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PHOTOGRAPHIC ELEMENTS HAVING GELATINOUS COATING COMPOSITIONS CONTAINING AMPHOTERIC SURFACE ACTIVE AGENTS

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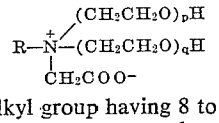
Int. Cl. G03c 1/02
U.S. Cl. 96—94 12 Claims

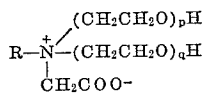
ABSTRACT OF THE DISCLOSURE

Gelatinous photographic coating compositions containing as a coating aid an amphoteric surface active agent having the following general formula:



wherein R is an alkyl group having 8 to 18 carbon atoms, p and q are each integers greater than zero and $p+q$ is an integer from 2 to 18. A photographic material containing the above compounds has good wettability for photographic developer.

This invention relates to an improved photographic element adapted for photographic purposes, which contains as a coating aid an amphoteric surface active agent having the following general formula:



wherein R is an alkyl group having 8 to 18 carbon atoms, p and q are each integers greater than zero, $p+q$ is an integer from 2 to 18.

In general, as a support for a photographic product, there have been known nitrocellulose, triacetyl cellulose, polycarbonate, polyester, other synthetized macromolecular materials, glass plate, papers, etc. On such a support is coated a silver halide photographic emulsion layer directly or through a substratum. The substratum contributes to adhere strongly the photographic emulsion layer onto the support. Further, a photographic product is usually coated with a thin gelatin layer on the photographic silver halide emulsion layer in order to prevent sticking of the emulsion layer to the surfaces of similar materials or different materials and to prevent the formation of scratches by pressing. Therefore, since a photographic product generally consists of many layers as mentioned above, a photographic silver halide emulsion layer or a protective layer cannot be uniformly coated without the aid of a surface active agent for spreading uniformly the coating gelatinous solution and improving the wetting property of the coating solution. The use of such a surface active agent also prevents the formation of foams and repellencies.

As one embodiment of applying a gelatinous solution on a support in multilayers, there is the production of a color film wherein three different photographic silver halide emulsions are coated continuously on a support in three layers. The coating problems in the case where a gelatin layer or other colloid layer is coated on a gelatinous layer are completely different from the case where a gelatinous layer is directly coated on a support. In particular, this is true in the case where the emulsion

while set and in a chilled set condition to to be overcoated with another emulsion or with a protective gelatin coating.

That is, in this case, the surface of a support must be uniformly wetted with a coating solution, and the surface of the layer formed from the coating solution by setting or drying, must be uniformly wetted with an overcoating solution.

Moreover, it is desirable that a dried surface is easily wetted with an aqueous solution for that the photographic film or paper is easily wetted with a treating solution in a photographic processing such as development and that there is no unevenness and no foaming.

Beside the above-mentioned unevenness in coating caused by the lack of good wetting property, there occurs spot-like unevenness caused by hydrophobic materials contained in gelatin such as a small amount of fat. In this case, the surroundings of the hydrophobic materials are reduced in the thickness of coating to form spots and a phenomenon called repellence or comet occurs. Commercially available gelatin generally contains a small amount of fat inevitably and hence in order to prevent the formation of the comet, etc., which is considered to be caused by the presence of the fat, the addition of a surface active agent is necessary.

Hitherto, saponin has been broadly used in the photographic industry as a spreading agent, and it can be further utilized in a larger range than other various surface active agents. However, saponin is a naturally occurring substance and may show decided variations in quality from batch to batch.

For this reason, as the surface active agents for photographic industry, synthetic materials have recently been used. There are many patents about such surface active agents in which, however, besides the use for the spreading agent, many merits by the surface active agents are described, such as, antistatic effect, improvement of the solubility of couplers, improvement of the permeability of treating solutions, reduction of troubles caused by water drops, vanishing of bubbles in the case where a gelatin sol is applied on a chilling-set emulsion layer, promotion of increase in photographic sensitivity by development, prevention of a support from being contaminated by halation-preventing dyes, and the like. However, almost all of these synthetic surface active agents are very peculiar to these effects and hence in some cases, they give good effects to a specific photographic emulsion and a gelatin composition but in other case, they are completely useless to other compositions in the improvement of wetting property and the prevention of the formation of comets. Therefore, the uses of almost all synthetic surface active agents are limited. Then, the utilization of many different types of surface active agents to photographic industry have been proposed. Further, as the problems about conventional synthetic surface active agents there are recognized that the wettability of a coating solution to a substratum or an already coated emulsion layer does not always coincide with the wettability of another coating solution or a treating solution to coating formed by applying the former coating solution on a support, and, on the contrary, in the case of using an easily coatable coating solution, it is usually difficult to coat on thus coated layer with another coating solution. Similarly, about the formation of comets and wetting ability of coating, the case profitable to one is usually unprofitable to another.

