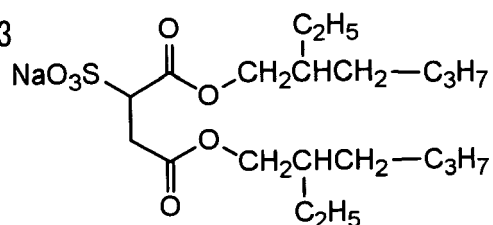
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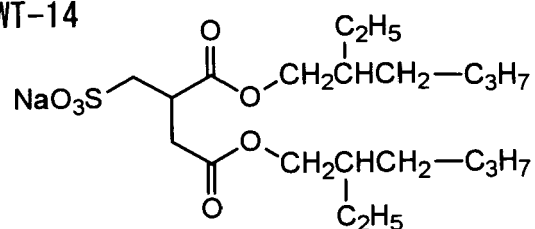
WT-12



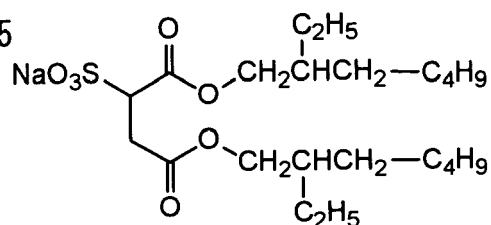
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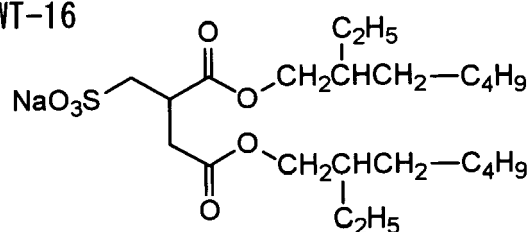
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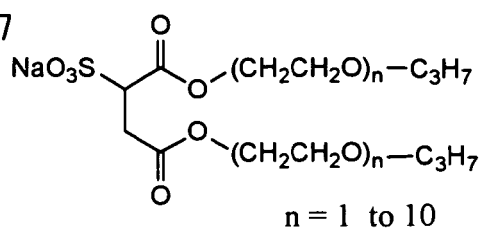
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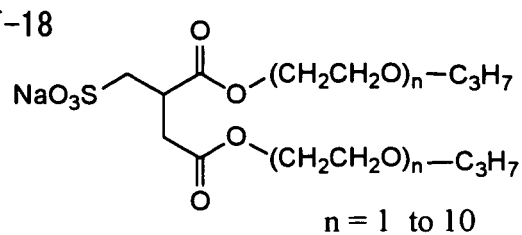
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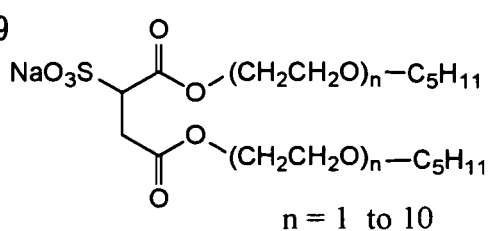
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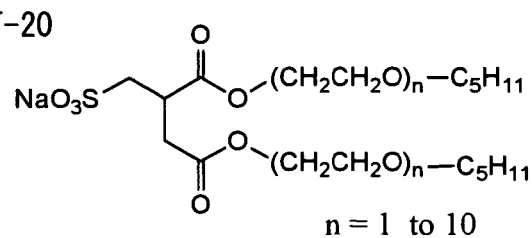
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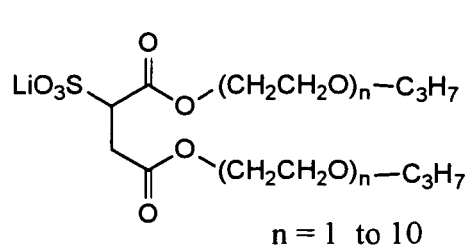
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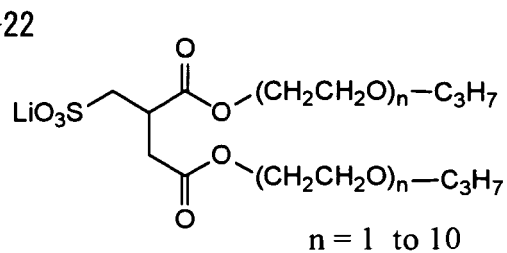
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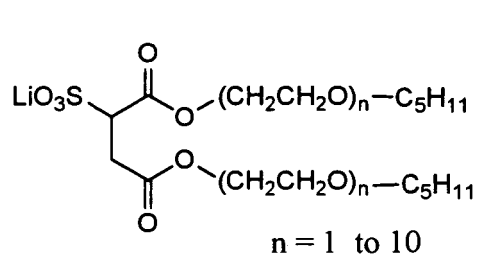
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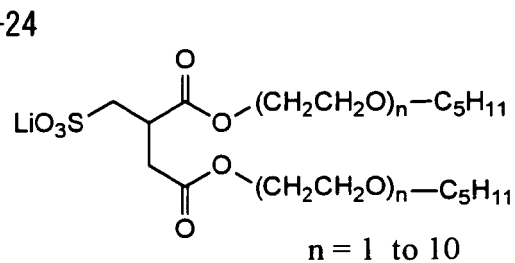
WT-22



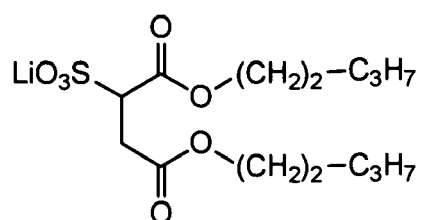
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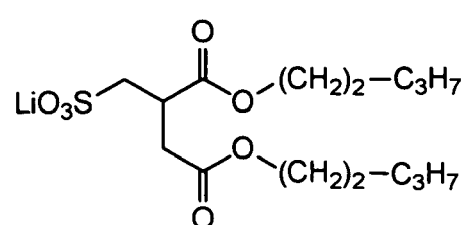
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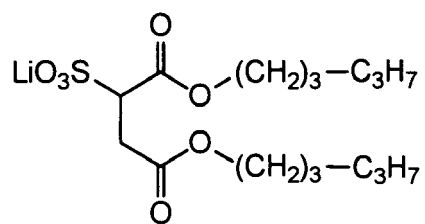
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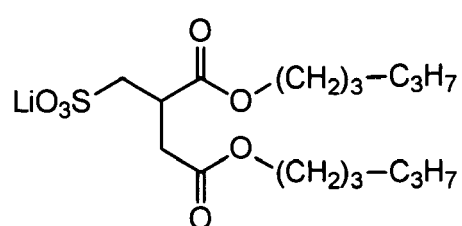
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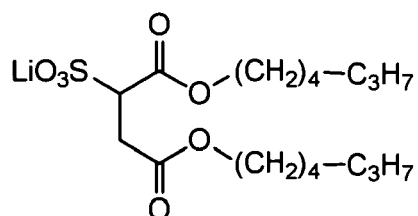
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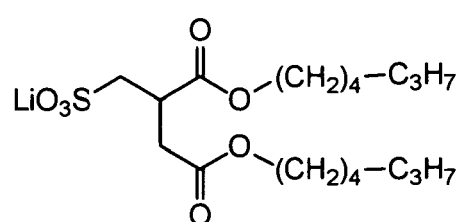
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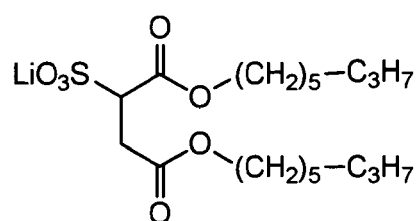
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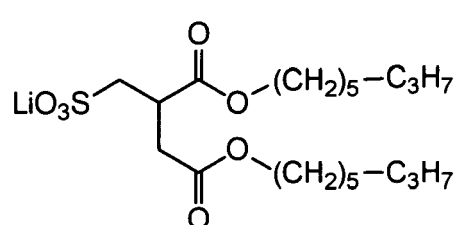
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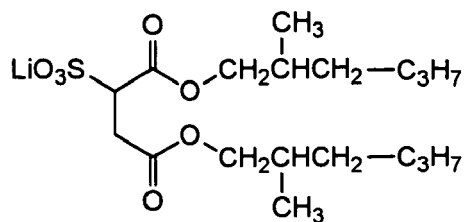
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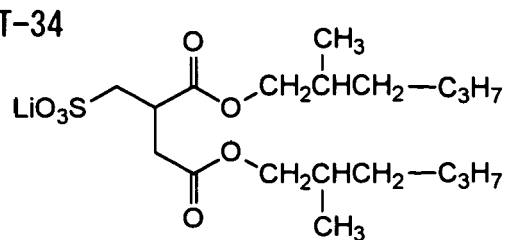
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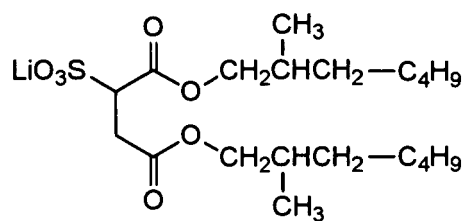
WT-33



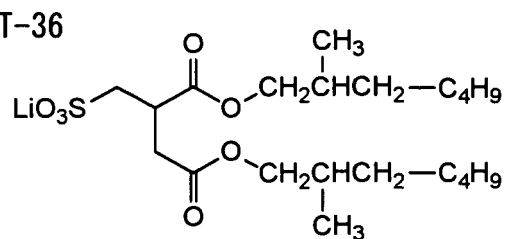
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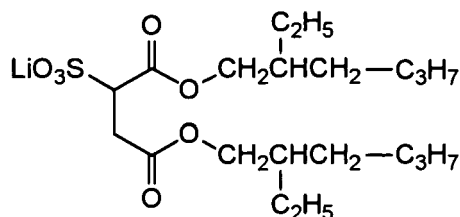
WT-35



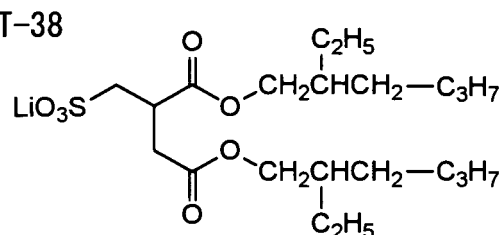
WT-36



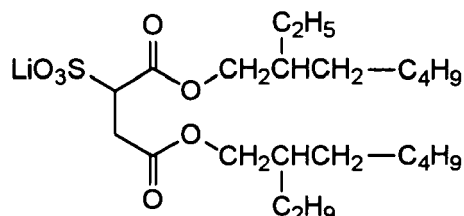
WT-37



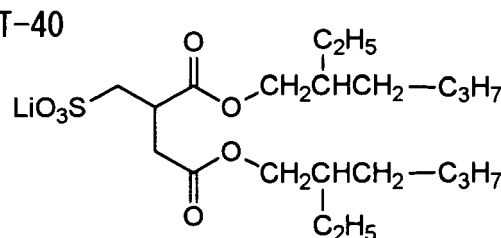
WT-38



WT-39

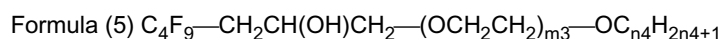


WT-40



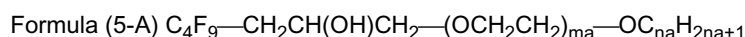
**[0063]** The coating amount of the compound represented by formula (4) is preferably in a range of from 0.1 mg/m<sup>2</sup> to 300 mg/m<sup>2</sup>, more preferably from 1 mg/m<sup>2</sup> to 150 mg/m<sup>2</sup>, and even more preferably from 5 mg/m<sup>2</sup> to 80 mg/m<sup>2</sup>.

**[0064]** Next, the nonionic fluorocarbon compound represented by formula (5) (hereafter, it is sometimes referred to as "the compound (5) of the present invention", or "the nonionic fluorocarbon compound of the present invention.") is explained in detail.



**[0065]** In the formula, m3 represents 15 to 60 and may be single or distributed. When there is a distribution, m3 represents an average value of them. m3 is preferably 20 to 40. n4 represents 8 to 24 and may be single or distributed. When there is a distribution, n4 represents an average value of them. n4 is preferably 10 to 20, more preferably 12 to 20, even more preferably 12 to 18, and particularly preferably 12 to 16.

**[0066]** As formula (5), preferred is the following formula (5-A).



**[0067]** In the formula, ma represents 20 to 40 ma is preferably 25 to 40, and may be single or distributed. When there is a distribution, ma represents an average value of them. na represents 12 to 18. na is preferably 12 to 16, and may be single or distributed. When there is a distribution, na represents an average value of them.

**[0068]** Specific examples of the compound represented by formula (5) described above are shown below, but the present invention is not restricted to these specific examples.

FS-101 :  $\text{C}_4\text{F}_9-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-(\text{OCH}_2\text{CH}_2)_{20}-\text{OC}_{18}\text{H}_{37}$

FS-102:  $\text{C}_4\text{F}_9-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-(\text{OCH}_2\text{CH}_2)_{21}-\text{OC}_{12}\text{H}_{25}$

FS-103 :  $\text{C}_4\text{F}_9-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-(\text{OCH}_2\text{CH}_2)_{23}-\text{OC}_{16}\text{H}_{33}$

FS-104:  $\text{C}_4\text{F}_9-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-(\text{OCH}_2\text{CH}_2)_{25}-\text{OC}_{12}\text{H}_{25}$

FS-105:  $\text{C}_4\text{F}_9-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-(\text{OCH}_2\text{CH}_2)_{40}-\text{OC}_{16}\text{H}_{33}$

FS-106:  $\text{C}_4\text{F}_9-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2-(\text{OCH}_2\text{CH}_2)_{32}-\text{OC}_{14}\text{H}_{29}$

**[0069]** The compound represented by formula (5) described above can be synthesized by the method described in Journal of Fluorine Chemistry, vol. 84, pages 53 to 61, 1997, and the like. That is, various derivatives can be synthesized by heating an epoxide compound having a fluoroalkyl group as a substituent and a compound having a hydroxy group in the presence of Lewis acid.

2. Aqueous coating composition containing the compounds represented by formulae (1) to (5) of the present invention

**[0070]** The compounds represented by formulae (1) to (5) are preferably used as surfactants in the aqueous coating composition for forming layers constituting the silver halide photosensitive material. When the compounds are used in a hydrophilic colloidal outermost layer of the silver halide photosensitive material, the use of the compounds is particularly

preferred from the standpoints of attaining effective antistatic performance and high-speed coating ability.

**[0071]** The coating composition containing the compounds represented by formulae (1) to (5) according to the present invention, as surfactants, is described below.

**[0072]** The aqueous coating composition of the present invention contains the compounds represented by formulae (1) to (5) according to the present invention and a medium for dissolving and/or dispersing the compounds. In addition, the coating composition may appropriately contain other components depending on the purpose.

**[0073]** An aqueous medium is preferred as a medium for the aqueous coating composition of the present invention. Examples of the aqueous medium include water and a mixed solvent of water and an organic solvent other than water (for example, methanol, ethanol, isopropyl alcohol, n-butanol, methyl cellosolve, dimethylformamide, acetone, and the like). In the present invention, the medium of the coating composition described above preferably contains 50% by weight or more of water.

