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ANTISTATIC PHOTOGRAPHIC FILMS

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Fig. 1

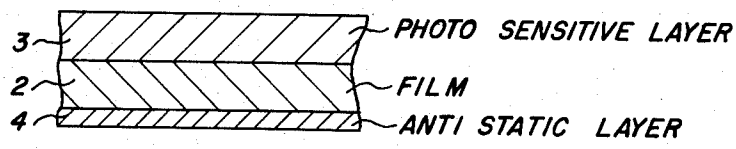
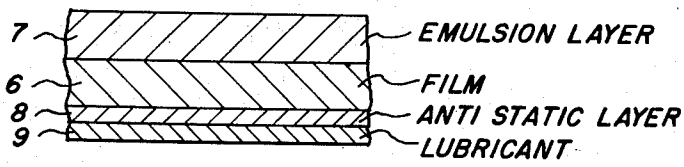


Fig. 2



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ANTISTATIC PHOTOGRAPHIC FILMS

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This invention relates to new photographic products. More particularly, this invention relates specifically to antistatic photographic films.

As is well known, the building up of electrical charges on photographic films presents serious difficulties. These charges can result from the rubbing of the film on surfaces such as the rollers and passageways of the cameras, or from the sudden elimination of the contact that was present between the film and another surface, as in the case e.g. when unrolling the windings from a spool and in so doing separating the emulsion side of one winding suddenly from the backing surface of the adjacent winding.

The electrical charges that are built up in this way on the film can attract dust, which is obviously undesirable and may be the source of luminous discharges that show up on the developed film as fogged areas of irregular shape.

It has been attempted to remedy these difficulties by applying layers of a different kind onto the film support, which layers may be classified in two general types.

The antistatic layers of the first type are such that they render the surface of the film support conductive and in this way permit the electrical charges to be discharged; they are comprised of hygroscopic substances and their effectiveness varies in direct proportion to the amount of relative humidity in the air. Antistatic layers of this first type are poorly suited to low relative humidities, because they are not conductive enough and, frequently, they are also poorly suited to high relative humidities because the hygroscopic layers then become sticky and the force that is required, for example, to separate the windings of films becomes greater, so that it is even possible to obtain higher charges than those that appear in the absence of these antistatic layers.

The antistatic layers of the second type are comprised of substances that have a tendency to take on charges of opposite polarity to that of the charges taken on by the subjacent support, or else that have a tendency to become even less charged than the support. Layers of this second type offer the advantages over the antistatic layers of the first type of being much less influenced by variations of relative humidity, and these layers of the second type may be preferred when it is possible to find one that is suitable for the film support that one has in mind.

An illustrative example of layers of this second type is comprised of an antistatic layer of cellulose acetate applied onto the cellulose nitrate film support. The cellulose acetate layer takes on a positive charge, although by regulating the thickness of the antistatic layer it is possible to obtain a film that practically does not become charged any more to a troublesome extent. Since the replacement of the cellulose nitrate films by other films, such as cellulose acetate films with a high degree of acetylation, cellulose mixed-ester films, films made of polyester or polyamid, etc., no antistatic layers of the second type are known that are satisfactory and, for want of something better, resort has been to layers of the first type, which are hygroscopic and conductive and which, as already pointed out, are not always satisfactory.

This invention has for a principal object a new photographic film with an antistatic layer, the effectiveness of which is independent of the degree of relative humidity

and which is satisfactory for at least all of the presentl known supports. Another object is to provide photo graphic film products comprised of a variety of base ma terials which have a styrene coating thereon of a certai thickness. Another object is to provide a method o making a new antistatic photographic film product. Othe objects will appear hereinafter.

The photographic film according to the broader aspect of the present invention involves a support, a photosensi tive emulsion layer on one side of the support and, o the other side, an antistatic layer made from a polyme containing styrene-derivative repeating units and pos sibly other repeating units, the nature and/or the propor tion of which in the polymer are such that they con tribute little or nothing to the antistatic effect of th layer.

The antistatic coating of the instant invention is a ho mopolymer of styrene or a copolymer of styrene, such as copolymer of styrene and of butadiene or another type o polymer containing styrene repeating units, such as a alkyd resin modified with styrene.

Inasmuch as such styrene materials are known chemi cal compositions which are commercially available, fur ther description thereof does not appear necessary.

The styrene-polymer layer may be deposited on th back surface of the film support by any of several coatin methods, e.g. by kiss-roll, dip single-surface coating, wic coating, etc., starting with a concentrated solution (abou 2/1000 to 8/1000) in a suitable solvent so as to obtai a dry layer that is 0.3 micron or less in thickness, pref erably 0.1 to 0.2 micron. The antistatic layers accord ing to this invention form a clear, transparent layer o the film without any undesirable physical or photographi effect.

Since the polystyrene antistatic layer has a relativel low resistance to abrasion, it may be advantageous to us a lubricant in connection with it by incorporating it in th layer itself or by applying it as a second coating. Pa affins, waxes or compounds such as stearic acid, glycerin oleate and the like can be used as the lubricant.

