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### 3,843,368 SILVER HALIDE PHOTOGRAPHIC LIGHT-SENSITIVE ELEMENT

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**20 Claims** 10

#### ABSTRACT OF THE DISCLOSURE

N-long chain amidoalkyl quaternary ammonium carboxylic acid betaine derivatives are superior coating aids 15 in forming photographic light-sensitive elements. Elements thus prepared.

## BACKGROUND OF THE INVENTION

#### (1) Field of the Invention

This invention relates to light-sensitive materials such as photographic films and photographic papers and more particularly to a photographic light-sensitive element prepared by adding an N-long chain amidoalkyl quaternary ammonium carboxylic acid betaine derivative to a photographic emulsion as a coating additive for a hydrophilic colloidal coating composition applied on a support such as synthetic films and papers or as an agent to improve the electrical discharge and adhesive properties of the surface of a base film or the surface layer of the applied photographic emulsion.

# (2) Description of the Prior Art

In general, cellulose esters, synthetic high molecular weight materials such as polystyrene, polycarbonate, and polyethylene terephthalate, glasses, papers, or a paper covered with a poly  $\alpha$ -olefin are employed as the support in photographic light-sensitive materials. Onto these supports, a silver halide photographic emulsion layer is either directly applied or applied via a subbing layer.

In many types of light-sensitive materials, a layer to protect the surface of a photographic emulsion layer is applied thereon to prevent the sticking of the surface of the light-sensitive material to the same or different kinds of light-sensitive materials, and damage to the surfaces of light-sensitive materials due to pressure.

In addition to the above, a coating layer made of gelatin, other hydrophilic colloids, or a vinyl polymer latex containing various additives such as a dyestuff, antistatic agent, hardening agent, coupler, and antihalation agent, for example, an antihalation layer, intermediate layer, filter layer, antistatic layer or the like is provided on the support of a photographic film.

As described above, a common photographic light-sensitive material comprises many layers and accordingly, it is necessary that a coating composition described above be uniformly applied in the form of a thin layer without any coating difficulties, such as repelling, at the time of the production of the photographic light-sensitive material.

In the production of photographic light-sensitive materials as described above, there are many cases in which several kinds of photographic emulsions or other coating compositions containing gelatin are simultaneously applied as multiple layers, for example, where different photographic emulsions are continuously applied onto a support to form three photographic emulsion layers in the production of a color photographic light-sensitive material.

In the case in which gelatin or other colloidal compositions are applied onto a gelatin colloidal layer, it is very

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difficult to obtain the required coating characteristics as compared with the case in which a gelatin colloidal composition is directly applied onto a support, particularly, in the case where an under layer is in a wet and cold state immediately after the application thereof.

As an example of the difficult problems caused in the coating process steps in the case of producing photographic light-sensitive materials, difficulties are encountered when a colloidal dispersion prepared by dispersing a mordant dyestuff into a dilute gelatin solution must be uniformly applied onto a support, and the layer of the colloidal dispersion is employed as an antihalation layer or filter layer in a photographic light-sensitive material.

In this case, it is very difficult to obtain a uniform dispersion of the mordant dyestuff and to coat such that no bubbling or repelling occurs and diffusion of the dyestuff from the coated mordant dyestuff layer to the adjacent photographic emulsion layer is prevented.

With respect to the surface properties of a photographic surface layer, fogging often occurs due to the friction between the emulsion surface and the back surface in the case that a number of printing papers are piled and when an emulsion surface contacts another different substance, for example, a rubber fingerstall which is used to roll up graphic paper.

Moreover, in the case when the emulsion surface of a photographic light-sensitive material is dried by facing the emulsion surface against the surface of a cloth belt of a ferrotype, there is the problem that the emulsion surface sticks to the surface of the cloth belt and this results not only in stains on the emulsion surface or damage thereto, but also results in a disturbance in smooth processing, thereby causing a lowering of the operational efficiency in the drying of photographic light-sensitive materials.

In order to eliminate the difficulties or disadvantages mentioned above, various types of surface active agents have been employed as coating additives for various compositions of photographic light-sensitive materials or to improve the surface characteristic properties of the surface layer of photographic materials. Particularly, saponin has been widely used as a coating additive in the photographic industries.