**[0074]** In the aqueous coating composition of the present invention, the compounds represented by formulae (1) to (5) each may be used individually or by mixing two or more thereof. Other surfactant may also be used in combination with the compounds of the present invention. As the surfactant that can be used in combination with the compounds of the present invention, an anionic surfactant, a cationic surfactant, or a nonionic surfactant are described. Also, the surfactant that can be used in combination may be a polymer surfactant or may be a fluorocarbon surfactant other than the surfactants of the present invention. The surfactant used in combination is preferably an anionic surfactant or a nonionic surfactant. The surfactants that can be used in combination are described, for example, in JP-A No. 62-215272, pages 649 to 706, Research Disclosure, Item 17643, pages 26 and 27 (Dec., 1978), Research Disclosure, Item 18716, page 650 (Nov., 1979), Research Disclosure, Item 307105, pages 875 and 876 (Nov., 1989), and the like.

**[0075]** A polymer compound is a representative example of the other component that can be used in the aqueous coating composition of the present invention. The polymer compound may be a polymer which is soluble in the aqueous medium (hereinafter referred to as "soluble polymer") or may be an aqueous dispersion of polymer (so-called polymer latex). The soluble polymer is not particularly limited but examples thereof include gelatin, poly(vinyl alcohol), casein, agar, gum arabic, hydroxyethyl cellulose, methyl cellulose, carboxymethyl cellulose, and the like. Examples of the polymer latex include homopolymer or copolymer of vinyl monomer (for example, an acrylate derivative, a methacrylate derivative, an acrylamido derivative, a methacrylamido derivative, a styrene derivative, a conjugated diene derivative, an N-vinyl compound, an O-vinyl compound, vinyl nitrile, and other vinyl compounds (for example, ethylene or vinylidene chloride)), and a dispersion of condensed polymer (for example, polyester, polyurethane, polycarbonate, or polyamide). Specific examples of the polymer compound include polymer compounds described in, for example, JP-A No. 62-215272, pages 707 to 763, Research Disclosure, Item 17643, page 651 (Dec., 1978), Research Disclosure, Item 18716, page 650 (Nov., 1979), Research Disclosure, Item 307105, pages 873 and 874 (Nov., 1989), and the like.

**[0076]** The aqueous coating composition according to the present invention may contain other various compounds, which may be either dissolved or dispersed in the medium. Examples thereof include a coupler, an ultraviolet absorber, an anti-color mixing agent, an antistatic agent, a scavenger, an antifoggant, a hardener, a dye, a rust-preventing agent, and the like. As described above, the aqueous coating composition according to the present invention is preferably used for forming a hydrophilic colloidal outermost layer of the silver halide photosensitive material, and in this case, in addition to the hydrophilic colloid (for example, gelatin) and the fluorocarbon compound of the present invention, the coating composition can contain a surfactant other than the above, a matting agent, a lubricant, a colloidal silica, a gelatin plasticizer, and the like.

(Photosensitive silver halide emulsion)

**[0077]** The photosensitive silver halide emulsion for use in the silver halide emulsion layer according to the present invention is described below.

#### 1) Halide composition

**[0078]** For the photosensitive silver halide grain used in the invention, silver chloride, silver bromochloride, silver bromide, silver iodobromide, or silver iodochlorobromide can be used. From the standpoint of rapid processing as described above, an average iodide content of the photosensitive silver halide grain is preferably in a range of from 0 mol% to 0.45 mol%. The average iodide content is preferably in a range of from 0.05 mol% to 0.40 mol%, and more preferably from 0.10 mol% to 0.30 mol%. The "average" iodide content of the photosensitive silver halide grain herein means an average value of the iodide contents obtained from halogen compositions of the respective photosensitive silver halide grains. The distribution of the halogen composition in a photosensitive silver halide grain may be uniform or the halogen composition may be changed stepwise, or it may be changed continuously. Further, a photosensitive silver halide grain having a core/shell structure can also be used.

## 2) Grain shape

**[0079]** Halogen conversion type (conversion type) grains as described in GB Patent No. 635,841 and USP No. 3,622,318 can be effectively used in the present invention. Halogen conversion is generally conducted by addition of an aqueous solution of halogen, which has a solubility product of halogen and silver being lower than that of a halogen composition on the surface of the grains before halogen conversion. For example, conversion is effected by adding an aqueous solution of potassium bromide and/or an aqueous solution of potassium iodide to tabular silver chloride grains or tabular silver chlorobromide grains, or by adding an aqueous solution of potassium iodide to tabular silver bromide grains or tabular silver iodobromide grains. It is preferred that the concentration of the aqueous solution to be added is low. A concentration of 30% or lower is preferred, and a concentration of 10% or lower is more preferred. The halogen solution for conversion is preferably added at a rate of 1 mol%/minute or lower per 1 mol of silver halide before halogen conversion. Further, a part or the whole of sensitizing dye and/or silver halide-adsorbing material may be present during the halogen conversion. Alternatively, fine grains of silver bromide, silver iodobromide or silver iodide may be added in place of the aqueous halogen solution for conversion. The grain size of the fine grain is generally 0.2  $\mu\text{m}$  or less, preferably 0.1  $\mu\text{m}$  or less, and particularly preferably 0.05  $\mu\text{m}$  or less. The halogen converting method that can be used in the present invention is not limited to the above, and various methods may be properly employed in combination depending on the purpose.

## 3) Method of grain formation

**[0080]** The method of forming photosensitive silver halide grain is well-known in the relevant art and, for example, methods described in JP-A No. 2-68539, USP No. 3,700,458, and Research Disclosure, Item 17029 (Jun., 1978) can be used.

## 4) Chemical sensitizing method

**[0081]** As a chemical sensitizing method for use in the present invention, the methods described in JP-A Nos. 2-68539, page 10, upper right column, line 13 to lower left column, line 16, JP-A Nos. 5-313282 and 6-110144 can be applied.

**[0082]** As the chemical sensitizing method for silver halide emulsion, specifically, in the presence of a silver halide-adsorbing compound, well-known method such as sulfur sensitizing method, selenium sensitizing method, reduction sensitizing method, or gold sensitizing method may be used individually or in combination.

**[0083]** Gold sensitizing method is a representative example of the noble metal sensitizing method, and a gold compound, mainly a gold complex salt, is used. Complex salt of noble metal other than gold, such as platinum, palladium, iridium, or the like may also be employed. Specific examples thereof are described in USP No. 2,448,060 and GB Patent No. 618,061.

**[0084]** As a sulfur sensitizer, in addition to a sulfur compound included in gelatin, various sulfur compounds such as thiosulfates, thioureas, thiazoles, rhodanines, and the like can be used. Specific examples thereof are described in USP Nos. 1,574,944, 2,278,947, 2,410,689, 2,728,668, 5,501,313, and 8,656,955. Examples of the selenium sensitizer are described in JP-A No. 6-110144.

**[0085]** The combined use of the sulfur sensitization by thiosulfate and the selenium sensitization or the gold sensitization is very useful. Examples of the reduction sensitizer include a tin (I) salt, amines, formamidinesulfinic acid, a silane compound, and the like.

## 5) Antifoggant and stabilizer

**[0086]** As an antifoggant and stabilizer usable in the invention, there are mentioned those described in JP-A. No. 2-68539, page 10, lower left column, 17 line to page 11, upper left column, line 7, *ibid.*, page 3, lower left column, line 2 to page 4, lower left column.

**[0087]** Specific examples thereof include the compounds known as a antifoggant and stabilizer, such as azoles (for example, benzothiazolium salts, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, nitroimidazoles, benztriazoles, aminotriazoles, and the like); mercapto compounds (for example, mercaptothiazoles, mercaptobenzthiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, mercaptotetrazoles, mercaptopyrimidines, mercaptotriazines, and the like); thioketo compounds such as oxazoline thione; azaindenes (for example, triazaindenes, tetraazaindenes (especially, 4-hydroxy-substituted (1,3,3a,7) tetraazaindenes), pentaazaindenes, and the like); benzenesulfonic acid, benzenesulfinic acid, benzenesulfonamide, and the like.

**[0088]** In particular, a nitron and a derivative thereof described is JP-A Nos. 607673 and 60-87322, a mercapto compound described in JP-A No. 60-80839, a heterocyclic compound described in JP-A No. 57-164735, a complex salt of a heterocyclic compound and an acid (for example, 1-phenyl-5-mercaptotetrazoles) and the like are preferably used.

**[0089]** In addition, purines, nucleic acids and polymer compounds described in Japanese Patent Application Publication (JP-B) No. 61-36213, JP-A No. 59-90844, and the like are also used. Among these, azaindenes, purines, and nucleic acids are particularly preferably used. The addition amount of the compound is from 0.5 mmol to 5.0 mmol, and preferably from 0.5 mmol to 3.0 mmol, per 1 mol of silver halide.

#### 6) Color-tone-improving agent

**[0090]** Color-tone-improving agents usable in the present invention are described in JP-A Nos. 62-276539, page 2, lower left column, line 7 to page 10, lower left column, line 20, and JP-A No. 3-94249, page 6, lower left column, line 15 to page 11, upper right column, line 19.

**[0091]** Specifically, assuming that a covering power of the silver halide emulsion is 60 or more, a dye having a maximum absorption wavelength in the wavelength range of from 520 nm to 560 nm and a dye having a maximum absorption wavelength in the wavelength range of from 570 nm to 700 nm can be added in at least one of the silver halide emulsion layer and the other layers in such an amount that the increase in transmission density due to the presence of the dye at the unexposed portion after development is 0.03 or less.

**[0092]** Typical examples of the silver halide emulsion layer having a covering power of 60 or more include a tabular grain emulsion, a fine grain emulsion, and the like. In particular, when the silver halide emulsion comprising tabular silver halide grains having a mean grain thickness of 0.4  $\mu\text{m}$  or less is used, or when a mixed emulsion of a surface-photo-sensitive emulsion with high iodide content and an emulsion comprising fine internally fogged silver halide grains is used, the effect for improving color tone becomes large.

**[0093]** Examples of the dyes used for improving color tone in the present invention include the combined use of a dye having a maximum absorption wavelength in the wavelength range of from 520 nm to 560 nm, preferably from 530 nm to 555 nm, and a dye having a maximum absorption wavelength in the wavelength range of from 570 nm to 700 nm, preferably from 580 nm to 650 nm. The maximum absorption wavelength herein means a maximum absorption wavelength obtained in the state where the dye is incorporated in the photosensitive material.

**[0094]** Examples of the dye for use in the present invention include those having the aforesaid maximum absorption wavelength selected from an anthraquinone dye, an azo dye, an azomethine dye, an indoaniline dye, an oxonol dye, a carbocyanine dye, a styryl dye, a triphenylmethane dye, and the like. Preferred examples thereof are selected from an anthraquinone dye, an azo dye, an azomethine dye, and an indoaniline dye, in consideration of stability to development treatment, durability to light, and influence on photographic performance such as desensitization, fogging, stain, and the like. Preferred compounds are described in JP-A No. 62-276539, page 3, upper left column, line 5 to page 9, upper left column, line 9.

**[0095]** These dyes can be incorporated in the emulsion layer or other hydrophilic colloidal layers (an intermediate layer, a protective layer, an antihalation layer, and a filter layer) by dispersing them according to various known methods. Specific examples of the method are described in JP-A No. 62-276539, page 9, upper left column, line 14 to page 10, lower left column, line 20.

#### 7) Spectral sensitizing dye

**[0096]** Examples of the spectral sensitizing dye for use in the present invention include those described in JP-A No. 2-68539, page 4, lower right column, line 4 to page 8, lower right column.

**[0097]** Specific examples thereof include a cyanine dye, a merocyanine dye, a complex cyanine dye, a complex merocyanine dye, a holopolar cyanine dye, a styryl dye, a hemicyanine dye, an oxonol dye, a hemioxonol dye, and the like.

**[0098]** Useful sensitizing dyes used in the present invention are described in USP Nos. 3,522,052, 3,617,197, 3,713,828, 3,615,643, 3,615,632, 3,617,293, 3,628,964, 3,703,377, 3,666,480, 3,667,960, 3,679,428, 3,672,897, 3,769,026, 3,556,800, 3,615,613, 3,613,638, 3,615,635, 3,705,809, 3,632,349, 3,677,765, 3,770,449, 3,770,440, 3,769,025, 3,745,014, 3,713,826, 8,567,458, 3,625,698, 2,526,632, and 2,503,776, JP-A No. 48-76525, Belgium Patent No. 691,807, and the like. The addition amount of the sensitizing dye is preferably in a range of 0.5 mmol or more and less than 4 mmol, and more preferably in a range of 0.5 mmol or more and 1.5 mmol or less, per 1 mol of silver halide.

**[0099]** Specific examples of the sensitizing dye include dyes II-1 to II-47 described in JP-A No. 2-68539, pages 5 to 8.

#### 8) Antistatic agent

**[0100]** In the present invention, surfactants described in JP-A No. 2-68539, page 11, upper left column, line 14 to page 12, upper left column, line 9 can be used as a coating aid, an antistatic agent, or a static-controlling agent.

**[0101]** Specific examples of the surfactant used for the aforesaid purpose include nonionic surfactants such as saponin (steroid type), alkylene oxide derivatives (for example, polyethylene glycol, a condensation product of polyethylene glycol/ propylene glycol, polyethylene glycol alkylethers, polyethylene glycol alkylarylethers, or silicone-polyethylene

oxide compounds), sugar-alkyl esters, and the like; anionic surfactants such as alkylsulfonate, alkylbenzenesulfonate, alkylnaphthalenesulfonate, alkylsulfate esters, N-acyl-N-alkyltaurines, sulfosuccinate esters, sulfoalkyl polyoxyethylene alkylphenyl ethers, and the like; amphoteric surfactants such as alkyl betaines, alkylsulfo betaines, and the like; and cationic surfactants such as aliphatic quaternary ammonium salts, aromatic quaternary ammonium salts, pyridinium salts, imidazolium salts, and the like.

**[0102]** Among these, anionic surfactants such as saponin, sodium dodecylbenzenesulfonate, sodium di-2-ethylhexyl- $\alpha$ -sulfosuccinate, sodium p-octylphenoxy ethoxyethanesulfonate, sodium dodecylsulfate, sodium triisopropyl naphthalenesulfonate, N-methyl-oleoyl taurine sodium salt, and the like; cationic surfactants such as dodecyltrimethylammonium chloride, N-oleoyl-N',N',N'-trimethylammonio diaminopropane bromide, dodecylpyridium chloride, and the like; betaine surfactants such as N-dodecyl-N,N-dimethylcarboxy betaine, N-oleoyl-N,N-dimethylsulfobutyl betaine, and the like; nonionic surfactants such as polyoxyethylene cetyl ether (average polymerization degree  $n = 10$ ), polyoxyethylene p-nonylphenol ether ( $n = 25$ ), bis(1-polyoxyethylene-oxy-2,4-di-t-pentylphenyl) ethane ( $n = 15$ ), and the like are particularly preferably used.

**[0103]** As the antistatic agent, the use of a nonionic surfactant, alkali metal salt of nitric acid, electrically conductive tin oxide, zinc oxide, vanadium pentaoxide, or a complex oxide in which the above is subjected to antimony-doping or the like, which are described in JP-A Nos. 60-80848, 61-112144, 62-172343, and 62-173459, and the like, is preferred.