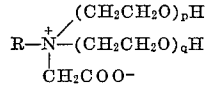
Further, it has been already known that a compound containing polyalkylene oxide has generally an effect for increasing the photographic sensitivity of a silver halide photographic product but in this invention it has been confirmed that only the coating property for a photographic product can be improved without giving influ-

ences on photographic properties, such as, photographic sensitivity, gamma, and fog.

Therefore, an object of this invention is to coat a photographic emulsion or a gelatin composition on a support without the formation of comets and the like, said photographic emulsion or the gelatin composition being, after it is formed into a layer on the support, easily wetted by a treating solution.

Another object of this invention is to coat a photographic emulsion or a gelatin composition on a support without the formation of comets and the like and without giving influences on the photographic properties, such as, photographic sensitivity, gamma, and fog, said photographic emulsion or the gelatin composition being, after it is formed into a layer on the support, easily and uniformly coated with a photographic emulsion or a gelatin composition.

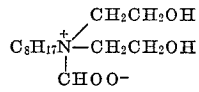
That is, the inventors have found that these objects can be attained by adding in a coating solution mainly consisting of gelatin a compound having the following general formula



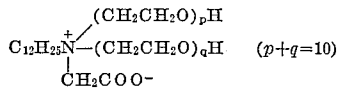
wherein R represents an alkyl group having 8 to 18 carbon atoms, p and q are integers greater than zero and $p+q$ is an integer of from 2 to 18.

As examples of such compounds, there are:

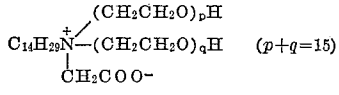
Compound 1



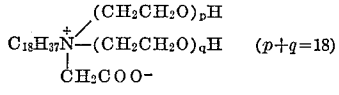
Compound 2



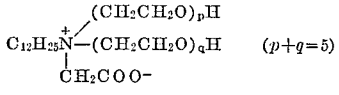
Compound 3



Compound 4



Compound 5



The above-mentioned compounds may be obtained by reacting an alkyl amine with ethylene oxide and then reacting the product with monochloroacetic acid.

These surface active agents may be added in a photographic coating solution in an amount of about 0.05–50 g., preferably 0.3–5 g. per 1 kg. of dried gelatin. These surface active agents may be used individually or as a mixture thereof, or may be used with other surface active agent.

The following examples will serve to understand the invention in detail while the invention is not by any means limited to them.

EXAMPLE 1

A gelatinous silver chlorobromide emulsion was prepared containing 8.0% gelatin and 4.5% silver salts. To one kilogram of this emulsion was added an aqueous solution having the following composition.

	Additive	Amount (mg.)
Sample No.:		
1	Nothing (Control)	0
2	Compound 1	20
3	do	50
4	do	100
5	Sodium dodecylbenzene sulfonate	100
6	Polyoxyethylenenonylphenyl ether (n=10)	100
7	Compound 1 and sodium dodecylbenzene sulfonate	{50 / 50

Thus prepared emulsion was coated on a subcoated film base by passing the film base under a coating roller so that the subcoated surface of the film base was dipped in the emulsion. The emulsion was immediately setted by chilled air but was not dried, and one kilogram gelatinous solution containing 20 g. of gelatin and 150 mg. of saponin was overcoated on the emulsion layer immediately without drying the emulsion as in the case of coating the emulsion.

In this case, the coating procedure of the protective coating solution was conducted by changing the passing speed of the film base that had been coated with the gelatinous silver halide emulsion to determine the maximum speed at which the protective coating solution was coated uniformly on the surface of the emulsion layer, which was defined as the limiting speed (the higher the limiting speed, the more profitable for the production). After the end of coating and drying, thus prepared film was examined about the number of portions where the coating of emulsion became uneven and the thickness of coating was thinned spot-likely, which are generally called "comets" (of course, the less the comet number, the better). The results were as follows.