However, saponin has the disadvantages of easily bubbling, shows remarkable fluctuations in its quality for the reason that saponin is a natural product, and has poor characteristics as a coating additive.

Furthermore, other various synthetic surface active agents have their own different peculiarities influencing the coating characteristics and surface characteristic properties of various photographic compositions or photographic coated layers and, as a result, their range of use is limited.

Therefore, a large number of different types of surface active agents are selected and employed in accordance with their specific uses.

In general, it is difficult to uniformly apply a coating composition to a support without any coating additive where an antistatic agent having a small surface activity is adopted.

However, when a conventionally well-known coating additive, such as the sodium salt of N-alkyltaurine, sodium alkylbenzenesulfonate, polyoxyethylene alkylether, or amidoalkyl quaternary ammonium sulfonic acid betaine disclosed in British Pat. No. 1,159,825, is used together with an antistatic agent, the antistatic property of such a system becomes inferior in many cases as is shown in the examples set forth hereunder.

# SUMMARY OF THE INVENTION

In accordance with the foregoing, it is a first object of this invention to eliminate the disadvantages of the prior art mentioned above and to provide an improved photo20

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graphic light-sensitive composition relating to coating characteristic properties such as anti-repellency, in the case when a solution containing gelatin or other hydrophilic colloidal solutions difficult to uniformly apply on a support is coated on a support such as a synthetic film or paper, or a photographic layer.

The second object of this invention is to provide a means by which a photographic emulsion or other hydrophilic colloidal composition can be applied on a support at high speed without being accompanied by bubbling, 10

repelling, or other coating troubles.

It is the third object of this invention to provide a means by which second and third gelatin-containing layers can be easily applied onto a first gelatin-containing photographic layer when each coating step is carried out 15 through separate coating machines, when the upper layers are concurrently applied to a subbing layer to form multiple layers on a support, and even when the upper layers are applied in order on a subbing layer to form multiple layers on a support.

It is the fourth object of this invention to provide a photographic light-sensitive material having an improved photographic antistatic layer for coating without deteriorating the antistatic property, even when a certain type of

antistatic agent is added.

Additionally, it is a fifth object of this invention to provide a photographic light-sensitive material in which fogging due to contact friction between a photographic emulsion surface and the same or different kind of substance is prevented.

It is the sixth object of this invention to provide a means by which the stickiness of the surface of a photographic

light-sensitive material can be eliminated.

The nature, principle, details, and utility of the invention will be more clearly apparent from the following 35 detailed description beginning with general considerations and concluding with specific examples constituting preferred embodiments of the invention.

# DETAILED DESCRIPTION OF THE INVENTION

The present inventors have found that the above various objects of the invention can be achieved by adding a long chain amidoalkyl quaternary ammonium carboxylic acid betaine derivative represented by the following gen- 45 eral formula to various photographic coating composi-

wherein R is a saturated or unsaturated hydrocarbon 55 group, such as an alkyl, alkenyl, etc., group containing from 7 to 21 carbon atoms, inclusive,  $R_1$  and  $R_2$  are members selected from the group consisting of alkyl radicals, hydroxyalkyl radicals, and polyalkyleneoxide chains each containing from 1 to 18 carbon atoms, such as ethylene 60 oxide, propylene oxide, etc., R3 and R4 each represents a member selected from the group consisting of hydrogen atom and alkyl radicals containing from 1 to 4 carbon atoms, n is an integer of 2 or more, most preferably 2 to 10, and x is 0 to 1.

Typical examples of the long chain amidoalkyl quaternary ammonium carboxylic acid betaine derivatives used according to the present invention are given below.

## Compound 1:

Compound 2:

$$\begin{array}{c} C_2H_5 \\ C_{11}H_{23}CONH(CH_2)_3-N-C_2H_5 \\ -1\\ CH_2COO- \end{array}$$

Compound 3:

Compound 4:

$$\begin{array}{c} CH_3 \\ C_{15}H_{31}CONH(CH_2)_2-\overset{+1}{N}-CH_2CH_2OCH_2CH_2OH \\ \vdots \\ CH_2CH_2COO- \end{array}$$

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Compound 5:

Compound 6:

Compound 7:

Compound 8:

Compound 9:

Compound 10:

Compound 11:

Compound 12:

in which p+q=5.