#### 9) Matting agent, lubricant, and plasticizer

**[0104]** Matting agents, plasticizers, and lubricants usable in the present invention are described in JP-A No. 2-68539, page 12, upper left column, line 10 to upper right column, line 10; *ibid.*, page 14, lower left column, line 10 to lower right column, line 1.

**[0105]** Specific examples of the matting agent include fine particles of homopolymer of poly(methyl methacrylate), fine particles of copolymer of methyl methacrylate and methacrylic acid, fine particles of an organic compound such as starch or the like, and fine particles of an inorganic compound such as silica, titan dioxide, strontium barium sulfate, or the like; as described in USP Nos. 2,992,101, 2,701,245, 4,142,894, and 4,396,706. The grain size thereof is preferably from 1.0  $\mu\text{m}$  to 10  $\mu\text{m}$ , and particularly preferably from 2  $\mu\text{m}$  to 5  $\mu\text{m}$ .

**[0106]** The surface layer of the photosensitive materials according to the present invention can contain a silicone compound described in USP Nos. 3,489,576 and 4,047,958, and the like, and colloidal silica described in JP-B No. 56-23139 as a lubricant. In addition to the above, paraffin wax, an ester of a higher fatty acid, and a starch derivative can be also employed.

**[0107]** The hydrophilic colloidal layer of the silver halide photosensitive material according to the present invention can contain polyols such as trimethylolpropane, pentanediol, butanediol, ethylene glycol, glycerine, or the like as a plasticizer. Moreover, the emulsion layer of the silver halide photosensitive material according to the present invention can include a plasticizer such as a polymer or an emulsified product to improve pressure characteristic.

**[0108]** For example, GB Patent No. 738,618 discloses the use of a heterocyclic compound, GB Patent No. 738,637 discloses the use of alkyl phthalate, GB Patent No. 738,639 discloses the use of an alkyl ester, USP No. 2,960,404 discloses the use of poly-alcohol, USP No. 3,121,060 discloses the use of carboxyalkyl cellulose, JP-A No. 49-5017 discloses the use of paraffin and a salt of carboxylic acid, and JP-B No. 53-28086 discloses the use of alkylacrylate and an organic acid. And the above methods can also be applied for the present invention.

#### 10) Hydrophilic colloid

**[0109]** As a binder or protective colloid, which can be used in the emulsion layer, intermediate layer, and surface protective layer of the silver halide photosensitive material according to the present invention, gelatin is used advantageously, but any other hydrophilic colloid can also be used.

**[0110]** As the hydrophilic colloid that can be used in the present invention, there are mentioned those described in JP-A No. 2-68539, page 12, upper right column, line 11 to lower left column, line 16.

**[0111]** For example, protein such as a gelatin derivative, a graft polymer of gelatin and other polymer, albumin, casein, or the like; a cellulose derivative such as hydroxyethyl cellulose, carboxymethyl cellulose, cellulose sulfate esters, or the like; a sugar derivative such as sodium alginate, dextran, a starch derivative, or the like; and various synthetic hydrophilic polymer including homopolymer such as poly(vinyl alcohol), poly(vinyl alcohol) partial acetal, poly(N-vinylpyrrolidone), poly(acrylic acid), poly(methacrylic acid), polyacrylamide, poly(vinyl imidazole), poly(vinyl pyrazole) or the like, and copolymer thereof can be used.

**[0112]** As gelatin, acid-processed gelatin or enzyme-processed gelatin as well as lime-processed gelatin may be used. Additionally, hydrolyzed gelatin or enzyme-decomposed gelatin can be used.

**[0113]** Among these, it is preferred to use dextran or polyacrylamide having an average molecular weight of 100,000 or less in combination with gelatin. The methods described in JP-A Nos. 63-68887 and 63-149641 are also useful in the

present invention.

#### 11) Hardener

**[0114]** The hydrophilic colloid incorporated in the emulsion layer and non-photosensitive layer used in the present invention may contain an inorganic or organic hardener. Examples of the hardener for use in the present invention are described in JP-A No. 2-68539, page 12, lower left column, line 17 to page 13, upper right column, line 6.

**[0115]** For example, a chrome salt (chrome alum, chrome acetate, or the like), aldehydes (formaldehyde, glyoxal, glutaraldehyde, or the like), an N-methylol compound (dimethylolurea, methyloldimethylhydantoin, or the like), a dioxane derivative (2,3-dihydroxy dioxane or the like), an active vinyl compound (1,3,5-triacryloyl-hexahydro-s-triazine, bis(vinylsulfonyl) methyl ether, N,N'-methylene bis-( $\beta$ -(vinylsulfonyl)propionamide), or the like), an active halogen compound (2,4-dichloro-6-hydroxy-s-triazine or the like), a mucohalogen acids (mucochloric acid, mucophenoxychloric acid, or the like), isooxazoles, dialdehyde starch, 2-chloro-6-hydroxy triazinyl gelatin, or the like can be used, individually or in combination. Among these, active vinyl compounds described in JP-A Nos. 53-41221, 53-57257, 59-162546, and 60-80846, and active halogen compounds described in USP No. 3,325,287 are preferable.

**[0116]** As a hardener, a polymer hardener can also be used effectively in the present invention. Specific examples of the polymer hardener used in the present invention include a polymer having an aldehyde group such as dialdehyde starch, polyacrolein, or an acrolein copolymer described in USP No. 3,396, 029; a polymer having an epoxy group described in USP No. 3,623,878; a polymer having a dichlorotriazine group described in USP No. 3,362,827, Research Disclosure, Item 17333 (1978) and the like; a polymer having an active ester group described in JP-A No. 56-66841; and a polymer having an active vinyl group or a polymer having a group to be a precursor thereof described in JP-A No. 56-142524, USP No. 4,161,407, JP-A No. 54-65033, Research Disclosure, Item 16725 (1978), and the like. Among these, a polymer in which an active vinyl group or a group to be a precursor thereof bonds to the main polymer chain by a long spacer, as described in JP-A No. 56-142524, is particularly preferred.

**[0117]** The hydrophilic colloidal layers included in the silver halide photosensitive material of the present invention are preferably hardened by the hardener described above so that the layers have a swelling ratio in water of 300% or less, and particularly preferably 230% or less.

#### 12) Support

**[0118]** Examples of the support used in the present invention are described in JP-A No. 2-68539, page 13, upper right column, line 7 to line 20. Specifically, as the support, a poly(ethylene terephthalate) film and a cellulose triacetate film are preferable.

**[0119]** The surface of the support is preferably subjected to corona discharge treatment, glow discharge treatment, or ultraviolet irradiation treatment, in order to improve adhesion strength between the support and the hydrophilic colloidal layer. Furthermore, an undercoat layer comprising styrene-butadiene latex, vinylidene chloride latex, or the like can be disposed on the support, on which a gelatin layer may be further provided.

**[0120]** An undercoat layer formed by using an organic solvent containing a polyethylene swelling agent and gelatin may be provided. The undercoat layer can be further improved in adhesion strength with the hydrophilic colloidal layer by applying surface treatment.

#### 13) Crossover cutting method

**[0121]** It is well known in the art that crossover light largely deteriorates sharpness. As a method for decreasing crossover light of a photosensitive material to 12% or less, USP No. 4,130,429 and JP-A No. 61-116354 disclose a method of absorbing light having a wavelength in accordance with the emission wavelength of an X-ray fluorescent screen by using a sensitizing dye or a pigment.

**[0122]** Furthermore, USP No. 4,800,150 discloses such a technique that a dye having a fine crystal dispersion form is provided between a support and an emulsion layer to decrease crossover light to 10% or less. Furthermore, JP-A No. 63-305345 discloses such a technique that an anionic dye is fixed in a specific layer by using a cationic polymer latex, and JP-A No. 1-166031 discloses such a technique that a dye fixing layer is provided as an undercoat layer. While all the methods described above may be applied for the photosensitive material of the present invention, a colored layer with a dye is preferably used as an undercoat layer where the dye is preferably fixed by the method described in JP-A No. 1-166031, and especially, the dye is preferably fixed in the undercoat layer in the form of a fine crystal dispersion described in USP No. 4,803,150. In the present invention any proper combination of the above methods are available.

**[0123]** Examples of preferred dye used in the present invention are described in JP-A No. 2-264944, page 4, lower left column, to page 9, upper right column.

**[0124]** As a mordant layer, those described in JP-A No. 2-264944, page 9, lower right column, to page 14, upper right

column can be used.

#### 14) Polyhydroxybenzenes

**[0125]** Examples of polyhydroxybenzenes for use in the present invention are described in JP-A No. 3-39948, page 11, upper left column to page 12, lower left column, and EP No. 452,772A.

**[0126]** Specifically, the compound represented by formula (III) described in JP-A No. 8-39948, page 11, upper left column and the specific compounds (III)-1 to (III)-25 described in the same publication, page 11, lower left column to page 12, lower left column are described.

**[0127]** It is enough that the addition amount of the polyhydroxybenzene compound is less than  $5 \times 10^{-1}$  mol per 1 mol of silver halide. Preferably, the addition amount of the polyhydroxybenzene compound is in a range of from  $5 \times 10^{-3}$  mol to  $1 \times 10^{-1}$  mol per 1 mol of silver halide.

**[0128]** The silver halide photosensitive material of the present invention has, on a support, a silver halide emulsion layer (photosensitive layer) including photosensitive silver halide grains and at least one non-photosensitive hydrophilic colloidal layer such as an intermediate layer, a surface protective layer, a back layer, a back surface protective layer, an antihalation layer, a filter layer, or the like. Other matters used herein, such as an emulsion sensitizing method or various additives, are not particularly limited, and for example, those described in JP-A No.2-68539 and the like can be preferably used.

#### 15) Surface protective layer and back surface protective layer

**[0129]** The silver halide photosensitive material of the present invention preferably has a surface protective layer and a back surface protective layer. The surface protective layer and the back surface protective layer contain various compounds by using hydrophilic colloid such as gelatin as a binder. In the case where the main component of the layer is gelatin, the use of an antiseptic is necessary. Further, the layer preferably contains a matting agent, a lubricant, a plasticizer, an antistatic agent, a surfactant, a hardener, a viscosity increasing agent, a dye, an electrically conductive material, and the like, depending on needs.

**[0130]** As the preferred embodiment of the silver halide photosensitive material of the present invention, the outermost layer has non-photosensitive hydrophilic colloid as a binder, and contains the compound represented by formula (1) described above. It is more preferred that the outermost layer contains the compound represented by formula (1) and at least one of an anionic fluorocarbon compound and an anionic hydrocarbon compound. The anionic fluorocarbon compound is preferably the compound represented by formula (1) described above, and the anionic hydrocarbon compound is preferably the compound represented by formula (2) described above.

#### 16) Method of development treatment

**[0131]** The method of development treatment used for the silver halide photosensitive material of the present invention can be selected from the methods described in JP-A No. 2-103037, page 16, upper right column, line 7 to page 19, lower left column, line 15; JP-A No. 2-115837, page 3, lower right column, line 5 to page 6, upper right column, line 10; and JP-A No. 2000-112078, page 34, left column, line 42 to page 35, left column, line 2.

**[0132]** For a rapid coating, where coating is performed at a speed of from 40 m/second to 250 m/second, it is particularly preferred to use the silver halide photosensitive materials of the present invention

## II. Packaging material

**[0133]** The packaged body used in the present invention has a constitution, in which a laminate comprising a sheet of the photographic silver halide material described above and a non-photosensitive plate material referred to as protection cardboard is packed with a light shielding sack-shaped material.

**[0134]** For the protection cardboard used in the present invention, a non-photosensitive plate material having a layer coated with an organic material on the surface thereof is employed.

#### 1) Non-photosensitive plate material

**[0135]** Next, the non-photosensitive plate material used in the present invention is explained.

**[0136]** The non-photosensitive plate material used in the present invention is a plate material on which plural sheets of the silver halide photosensitive material are piled to constitute a laminate therewith, and generally referred to as protection cardboard. Hereinafter "protection cardboard" is used in the following explanation.

**[0137]** As a raw material of the protection cardboard used in the present invention, any pulp manufactured by any

manufacturing method may be employed. Specifically, mechanical pulp, chemical pulp, or semi-chemical pulp can be used, and cellulose pulp such as pulp of wastepaper can be properly mixed therewith. Usually, natural wood pulp such as conifer pulp, broad-leaved tree pulp, and mixed pulp thereof are used. For example, conifer kraft pulp (NBKP; Nadelholz Bleached Kraft Pulp) as exemplified in pulp comprising 100% of pine, and broad-leaved tree pulp (LBKP; Laubholz Bleached Kraft Pulp) are preferably used.

**[0138]** The raw material of protection cardboard used in the present invention may be bleached or unbleached. A bleached protection cardboard is preferred. As the bleaching method, the ECF (Elemental Chlorine Free) method is preferred.

**[0139]** The raw material of the protection cardboard used in the present invention may be prepared by cutting fibers by a beater to make a fiber length distribution to a desired range. The fiber length distribution can be adjusted by controlling the processing amount and the pressure of the beater.

**[0140]** Compounds which are usually used in the stencil paper manufacturing process can be properly used. For example, a sizing agent such as alkylketene dimer, a fixing agent such as cationic starch or polymer, or the like may be also used.

**[0141]** The papermaking method is not particularly limited. Any papermaking methods known in the art can be applied. As the paper machine, a cylinder machine or Fourdrinier paper machine can be used, but Fourdrinier paper machine is preferably employed.

**[0142]** The protection cardboard used in the present invention is preferably subjected to surface treatment to maintain storage stability in a packaged embodiment. Various types of surface treating method are there, but a surface coating method with an organic substance is preferred. The organic substance used in the coating described above is not limited, but especially, when used for storing the silver halide photographic material, a packaging material coated with cationic starch or poly(vinyl alcohol) is preferably used. Poly(vinyl alcohol) is preferably coated in a coating amount of from 0.04 g/m<sup>2</sup> to 0.90 g/m<sup>2</sup> per one side, more preferably from 0.08 g/m<sup>2</sup> to 0.60 g/m<sup>2</sup> per one side, and even more preferably from 0.12 g/m<sup>2</sup> to 0.48 g/m<sup>2</sup> per one side. Poly(vinyl alcohol) is preferably coated on both sides of the packaging material.

In addition, as another surface treating method, a coating method using an ultraviolet curing resin is also preferably used. Specifically the ultraviolet curing resin described in JP-B No.4-13697 can be used. The thickness of the ultraviolet curing resin-coated layer is preferably in a range of from 0.05 to 15 μm, and more preferably from 0.1 μm to 5 μm. A density of the packaging material used in the present invention is preferably in a range of from 0.70 g/m<sup>3</sup> to 0.90 g/m<sup>3</sup>, more preferably from 0.75 g/m<sup>3</sup> to 0.85 g/m<sup>3</sup>, and even more preferably from 0.77 g/m<sup>3</sup> to 0.81 g/m<sup>3</sup>.

## 2) Light shielding sack-shaped material

**[0143]** The packaging material used in the present invention has a sufficient light-shielding ability to prevent the silver halide photosensitive material from exposing to undesired light. Further preferably, the packaging material comprises a packaging material having low oxygen permeability and low vapor permeability.