For a still further understanding of our invention refe ence may be made to the attached drawing forming part of the present application. In the attached draw ing FIG. 1 is a sectional view on an enlarged scale of film product in accordance with the invention. FIG. likewise is a sectional view on an enlarged scale of a other embodiment of the present invention.

Referring ot FIG. 1, the film base is shown at **2**. Th may be any one of several different bases as will be ap parent as the description proceeds. The base carries usual photographic emulsion layer **3** on one side. Th other side carries the thin polystyrene layer **4** of the pre ent invention.

FIG. 2 is similar to FIG. 1 in showing a film base emulsion layer **7**, and polystyrene layer **8**. However, i this embodiment the polystyrene layer is overcoated wi a thin layer of lubricant **9**.

A still further understanding of our invention will b had from a consideration of the following specific exan ples which are set forth for illustrating certain preferre embodiments.

EXAMPLE I

A solution of 0.35 part by weight of polystyrene havi a molecular weight of about 800,000 in 99.65 parts b weight of trichloroethylene is prepared. The solution applied as a backing on a cellulose acetate support wi 43.6% acetyl by the kiss-roller method and is then drie A conventional gelatin-silver halide emulsion is coate onto the substrated surface of the support. The optic aspect of the backing layer of the obtained film is goo While at 26° C. and a relative humidity of 35% a chec

product that does not have the polystyrene layer takes on a positive charge of 2590 v./cm., the product with the polystyrene layer according to the invention takes on, under the same conditions, a positive charge of only 172 v./cm.

EXAMPLE II

A photographic product like that of Example I is prepared by using as the ingredients of the antistatic layer a solution of 0.65 part by weight of a copolymer of styrene and butadiene in 99.35 parts by weight of trichloroethylene. Under the conditions specified in Example I the product takes on a negative charge of only 320 v./cm.

EXAMPLE III

0.65 part by weight of polystyrene are dissolved in 99.35 parts by weight of trichloroethylene and the solution is applied as a backing layer onto a support identical to that of Example I. After drying, a solution of 0.2 part by weight of stearic acid in 99.8 parts by weight of type F oil (essence) is applied onto the aforementioned layer. A gelatin-silver halide emulsion is coated on the substrated side of the support. Under the conditions specified in Example I the obtained product takes a positive charge of only 289 v./cm.

The optical aspect of the backing layer of the obtained film is satisfactory. This is also true of the backing layers prepared as indicated in the following examples.

In the same way as in Example I, other photographic films are prepared by using as the ingredients for the antistatic layer the solutions indicated in Examples IV to VI where the quantities are indicated in parts by weight.

EXAMPLE IV

Styrene-butadiene copolymer	0.65
Trichloroethylene	99.35

Under the conditions indicated in Example I, the obtained product takes on a negative charge of 96 v./cm.

EXAMPLE V

We proceed as in Example III, using for the antistatic coating a solution of 0.65 part of polystyrene in 99.35 parts of trichloroethylene and, for the lubricant coating a solution of 0.25 part of paraffin in 99.75 parts of hexane.

Under the conditions indicated in Example I, the obtained product takes on a positive charge of 340 v./cm.

EXAMPLE VI

Polystyrene	0.65
Glycerin oleate	0.25
Trichloroethylene	99.10

Under the conditions indicated in Example I, the obtained product in which the lubricant is incorporated in the antistatic layer takes on a positive charge of 410 v./cm.

The following Examples VII to IX describe the application of this invention to products, the support of which is comprised of different film base materials from that described in the above examples.

EXAMPLE VII

A solution is prepared of 0.50 part by weight of polystyrene in a solvent mixture of 89.50 parts of trichloroethylene and 10 parts by weight of ortho-chlorophenol. The solution is applied as a backing layer on a 0.20 mm. thick support of ethylene glycol polyterephthalate, and a gelatin-silver halide emulsion is applied to the substrated side of the support.

While a check product that does not have the layer according to this invention takes on a positive charge of 2400 v./cm., the product with the polystyrene layer of this invention takes on a negative charge of 100 v./cm.

EXAMPLE VIII

A solution is prepared of 0.65 part by weight of a copolymer of styrene and butadiene, in a solvent mixture of 91 parts by weight of trichloroethylene and 8.35 parts by weight of ortho-chlorophenol. The solution is applied as a backing layer on 0.14 mm. thick polyundecanamid film and dried. A gelatin-silver halide emulsion is coated on the substrated side of the support. Under the conditions indicated in Example I, the thus obtained product takes on a positive charge of 710 v./cm., whereas a similar product without the antistatic layer according to this invention takes on a positive charge of 2240 v./cm.

EXAMPLE IX

A solution is prepared of 0.65 part by weight of polysytrene in a solvent mixture of 90 parts by weight of trichloroethylene and 9.36 parts by weight of ortho-chlorophenol. The solution is applied as a backing on a sheet comprised of a copolymer of modified polyvinyl chloride. A gelatin-silver halide emulsion is coated on the substrated side of the support. Under the conditions indicated in Example I the obtained product takes on a positive charge of 2000 v./cm., whereas a similar product without the antistatic layer according to the invention takes on a positive charge of 6000 v./cm.