A process for synthesizing the amidoalkyl quaternary ammonium carboxylic acid betaine derivatives according 65 to the present invention will now be described.

# EXAMPLE OF SYNTHESIS (Compound 3)

Compound A

 $C_{15}H_{31}CONH(CH_2)_3N(CH_3)_2 + ClCH_2COONa$  -CH<sub>3</sub> C<sub>15</sub>H<sub>31</sub>CONH(CH<sub>2</sub>)<sub>3</sub>N—CH<sub>3</sub> CH2COO-

256 g. (1 mol) of palmitic acid and 122.4 g. (1.2 mol) of 3-dimethylaminopropylamine were subjected to heating and refluxing in an N2 gas stream at a temperature of 180° C. for 6 hours. Water and excess amine produced thereby were removed from the system.

After the reaction, unreacted palmitic acid and amine were further distilled off under reduced pressure and, as a result, 330 g. of a light yellowish white solid was obtained. This crude crystal was subjected to refining by recrystallizing the crystal twice with 2.5 times the quantity 20 of methanol, and 190 g. of compound A being in the form of minute white crystal was obtained.

Next, 170 g. (0.5 mol) of the thus obtained compound A was dissolved in about 250 ml. of ethanol to prepare a solution. To the resulting solution, an aqueous sodium 25 monochloroacetate solution which was prepared by dissolving 57 g. (0.6 mol) of ClCH2COONa in 24 ml. of water was added, and the system subjected to refluxing for 5 hours. The resulting product was cooled, washed with petroleum ether, concentrated and dried.

Thereafter, ethanol was added to the resulting product and the mixture dissolved by heating. The by-product insoluble sodium chloride and excess of sodium monochloroacetate produced as a result of the heating were filtered off from the system. Then, ethanol was distilled 35off and the product dried to obtain 210 g. of minute white

The resulting product was compound 3. It is soluble in water or alcohol, and the surface tension of a 1% aqueous solution of the compound is 31 dynes/cm.

The other compounds according to the present invention can be synthesized in a similar manner as above by employing appropriate starting materials but it is to be noted that the process for synthesizing the compounds is 45 not limited to the above described process.

A surface active agent employed in the present invention may be added in an amount of from 0.01 to 50 g. per 1 kg. of a photographic coating composition and, generally, from 0.1 to 5 g. of the surface active agent is suit-

It is desirable that the addition of the surface active agent be carried out in the form of a solution which is prepared by dissolving the surface active agent in water, methanol, or other solvents miscible with water.

The particularly favorable characteristic features obtained by the addition of a surface active agent according to this invention reside in the fact that an extremely uniform coated film can not only be obtained coating at than 50 m./min.). In addition, the effects of an antistatic agent which is added for imparting an antistatic property to the coated film are not deteriorated, and problems such as friction fogging or sticking of printing papers or sensitive materials can be eliminated.

Furthermore, even when a large quantity of these surface active agents are added to a photographic emulsion, yellow fogging or other unfavorable influences with respect to photographic properties encountered in the case 70 of using polyoxyethylene nonionic surface active agents cannot be observed.

Moreover, even if the surface active agents according to this invention are employed together with other anionic, cationic, nonionic, or amphoteric surface active agents, 75

there occur no problems. In this case, these surface active agents may be added to the same or different layer of a photographic light-sensitive material than the layer to which the surface active agent of this invention is added.

Surface active agents other than those of the present invention which may be jointly used therewith, as described above, are, for example, disclosed in "Kaimen Kasseizai no Gosei to Sono Oyo (Synthesis of Surface Active Agent and the Application Therefore)" (1964 edition) authored by Ryohei Oda and Kazuhiro Teramura and published by Maki Shoten.

The surface active agents according to the present invention may be added to various hydrophilic colloidal coating compositions generally employed in the photographic field and/or non-aqueous coating compositions.