**[0144]** Preferably, oxygen permeability is 50 mL·atm<sup>-1</sup>m<sup>-2</sup>day<sup>-1</sup> or lower (at 25°C), and vapor permeability is 10 g·atm<sup>-1</sup>m<sup>-2</sup>day<sup>-1</sup> or lower (at 25°C). Preferably, oxygen permeability is 50 mL·atm<sup>-1</sup>m<sup>-2</sup>day<sup>-1</sup> or lower (at 25°C), more preferably 10 mL·atm<sup>-1</sup>m<sup>-2</sup>day<sup>-1</sup> or lower (at 25°C), and even more preferably 1.0 mL·atm<sup>-1</sup>m<sup>-2</sup>day<sup>-1</sup> or lower (at 25°C). Preferably, vapor permeability is 10 g·atm<sup>-1</sup>m<sup>-2</sup>day<sup>-1</sup> or lower (at 25°C), more preferably 5 g·atm<sup>-1</sup>m<sup>-2</sup>day<sup>-1</sup> or lower (at 25°C), and even more preferably, 1 g·atm<sup>-1</sup>m<sup>-2</sup>day<sup>-1</sup> or lower (at 25°C). The oxygen permeability used herein means a value obtained by the measurement at the condition B defined in JIS Z0208. The vapor permeability used herein means vapor transmittance obtained by the measuring method defined in JIS K7129-1992 wherein the measurement condition is at 40°C and relative humidity of 90%RH.

**[0145]** As specific examples of the packaging material having low oxygen permeability and/or low vapor permeability, reference can be made to, for instance, the packaging material described in JP-A Nos. 8-254793 and 2000-206653. Details thereof are described below.

**[0146]** Specific examples of the raw material of the packaging material include polyethylene resin, nylon resin, polypropylene resin, poly(ethylene terephthalate) resin, polyamido resin, ethylene-vinyl alcohol copolymer resin, ethylene-vinyl acetate copolymer resin, acrylonitrile-butadiene copolymer resin, cellophane resin, vinylon resin, vinylidene chloride resin, and the like. Polypropylene resin and nylon resin used for the packaging material may be stretched and further may be overcoated with vinylidene chloride resin thereon. Concerning polyethylene resin, high density polyethylene resin or low density polyethylene resin can be used. Synthetic resin such as epoxy-phosphoric acid resin (polymers described in JP-A Nos. 63-63037 and 57-32952), and pulp can be also used.

**[0147]** The packaging material preferably consists of a single material. When used as film, the film is laminated with adhesive, but may be a coated layer, or monolayered film may also be available. It is more preferred to use various gas barrier film such as aluminum foil or aluminum deposited synthetic resin, for example, between the above synthetic resin film. The total film thickness of the laminated film or the monolayered film is preferably in a range of from 1 μm to 3,000 μm, more preferably from 10 μm to 2,000 μm, and even more preferably from 50 μm to 1,000 μm.

**[0148]** As the raw material of the packaging material, among the polymers described above, it is preferred to use polyethylene (PE), nylon (Ny), vinylidene chloride resin (PVDC) coated nylon (KNy), non-stretched polypropylene (CPP), stretched polypropylene (OPP), PVDC coated polypropylene (KOP), poly(ethylene terephthalate) (PET), PVDC coated cellophane (KPT), or polyethylene-vinyl alcohol copolymer (Eval). The use of the aforesaid resin can easily bring about the packaging material having the mechanical strength, the oxygen permeability, and the vapor permeability required in the present invention.

**[0149]** As the raw material of the packaging material, an inorganic compound deposited polymer material can also be used where the polymer material may be the aforesaid or well-known material. The inorganic compounds used for vapor deposition include aluminum, aluminum oxide ( $\text{Al}_2\text{O}_3$ ), silicone oxide ( $\text{SiOx}$ ), and the like. The film thickness of deposited film is in a range of from 50 Å to 1,000 Å. Well-known depositing methods such as a chemical vapor depositing method, a physical vapor depositing method, a vapor depositing method, a sputtering method, and the like can be employed. In the case where the packaging material has a multi-layered structure, the film thickness of each layer may be properly adjusted depending on the demand for the light shielding ability, the oxygen permeability, the vapor permeability, the mechanical strength, and the like, but as the whole packaging material, the total thickness is fallen in 500  $\mu\text{m}$  or less. The method of producing the multi-layered packaging material is not particularly limited, but for example, includes a method of combining a resin layer and the other resin layer with an adhesive, a method of combining a resin layer and the other resin layer with a melt-type resin, an extruding method, a laminating method, and the like.

**[0150]** Specific examples of the raw material of the packaging material include the following materials, but the invention is not limited to these. The layer constitution of (outermost portion)/ (intermediate portion)/ (contacted portion with the photothermographic material) is shown below.

- (1) PET/ Ny/ CPP
- (2) KOP/ Ny/ PE
- (3) OPP/  $\text{Al}_2\text{O}_3$ / PET/ CPP
- (4) Ny/  $\text{Al}_2\text{O}_3$ / PE
- (5) PET/ PE/ Al/ Ny/ PE
- (6) KOP/ Ny/ PE
- (7)  $\text{SiOx}$ / PET/  $\text{Al}_2\text{O}_3$ / PET
- (8) KPT/ PE/ Ny/ PE
- (9) PET/ KNy/ PE
- (10) OPP/ Eval/ PE

**[0151]** To adjust oxygen permeability and vapor permeability of the packaging material in the above specified range, for example, raw materials and the thickness of the constituent layer are properly selected.

**[0152]** All publications, patent applications, and technical standards mentioned in this specification are herein incorporated by reference to the same extent as if each individual publication, patent application, or technical standard was specifically and individually indicated to be incorporated by reference.

## EXAMPLES

**[0153]** The present invention is specifically explained by way of Examples below, which should not be construed as limiting the invention thereto.

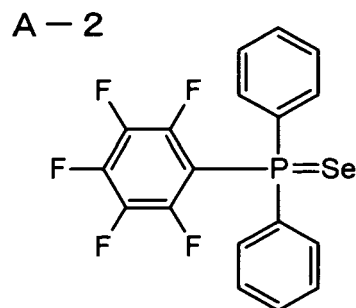
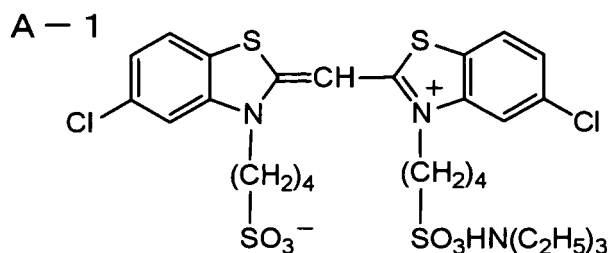
### EXAMPLE 1

#### 1. Preparation of Sample

##### <Preparation of Silver Halide Emulsion>

**[0154]** A solution was prepared by adding 4 g of sodium chloride, 4 g of potassium iodide, and 20 g of gelatin to 1 liter of water. The solution was kept at 70°C while stirring in a reaction vessel, and thereto were added 400 mL of an aqueous solution containing 83 g of silver nitrate and 190 mL of an aqueous solution containing 57 g of potassium bromide over 16 minutes by controlled double jet method. After adding an aqueous solution containing from 0.1 mol to 0.85 mol of ammonia, 250 mL of an aqueous solution containing 123 g of silver nitrate and 275 mL of an aqueous solution containing 82.5 g of potassium bromide were added over 20 minutes by controlled double jet method, and subjected to physical ripening for 18 minutes while keeping the temperature. Thereafter, the pH was neutralized using an aqueous solution of acetic acid and the mixture was cooled to 35°C followed by removing soluble salts by sedimentation method. Then, the resulting mixture is warmed to 40°C, and thereto were added 23.7 mL of a 50% by weight solution of trimethylol

propane, 42 mg of Proxel, 32.5 g of gelatin, and sodium polystyrenesulfonate (average molecular weight of 600,000) as a viscosity increasing agent and the pH was then adjusted to 6.6 using sodium hydroxide aqueous solution. The thus-prepared emulsion was warmed to 49°C and thereto were added 41 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, 150 mg of sensitizing dye A-1, 0.93 mg of chloroauric acid, and 165 mg of potassium thiocyanate. After 15 minutes, 25 mg of 4,7-dithia-1,10-decanediol was added thereto, and 10 minutes later, 2.6 mg of sodium thiosulfate, 0.9 mg of selenium sensitizer A-2, and 1.76 g of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene were added and then the mixture was cooled down quickly and solidified, to prepare an emulsion. Grains in thus prepared silver halide emulsion had a crystal habit of rounded tetradecahedral form and an equivalent spherical diameter of from 0.45 μm to 1.14 μm. The grain size was measured by a Mastersizer.



#### <Preparation of Emulsion Coating Solution and Coating>

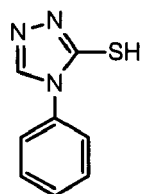
**[0155]** The emulsion coating solution was prepared by adding the following agents in the amounts described below per 1 kg (1.52 mol of silver) of the above emulsion.

Gelatin	38.2 g
Sodium polystyrenesulfonate (weight-average molecular weight of 600,000)	1.4 g
Polyacrylamide (weight-average molecular weight of 45,000)	27.2 g
Compound A-3	24.3 mg
Compound A-4	92.0 mg
Compound A-5	73.5 mg
Compound A-6	105.0 mg
Compound A-7 (BFV)	73.5 mg
Compound A-8 (KMF)	105.0 mg
Palladium chloride	19.9 μmol
1,3-Dihydroxy benzene	1.2 g
1,2-Bis(vinylsulfonyl acetamido)ethane	1.2 g
DV-759L manufactured by Dainippon Ink and Chemicals, Inc. (20% by weight aqueous solution) (mixed latex dispersion of acrylic ester polymer and SiO <sub>2</sub> )	45.0 mL

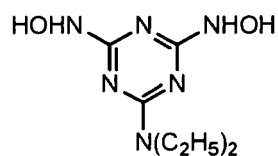
**[0156]** Water was added to give a total amount of 2,400 mL.

**[0157]** This coating solution was coated on both sides of a polyester support having a thickness of 0.18 mm so that the amount of coated silver became 2.2 g/m<sup>2</sup> per one side.

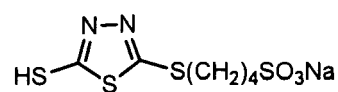
A - 3



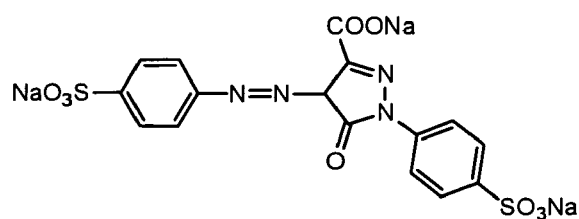
A - 4



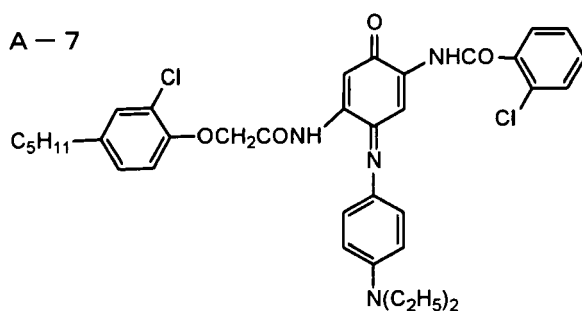
A - 5



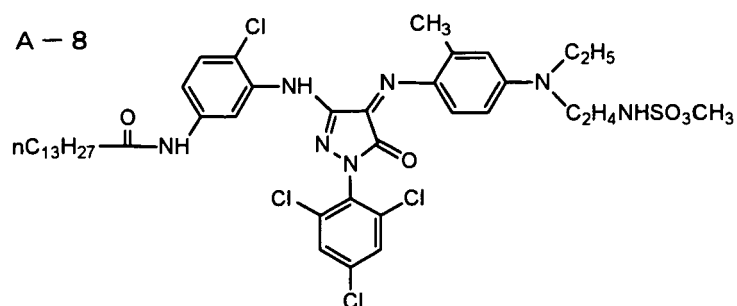
A - 6



A - 7



A - 8



# <Preparations of Coating Solution of Surface Protective Layer and Coating>

**[0158]** The coating solutions for the surface protective layer were prepared by adding the surfactant of the invention or the comparative surfactant as described below. Then, samples were prepared by coating them on both emulsion layer sides at a coating speed of 160 m/second.

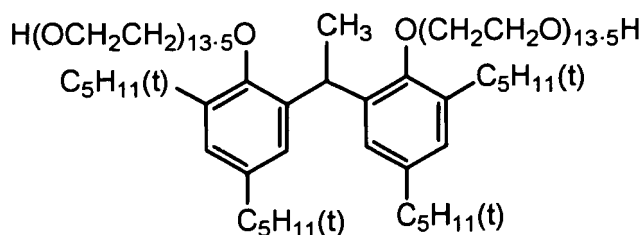
**[0159]** Each component was adjusted to be the coating amount described below, and was coated.

Gelatin	0.78 g/m <sup>2</sup>
Poly(methyl methacrylate) (matting agent, mean particle diameter of 3.7 μm)	46.7 mg/m <sup>2</sup>

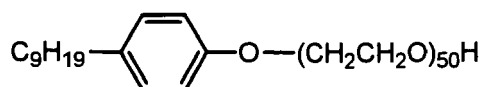
(continued)

Proxel	0.37 mg/m <sup>2</sup>
Sodium polyacrylate (weight-average molecular weight of 40,000)	0.98 mg/m <sup>2</sup>
Surfactant of the invention or comparative surfactant	(See Table 2)
Compound A-9	40.5 mg/m <sup>2</sup>
Compound A-10	2.16 mg/m <sup>2</sup>
Snowtex C manufactured by Nissan Chemical Industries, Ltd. (colloidal silica having a mean particle diameter of about 10 nm)	0.18 g/m <sup>2</sup>

## A - 9



## A - 10



## 2. Performance Evaluation

## &lt;Evaluation of Coated Surface State&gt;

**[0160]** In order to evaluate the coated surface state, a number of coating defects, referred to as repellency, on each sample was counted. The repellency herein means a spot-like defect where the outermost surface protective layer is partially thin or is not coated partially. The obtained samples are evaluated and expressed by a relative value based on the comparative sample when the number of the defects occurred in the comparative sample is taken as 100.

## &lt;Static test&gt;

**[0161]** The coated samples each was cut into a sheet state and stored under an atmosphere of 25°C and 60%RH for a period of one hour, and thereafter contacted with the protection cardboard of the present invention or the comparative protection cardboard. The prepared set was sealed in a sack-shaped material and pressed with a load of 90 g/cm<sup>2</sup>, and left under a condition of 25°C for a period of 3 days while loaded. The samples were evaluated as follows. Hi-SCREEN B-2 (manufactured by Fuji Photo Film Co., Ltd.) was pasted inside of a cassette Fuji EC CASSETTEN (manufactured by Fuji Photo Film Co., Ltd.). Thereafter, the screen was rubbed with fibers under a condition of 25°C and 25%RH, and coated with a cleaner for X-ray intensifying screens manufactured by Fuji Photo Film Co., Ltd. (trade name: Fuji AS cleaner) and acetone or chloroform to remove the film, so that the surface electrostatic voltage of the screen surface was controlled within a range of from 3 kV to 4 kV measured by using an electrostatic voltage measuring apparatus M2 (trade name, available from Shishido Electrostatics Co., Ltd.). And then, the sample of the invention and the comparative sample were set in the cassette prepared above. After being left in a dark condition of 25°C and 25%RH for 30 minutes, the test samples were taken out from the cassette, and developed by using an automatic developing apparatus CEPROS-M2 (trade name, manufactured by Fuji Photo Film Co., Ltd.) with Developer CED-1 (manufactured by Fuji Photo Film Co., Ltd) at 34°C for 25 seconds (total processing time of 90 seconds). As the fixing solution, Fixer CEF-1 (manufactured by Fuji Photo Film Co., Ltd.) was used and water washing was carried out by using tap water.

