United States Patent Office

3,457,076

Patented July 22, 1969

3,457,076

ANTISTATICALLY FINISHED PHOTOGRAPHIC FILM

Yasushi Yano, Odawara-shi, Wataru Ueno, Ashigarakami-gun, Fumihiko Nishio, Odawara-shi, and Yosuke Nakajima, Ashigarakami-gun, Japan, assignors to Fuji Shashin Film Kabushiki Kaisha, Kanagawa-ken, Japan

No Drawing. Continuation-in-part of application Ser. No. 339,900, Jan. 24, 1964. This application Nov. 29, 1967, Ser. No. 686,755

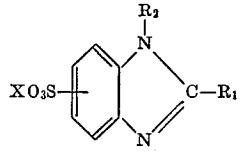
Claims priority, application Japan, Jan. 30, 1963, 38/4,019

Int. Cl. G03c *1/82*

U.S. Cl. 96—87 5 Claims

ABSTRACT OF THE DISCLOSURE

A finished photographic film comprising a support, a photosensitive emulsion layer and at least one auxiliary layer, containing as an antistatic agent a compound of the formula:



wherein R_1 represents an alkyl group, R_2 represents an aralkyl group, total carbon number of R_1 and R_2 being less than 25, and X represents a member selected from the group consisting of hydrogen, an alkali metal and ammonium.

This application is a continuation-in-part of our invention Ser. No. 339,900 filed Jan. 24, 1964, now abandoned.

This invention relates to an antistatically finished photographic film.

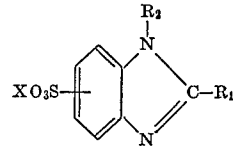
Accumulation of static electricity during the manufacture and the use of a photographic film often results in various troubles. Such electrostatic charges on the film are created at the contact portion of a roller with a film and at the gate of a camera or during the course of other film treatments where the friction between the film and other substances and stripping-off takes place. Upon the discharge of static electricity so deposited, the film is sensitized to form irregular static marks after it has been developed. All kinds of film supporting materials are hydrophobic possessing high electrostatic capacity which, therefore, tend to be charged with a lot of static electricity on the manufacture processing or on the use thereof. Since the defects of the discharge become more serious as the sensitivity of film emulsion becomes higher.

The static marks also appear when a roll film is wound or rewound at a speed as high as the adhesion takes place as the result of stripping between the base face and the emulsion face.

Various types of antistatic agent have hitherto been used for avoiding the static charge of a photographic film. Such an agent often includes those having hydroscopic properties which are capable of giving electroconductivity to the film thereby bleeding off the static charge. However, most of such agents are not always sufficient for the practical application to the photographic film because of their poor low-temperature characteristics especially on applying to a new high-sensitive emulsion, of their degradation of antistatic effect with the time lapse and of adhesion problem at elevated temperatures.

The object of this invention is to provide a new, effective and facile method for preventing the static charge of a highly sensitive film.

The above object is now attained by adding to at least one of an emulsion laper and auxiliary layers, such as an emulsion-protective layer, anti-curl layer, halation-protective layer, etc. an alkylbenzimidazole sulfonic acid derivative having the following structure:



(wherein

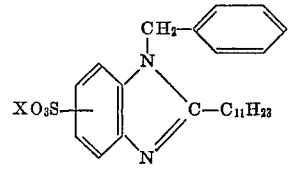
R_1: an alkyl group

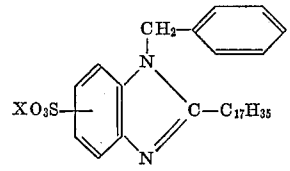
R_2: an aralkyl group (the total carbon numbers of R_1 and R_2 being less than 25)

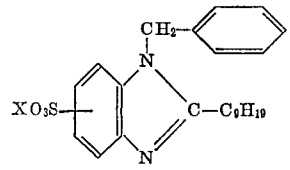
X: hydrogen, an alkali metal or an ammonium),

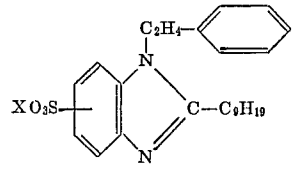
and/or by coating on at least one of the above layers and a support.