As typical hydrophilic colloid or binder compositions there are, for example, gelatin, colloidal albumin, polysaccharides, cellulose derivatives, and colloids of synthetic polymers such as polyvinyl alcohol and polyacrylamide. Since the hydrophilic colloid or binder is of secondary importance to the main concepts of the present invention, any of those hydrophilic colloids as are generally used in the photographic art may be used in the present inven-

Further, the coating properties of non-aqueous coating compositions comprising an hydrophobic binder such as a water-insoluble polymer, e.g., a polyalkylacrylate, a polyalkylmethacrylate, etc., in an organic solvent, such as methanol, ethanol, acetone, ethylene chloride, etc., can be improved in accordance with the present invention, whether used alone or as mixtures thereof. The nonaqueous coating compositions to which the compound of this invention can be added is quite useful when applied to the surface of photographic supports to provide an antistatic property thereto.

The surface active agents according to the present invention may be employed with all well-known silver halide emulsions of various compositions which may be chemically sensitized with sulfur, selenium polyalkylene oxides, or compounds containing such materials as a component thereof. The emulsions may also be spectrally sensitized with a sensitizing dye such as a cyanine or merocyanine dye.

The colloidal layer coating compositions applied with the surface active agent of the present invention may contain various photographic hardening agents, for example, inorganic hardening agents such as chromium alum, or chromium acetate, both well known in the art, or organic hardening agents such as formaldehyde, mucochloric acid, active halogen compounds, active vinyl compounds, or ethyleneimine compounds.

The photographic light-sensitive elements containing the surface active agents according to this invention may further contain various emulsion stabilizers such as azaindenes, and phenylmercaptotetrazole which are well known, antifogging agents, and other various additives required for producing a photographic light-sensitive element, for example, surface treating agents such as silicone, ordinary speed, but also with high speed coating (more 60 fluorine-containing compounds, or esters of fatty acids, and various color couplers, dyestuffs, plasticizers, or the like used in a color light-sensitive element.

In order to indicate still more clearly the nature and utility of the invention, the following specific examples of practice constituting preferred embodiments of the invention and results are set forth. It will be understood that these examples are presented as illustrative only, and that they are not intended to limit the scope of the invention.

## EXAMPLE 1

A series of emulsions was prepared by adding the compound according to the present invention or a comparative compound as a coating additive to 1 kg. of a sensitive negative photographic emulsion containing 7% by weight (unless otherwise indicated, percent is by

weight hereinafter) gelatin and 8% silver iodobromide at the ratio set out in Table 1.

Each emulsion thus prepared was applied to a triacetyl cellulose support which had been preliminary subbed.

Immediately after cold setting of the emulsion layer, a composition for a surface protecting layer prepared by adding 200 mg. of saponin to 1 kg. of a 2.5% aqueous gelatin solution was applied thereon and, for the resulting surface protecting layer, the comet number and critical speed were examined.

TABLE 1

Coating additive	Quantity added (g.) to 1 kg. of emulsion	Comet number* (number/ m.²)	Critical speed** (m./min.)	15
Compound:				
5	0, 125 0, 125	0	>30 >30	
Sodium dodecylbenzenesulfonate (for comparison)  Polyoxyethylene nonylphenyl-	0. 125	0	<b>&lt;</b> 5	
ether (n=10) (for comparison) None	0.125	20 20	20-30 8	20

As is apparent from Table 1, when the compound according to the present invention was employed, the critical speed was high and no comet was observed.

On the other hand, in case of employing sodium 30 dodecylbenzenesulfonate, a typical anionic surface active agent, the critical speed was low, and in case of employing polyoxyethylene nonylphenylether (n=10), although the critical speed was elevated, the comet number was increased.

Finally, in the case of employing the compound of this invention, no unfavorable influence was observed with respect to the photographic properties of a photographic light-sensitive material, e.g., fog or sensitivity.

Example 1 thus shows the surface properties of the 40 layer containing the compound of this invention are improved, and that the layer (gelatin layer) which is coated on the surface thereof can be coated without repelling.

