

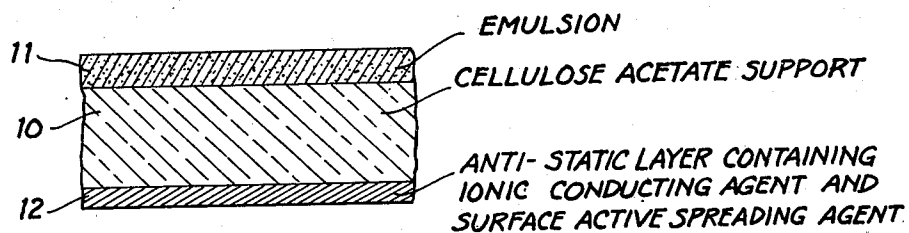
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ANTISTATIC PHOTOGRAPHIC FILM

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ANTISTATIC PHOTOGRAPHIC FILM

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This invention relates to photographic film and particularly to a film protected against static.

The accumulation of electrical charges on photographic film has been the cause of considerable trouble. These charges are produced by the friction of the film moving over rollers or past the gates of a camera, or by the separation of the emulsion from the backing side, upon unreeling of a large roll, and when discharged are manifested as irregular fogged patterns in the emulsion of the film after it has been developed. These static effects are particularly noticeable in films provided with cellulose nitrate supports, although they are also evident on cellulose acetate supports, particularly since the advent of high speed emulsions. Static markings on film are thought to result also upon separation of emulsion from paper during unwinding of a stock roll when the roll was wound at a humidity sufficiently high to impart sticking.

Attempts have been made to overcome static in photographic film by the application of various layers to the film support. These layers have in general consisted of materials designed to dissipate the electric charges by providing the film with a conducting surface. Materials which absorb moisture and therefore provide a conducting surface have frequently been employed. Most of these methods have not proven entirely satisfactory with the newer high speed emulsions.

It is therefore an object of the present invention to provide a novel and effective means of protecting a sensitive photographic film against static. A further object is to provide a method of coating photographic film to reduce its static tendency. A still further object is to provide a suitable means for protecting cellulose acetate films, especially cellulose triacetate films, against static. Other objects will appear from the following description of our invention.

These objects are accomplished by coating photographic film base with a mixture of certain surface-active agents as explained more fully hereinafter.

The accompanying drawing shows sectional views of film constructed according to our invention.

In general, the mixtures which comprise our invention consist of (1) certain ionic organic materials (which, incidentally, are surface-active) which act primarily as conductors in the mixture, and (2) ionic organic materials of lesser ionic activity than class 1 which are surface-active and which function primarily as spreading agents in the mixture, producing clear, even, and transparent coatings on the film. These compounds

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of the second class may even be completely non-ionic. The ratio of the components in the mixture may vary within wide limits. The conducting agent should be present in amounts from about 30% to 95% of the mixture of surface-active agents.

The two components may be further differentiated by their surface resistivity. Thus if the spreading agent is applied by itself from a 1% solution onto a sheet of cellulose acetate, the sheet dried and the surface resistivity measured, this resistance then is greater than 10^{12} ohms. On the other hand, if a mixture of 95% conductor and 5% spreading agent is applied from a 1% solution, the surface resistivity then is less than 10^{12} ohms and preferably lower than about 10^{10} ohms.

The surface resistivity is measured by placing two parallel electrodes on the film, at a fixed relative humidity of 50%; these electrodes are long compared to the distance between them, so as to avoid end effects. The observed resistance reading is divided by the distance between electrodes, and multiplied by their length, to obtain the surface resistivity.

The ionic surface-active materials serving as conductors according to our invention are as follows:

1 (a) The alkali metal or amine salts of sulfonated naphthalene formaldehyde condensates. These products are sold under the trade names Tamol NNO and Tamol P by Rohm and Haas and under the trade name Daxad 11 by Dewey and Almy Chemical Company. Other varieties are Darvan No. 1 (R. T. Vanderbilt Co.), Blancol, and Lomar PW (Jacques Wolf & Co.). They are relatively neutral amorphous solid products having little or no odor, are quite soluble in water, and are compatible with water-organic solvent mixtures. When dissolved in water at low concentrations, they give essentially clear colorless solutions without odor which do not decompose with standing. More concentrated solutions have a slight yellowish color. (See Ullmann, *Enzyklopadie der technischen Chemie*, 2nd Auflage (1930) 5 Band, page 686; H. Wagner, "Chemiker Zeitung," vol. 46 (1922), page 801; U. S. Patent 1,336,759.