The compounds to be used in this invention are exemplified as follows:

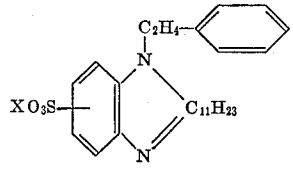








and



X in above formulae may be optionally replaced either with hydrogen, an alkali metal or an ammonium group.

If the number of total carbon atoms of R_1 and R_2 amounts to 25 or greater, the ratio of hydrophilic group to hydrophobic group reduces with the decrease in the antistatic activity.

According to this invention, the static charge which occurs upon handling the films, for instance, when charging a film into a cassette and loading into a camera, can be effectively inhibited even at a lower temperature with-

out accompanying any decrease in the antistatic effect for a long period of time.

Moreover, the above-mentioned substance has such advantages that it gives to the film a proper electroconductivity and lowers the static or dynamic friction modulus without causing adhesion at elevated temperatures. The above compound is readily soluble in such solvents as water, methanol, etc., and is an excellent antistatic agent which on admixing to a photographic emulsion, does not influence to the photographic characters such as sensitivity, gamma, fog, etc. as well as to the viscosity, specific weight, coagulation temperature and pH of the photographic emulsion.

It has already been disclosed in the specification of British Patent No. 847,884 that the compound of aforementioned structural formula in which R_2 is, however, a hydrogen atom can be applied to the back of a film as an antistatic agent. However, the derivative of this invention wherein R_2 is an aralkyl group is remarkably advantageous in solubility and, especially upon applying to a photographic film, possessing extremely long-lasting antistatic activity as compared with the aforesaid known derivative. Moreover, the derivative of this invention wherein R_2 is an aralkyl group gives less photographic fogging than the known derivative of the British patent as illustrated in Example 5 shown below.

The antistatic agent of this invention may be applied at the proportion of from 0.01 to 20 g. per square meter of the photographic film. Particularly, from 0.04 to 0.4 g. is desirable. However, the above range should of course be varied depending upon the type, shape of the film used or upon the manner of coating.

The compound of this invention may be applied to the back of the film either by spray-coating on its surface as the form of the solution in water, organic solvents or in their mixture, or by immersing the back in such a solution followed by drying. It may also be incorporated to binders, such as, gelatin, polyvinyl alcohol, cellulose acetate phthalate, cellulose acetate, etc.

The invention may be also applied for the antistatic treatment of film or shaped articles of cellulose ester, polyester, polystyrene, polycarbonate, polyethylene, polypropylene and the like vinyl type resins.

The antistatic activity is measured in this invention in accordance with the following methods:

(1) A film strip is rolled with two rubber rolls at each relative moisture of 30% and 65%, then the amount of static electricity charged is measured by means of a Faraday box.

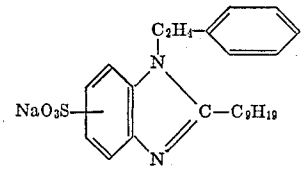
(2) An unexposed film is placed on a rubber sheet and is stripped after pressing with a rubber roll to form static marks on the film.

(3) A measurement of intrinsic surface resistance of the fiilm.

The invention will be further described by following examples, which are shown not for the purpose of limiting it.

Example 1

Solutions of 0.10 g. of an alkylbenzimidazole sulfonate represented by the formula:



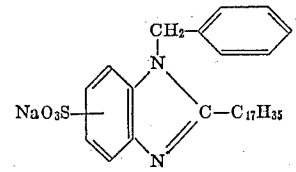
in each 100 cc. of water (A) and methanol (B) were sprayed on the surfaces of high sensitive X-ray films and dried respectively.

Films each treated with solution (A) and solution (B) were found to have no static marks at the relative humidity of 30% after the static mark generation test, while untreated films had remarkable static marks thereon.

The amount of static charge of the film treated with solution (A) at the relative humidity of 30% was 21 v., 8 v. with solution (B) and 200 v. with no solution treatment respectively. (The difference of the effects between solutions (A) and (B) is due to the state of swelling of gelatin by the attack of solvent and to the difference in the concentrations of the antistatic agent remaining on the film surface depending upon the variety of evaporation speeds.)

Example 2

Solution of 0.25 g. of an alkylbenzimidazole sulfonate having the formula



in each 100 cc. of water (A) and methanol (B) were prepared. High sensitive X-ray films were immersed in each solution and dried to give antistatically finished films free from the formation of static marks after being subjected to the static mark generating tests. Whereas, non-treated films gave considerable spotty static marks.