## EXAMPLE 2

Firstly, a photographic emulsion was prepared by adding 5 ml. of a 4% aqueous solution of saponin as a coating additive to 1 kg. of a sensitive emulsion for X-ray photography containing 9% gelatin and 9% silver halide.

Secondly, a composition for a surface protecting layer was prepared by adding 100 ml. of a 10% aqueous solution of saponin as an antistatic agent and 10 ml. of a 2.5% aqueous solution of compound 1 of the present invention as a coating additive to 1 kg. of a 7% gelatin solution.

The photographic emulsion and the coating composi- 55 tion were concurrently applied on a triacetyl cellulose support on which a subbing layer was preliminarily applied so as to form dried films of a thickness of  $5\mu$  and  $1\mu$ , respectively, in accordance with the multiple layer coating method. The layers thus applied were subjected to 60 cold setting and then dried.

Another composition for a surface protecting layer was prepared in a manner similar to that described above except for adding no compound of this invention as a coating additive. Furthermore, other compositions for use 65 as a surface protecting layer were prepared in a manner similar to that described above except for adding three kinds of well-known coating additives instead of the compounds of the present invention.

These coating compositions and the above photo- 70 graphic emulsions were applied onto supports and dried in a manner similar to that described above, and the results relating to the coating characteristics of an applied film surface and the effects of the antistatic agent added are shown in Table 2.

TABLE 2

5	Coating additive	Quantity added (g.) to 1 kg. of protecting layer composition	number	Static mark**
	Compound:  1 2 Comparative compound:	0, 25 0, 25	0	No occurrence. Do.
10	I	0. 25	1	Considerable occurrence.
	II III None (only saponin)	0. 25 0. 25	0 3 5	Do. Do. Slight
	(biii) napoinii, a			occurrenci.

\*Repelling number: The repellence number is calculated by counting
the number of repellencies per unit square of coating.

\*\*Static mark: An unexposed film is placed on a rubber sheet and the
film is pressed with a rubber roller to impart a certain friction. Then, the
film is peeled off and subjected to developing by the use of a prescribed
developing agent as describe below:

Thereafter the number of static marks occurring on the resulting film is examined.

NOTE:

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Comparative Compound I:

Comparative Compound II:

Comparative Compound III:

$$\begin{array}{c} CH_3\\ C_{15}H_{31}CONH(CH_2)_3 \overset{1}{N} - CH_3\\ \overset{1}{C}H_2CH_2CH_2SO_3 - \\ \end{array}$$

As is apparent from Table 2, the compound according to this invention is not only excellent as a coating additive, but also will not deteriorate the antistatic property and is rather improved even in the case when an antistatic agent having a low surface activity such as saponin is jointly used. Furthermore, there were no unfavorable effects on the photographic properties due to the addition of the compound according to this invention.

On the other hand, it was observed that a cyan comparative compound III had a tendency to increase fogging.

## EXAMPLE 3

A photographic emulsion was prepared by adding 5 ml. of a 4% aqueous solution of saponin as a coating additive to 1 kg. of silver iodobromide emulsion containing a coupler together with dibutyl phthalate. The emulsion thus prepared was applied onto a triacetyl cellulose support on which a subbing layer had been preliminarily applied. The emulsion had a dried film thickness of  $3\mu$ .

Further, a composition consisting of 50 parts of gelatin, 6 parts of a dyestuff and 5 parts of a mordant was diluted with water so that the content of gelatin was 1.6% by weight. To separate portions of the resulting solution compound 1 of the present invention and comparative coating additives I, II, III, and IV were added in an amount of 2.5% and 7.5%, with respect to the weight of gelatin, to thereby provide separate coating compositions. Each of the coating compositions thus prepared was applied onto the above described photographic emulsion layer and

<sup>\*</sup>Comet: The term means a spot-like thin coated portion formed by tailing of the coating composition.

\*\*Critical speed: The maximum speed at which a gelatin solution for a protecting layer can be uniformly applied onto an emulsion layer is the critical speed for the protecting layer.

the wetting condition and repelling number determined with the results being shown in Table 3.