1 (b) Alkali metal-alkyl phosphates, for example, sodium potassium ethyl phosphate and sodium potassium amyl phosphate, sold by Monsanto Chemical Company.

1 (c) Alkali metal, ammonium, or amine salts of cellulose sulfate or cellulose acetate sulfate. These include the sodium or ammonium salts of cellulose acetate sulfate containing from 6 to

20% of sulfur (Crane U. S. application Serial No. 104,482, filed July 13, 1949); cellulose di-N-butyl amine sulfate, cellulose diethanolamine sulfate, and cellulose N,N'-diethylcyclohexylamine sulfate.

The mixtures which comprise our invention are composed of an agent selected from class 1a, 1b, or 1c, and an agent selected from class 2 or class 3.

Class 2 comprises surface-active agents, ionic in character, but not capable of giving sufficient conductivity to be employed as class 1 agents. They have been found to be compatible with those of class 1, and to permit the application of thin, even, transparent coatings, free from streaks, blemishes, haze, and reticulated areas. The agents of class 1, if used alone, run into these difficulties and do not yield a commercially acceptable product.

2(a) Alkyl aryl sulfonates. Examples are Nacconol NR, (National Aniline Co.), Santomerse D—sodium dodecyl benzene sulfonate (Monsanto Chemical Co.), Sorbit P—sodium alkyl naphthylene sulfonate (Alrose Chemical Co.), and Padasol—sodium dodecyl benzene sulfonate (Jacques Wolf & Co.).

2(b) The sodium salt of a fatty alcohol sulfate. Examples are Duponol D (principally C₁₆ and C₁₈ alcohols) and Duponol 80 (sodium octyl alcohol sulfate) both sold by Du Pont; and Tergitol 08 (sodium sulfate derivative of 2-ethyl-hexanol-1), sold by Carbide and Carbon Chemicals Corp.

2(c) The sodium salt of sulfated higher fatty esters, for example, Surfax WO sold by the E. F. Houghton & Co.

Class 3 comprises non-ionic surface-active agents of the following nature:

3(a) Mixed fatty acid alkylolamine condensates. Examples are Ninol 400 and Ninol 737, sold by Ninol Laboratories; also Dianol G (Quaker Chemical Co.); and the Alrosols (Alrose Chemical Co.).

3(b) Alkylated aryl polyether alcohol. Example: Triton X-45 (Rohm & Haas Co.).

3(c) Esters of polyhydric alcohols such as sorbitan or mannitan, with higher fatty acids such as lauric, palmitic, oleic, ricinoleic, and stearic acids. Examples are Span 20, sorbitan monolaminate; Span 40, sorbitan monopalmitate; and Span 85, sorbitan trioleate; all sold by the Atlas Powder Co. of Wilmington, Delaware.

3(d) Esters of polyethylene glycol with the higher fatty acids, for example, the Quakesters (Quaker Chemical Products Corporation).

When used to prevent static on sensitive photographic film, the mixtures of our invention may be incorporated in the sensitive emulsion layer, in an overcoating layer, or as a backing layer. Our anti-static agents possess such physical properties that when applied from solvent solution to the back of a cellulose ester film, they form a clear, transparent layer on the film without any undesirable physical or photographic effects. They are therefore preferably applied in this way.

The following examples illustrate methods of applying the mixture of surface-active agents according to our invention.