	Limiting speed (m./min.)	Comet No./sq.m.
Sample No.:		
1	6	20
2	15	5
3	Above 20	2
4	Above 20	0
5	Above 5	0
6	Above 20	Above 20
7	Above 20	0

As shown in the above table, by the process of this invention (sample Nos. 2, 3, 4 and 7), the conditions of the high limiting speed and less comet number were obtained, while by the addition of a typical anion surface active agent, sodium dodecylbenzene sulfonate (sample No. 5), the limiting speed at which the comet number was less was low. Further, by the addition of a typical nonionic surface active agent, polyoxyethylene nonylphenyl ether (sample No. 6), the limiting speed was increased but the comet number was also increased. Moreover, in an embodiment of this invention, wherein Compound 1 in this invention was used with sodium dodecylbenzene sulfonate (sample No. 7), the conditions of the high limiting speed and less comet number were obtained. When the photographic products that had been prepared by the process of this invention were developed with a commercially available metol-hydroquinone developer, no bad influences were observed on the photographic properties, such as, photographic sensitivity, gamma, and fog.

EXAMPLE 2

A photographic emulsion containing 75 g. of gelatin, 62 g. of silver iodobromide, 150 mg. of saponin, and

60 mg. of polyoxyethylene nonylphenyl ether (n=15) per 1 kg. of emulsion was coated on a film base as in Example 1. After drying, a protective coating solution containing 1.5 g. of gelatin per 1 kg. and the following surface active agent was applied on it.

Additives		Amount [1]
Sample No.:		
1	Nothing (control)	0
2	Compound 2	20
3	do	50
4	do	100
5	Sulfuric acid ester of lauryl alcohol	100
6	Sodium dodecylbenzene sulfonate	100
7	Polyoxyethylene nonylphenyl ether	100

[1] mg./kg. of gelatin solution.

Thus coated and dried samples were examined about the comet number. Further, a developing solution was dropped onto the sample that has been placed horizontally and the contact angle was measured by a microscope having a low magnifying power. If the contact angle is large, the film is not easily wetted when it is dipped into the developer and the large contact angle causes attaching of foams and the formation of unevenness. Therefore, the contact angle is preferably small. The measured comet number and contact angle were shown in the following table.

	Contact angle,°	Comet number
Sample No.:		
1	47	Above 20
2	40	3
3	30	0
4	23	0
5	50	0
6	53	0
7	30	15

As clear from the above table, in the case of this invention, the contact angle was small and the comet number was small. In the cases of using a typical anion surface active agent, sulfuric acid ester of lauryl alcohol (sample No. 5) and sodium dodecylbenzene sulfonate (sample No. 6), the comet number was reduced but the contact angle was increased and the surface of the film became water-repellent. Further, in the case of using a typical nonionic surface active agent, polyoxyethylene nonylphenyl ether (n=10) (sample No. 7), it was impossible to remove comets completely.

When the photographic product prepared by the process of this invention was developed by a commercially available phenidonehydroquinone developer, no bad influences were observed on the photographic properties, such as, photographic sensitivity, gamma, and fog.

EXAMPLE 3

An emulsion was prepared by adding a panchromatic color sensitizer, a stabilizer and a hardening agent into 100 parts of a silver iodobromide gelatin emulsion that has been chemically sensitized with a sulfur-containing sensitizer and a gold salt sensitizer in accordance with a conventional method. Apart from this, a solution of 10 parts 1-hydroxy-N-dodecyl-2-naphthamide in 10 parts of dibutyl phthalate was dispersed in 100 parts of a 10% gelatin solution using sodium butylnaphthalene sulfonate. Into 100 parts of the above-prepared silver halide photographic emulsion was added 10 parts of thus prepared dispersion containing the coupler. The emulsion was further added with 2 cc. of a 2% methanol solution of the compound shown in the following table and applied on a subcoated film base as in Example 1. Thus

obtained intermediate film product was, without being dried, immediately coated with a gelatin solution containing 20 g. of gelatin, 200 mg. of dodecylbenzene sulfonic acid, and 800 mg. of saponin per 1 kg. as in the case of coating the emulsion.

Additive		Limiting speed (m./min.)
Sample No.:		
1	Nothing (control)	0
2	Compound 3	15
3	Saponin	3
4	Sodium dodecylbenzene sulfonate	3
5	Polyoxyethylene nonylphenyl ether (n=10)	0

Thus, in the case of this invention (sample No. 2), the limiting speed was extremely superior to the cases of using other known typical surface active agents (3, 4 and 5). Further, the color tone, gradation, and photographic sensitivity of the photographic product were not reduced by color development.