The results of the measurement of the static electricity charged were shown in the following table. As is clear from the table, the film thus treated has excellent antistatic property.

	Static charge (v.)	
Solution	30% R.H.	65% R.H.
A	20	0
B	0	0
Non-treated	200	5

The intrinsic surface resistance of the film treated with solution (A) was 1×10^{12} ohms at the relative humidity (R.H.) of 28%. No degradation of the antistatic activity was noticed over a long period.

Example 3

To 1 kg. of 2% gelatin solution were added 75 cc. of an aqueous solution of 1 g. of the alkylbenzimidazole sulfonate in 100 cc. of water, prepared as in Example 2, and conventional hardening and surface active agents. The resulted solution was applied as a protective layer to an X-ray film by coating followed by drying to the thickness of 1.5μ.

Static mark generating test at the relative humidity of 30% to the film thus treated showed substantial absence of static marks, whereas the non-treated film gave considerable marks.

Static charge at 30% relative humidity was 50 v. for the treated film and 210 v. for the untreated one.

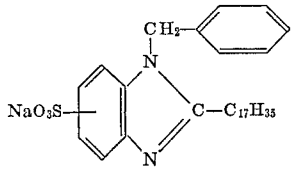
Example 4

A solution of 1 g. of the alkylbenzimidazole sulfonate as described in Example 1 in 100 cc. of distilled water was mixed with a solution comprising 2 g. of cellulose acetate phthalate, 2 g. of triethanolamine and 600 cc. of methanol. The mixture of above solutions was sprayed on the back face of a cellulose triacetate film. The reverse face was coated with a cinematographic negative emulsion together with a subbing layer. The intrinsic surface resistance at 30% relative humidity was 9×10^{11} ohms at the back face of the treated film, whereas that of the back face of the non-treated film was 5×10^{14} ohms.

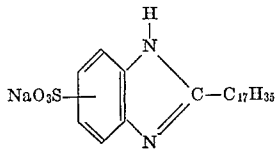
Example 5

To 2 kg. of a 2% gelatin solution were added 0.2 g. chrome alum and 0.4 g. of saponin, then the resulted solution was divided into two portions. One was incorporated with 100 cc. of a 1% aqueous solution of the following compound (I) described in Example 2. Another was ad-

mixed with 100 cc. of a 1% aqueous solution of Ultrabon W (manufactured by Ciba Ltd.) shown by the following formula. (The latter compound was disclosed in aforementioned British patent).



(I)



(II)

Two solutions thus prepared were respectively sprayed on high sensitive X-ray photographic emulsion layers as the protective layers and dried into the thickness of 1.5μ.

Two types of films thus prepared were subjected to static charge tests in which one measured immediately after the coating treatment and another measured after it had been left for 120 hours at a temperature of 50° C. and at a relative humidity of 80%. The results obtained are shown in the following table.

Compound	Immediately after coating (v.)	After 120 hrs. at 50° C., 80% R.H. (v.)
(I)	20	20
(II)	20	60

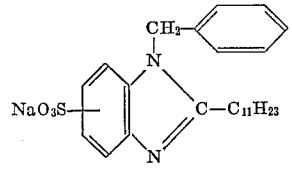
As is clear from the table, the film treated with (II) shows the degradation of antistatic activity as time elapses. Whereas, no change in the static activity is observed in the film treated with (I).

Further, the two types of the X-ray photographic films prepared above and control sample of an X-ray photographic film prepared by the same conditions but containing neither compound I nor compound II were developed and the state of fogging (optical density) was observed. The results are shown in the following table.

Compound:	Photographic fogging (optical density)
Non(control)	0.10
(I)	0.10
(II)	0.15

As clear from the above table, Compound I of this invention gave substantially no bad influence on the formation of fogs whereas the fog formation was increased by the addition of Compound II disclosed in the British patent.

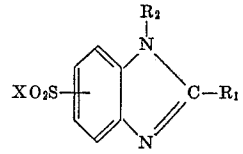
Example 6



150 cc. of a 1% aqueous solution of sodium alkyl benzimidazole sulfonate represented by above formula was added to 200 cc. of a 6% aqueous gelatin solution. The resulting solution was further mixed with 0.4 g. of chrome alum and 0.1 g. of saponin, and then the mixture was applied to a cellulose triacetate film base and dried. The opposite side of the film was coated with a high-sensitive negative emulsion. The static charge of the film under 30% in relative humidity was 35 v., while the charge was 200 v. in the case where the benzimidazole derivative compound had not been incorporated in the back layer.