**[0162]** The static marks occurred in the developed samples prepared above were observed and evaluated according to the following criteria.

Rank:	Standard
1:	Occurrence of static mark was not observed at all.
2:	Occurrence of static mark was observed in a small degree.
3:	Occurrence of static mark was observed in a middle degree.
4:	Occurrence of static mark was observed to a high degree.
5:	Occurrence of static mark was observed almost all over the surface.

**[0163]** Results of the evaluation including the results obtained in other Examples are shown in Table 2.

**[0164]** It can be seen from the results that the use of compounds of the present invention is very effective with respect to decreasing the repelling trouble. Moreover, the use of the protection cardboard of the present invention stabilizes the electrostatic characteristics.

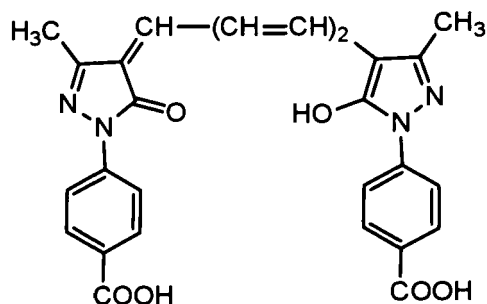
## EXAMPLE 2

### 1. Preparation of Undercoated Support

#### 1) Preparation of Dye D-1 for Undercoat Layer

**[0165]** The following dye was dispersed using a ball mill by the method described in JP-A No. 68-197943.

D - 1

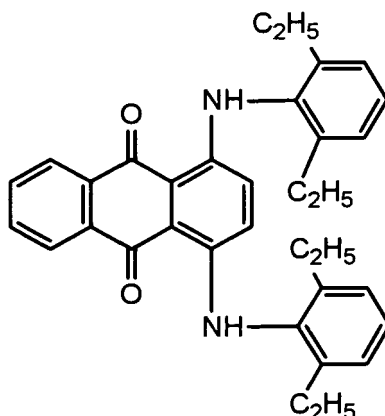


**[0166]** 434 mL of water, 791 mL of a 6.7% by weight aqueous solution of surfactant Triton X-200 were poured into a ball mill of 2 liters. 20 g of the dye was added to the mixture, and then 400 mL of zirconium oxide (ZrO) beads (diameter of 2 mm) was added thereto and the mixture was powdered for 4 days. Thereafter, 160 g of a 12.5% by weight aqueous solution of gelatin was added. After the mixture was subjected to defoaming treatment, ZrO beads were removed by filtration. The observation of the obtained dye dispersion revealed that the dispersion comprised pulverized dyes having a broad particle diameter distribution such as the diameter is from 0.05  $\mu\text{m}$  to 1.15  $\mu\text{m}$  and a mean particle diameter of 0.37  $\mu\text{m}$ . Furthermore, the dye particles having a particle diameter of 0.9  $\mu\text{m}$  or more were removed by centrifugal separation to obtain dispersion D-1.

#### 2) Preparation of Support

**[0167]** The surfaces of the biaxially tented poly(ethylene terephthalate) film having a thickness of 183  $\mu\text{m}$  were subjected to corona discharge treatment. Thereafter, the first undercoat solution comprising the following composition was coated on one surface with a wire bar coater so that the coating amount became 5.1  $\text{mL}/\text{m}^2$ , and dried at 175°C for one minutes. Then, the first undercoat layer was disposed on the opposite side in a similar manner. Poly(ethylene terephthalate) film including 0.04% by weight of dye D-2 having the following structure was used.

## D - 2



## - Composition of First Undercoat Layer -

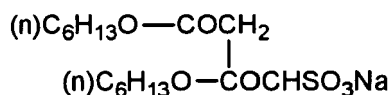
**[0168]** The amount of coating solution was 4.9 mL per 1 m<sup>2</sup> of one side of the support. The coating amount of each additive per 1 m<sup>2</sup> of one side of the support is as follows.

Butadiene-styrene copolymer latex (on the basis of solid content)	0.31 g
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(Note: the latex solution contains compound A-11 having the following structure in an amount of 0.4% by weight with respect to latex solid content as emulsified dispersion)

Sodium salt of 2,4-dichloro-6-hydroxy-s-triazine	8 mg
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## A - 1 1



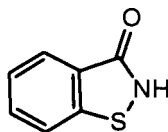
**[0169]** Furthermore, on both sides of the support having thereon the first undercoat layer, a second undercoat solution comprising the following composition was overcoated with a wire bar coater so that the coating amount became the amount described below, and dried at 150°C.

## - Composition of Second Undercoat Layer -

**[0170]** The coating amount of each compound per 1 m<sup>2</sup> on one side is shown below.

Gelatin	81 mg
C <sub>12</sub> H <sub>25</sub> O(CH <sub>2</sub> CH <sub>2</sub> O) <sub>10</sub> H	3.8 mg
A-12	0.28 mg
Matting agent (poly(methyl methacrylate) particles, mean particle diameter of 2.5 μm)	2.3 mg
Polymer latex (ethylacrylate/ acrylic acid (= 95/ 5))	8.2 mg
Dye dispersion D-1	8.2 mg
Acetic acid	0.6 mg

A - 1 2

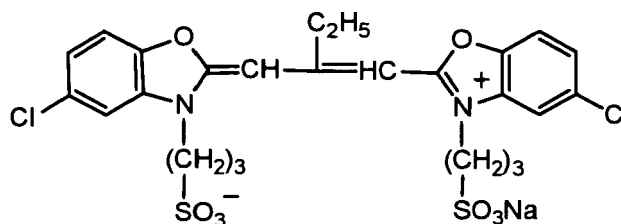


## 2. Preparations of Coating Solution

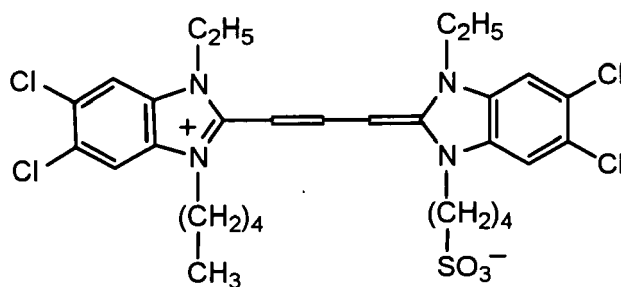
## 1) Preparation of Silver Halide Emulsion T-1

**[0171]** A solution was prepared by adding 6 g of potassium bromide and 7 g of gelatin to 1 liter of water. The solution was kept at 55°C while stirring in a vessel, and thereto were added 37 mL of an aqueous solution containing 4.00 g of silver nitrate and 38 mL of an aqueous solution containing 5.9 g of potassium bromide over 37 seconds by controlled double jet method. After adding 18.6 g of gelatin, the mixture was heated to 70°C and then 89 mL of an aqueous solution containing 9.8 g of silver nitrate was added over 22 minutes. After adding thereto 7 mL of a 25% aqueous solution of ammonia, the mixture was subjected to physical ripening for 10 minutes while keeping the temperature. And then, 6.5 mL of 100% acetic acid solution was added. Successively, an aqueous solution containing 153 g of silver nitrate and an aqueous potassium bromide solution were added over 35 minutes by controlled double jet method while keeping the pAg at 8.5. After the pBr was adjusted to 2.8 using silver nitrate aqueous solution, 15 mL of a 2 mol/L potassium thiocyanate solution was added and the mixture was subjected to physical ripening for 5 minutes, while keeping the temperature, and then cooled down to 35°C. Thereby, monodispersed pure silver bromide tabular grains having a mean projected area equivalent diameter of 1.10  $\mu\text{m}$ , a mean grain thickness of 0.165  $\mu\text{m}$ , and a variation coefficient of a diameter distribution of 18.5% was obtained. Thereafter, soluble salts were removed by sedimentation method. The resulting mixture was warmed again to 40°C, and then, 30 g of gelatin, 2.35 g of phenoxyethanol, and 0.8 g of sodium polystyrenesulfonate as a viscosity increasing agent were added. The pH and pAg were adjusted to 5.90 and 8.25, respectively, using sodium hydroxide solution and silver nitrate solution. This emulsion was subjected to chemical sensitization while stirring and keeping the temperature at 56°C. However, prior to and during the chemical sensitization, fine silver iodide grains were added in an amount of 0.05 mol% per 1 mol of monodispersed pure silver bromide tabular grain. 0.043 mg of thiourea dioxide was added followed by subjecting to reduction sensitization while keeping the state for 22 minutes. And then, 20 mg of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, 400 mg of sensitizing dye A-13, and 2 mg of A-14 were added. Further, 0.83 mg of calcium chloride was added. Successively, 1.5 mg of sodium thiosulfate as a sensitizer, 2.2 mg of A-2, 2.6 mg of chloroauric acid, and 90 mg of potassium thiocyanate were added thereto, and after 40 minutes, the mixture was cooled to 35°C. Thereby, tabular silver halide emulsion T-1 was prepared. Silver halide grains in the obtained silver halide emulsion T-1 had an average iodide content of 0.1 mol%.

A - 1 3



## A - 1 4



## 2) Preparation of Silver Halide Emulsion T-2

**[0172]** Silver halide emulsion T-2 was prepared in a similar manner to the process in the preparation of silver halide emulsion T-1 except that the addition amount of fine silver iodide grains prior to and during the chemical sensitization was changed to 0.5 mol% respectively. Silver halide grains in the obtained silver halide emulsion T-2 had an average iodide content of 1.0 mol%.

## 3) Preparations of Sample

## - Preparation of Coating Solution T-1 for Emulsion Layer -

**[0173]** The coating solution for emulsion layer T-1 was prepared by adding the following compounds to give the coating amount as follows.

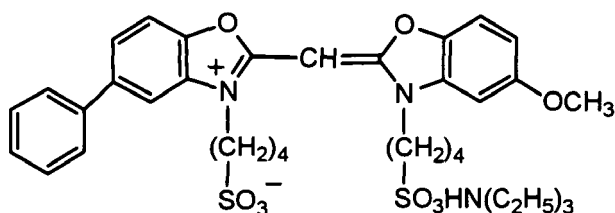
Emulsion T-1 (on the basis of Ag content)	1.09 g/m <sup>2</sup>
Dextran (average molecular weight of 39,000)	0.21 g/m <sup>2</sup>
Sodium polystyrenesulfonate (average molecular weight of 600,000)	19 mg/m <sup>2</sup>
Hardener (1,2-bis(vinylsulfonyl acetamido)ethane)	26 mg/m <sup>2</sup>
A-3	0.2 mg/m <sup>2</sup>
A-4	1.1 mg /m <sup>2</sup>
A-15	4.1 mg/m <sup>2</sup>
A-16	0.1 g/m <sup>2</sup>
A-17	0.02 g/m <sup>2</sup>

## - Preparation of Coating Solution T-2 for Emulsion Layer -

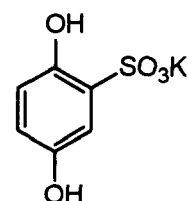
**[0174]** The coating solution for emulsion layer T-2 was prepared by adding the following compounds to give the coating amount as follows.

Emulsion T-2 (on the basis of Ag content)	0.66 g/m <sup>2</sup>
Dextran (average molecular weight of 39,000)	0.13 g/m <sup>2</sup>
Sodium polystyrenesulfonate (average molecular weight of 600,000)	11 mg/m <sup>2</sup>
Hardener (1,2-bis(vinylsulfonyl acetamido)ethane)	27 mg/m <sup>2</sup>
A-3	0.1 mg/ m <sup>2</sup>
A-4	0.6 mg/ m <sup>2</sup>
A-5	0.45 mg/ m <sup>2</sup>
A-7	0.34 g/ m <sup>2</sup>
A-15	1.2 mg/ m <sup>2</sup>
A-16	0.06 g/ m <sup>2</sup>

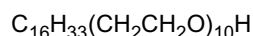
A - 1 5



A - 1 6



A-17



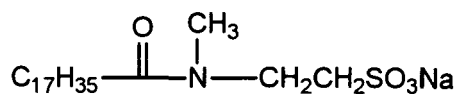
- Preparation of Coating Solution for Surface Protective Layer -

**[0175]** Preparations of the coating solution for surface protective layer using the surfactant of the invention or the comparative surfactant were conducted as follows.

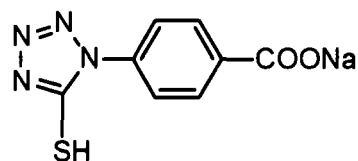
**[0176]** Composition of coating solution for surface protective layer; and coating amount:

Gelatin	0.966 g/ m <sup>2</sup>
Sodium polyacrylate	0.023 g/ m <sup>2</sup>
4-Hydroxy-6-methyl-1,3,3a,7-tetraazaindene	0.015 g/ m <sup>2</sup>
Poly(methyl methacrylate) particles (mean particle diameter of 3.7 μm)	0.087 g/ m <sup>2</sup>
Proxel (the pH being adjusted to 7.4 with sodium hydroxide)	0.5 mg/ m <sup>2</sup>
Surfactant of the invention or comparative surfactant	(See Table 2)
A-17	0.045 g/ m <sup>2</sup>
A-18	6.5 mg/ m <sup>2</sup>
A-19	1.7 mg/ m <sup>2</sup>

A - 1 8



A - 1 9



### 3. Coating

**[0177]** On both sides of the undercoated support prepared above, the coating solutions T-1 and T-2 for the emulsion layer, and the coating solution for the surface protective layer were coated by a simultaneous extruding method at a coating speed of 160 m/second to form emulsion layers and a surface protective layer thereby. The amount of coated silver was 1.75 g/m<sup>2</sup> per one side.

### 4. Performance Evaluation

**[0178]** The obtained samples were evaluated similar to Example 1. Results of the evaluation including the results

obtained in other Examples are shown in Table 2.

[0179] It can be seen from the results that the use of compounds of the present invention is very effective with respect to decreasing the repelling trouble.

[0180] Moreover, the use of the protection cardboard of the present invention stabilizes the electrostatic characteristics.