EXAMPLE 4

After adding an orthochromatic sensitizer, a stabilizer, and a hardening agent into 100 parts of a silver chlorobromide gelatin emulsion prepared by a conventional method, the emulsion was added with 5 parts of a 5% aqueous solution of 1-(4'-phenoxy - 3 - sulfophenyl)-3-heptadecyl-5-pyrazolone and then 2 cc. of a 2% aqueous solution of the compound shown in the following table. The emulsion was applied on a subcoated film base followed by drying. On thus formed emulsion layer was applied a 2% gelatin solution containing a hardening agent and 1 g./liter of saponin with a coating speed of 5 m./min.

Additive		Comet No./sq. m.
Sample No.:		
1	Nothing (control)	Above 20
2	Compound 4	0
3	Sodium dodecylbenzene sulfonate	5
4	Polyoxyethylene nonylphenyl ether (n=10)	Above 20
5	Compound 4 and Sodium dodecylbenzene sulfonate	0

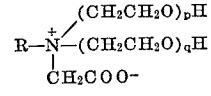
As clear from the above table, the case of using the process of this invention showed no comet number.

EXAMPLE 5

The process of Example 4 was carried out in the same manner except using Compound 5 instead of Compound 4 and almost same results were obtained.

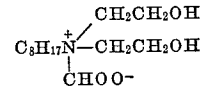
What is claimed is:

1. A photographic element comprising a support having thereon at least one light-sensitive silver halide gelatinous emulsion layer, said layer containing a compound having the following general formula

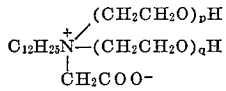


wherein R represents an alkyl group having from 8 to 18 carbon atoms, p and q are each integers greater than zero, and $p+q$ is an integer from 2 to 18.

2. The photographic element according to claim 1 wherein said compound is shown by the following formula

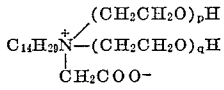


3. The photographic element according to claim 1 wherein said compound is shown by the following formula



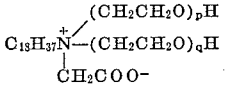
wherein p and q are each integers greater than zero and $p+q=10$.

4. The photographic element according to claim **1** wherein said compound is shown by the following formula



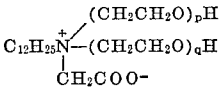
wherein p and q are each integers greater than zero and $p+q=15$.

5. The photographic element according to claim **1** wherein said compound is shown by the following formula



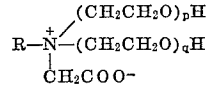
wherein p and q are each integers greater than zero and $p+q=18$.

6. The photographic element according to claim **1** wherein said compound is shown by the following formula



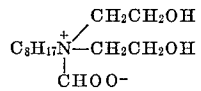
wherein p and q are each integers greater than zero and $p+q=5$.

7. A photographic element comprising a support having thereon at least one light-sensitive silver halide gelatinous emulsion and at least one subsidiary layer, at least one of said layers containing a compound having the following general formula

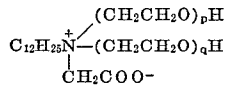


wherein R represents an alkyl group having from 8 to 18 carbon atoms, p and q are each integers greater than zero and $p+q$ is an integer from 2 to 18.

8. The photographic element according to claim **6** wherein said compound is shown by the following formula

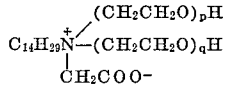


9. The photographic element according to claim **6** wherein said compound is shown by the following formula



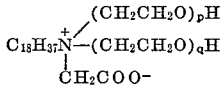
wherein p and q are each integers greater than zero and $p+q=10$.

10. The photographic element according to claim **6** wherein said compound is shown by the following formula



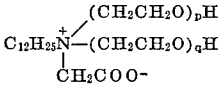
wherein p and q are each integers greater than zero and $p+q=15$.

11. The photographic element according to claim **6** wherein said compound is shown by the following formula



wherein p and q are each integers greater than zero and $p+q=18$.

12. The photographic element according to claim **6** wherein said compound is shown by the following formula



wherein p and q are each integers greater than zero and $p+q=5$.

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J. TRAVIS BROWN, *Primary Examiner.*