Example 1.—A mixture of 90% of the sodium salt of a sulfonated naphthalene formaldehyde condensate (Daxad 11) and 10% of the sodium salt of an alkyl aryl sulfonate (Padasol) was dissolved as a 1% solution in a solvent consisting of 35% water and 65% methyl alcohol. This solu-

tion was applied as a backing to a roll of cellulose triacetate film base by means of a dip roller and dried. The film was then further coated on the reverse side with a suitable subbing layer and a gelatino-silver halide emulsion. This film showed good optical appearance of the backing. A second sample of film was coated in the same way except that no surface-active agent mixture was applied to it. These two films were then brought to equilibrium with 50% relative humidity and tested for electrical conductance with the following results:

	Backing Resistivity
Untreated film.....	Greater than 10 ¹⁴ ohms.
Film with mixture of surface-active agents.....	0.05×10 ¹⁰ ohms.

While the concentration of the mixture of surface-active agents in the anti-static layer is not highly critical, we have found that a solution of between 0.5% and 2.0% by weight is most effective.

Example 2.—A solvent was made up consisting of 40% water and 60% methyl alcohol. To this was added 0.6% of a mixture consisting of 5 parts cellulose acetate sodium sulfate and 1 part of the sodium salt of an alkyl aryl sulfonate (Padasol). A sheet of cellulose triacetate film coated with this solution, dried and measured at 50% R. H., had a surface resistance of 0.2×10¹⁰ ohms, whereas the untreated film measured over 10¹⁴ ohms.

Example 3.—A solvent was made up consisting of 40% water and 60% methyl alcohol. To this was added 0.6% of a mixture consisting of 5 parts cellulose diethanolamine sulfate and 1 part of the sodium salt of an alkyl aryl sulfonate (Padasol). A sheet of cellulose triacetate film coated with this solution, dried and measured at 50% R. H., had a surface resistance of 8.2×10¹⁰ ohms.

Example 4.—A solvent was made up consisting of 40% water and 60% methyl alcohol. To this was added 0.4% of a mixture consisting of equal parts of Darvan No. 1 and Santomerse D. A sheet of cellulose triacetate film, coated with this solution, dried and measured at 50% R. H., had a surface resistance of 0.46×10¹⁰ ohms.

Example 5.—A solution was made up and coated on cellulose triacetate film in the same way as Example 4, except that Duponol D was substituted for Santomerse D. The resistance was found to be 0.3×10¹⁰ ohms.

Example 6.—A solution of equal parts of Lomar PW and Surfax 1288 was made up and coated in the same way as in Example 4. The resistance was found to be 0.76×10¹⁰ ohms.

Certain types of backings are composed principally of gelatin, and it is desirable, for static control, to bring the surface resistance of such backings near the value of 10¹⁰ ohms. This is accomplished, we have discovered, by the addition of mixtures composed of class 1a, 1b or 1c, together with one of the following: Igepon T, which is the sodium salt of lauryl methyl taurine; Arctic Syntex T (a substituted amide sodium salt of alkyl taurate); sodium polyethylene glycol sulfate; the ammonium salt of polyacrylic acid. A suitable mixture may also be had by combining two of the last four materials mentioned. All of these mixtures consist of approximately equal parts, and have the additional desirable property of retaining clarity in the gelatin backing.

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When added to a gelatin coating, either a backing layer or the emulsion itself, our agents should be present in an amount of at least 5% of the weight of the gelatin, and preferably in an amount not over 25% of the weight of the gelatin. Aqueous solutions only are used when dealing with gelatin.

When coated from solution in an organic solvent, any suitable solvent, such as an aqueous solution of methyl alcohol, ethyl alcohol, or methyl Cellosolve, or a hydrocarbon such as benzene, may be used. We prefer to use a 20% to 95% solution of methyl alcohol in water.

In the accompanying drawing, the single figure is a sectional view of a photographic film constructed according to our invention. As shown therein, a film support 10 of cellulose acetate has coated thereon a layer 11 of gelatin-silver halide emulsion and on the opposite side a layer 12 of a mixture of an ionic, organic agent having marked conductive properties and a surface-active agent capable of spreading the conducting material into a clear, continuous, homogeneous, and transparent film of sub-microscopic thickness.

It will be understood that our invention is capable of numerous modifications within the scope of the appended claims.