### EXAMPLE 3

#### 1. Preparations of Sample

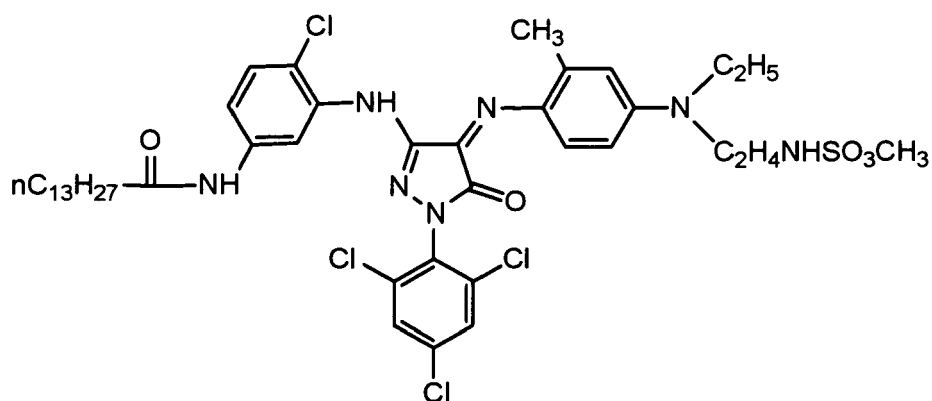
##### <Preparation of Silver Halide Emulsion>

[0181] A liquid was prepared by adding 21 g of gelatin, 10.7 g of ammonium nitrate, 0.3 g of potassium bromide, and 0.07 g of silver nitrate to 1 liter of water. The liquid was kept at 42°C while stirring in a reaction vessel, and thereto were added: an aqueous solution containing 85.7 g of silver nitrate and 0.71 g of ammonium nitrate; and an aqueous solution containing potassium bromide over 19 minutes and 10 seconds by controlled double jet method. After starting the double jet addition, 2.4 mL of a 25% by weight aqueous solution of ammonium was added, and after t minutes, the mixture was neutralized using 0.71 g of glacial acetic acid. Thereafter, an aqueous solution containing 85.7 g of silver nitrate and 0.71 g of ammonium nitrate; and an aqueous solution containing 39.6 g of potassium bromide, 1.17 g of potassium iodide, and 0.52 mg of  $K_3IrCl_6$  were added over 8 minutes and 40 seconds by controlled double jet method. In this step, the time t was adjusted so that the obtained grains had a mean equivalent spherical diameter of 0.21  $\mu m$ . And then, the mixture was cooled to 35°C and soluble salts were removed by sedimentation method. Thereafter, the resulting mixture was heated to 60°C, and thereto were added 156 g of gelatin and 5 g of 2-phenoxyethanol. The pH was adjusted to 6.70 with sodium hydroxide and sulfuric acid. Thereafter, 56 mg of 1-phenyl-mercaptotetrazole, 4.79 mg of sodium thiosulfate, 124 mg of 4,7-dithia-1,10-decanediol, 49.57 mg of  $HAuCl_4$ , and 43.4 mg of potassium thiocyanate were added thereto. After T minutes, 0.91 g of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene was added to the mixture. Then the mixture was cooled down quickly and solidified.

##### <Preparation of coating solution for emulsion layer >

[0182] To the emulsion prepared above in an amount of 1 kg were added 0.2 g of 2,4-dihydroxybenzaldehyde oxime, 0.66 g of potassium bromide, 3.26 g of sodium p-toluenesulfonate, 0.10 g of sodium 3-(5-mercapto-1-tetrazoyl)benzenesulfonate, 28 mg of lipoic acid, 0.8 g of 1,3-hydroxybenzene, 82 mg of 3,4-dimethylthiazoline-2-thione, 21 mg of compound A-7, 6.4 mg of compound I, and 0.60 g of sodium salt of 2,4-dichloro-6-hydroxy-1,3,5-triazine, and then, water was added thereto to give a total volume of 1,043 mL. The prepared solution was coated on a blue colored poly(ethylene terephthalate) support having a thickness of 175  $\mu m$ , which is biaxially tentered and thereafter on which the first undercoat comprising styrene-butadiene (0.3 g/m<sup>2</sup>) and the second undercoat comprising gelatin (0.1 g/m<sup>2</sup>) were conducted, to provide 109 mL/m<sup>2</sup>, and dried. The obtained grains had a crystal habit of cubic form and a mean equivalent spherical diameter of 0.21  $\mu m$ . Concerning the prepared sample, an amount of coated silver was 7.35 g/m<sup>2</sup> and an amount of coated gelatin was 12.0 g/m<sup>2</sup>.

#### Compound I



## &lt;Preparation of Coating Solution for Surface Protective Layer&gt;

**[0183]** To 1 kg of lime-processed gelatin using bovine bone as a raw material (pH 6.0, gelling strength of 260 g, and Ca content of 2,700 ppm) were added 9,865 mL of water, 921 mL of methanol, 28.8 g of PMMA particles (mean particle diameter of 5.5  $\mu\text{m}$ ) as a matting agent, 4.5 g of compound A-9 described above, 0.40 g of FSA-28, and the surfactant of the invention or the comparative surfactant (shown in Table 2), and then the pH was adjusted to 5.1 with phosphoric acid. Thereafter, 209 g (on the basis of solid content) of Voncoat DV-759 (manufactured by Dainippon Ink & Chemicals, Inc.) and 3.56 g of sodium salt of 2,4-dichloro-6-hydroxy-1,3,5-triazine were added thereto. The prepared solution was coated on the emulsion layer so that the amount of coated gelatin became 2.21 g/m<sup>2</sup>, and dried.

## &lt;Coating&gt;

**[0184]** The above emulsion layer and surface protective layer were coated on both sides of the support at a coating speed of 40 m/second so that the amount of coated silver became 7.35 g/m<sup>2</sup> per one side and an amount of coated gelatin became 14.2 g/m<sup>2</sup> per one side. In the case where the emulsion layer and surface protective layer were coated only on one side, the layer described below was coated on the side having no emulsion layer.

## &lt;Preparation of Coating Solution for Back Layer&gt;

**[0185]** To 1 kg of gelatin which is the same as that used in the surface protective layer were added 1 g of Proxel (manufactured by Imperial Chemical Industries), 3.5 g of sodium salt of 2,4-dichloro-6-hydroxy-1,3,5-triazine, 0 mL to 1,514 mL of Snowtex C manufactured by Nissan Chemical Industries, Ltd. (20% by weight liquid, mean particle diameter of 10 nm) and 0 mL to 1500 mL of polymer latex [poly(ethyl acrylate/ methacrylic acid) = 97/ 3] were added, and then water was added to the mixture to give a total amount of 9,730 mL. The prepared solutions were coated to form a single layer or multilayer on the backside of the single-sided coated photosensitive material coated with the emulsion layer and surface protective layer, so that the amount of coated gelatin became of 11 g/m<sup>2</sup>, and dried.

## &lt;Preparation of Coating Solution for Back Surface Protective Layer&gt;

**[0186]** The coating solution for back surface protective layer was prepared using the same additives as those used in the surface protective layer on the emulsion layer side except that the matting agent having a mean particle diameter of 8  $\mu\text{m}$  was used and Snowtex C was added so that the coating amount thereof became 0 g/m<sup>2</sup> to 0.6 g/m<sup>2</sup> on the basis of solid content. The prepared solution was coated to form a single layer or multilayer, so that the amount of coated gelatin became of 1.7 g /m<sup>2</sup>, and dried.

## 2. Performance Evaluation

**[0187]** The obtained samples were evaluated similar to Example 1. Results including the results obtained in other Examples are shown in Table 2. It can be seen from the results that the use of compounds of the present invention is very effective with respect to decreasing the repelling trouble. Moreover, the use of the protection cardboard of the present invention stabilizes the electrostatic characteristics.

## EXAMPLE 4

## 1. Preparations of Sample

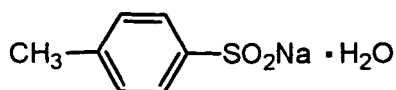
## &lt;Preparation of Silver Halide Emulsion&gt;

## 1) Preparation of Silver Iodobromide Emulsion (O)

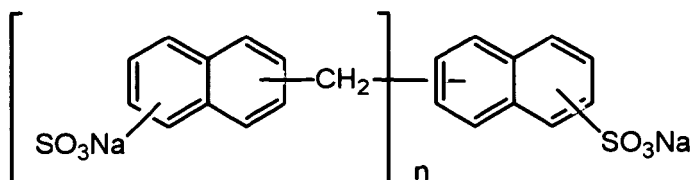
**[0188]** 39 g of gelatin was dissolved in 1 liter of water. This solution was kept at 65°C while stirring in a vessel, and thereto were added 6.4 mg of sodium thiosulfate, 1.3 g of acetic acid, 1.4 g of ammonium hydroxide, 15 mg of silver nitrate, 61 mg of potassium bromide, and 3.8 g of the following compound A. Thereafter, 560 mL of an aqueous solution containing 192 g of silver nitrate and 0.77 g of ammonium nitrate, and 470 mL of an aqueous solution containing potassium hexachloroiridate (III) so that the molar ratio of iridium/ final silver halide became  $2.3 \times 10^{-7}$  and further containing 130 g of potassium bromide were added thereto by controlled double jet method. Thereafter, 0.11 g of potassium iodide was added to obtain cubic monodispersed silver iodobromide grains having a mean grain size of 0.51  $\mu\text{m}$ . Compound B described below was added to the above emulsion, and after desalting treatment, 48 g of gelatin, 0.45 g of sodium

polystyrenesulfonate, and 2.8 g of phenoxyethanol were added thereto, and the pH was adjusted to 6.2. Then, 1.4 mg of sodium thiosulfate and 3.9 mg of chloroauric acid were added followed by subjecting to chemical sensitization at 62°C. After adding 0.38 g of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, the mixture was cooled down quickly and solidified.

Compound A



Compound B



## 2) Preparation of Silver Iodobromide Emulsion (P)

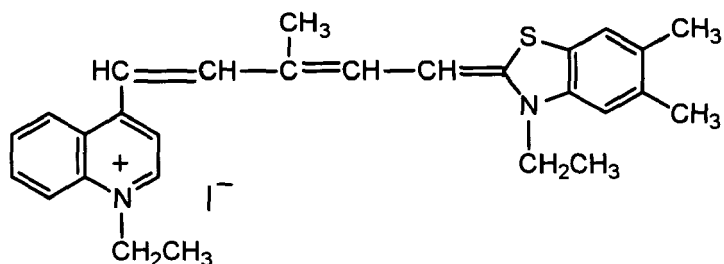
**[0189]** 38 g of gelatin was dissolved in 1 liter of water in a vessel while keeping at 55°C, and thereto were added 6.4 mg of sodium thiosulfate, 1.3 g of acetic acid, 0.80 g of ammonium hydroxide, 6.1 mg of silver nitrate, 61 mg of potassium bromide, and 3.8 g of the above compound A. Thereafter, 590 mL of an aqueous solution containing 190 g of silver nitrate and 0.77 g of ammonium nitrate, and 450 mL of an aqueous solution containing potassium hexachloroiridate (III) so that the molar ratio of iridium/ final silver halide became  $9.0 \times 10^{-7}$  and further containing 130 g of potassium bromide were added by controlled double jet method. Thereafter, 0.14 g of potassium iodide was added to obtain cubic mono-dispersed silver iodobromide grains having a mean grain size of 0.36  $\mu\text{m}$ . To the above emulsion, sodium polystyrenesulfonate having an average molecular weight of 50,000 was added, and after desalting treatment, 48 g of gelatin, 0.14 g of nucleic acid base mixture, 0.16 g of potassium bromide, and 2.2 g of phenoxyethanol were added and the pH was adjusted to 6.0. Then, 4.1 mg of sodium thiosulfate and 7.4 mg of chloroauric acid were added followed by subjecting to chemical sensitization at 60°C. After adding 0.37 g of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene, the mixture was cooled down quickly and solidified.

## 3) Preparation of Coating Solution for Emulsion layer

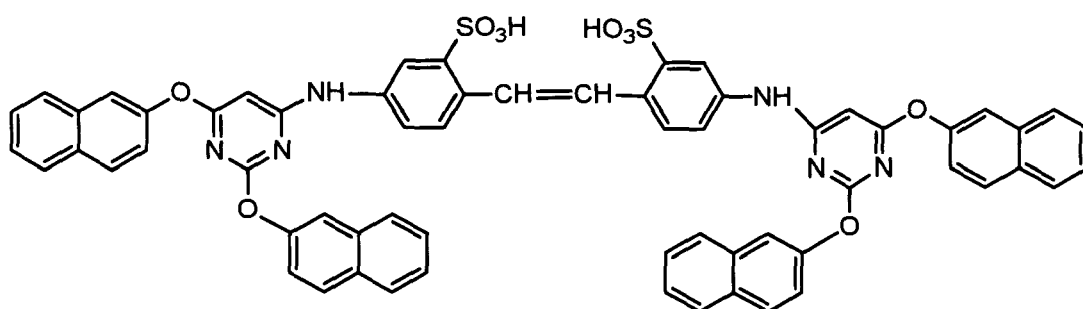
**[0190]** The coating solution was prepared by mixing the emulsion (O) and the emulsion (P) to give a silver halide molar ratio of 1/ 2.1 and adding the following additives in the amount described below per 1 mol of silver halide.

Spectral sensitizing dye (D-1)	$3.6 \times 10^{-5}$ mol
Super sensitizer (Compound D)	$1.5 \times 10^{-4}$ mol
3-Allyl-2,6-dimethylbenzothiazolium bromide	$5.7 \times 10^{-4}$ mol
Compound E	$2.5 \times 10^{-4}$ mol
Polyacrylamide (molecular weight of 40,000 to 50,000)	9.3 g
Poly(ethylacrylate/ methacrylic acid) latex	1.8 g
1,2-Bis(vinylsulfonyl acetamido)ethane	1.8 g
1,3-Bis(vinylsulfonyl acetamido)propane	0.59 g

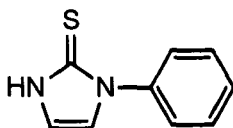
## Spectral sensitizing dye D-1



## Compound D



## Compound E



## 4) Preparation of Coating Solution for Emulsion Surface Protective Layer

**[0191]** The vessel was warmed to 65°C and the coating solution for the emulsion surface protective layer was prepared by adding the following additives according to the following composition.

<Formula of Coating Solution for Surface Protective Layer>

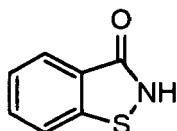
**[0192]**

a) Gelatin	100 g
b) Polyacrylamide (molecular weight of 40,000 to 50,000)	12 g
c) Sodium polystyrenesulfonate	0.15 g
d) 1,2-Bis(vinylsulfonyl acetamido)ethane	1.4 g
e) 1,3-Bis(vinylsulfonyl acetamido)propane	0.46 g
f) Poly(methyl methacrylate) particles (mean particle diameter of 2.8 μm)	2.6 g
g) Poly(methyl methacrylate) particles (mean particle diameter of 0.7 μm)	3.0 g
h) Surfactant of the inventive or comparative surfactant	(See Table 2)

(continued)

i) $C_{16}H_{33}O-(CH_2CH_2O)_{10}-H$	3.3 g
j) Sodium polyacrylate (molecular weight of about 100,000)	3.7 g
k) Sodium hydroxide (1N)	3 mL
l) Methanol	78 mL
m) Compound G	52 mg

### Compound G



#### 5) Preparation of Coating Solution for Back Layer

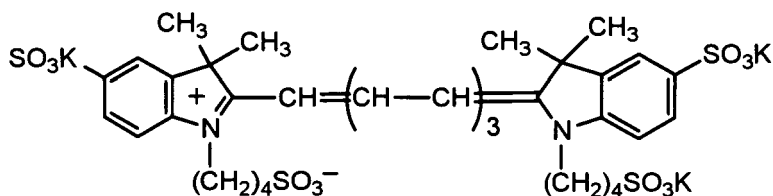
**[0193]** The vessel for preparing the coating solution for back layer was heated to 65°C and the following additives according to the following composition were added thereto, to obtain the coating solution for the back layer.