TABLE 3

Coating additive	Quantity added, wt. percent of compound/g. gelatin	Repelling number (number/ 100 m.²)	Wetting range (percent)*	10
Compound:				
1	2. 5 2. 5	0	100 100	
I	- 2. 5 7. 5	83 75	73 75	15
Ш	2.5 7.5	55 <b>35</b>	71 80	
m	2. 5 7. 5	50 <b>33</b>	87 95	90
IV	- 2. 5 7. 5	53 24	83 91	20

\*Wetting range: The extent of wetting of a photographic emulsion layer wetted with a coating composition compared to a value of 100 (the completely wetted range (width of base) of the emulsion layer) represented by a relative percentage.

Note: Dyestuff:

Mordant:

$$\begin{array}{c|c} CH_2 - CH \\ \hline N \\ CH_3 \end{array}$$

Comparative coating additive (I):

Comparative coating additive (II): Saponin. Comparative coating additive (III):

C<sub>12</sub>H<sub>15</sub>NHCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub> CH<sub>2</sub>NHCH<sub>2</sub>COONa

Comparative coating additive (IV):

As will be understood from Table 3, the coating compositions to which comparative compounds (I) through (IV) were added showed a high repelling number and unfavorable wetting. Particularly, comparative compound (I) promoted the diffusion of dyestuffs to the adjacent photographic emulsion layer to thereby decrease the sensitivity of the adjacent photographic emulsion layer, and comparative compound (IV) caused dyestuff coagulation to produce a yellow precipitate.

On the other hand, no disadvantages as mentioned above were observed and a uniform coating film was ob- 75 containing 5% silver bromide and 15% gelatin.

tained in the case when the compounds according to the present invention were employed.

EXAMPLE 4

An antistatic composition having the following composition was applied to a polyethylene terephthalate film support having a thickness of 0.1 mm. and dried (dried film thickness  $0.2\mu$ ).

.,		
	Antistatic composition:	G.
	10% methanol solution of compound 5 of this	
	invention	1
	5% (methylene chloride:methanol=92:8) solu-	
5	tion of cellulose triacetate	12
	Phenol	2
	Ethane tetrachloride	8
	Ethylene chloride	
	Methanol	5
		-

A silver halide photographic emulsion was then applied onto the opposite surface of the support thus coated with the antistatic composition. The emulsion was then dried.

With respect to the photographic film thus prepared, the surface resistivity of the back surface of the film measured at 30% RH was  $8\times10^{10}$  ohm. This result was low as compared to the surface resistivity  $(8\times10^{14}$  ohm) of an untreated film, and an excellent antistatic effect was thus observed.

#### EXAMPLE 5

A photographic emulsion was prepared by adding 25 ml. of a 2% methanol solution of compound 3 of the present invention, a color sensitizer, antifogging agent, fluorescent brightening agent, hardening agent, and matting agent at art recognized quantities to 1 kg. of a silver haldie photographic emulsion containing 5% silver chlorobromide, including 50 mol percent of silver bromide, and 6% gelatin.

The photographic emulsion thus prepared was applied onto a photographic baryta paper weighing 85 g./m.<sup>2</sup> in such a manner that the quantity of silver chlorobromide was 2.5 g./m.<sup>2</sup>. The emulsion was dried to produce a photographic paper.

As a comparative sample, another photographic paper was produced as above except that the compound of the present invention was removed from the emulsion composition.

After the exposure of these samples, the exposed photographic papers were subjected to ordinary developing and fixing treatments.

Then, each photographic paper thus treated was dried by the use of an MD-2 type dryer for copying photographic paper (manufactured by Japou Kabushiki Kaisha) at a temperature of 80°-95° C. for 40-80 seconds in such a manner that the emulsion surface of the photographic paper was caused to closely contact the cloth belt of the dryer.

As a result, the photographic paper including the compound of the present invention was dried without sticking to the cloth belt, but the photographic papers of the comparative samples dried and stuck to the cloth belt.

# EXAMPLE 6

A series of photographic emulsions were prepared by adding a compound of the present invention or a comparative compound as shown in Table 4 in the quantity indicated in the same table. Further, a color sensitizer, antifogging agent, fluorescent brightening agent, hardening agent, and matting agent at art utilized quantities were added to 1 kg. of a photographic silver bromide emulsion containing 5% silver bromide and 15% gelatin.