We claim:

1. An anti-static photographic film comprising a cellulose ester support having thereon a sensitive silver halide emulsion layer and in one of the layers of the film a mixture of (1) a surface-active ionic conductor material selected from the class consisting of salts of sulfonated naphthalene formaldehyde condensates selected from the group consisting of alkali metal and amine salts, alkali metal alkyl phosphates, and cellulose sulfates in which one valence of the sulfate is satisfied by a radical selected from the group consisting of alkali metal, ammonium and amine, and (2) a surface-active spreading agent selected from the class consisting of esters of polyhydric alcohols with higher fatty acids, alkyl aryl sulfonates, sodium salts of fatty alcohol sulfates, sodium salts of sulfated higher fatty esters, mixed fatty acid alkylamine condensates, and alkylated aryl polyether alcohols, said surface-active conductor comprising from about 30% to about 95% of said mixture.

2. An anti-static photographic film comprising a cellulose ester support having thereon a sensitive silver halide emulsion layer and in one of the layers of the film a mixture of an alkali metal salt of a sulfonated naphthalene formaldehyde condensate and an alkali metal salt of an alkyl aryl sulfonate, said alkali metal salt of a sulfonated naphthalene formaldehyde condensate comprising from about 30% to about 95% of said mixture.

3. An anti-static photographic film comprising a substantially fully esterified cellulose lower fatty acid ester support having on one side thereof a sensitive silver halide emulsion layer and on the other side a coating of a mixture of an alkali metal salt of a sulfonated naphthalene formaldehyde condensate and an alkali metal salt of an alkyl aryl sulfonate, said alkali metal salt of a sulfonated naphthalene formaldehyde condensate comprising from about 30% to about 95% of said mixture.

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4. An anti-static photographic film comprising a substantially fully esterified cellulose lower fatty acid ester support having on one side thereof a sensitive silver halide emulsion layer and on the other side a coating of a mixture of 90% of the sodium salt of a sulfonated naphthalene formaldehyde condensate and 10% of the sodium salt of dodecyl benzene sulfonate.

5. An anti-static photographic film comprising a substantially fully esterified cellulose lower fatty acid ester support having on one side thereof a sensitive silver halide emulsion layer and on the other side a coating of a mixture of cellulose acetate sodium sulfate and the sodium salt of an alkyl aryl sulfonate, said cellulose acetate sodium sulfate comprising from 30% to 95% of said mixture.

6. An anti-static photographic film comprising a substantially fully esterified cellulose lower fatty acid ester support having on one side thereof a sensitive silver halide emulsion layer and on the other side a coating of a mixture of cellulose diethanolamine sulfate and the sodium salt of an alkyl aryl sulfonate, said cellulose diethanolamine sulfate comprising from 30% to 95% of said mixture.

7. An anti-static photographic film comprising a substantially fully esterified cellulose lower fatty acid ester support having on one side thereof a sensitive silver halide emulsion layer and on the other side a coating of a mixture of an alkali metal salt of a sulfonated naphthalene formaldehyde condensate and the sodium salt of a higher fatty alcohol sulfate, said alkali metal salt of a sulfonated naphthalene formaldehyde condensate comprising from about 30% to about 95% of said mixture.

8. An anti-static photographic film comprising a substantially fully esterified cellulose lower fatty acid ester support having on one side thereof a sensitive silver halide emulsion layer and on the other side a coating of a mixture of a sulfonated naphthalene formaldehyde condensate and the sodium salt of a sulfated higher fatty ester, said alkali metal salt of a sulfonated naphthalene formaldehyde condensate comprising from about 30% to about 95% of said mixture.

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References Cited in the file of this patent UNITED STATES PATENTS

Number	Name	Date
1,534,019	Shepherdson et al.	Apr. 21, 1925
2,118,059	Slack et al.	May 24, 1938
2,184,171	Sponsel et al.	Dec. 19, 1939
2,244,512	Brandt	June 3, 1941
2,386,627	Nadeau et al.	Oct. 9, 1945
2,413,428	Billings	Dec. 31, 1946
2,494,054	Nadeau et al.	Jan. 10, 1950

FOREIGN PATENTS

Number	Country	Date
278,485	Great Britain	Oct. 13, 1927

OTHER REFERENCES

Schwartz and Perry, "Surface Active Agents," 1949, Interscience Publishers, Inc., New York, page 424 cited.