<Formula of Coating Solution for Back Layer>

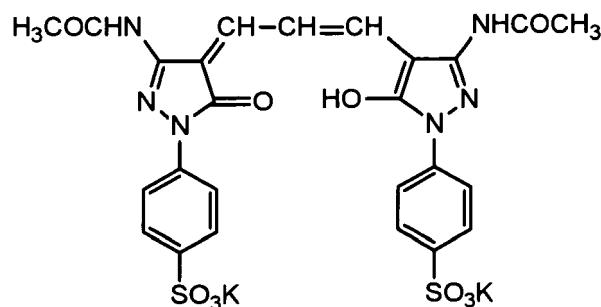
#### [0194]

a) Gelatin	100 g
b) Antihalation dye (Compound H)	2.3 g
c) Sodium polystyrenesulfonate	1.7 g
d) Poly(ethyl acrylate/methacrylic acid) latex	3.3 g
e) 1,2-Bis(vinylsulfonyl acetamido)ethane	2.5 g
f) 1,3-Bis(vinylsulfonyl acetamido)propane	0.84 g
g) Compound G	45 mg
h) A-7	0.28 g
i) Compound J	84 mg
j) Phosphoric acid	0.40 g

### Compound H



## Compound J



## 6) Preparation of Coating Solution for Back Surface Protective Layer

**[0195]** The vessel for preparing the coating solution for back surface protective layer was warmed to 65°C and the following additives according to the following composition were added thereto, to obtain the coating solution for the back surface protective layer.

<Formula of Coating Solution for Back Surface Protective Layer>

**[0196]**

a) Gelatin	100 g
b) Sodium polystyrenesulfonate	0.3 g
c) 1,2-Bis(vinylsulfonyl acetamido)ethane	1.3 g
d) 1,3-Bis(vinylsulfonyl acetamido)propane	0.43 g
e) Poly(methyl methacrylate) particles (mean particle diameter of 5.8 μm)	3.3 g
f) Surfactant of the inventive or comparative surfactant	(See Table 2)
g) C <sub>16</sub> HH <sub>33</sub> O-(CH <sub>2</sub> CH <sub>2</sub> O) <sub>10</sub> -H	2.9 g
h) Sodium polyacrylate (molecular weight of about 100,000)	1.3 g
i) Sodium hydroxide (1N)	7 mL
j) Methanol	110 mL
k) Compound G	45 mg

## 7) Coating

**[0197]** The coating solution for the back layer and the back surface protective layer prepared above were coated on one side of the poly(ethylene terephthalate) support at a coating speed of 160 m/second so that: the coating solution for the back layer gave the coating amount of gelatin of 2.4 g/m<sup>2</sup>; the coating solution for the back surface protective layer gave the coating amount of gelatin of 1.4 g/m<sup>2</sup>; and so that the total amount of gelatin became 3.8 g/m<sup>2</sup>. Successively, the coating solution for the emulsion layer and the surface protective layer were coated on the opposite side of the support so that the coating solution for the emulsion layer gave the coating amount of silver of 2.8 g/m<sup>2</sup> and so that the coating solution for the surface protective layer gave the coating amount of gelatin of 1.2 g/m<sup>2</sup>.

## 2. Performance Evaluation

**[0198]** The obtained samples were evaluated similar to Example 1. Results including the results obtained in other Examples are shown in Table 2. It can be seen from the results that the use of compounds of the present invention is very effective with regard to decreasing the repelling trouble. Moreover, the use of the protection cardboard of the present invention stabilizes the electrostatic characteristics.

## EXAMPLE 5

## 1. Preparations of Sample

## (Preparation of Silver Halide Emulsion A-1)

**[0199]** 1,178 mL of an aqueous solution containing 0.8 g of potassium bromide and 3.2 g of acid-processed gelatin having an average molecular weight of 20,000 were stirred while keeping the temperature at 35°C. Thereafter, an aqueous solution containing 1.6 g of silver nitrate, an aqueous solution containing 1.16 g of potassium bromide, and an aqueous solution containing 1.1 g of acid-processed gelatin having an average molecular weight of 20,000 were added thereto by triple jet method over 45 seconds. The concentration of the silver nitrate solution was 0.3 mol/L. Thereafter, the mixture was heated to 75°C over 20 minutes, and 26 g of gelatin having an average molecular weight of 100,000 was added thereto. Then, an aqueous solution containing 209 g of silver nitrate and an aqueous solution comprising 99.9 mol% of potassium bromide and 0.1 mol% of potassium iodide were added by controlled double jet method in an accelerated flow rate over 75 minutes while keeping the pAg at 8.5. After adding gelatin having an average molecular weight of 100,000, the mixture was subjected to desalting treatment by the conventional way. Thereafter the mixture was dispersed by adding gelatin having an average molecular weight of 100,000, and the pH and pAg was adjusted to 5.8 and 8.0 at 40°C respectively, to obtain an emulsion. The obtained emulsion contained 1 mol of silver and 60 g of gelatin, per 1 kg of the emulsion. Grains in thus prepared silver halide emulsion were tabular grains having a mean equivalent circular diameter of 1.5  $\mu\text{m}$ , a variation coefficient of an equivalent circular diameter distribution of 22%, a mean grain thickness of 0.10  $\mu\text{m}$ , and a mean aspect ratio of 15.

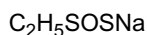
## (Preparation of Silver Halide Emulsion B-1)

**[0200]** 1,178 mL of an aqueous solution containing 0.8 g of potassium bromide and 1 g of gelatin having an average molecular weight of 20,000 were stirred while keeping the temperature at 35°C. Thereafter, an aqueous solution containing 0.74 g of silver nitrate and an aqueous solution containing 0.54 g of potassium bromide were added thereto by controlled double jet method over 45 seconds. The concentration of the silver nitrate solution was 0.2 mol/L. Thereafter, the mixture was heated to 68°C over 30 minutes and 13 g of succinated gelatin having an average molecular weight of 100,000 was added thereto. Thereafter, an aqueous solution containing 237 g of silver nitrate and an aqueous solution of potassium bromide were added by controlled double jet method in an accelerated flow rate over 45 minutes while keeping the pAg at 8.5. After adding gelatin having an average molecular weight of 100,000, the mixture was subjected to desalting treatment by the conventional way. Thereafter the mixture was dispersed by adding gelatin having an average molecular weight of 100,000, and the pH and pAg was adjusted to 5.8 and 8.0 at 40°C respectively, to obtain an emulsion. The obtained emulsion contained 1 mol of silver and 60 g of gelatin per 1 kg of the emulsion. Grains in thus prepared silver halide emulsion were tabular grains having a mean equivalent circular diameter of 2.0  $\mu\text{m}$ , a variation coefficient of an equivalent circular diameter distribution of 30%, a mean grain thickness of 0.09  $\mu\text{m}$ , and a mean aspect ratio of 22.

## (Chemical Sensitization)

**[0201]** Thus prepared emulsions each was stirred and subjected to chemical sensitization, while keeping the temperature at 52°C. At first, thiosulfonic acid compound-1 was added in an amount of  $7 \times 10^{-5}$  mol per 1 mol of silver halide, sequentially fine silver iodide grains having a mean diameter of 0.03  $\mu\text{m}$  were added in an amount of 0.15 mol% with respect to total amount of silver. Thereafter, potassium thiocyanate was added in an amount of  $6 \times 10^{-4}$  mol equivalent per 1 mol of silver halide, and then A-13 in an amount of  $1 \times 10^{-3}$  mol equivalent per 1 mol of silver halide and A-14 solution in an amount of  $3 \times 10^{-6}$  mol equivalent per 1 mol of silver halide were added, and further, calcium chloride was added thereto. Thereafter, a solution of A-15 described below was added in an amount of  $2 \times 10^{-4}$  mol equivalent per 1 mol of silver halide. Successively, aurochloric acid in an amount of  $2 \times 10^{-5}$  mol equivalent per 1 mol of silver halide and potassium thiocyanate in an amount of  $6 \times 10^{-4}$  mol equivalent per 1 mol of silver halide were added, and then, sodium thiosulfate in an amount of  $1 \times 10^{-5}$  mol equivalent per 1 mol of silver halide and selenium sensitizer A-2 in an amount of  $4 \times 10^{-6}$  mol equivalent per 1 mol of silver halide were added thereto. 60 minutes later, the resulting mixture was cooled to 35°C and thereby the chemical sensitization of the emulsion was finished.

Thiosulfonic acid compound-1



(Preparation of Coating Solution for Emulsion Layer)

**[0202]** Each compound was added to the emulsion to give the following coating amount.

5		<Coating amount per 1 m <sup>2</sup> of one side>
	Amount of coated silver	1.30 g
	Gelatin	1.20 g
	Sodium polystyrenesulfonate (average molecular weight of 600,000)	39 mg
10	A-3	0.22 mg
	A-4	1.6 mg
	A-15	3.7 mg
	A-16	143 mg
	D-2 (on the basis of solid content)	19.7 mg
15	1,2-Bis (vinylsulfonyl acetamido)ethane	60 mg

**[0203]** At this time, the amount of the coating solution was 50.5 mL per 1 m<sup>2</sup> of one side.

20 (Preparation of Coating Solution for Surface Protective Layer)

**[0204]** Each compound was added to give the following coating amount.

		<Coating amount per 1 m <sup>2</sup> of one side>
25	Gelatin	0.767 g
	Sodium polyacrylate (average molecular weight of 400,000)	26 mg
	Sodium polystyrenesulfonate (average molecular weight of 600,000)	0.9 mg
	Poly(methyl methacrylate) particles (mean particle diameter of 3.7 μm) (on the basis of solid content)	70 mg
30	A-17	34.6 mg
	A-18	6.8 mg
	A-19	2.1 mg
	A-5	0.5 mg
	Surfactant of the invention or comparative surfactant	(See Table 2)
35	Antiseptic G	0.9 mg
	p-Benzoquinone	0.7 mg

40 **[0205]** The pH of the coating solution for surface protective layer was adjusted to 6.6 using a small quantity of sodium hydroxide. The amount of the coating solution was 9.4 mL per 1 m<sup>2</sup> of one side.

(Coating)

45 **[0206]** On both surfaces of the undercoated support prepared in Example 2, simultaneous coating by an extruding method was subjected in order of the emulsion layer and surface protective layer from the support side, at a coating speed of 160 m/second, and dried at 185°C.

## 2. Performance Evaluation

50 **[0207]** The obtained samples were evaluated similar to Example 1. Results including the results obtained in other Example are shown in Table 2. It can be seen from the results that the use of compounds of the present invention is very effective with respect to decreasing the repelling trouble. Moreover, the use of the protection cardboard of the present invention stabilizes the electrostatic characteristics.

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## EXAMPLE 6

## 1. Preparations of Silver Halide Photosensitive Material

**[0208]** Silver halide photosensitive material Nos. 6-1 to 6-7 were prepared similar to Example 2 except that the surfactants added in the surface protective layer were changed to the compound shown in the following Table

1. The addition amounts thereof are shown in Table 1.

## 2. Preparations of Protection Cardboard

**[0209]** NBKP (Nadelholz Bleached Kraft Pulp) pulp made from conifers and LBKP (Laubholz Bleached Kraft Pulp) pulp made from broad-leaved trees were mixed in a ratio of 50% by weight/ 50% by weight and beaten. An acrylamido type paper power enhancer was added to the virgin pulp prepared above and then alkylketene dimer and cationic starch were added thereto and mixed to form a paper having triple-layered structure. Thus prepared paper was dewatered by a press roller and dried so that the surface temperature became from 120°C to 150°C and the moisture content became from 2% by weight to 3% by weight.

## 1) Protection Cardboard A

**[0210]** Sequentially, poly(vinyl alcohol) was coated on the prepared paper surface so that the coating amount thereof became 0.24 g/m<sup>2</sup>. Thereby, the protection cardboard having a moisture content of from 7% by weight to 8% by weight of the present invention was prepared.

## 2) Protection Cardboard C (Comparative)

**[0211]** The comparative protection cardboard having a moisture content of from 7% by weight to 8% by weight without any overcoat was prepared.

## 3. Performance Evaluation

## 1) Preparations of Sample for Measurement

**[0212]** The prepared photosensitive materials each were stored under an atmosphere of 25°C and 60%RH for a period of 1 hour, and then samples for measurement were prepared as follows.

Sample a: Simple photosensitive material;

Sample b: the photosensitive material was contacted with the protection cardboard A of the present invention. And then the combined set was sealed in a sack-shaped material and left at 25°C for 3 days with a load of 90 g/cm<sup>2</sup>. Thereafter, the photosensitive material was taken out;

Sample c: the photosensitive material was contacted with the comparative protection cardboard C. And then the combined set was sealed in a sack-shaped material and left at 25°C for 3 days with a load of 90 g/cm<sup>2</sup>. Thereafter, the photosensitive material was taken out.

## 2) Measurement of Surface Resistance

**[0213]** The above samples were conditioned at 25°C and 25%RH for 1 hour. The surface resistance (log SR) of the sample was measured by using R12704 (trade name, available from Advantest Co. Ltd.) while loading voltage thereon for 50 seconds.

**[0214]** Results are shown in Table 1. The smaller is the log SR value, the shorter is the time period for electric leakage, and namely the slower is the discharge.

TABLE 1

Sample No.	Coated Compound						LogSR (contacted)		
	Coating amount (mg/m <sup>2</sup> )						Sample a	Sample b	Sample c
6-1	WO-1 1.42	WO-3 3.11	WE-1 17.5	-	-	-	12.5	13.0	12.6
	Compound 1	Compound 2	Compound 3	Compound 4	Compound 5	Compound 6			
6-2	FS-1 1.14	WS-20 17.5	-	-	FS-104 4.67	-	12.1	12.8	12.3
6-3	FS-1 1.14	WS-20 14.2	WT-13 7.4	-	FS-104 4.67	-	12.3	12.9	12.5
6-4	FS-1 1.14	WS-20 14.2	-	WH-5, 13 4.4, 3.0	FS-104 4.67	-	12.7	13.3	12.9
6-5	FS-1 1.14	WS-20 14.2	WT-7 8.9	-	FS-104 4.67	-	12.4	12.9	12.5
6-6	-	WS-45 13.5	WT-13 7.4	-	-	1-50 4.67	12.4	12.7	12.5
6-7	FS-1 1.14	WS-45 13.5	WT-13 7.4	-	FS-105 4.67	-	12.2	12.8	12.4

**[0215]** While the difference in log SR between sample a, which is a simple photosensitive material, and sample b, which is the case of contacting with the protection cardboard C, was from 0.3 to 0.7, the difference in log SR between sample a and sample c, which is the case of contacting with the protection cardboard A, was smaller and was from 0.1 to 0.2. Namely, the use of a packaging material whose surface is coated with an organic compound of the present invention can depress the variation of surface resistances of the photosensitive material, which is contacted with the protection cardboard.