Each photographic emulsion thus prepared was applied onto a photographic baryta paper (150 g./m.2 weight) in such a manner that the quantity of silver bromide was 3 g./m.2. The emulsion was then dried to produce a photographic paper.

Each resulting photographic paper was treated as described in Example 5. Then, each treated photographic paper was dried employing the same dryer as in Example 5 at 80°-95° C. for 80-180 seconds in such a manner that the emulsion surface of the photographic paper closely 10 contacted the cloth belt of the dryer.

After drying each photographic paper, the stickiness between the cloth belt and the photographic paper was as shown in Table 4.

TABLE 4

Additive	Quantity added (g.)/ 1 kg. of emulsion	Stickiness
Compound 3 of this invention	0.5	No sticking.
	1.0	Do.
Compound 6 of this invention	0.5	Do.
	1.0	Do.
Comparative compound:	0.5	G41-1-1
1	0.5 1.0	Sticking. Do.
II	1.0	Do.
iii	1.0	$\mathbf{D_0}$ .

Note: Comparative compound:

I=Saponin. II=Sodium dodecylsulfate. III=Saccharose monolauric ester.

As is apparent from Table 4, no sticking was observed and a favorable drying characteristic could be obtained  $\ ^{40}$ using a compound according to the present invention.

## **EXAMPLE 7**

A series of emulsions were prepared by adding a com- 45 pound according to this invention or a comparative compound as shown in Table 5 at a quantity as indicated in the same table. Further, a sensitizing dye, antifogging agent, fluorescent brightening agent, hardening agent, and matting agent at art recognized quantities were added to 50 1 kg. of a silver halide photographic emulsion containing 7.5% gelatin and 7.5% of silver chlorobromide including 30 mol percent of silver bromide.

Each photographic emulsion thus prepared was applied onto a photographic baryta paper (paper weight 55 g./ m.2) in such a manner that the quantity of silver chlorobromide was 2 g./m.2. The emulsion was then dried to produce a photographic paper.

Each resulting photographic paper was subjected to the friction fogging test described below in its unexposed state 60 with the results being indicated in Table 5.

# METHOD OF FRICTION FOGGING TEST

A stainless steel needle having a pointed end of a hemispherical shape (diameter 3 mm.) was weighted at 10 g., 50 g., 100 g., 200 g., 300 g., 400 g. and 500 g. The pointed end of the needle was caused to contact the emulsion surface of each sample to be examined, and the pointed end of the needle was moved at a speed of 10 cm./sec. across 70 the emulsion while in contact therewith.

Then, each sample thus treated was subjected to ordinary developing and fixing treatments and, as a result, the degree of friction fogging occurring in connection with each amount of weighting was examined.

5	Compound	Quantity added (g.)/ 1 kg. of emulsion	Weight (g.) at which fric- tion fogging occurred	Preventing effect
	Compound 3 of the invention.	0. 5 1. 0	300 400	Effective. Do.
	Compound 6 of the invention.	$0.5 \\ 1.0$	300 500	Do. Do.
10	Comparative compound:	0.5 1.0	50 50	Ineffective.
	п	0.5 1.0	50 50	Do. Do.
15	111	0.5 1.0	50 100	Do. Slightly effective.
	IV	0.5 1.0	50 50	Ineffective. Do.
20	Nothing		50	Do.

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OTE:
Comparative compound:
I=Sodium dodecylbenzenesulfonate.
II=Saponin.
III=Saccharose monolauric ester.
IV=Sodium dodecylsulfate.

As will be understood from Table 5, the effect of preventing friction fogging was remarkable in the photographic papers containing the compounds according to this invention as compared with those containing no compound of the invention or those containing any comparative compound recited above.