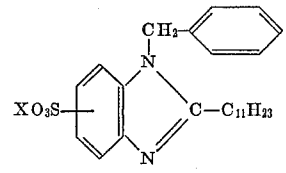
What is claimed is:

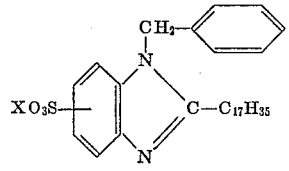
1. An antistatically finished photographic film comprising a support, a photosensitive emulsion layer and at least one auxiliary layer, at least one of said layers containing an alkylbenzimidazole sulfonic acid derivative having the following formula

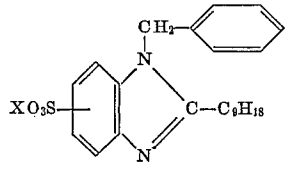


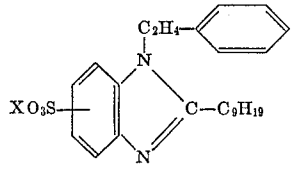
wherein R_1 represents an alkyl group, R_2 represents an aralkyl group, total carbon number of R_1 and R_2 being less than 25, and X represents a member selected from the group consisting of hydrogen, an alkali metal and an ammonium group.

2. The antistatically finished photographic film as claimed in claim 1 wherein said alkylbenzimidazole sulfonic acid derivative is a member selected from the group consisting of the compounds having the following formulas

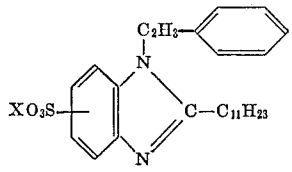






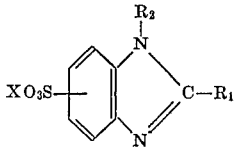


and



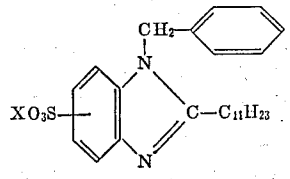
wherein X represents a member selected from the group consisting of hydrogen, an alkali metal, and ammonium.

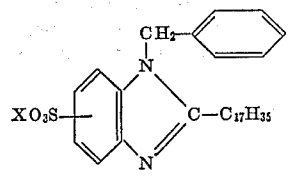
3. An antistatically finished photographic film comprising a support, a photosensitive emulsion layer and at least one auxiliary layer, at least one of said support and said layer having a coating containing an alkylbenzimidazole sulfonic acid derivative having the following formula

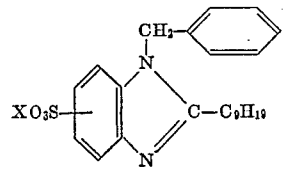


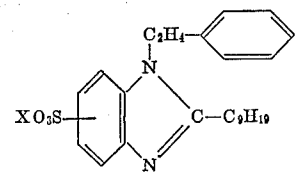
wherein R_1 represents an alkyl group, R_2 represents an aralkyl group, total carbon number of R_1 and R_2 being less than 25, and X represents a member selected from the group consisting of hydrogen, an alkali metal and an ammonium group.

4. The antistatically finished photographic film as claimed in claim 3 wherein said alkylbenzimidazole sulfonic acid derivative is a member selected from the group consisting of the compounds having the following formulas

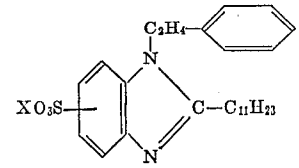








and



wherein X represents a member selected from the group consisting of hydrogen, an alkali metal and ammonium.

5. The antistatically finished photographic film as claimed in claim 3 wherein at least one of said layers contains said alkylbenzimidazole sulfonic acid derivative.

References Cited

UNITED STATES PATENTS

2,992,108 7/1961 Knox et al. ---------- 96—85

FOREIGN PATENTS

847,884 9/1960 Great Britain.

NORMAN G. TORCHIN, Primary Examiner

RONALD H. SMITH, Assistant Examiner

U.S. Cl. X.R.

96—94