**[0216]** The surfactants used for comparison are shown below.

WE-1 :	$C_8H_{17}-C_6H_4-O(CH_2CH_2O)_nCH_2CH_2SO_3Na$	n=3 in average
WO-1 :	$C_8F_{17}SO_2N(C_3H_7)(CH_2CH_2O)_n(CH_2)_4SO_3Na$	n=5 in average
WO-2 :	$C_8F_{17}SO_3K$	
WO-3 :	$C_8F_{17}SO_2N(C_3H_7)(CH_2CH_2O)_nH$	n=15 in average

TABLE 2

Sample No.	Coated Side	Comparative Compound			Compound of the Invention					Repellency	Static Test	
					Compound 1	Compound 2	Compound 3	Compound 4	Compound 5		Protection Cardboard C	Protection Cardboard A
Comparative 1-1	Emulsion layer side	WO-1	WO-3	WE-1						100	4	3
Comparative 1-2	Emulsion layer side				FS-1	WS-20				256		
Invention 1-1	Emulsion layer side				FS-1	WS-20	WT-13		FS-104	32	5	2
Invention 1-2	Emulsion layer side				FS-1	WS-20		WH-5,13	FS-104	44	4	2
Comparative 2-1	Emulsion layer side	WO-1	WO-3	WE-1						100	4	4
Comparative 2-2	Emulsion layer side	FS-1				WS-20				231		
Comparative 2-3	Emulsion layer side				FS-7	WS-45				195		
Invention 2-1	Emulsion layer side	FS-1				WS-20	WT-13		FS-104	10	5	2
Invention 2-2	Emulsion layer side				FS-1	WS-20		WH-5,13	FS-104	22		41
Invention 2-3	Emulsion layer side				FS-1	WS-20	WT-7		FS-104	15	4	2
Invention 2-4	Emulsion layer side				FS-7	WS-20	WT-7		FS-104	12	5	2
Comparative 3	Emulsion layer side	WO-1		WE-1						100	3	4
Invention 3-1	Emulsion layer side				FS-1	WS-20		WH-5.13		46	4	2

(continued)

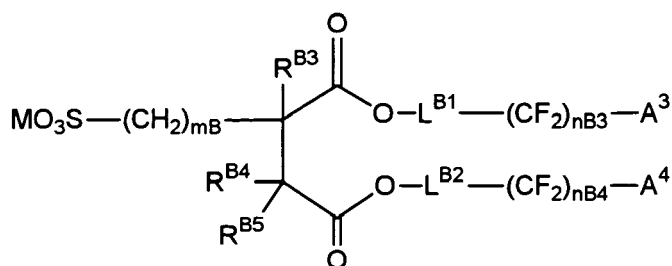
Sample No.	Coated Side	Comparative Compound			Compound of the Invention					Repellency	Static Test	
					Compound 1	Compound 2	Compound 3	Compound 4	Compound 5		Protection Cardboard C	Protection Cardboard A
Invention 3-2	Emulsion layer side				FS-1	WS-20		WH-5. 13		46	4	2
Invention 3-2	Back side				FS-1	WS-20		WH-5, 13		37	3	2
Invention 3-3	Emulsion layer side				FS-1	WS-20	WT-13		FS-1 04	32	4	1
Invention 3-4	Emulsion layer side				FS-1	WS-20	WT-7			29	3	1
Comparative 4	Emulsion layer side	WO-1	WO-2	WE-1						100	3	2
Comparative 4	Back side	WO-1	WO-2	WE-1						100	3	3
Invention 4-1	Emulsion layer side				FS-1	WS-20	WT-13			21	4	1
Invention 4-1	Back side				FS-1	WS-20	WT-13			12	3	1
Comparative 5	Emulsion layer side	WO-1	WQ-3	WE-1						100	4	3
Invention 5-1	Emulsion layer side				FS-1	WS-20	WT-13		FS-104	32	4	2
Invention 5-2	Emulsion tayer side				FS-7	WS-20	WT-13		FS-104	25	5	2
Invention 5-3	Emulsion tayer side				FS-7	WS-20	WT-7		FS-104	17	4	1
Invention 5-4	Emulsion layer side				FS-7	WS-45	WT-7		FS-104	26	4	1
Invention 5-8	Emulsion layer side				FS-7	WS-20		WH-8, 17	FS-104	27	4	2

- [0217] The coating amount of each compound described in Table 2 is as follows.
- [0218] (Comparative 1) WO-1: 1.72 mg/m<sup>2</sup>; WO-3: 1.48 mg/m<sup>2</sup>; WE-1: 4.85 mg/m<sup>2</sup>.
- [0219] (Invention 1-1) FS-1: 1.38 mg/m<sup>2</sup>; WS-20: 3.88 mg/m<sup>2</sup>; WT-13: 2.1 mg/m<sup>2</sup>; FS-104: 2.22 mg/m<sup>2</sup>.
- [0220] (Invention 1-2) FS-1: 1.38 mg/m<sup>2</sup>; WS-20: 3.88 mg/m<sup>2</sup>; WH-5: 1.3 mg/m<sup>2</sup>; WH-13: 0.8 mg/m<sup>2</sup>; FS-104: 2.22 mg/m<sup>2</sup>.
- [0221] (Comparative 2) WO-1: 1.42 mg/m<sup>2</sup>; WO-3: 3.11 mg/m<sup>2</sup>; WE-1: 17.5 mg/m<sup>2</sup>.
- [0222] (Invention 2-1) FS-1: 1.14 mg/m<sup>2</sup>; WS-20: 14.2 mg/m<sup>2</sup>; WT-13: 7.4 mg/m<sup>2</sup>; FS-104: 4.67 mg/m<sup>2</sup>.
- [0223] (Invention 2-2) FS-1: 1.14 mg/m<sup>2</sup>; WS-20: 14.2 mg/m<sup>2</sup>; WH-5: 4.4 mg/m<sup>2</sup>; WH-13: 3.0 mg/m<sup>2</sup>; FS-104: 4.67 mg/m<sup>2</sup>.
- [0224] (Invention 2-3) FS-1: 1.14 mg/m<sup>2</sup>; WS-20: 14.2 mg/m<sup>2</sup>; WT-7: 8.9 mg/m<sup>2</sup>; FS-104: 4.67 mg/m<sup>2</sup>.
- [0225] (Invention 2-4) FS-7: 0.97 mg/m<sup>2</sup>; WS-20: 14.2 mg/m<sup>2</sup>; WT-7: 8.9 mg/m<sup>2</sup>; FS-104: 4.67 mg/m<sup>2</sup>.
- [0226] (Comparative 3) WO-1: 3.42 mg/m<sup>2</sup>; WE-1: 73.4 mg/m<sup>2</sup>.
- [0227] (Invention 3-1, 3-2) FS-1: 2.74 mg/m<sup>2</sup>; WS-20: 58.7 mg/m<sup>2</sup>; WH-5: 18.7 mg/m<sup>2</sup>; WH-13: 12.5 mg/m<sup>2</sup>.
- [0228] (Invention 3-2 (Back side)) FS-1: 2.06 mg/m<sup>2</sup>; WS-20: 44.2 mg/m<sup>2</sup>; WH-5: 14.1 mg/m<sup>2</sup>; WH-13: 9.4 mg/m<sup>2</sup>.
- [0229] (Invention 3-3) FS-1: 2.74 mg/m<sup>2</sup>; WS-20: 58.7 mg/m<sup>2</sup>; FS-104: 8.22 mg/m<sup>2</sup>.
- [0230] (Invention 3-4) FS-1: 2.74 mg/m<sup>2</sup>; WS-20: 58.7 mg/m<sup>2</sup>; WT-7: 31 mg/m<sup>2</sup>.
- [0231] (Comparative 4 (Emulsion layer side)) WO-1: 0.95 mg/m<sup>2</sup>; WO-2: 0.7 mg/m<sup>2</sup>; WE-1: 17.2 mg/m<sup>2</sup>.
- [0232] (Comparative 4 (Back side)) WO-1: 0.81 mg/m<sup>2</sup>; WO-2: 0.5 mg/m<sup>2</sup>; WE-1: 20.2 mg/m<sup>2</sup>.
- [0233] (Invention 4-1 (Emulsion layer side)) FS-1: 0.52 mg/m<sup>2</sup>; WS-20: 17.2 mg/m<sup>2</sup>; WT-13: 10.4 mg/m<sup>2</sup>.
- [0234] (Invention 4-1 (Back side)) FS-1: 0.64 mg/m<sup>2</sup>; WS-20: 20.2 mg/m<sup>2</sup>; WT-13: 9.1 mg/m<sup>2</sup>.
- [0235] (Comparative 5) WO-1: 1.22 mg/m<sup>2</sup>; WO-3: 3.18 mg/m<sup>2</sup>; WE-1: 17.8 mg/m<sup>2</sup>.
- [0236] (Invention 5-1) FS-1: 1.64 mg/m<sup>2</sup>; WS-20: 14.2 mg/m<sup>2</sup>; WT-13: 9.1 mg/m<sup>2</sup>; FS-104: 5.56 mg/m<sup>2</sup>.
- [0237] (Invention 5-2) FS-7: 1.39 mg/m<sup>2</sup>; WS-20: 14.2 mg/m<sup>2</sup>; WT-13: 9.1 mg/m<sup>2</sup>; FS-104: 5.56 mg/m<sup>2</sup>.
- [0238] (Invention 5-3) FS-7: 1.39 mg/m<sup>2</sup>; WS-20: 14.2 mg/m<sup>2</sup>; WT-7: 10.9 mg/m<sup>2</sup>; FS-104: 5.56 mg/m<sup>2</sup>.
- [0239] (Invention 5-4) FS-7: 1.39 mg/m<sup>2</sup>; WS-45: 13.5 mg/m<sup>2</sup>; WT-7: 10.9 mg/m<sup>2</sup>; FS-104: 5.56 mg/m<sup>2</sup>.
- [0240] (Invention 5-5) WS-45: 13.5 mg/m<sup>2</sup>; WH-5: 14.1 mg/m<sup>2</sup>; WH-13: 9.4 mg/m<sup>2</sup>; 1-50: 2.5 mg/m<sup>2</sup>.
- [0241] (Invention 5-6) WS-45: 13.5 mg/m<sup>2</sup>; WT-13: 12.8 mg/m<sup>2</sup>; 1-73: 2.5 mg/m<sup>2</sup>.
- [0242] (Invention 5-7) WS-45: 13.5 mg/m<sup>2</sup>; WT-7: 14.1 mg/m<sup>2</sup>; 2-20: 2.3 mg/m<sup>2</sup>.
- [0243] (Invention 5-8) FS-7: 1.39 mg/m<sup>2</sup>; WS-45: 13.5 mg/m<sup>2</sup>; WH-8: 14.1 mg/m<sup>2</sup>; WH-17: 9.4 mg/m<sup>2</sup>; FS-104: 5.56 mg/m<sup>2</sup>.

## Claims

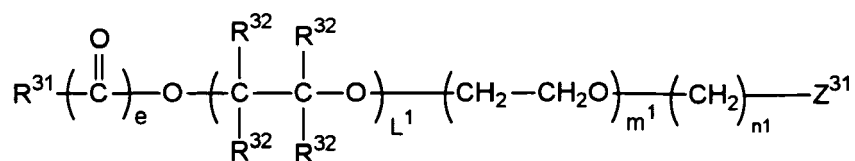
1. A silver halide photosensitive material comprising, on at least one side of a transparent support, at least one photosensitive silver halide emulsion layer, and containing an anionic fluorocarbon compound represented by the following formula (1), an anionic hydrocarbon compound represented by the following formula (2), and at least one of an anionic hydrocarbon compound represented by the following formula (3) or an anionic hydrocarbon compound represented by the following formula (4):

Formula (1)



wherein R<sup>B3</sup>, R<sup>B4</sup>, and R<sup>B5</sup> each independently represent a hydrogen atom or a substituent; A<sup>3</sup> and A<sup>4</sup> each independently represent a fluorine atom or a hydrogen atom; nB3 and nB4 each independently represent an integer of from 4 to 8; L<sup>B1</sup> and L<sup>B2</sup> each independently represent an alkylene group, an alkyleneoxy group, or a divalent linking group formed by combining groups selected from among these groups; mB represents 0 or 1; and M represents a cation;

## Formula (2)

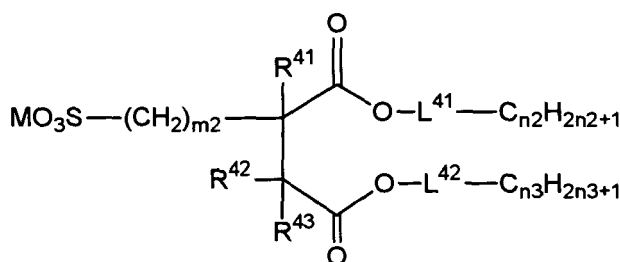


wherein  $R^{31}$  represents an alkyl group or alkenyl group having 6 to 25 carbon atoms;  $R^{32}$ s may be identical or different from one another and each represent a hydrogen atom, an alkyl group having 1 to 14 carbon atoms, an alkenyl group having 1 to 14 carbon atoms, an aralkyl group having 7 to 20 carbon atoms, or an aryl group having 6 to 18 carbon atoms;  $L^1$  represents an integer of from 0 to 10;  $m^1$  represents an integer of from 0 to 30;  $n^1$  represents an integer of from 0 to 4;  $L^1$  and  $m^1$  do not simultaneously represent 0;  $e$  represents 0 or 1;  $Z^{31}$  represents an  $\text{OSO}_3\text{M}$  group or an  $\text{SO}_3\text{M}$  group; and  $\text{M}$  represents a cation;

Formula (3)  $R^3 \text{-(L}^3\text{)}_b \text{-Z}^3$ 

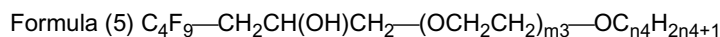
wherein  $R^3$  represents an alkyl group, alkylene group, or aralkyl group having 6 to 24 carbon atoms;  $L^3$  represents an alkylene group having a hydroxy group and 3 to 5 carbon atoms, a vinylene group, a vinylenealkylene group, or a divalent linking group formed by combining groups selected from among these groups;  $b$  represents 0 or 1;  $Z^3$  represents an  $\text{OSO}_3\text{M}$  group or an  $\text{SO}_3\text{M}$  group; and  $\text{M}$  represents a cation; and

## Formula (4)



wherein  $R^{41}$ ,  $R^{42}$ , and  $R^{43}$  each independently represent a hydrogen atom or a substituent;  $n_2$  and  $n_3$  each independently represent an integer of from 1 to 5;  $L^{41}$  and  $L^{42}$  each independently represent an alkylene group having no fluorine atoms, an alkyleneoxy group, or a divalent linking group formed by combining groups selected from among these groups;  $m_2$  represents 0 or 1; and  $\text{M}$  represents a cation.

2. The silver halide photosensitive material according to claim 1, wherein, in formula (3),  $L^3$  is an alkylene group having a hydroxy group and 3 to 5 carbon atoms.
3. The silver halide photosensitive material according to claim 1, wherein, in formula (3),  $L^3$  is a vinylenealkylene group.
4. The silver halide photosensitive material according to claim 1, wherein, in formula (3),  $L^3$  is a divalent linking group formed by combining an alkylene group and a vinylene group.
5. The silver halide photosensitive material according to claim 1, wherein the silver halide photosensitive material further contains a nonionic fluorocarbon compound represented by the following formula (5):



wherein  $m_3$  represents an integer of from 15 to 60, and  $n_4$  represents an integer of from 8 to 24.

6. A packaged body in which a laminate formed by stacking a sheet of the silver halide photosensitive material according to claim 1 and a non-photosensitive plate material having a layer coated with an organic material on the surface thereof is packed and sealed with a light shielding sack-shaped material.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 06 01 4800

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CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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