From the instant and foregoing examples, it will be understood that the compounds according to the present invention have very favorable characteristic features in comparison with well-known compounds.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. In a process for forming a gelatino-silver halide light-sensitive photographic material comprising at least one photographic layer coated on a photographic support, the improvement which comprises preparing a photographic coating composition containing as a coating aid 0.01 to 50 g./kg. of said coating composition of a compound having the following formula:

in which R is a saturated or unsaturated hydrocarbon group containing from 7 to 21 carbon atoms, inclusive, R<sub>1</sub> and R<sub>2</sub> are members selected from the group consisting of alkyl radicals, hydroxyalkyl radicals, and polyalkyleneoxide chains each containing from 1 to 18 carbon atoms, inclusive, R<sub>3</sub> and R<sub>4</sub> each represents a member selected from the group consisting of hydrogen atom and alkyl radicals containing from 1 to 4 carbon atoms, inclusive, n is an integer of 2 or more, and x is 0 or 1, and applying said photographic coating composition containing said coating aid as a layer on said photographic support, said applied layer being an initially coated layer on said support, a layer on the surface of 75 said support opposite the surface carrying a light-sensitive

13 14 layer, or as a layer adjacent another photographic layer. 11. The process of Claim 1 wherein said compound is 2. The process of Claim 1 wherein said compound is C7H15CONH(CH2)2  $C_{11}H_{23}CONH(CH_2)_3-\stackrel{+}{N}-CH_3$ cH2C00 5 CH,COO-12. The process of Claim 1 wherein said compound is 3. The process of Claim 1 wherein said compound is  $C_2H_5$ C21H43CONH(CH2)3-N-CH3 C<sub>11</sub>H<sub>23</sub>CONH(CH<sub>2</sub>)<sub>3</sub>—N-C<sub>2</sub>H<sub>5</sub> 10 сн₃соо-ĊH₂COO-13. The process of Claim 1 wherein said compound is 4. The process of Claim 1 wherein said compound is (CH2CH2O)pH  $C_{11}H_{23}CONH(CH_2)_3-\overset{\dagger}{N}-(CH_2CH_2O)_qH$ C15H31CONH(CH2)3-15 ĊH₂COOin which p+q=5. 5. The process of Claim 1 wherein said compound is 14. The process of Claim 1 wherein the compound is present in an amount of from 0.1 to 5 grams per 1 kg. of the photographic composition. C<sub>15</sub>H<sub>31</sub>CONH(CH<sub>2</sub>)<sub>2</sub>—N—CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OH 15. The process of Claim 1 wherein the compound is CH2CH2COOpresent in a layer initially coated on said support. 16. The process of Claim 1 wherein said compound is 6. The process of Claim 1 wherein said compound is present in a photographic emulsion. 17. The process of Claim 1 wherein said compound is C<sub>17</sub>H<sub>33</sub>CONH(CH<sub>2</sub>)<sub>3</sub>—N—CH<sub>3</sub> present in an antistatic layer on the surface of said sup-ĊH₂CO'0port opposite the emulsion layer. 18. The process of Claim 1 wherein said photographic 7. The process of Claim 1 wherein said compound is element is a multi-layer color photographic element. 19. The process of Claim 1 wherein said photographic C<sub>17</sub>H<sub>35</sub>CONH(CH<sub>2</sub>)<sub>3</sub>—N—CH<sub>3</sub> element includes a hydrophobic colloid. 20. The process of Claim 1 wherein said compound is present in a photographic layer which is overcoated on 8. The process of Claim 1 wherein said compound is another photographic layer. 35 C<sub>11</sub>H<sub>23</sub>CONH(CH<sub>2</sub>)<sub>8</sub>—N—C<sub>4</sub>H<sub>9</sub> References Cited сп₃сн₂соо-UNITED STATES PATENTS 9. The process of Claim 1 wherein said compound is 3,113,026 12/1963 Sprung \_\_\_\_\_ 96—107 3,726,683 4/1973 Yamamoto et al. \_\_\_\_ 96-84 A C11H23CONH(CH2)2-.N—CH₃ RONALD H. SMITH, Primary Examiner снсоо-A. T. SURO PICÓ, Assistant Examiner  $CH_3$ U.S. Cl. X.R. 10. The process of Claim 1 wherein said compound is 96—50 PL, 107, 114.5; 117—34

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C<sub>17</sub>H<sub>85</sub>CONH(CH<sub>2</sub>)<sub>8</sub>—N—CH<sub>2</sub>CH<sub>2</sub>OH