Measurement of the charges taken by the films was determined as follows. A closed loop of film, which preferably has been exposed for 12 hours to conditioned atmosphere is passed over a small number of stainless-steel rollers and, after the initial neutralization of the charges by means of an ionizer, the deflection of a device for measuring charges is noted and the results are expressed by the intensity of the electrical field causing the same deflection and created by a metal plate maintained at a predetermined voltage level, of the same shape and of the same dimensions as the film and supposedly placed in the same position as the latter.

Table I shows the variations in the electrostatic charges of various films according to the invention as a function of the hygrometric conditions at 22° C. In each case the product according to the invention is compared to a test piece that does not have the antistatic layer, but is the same in every other respect.

Table I

HYGROMETRIC CONDITIONS

Support	50% RH, v./cm.	Polarity	60% RH, v./cm.	Polarity	84% RH, v./cm.	Polarity
Example I:						
Test Piece	600	+	600	+	280	+
Product according to the invention	200	+	160	+	120	+
Example VII:						
Test Piece	1,600	+	1,000	+	80	+
Product according to the invention	200	+	20	+	16	+
Example VIII:						
Test Piece	2,700	+	2,600	+	300	+
Product according to the invention	1,200	+	360	+	30	+
Example IX:						
Test Piece	250	+	150	+	150	+
Product according to the invention	100	+	100	+	20	+

It will be noted that the antistatic layers of the products according to the invention are of a very small thickness, e.g. on the order of 0.1 to 0.2 micron, which is a definite advantage when recovering waste from the products according to the invention. In fact, since the amount of polystyrene is very small in proportion to the amount of the cellulose derivative or other constituents of the support, the polystyrene does not cause any cloudiness or drop in mechanical properties in the products according to the invention. Moreover, the thinness of the poly-

styrene layer assures its good adherence to the support.

The present invention has also been tested under conditions other than those set forth above. That is, a roller charging apparatus similar to that used above was used except that it contained chromium plated rollers instead of stainless steel, and the charge was measured with a Faraday cylinder instead of measuring the field with a fieldmeter. Table II gives these roller-charging data.

Table II

	Coating 1, e.s.u./cm.[1]	Coating 2, e.s.u./cm.[1]
Check sample	+6.4	+7.5
Polystyrene plus Wax Sample	−1.0	+6.0

	Coating 1, e.s.u./cm.	Coating 2, e.s.u./cm.	Coating 3, e.s.u./cm.
Check Sample	+4.8	+3.9	+4.6
Polystyrene Sample	0	0	+0.5

[1] Charge in electrostatic units per cm. length of 35 mm. width film.

Static tests were made in which the film was run through 35 mm. miniature cameras, the charge again being measured with a Faraday cylinder. These data are given in Table III.

Table III

	Coating 1, e.s.u./cm.	Coating 2, e.s.u./cm.
Kodak 35 Camera:		
Check Sample	+7.2	+5.4
Polystyrene plus Wax Sample	+1.0	+1.0
Retina II-C Camera:		
Check Sample	+2.0	+6.2
Polystyrene plus Wax Sample	+1.0	+3.0

It can be seen from this data and particularly the runs in cameras that the effect of static was materially reduced by the styrene antistatic coating of the present invention.

In the above examples for convenience and consistency of operation, we have used trichloroethylene as the solvent for the styrene coating solutions with other solvents as chlorophenol incorporated when polyester film or the like is coated. However, our invention is not limited to these particular solvents. For example, other solvents such as other chlorinated solvents, esters, ketones, aromatic hydrocarbons, etc. may be used.

The invention has been described in detail with particular reference to the preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. As a new article of manufacture a photographic film product exhibiting improved antistatic properties, said product being comprised of a film base selected from the group consisting of cellulose acetate, ethylene glycol polyterephthalate, polyundecanamid, and a copolymer of polyvinyl chloride which carries a photographic gelatin-silver halide emulsion layer on one surface thereof and on the other surface an antistatic layer having a thickness of from about 0.1 to 0.3 micron and being characterized in that it consists essentially of a styrene resinous material selected from the group consisting of polystyrene and a copolymer of styrene and butadiene.

2. As a new article of manufacture a photographic film product exhibiting improved antistatic properties, said product being comprised of a cellulose acetate film base which carries a photographic gelatin-silver halide emulsion layer on one surface thereof and on the other surface an antistatic layer having a thickness of from about 0.1 to 0.3 micron and being characterized in that it consists essentially of a styrene resinous material selected from the group consisting of polystyrene and a copolymer of styrene and butadiene.

3. As a new article of manufacture a photographic film product exhibiting improved antistatic properties, said product being comprised of an ethylene glycol polyterephthalate film base which carries a photographic gelatin-silver halide emulsion layer on one surface thereof and on the other surface an antistatic layer having a thickness of from about 0.1 to 0.3 micron and being characterized in that it consists essentially of a styrene resinous material selected from the group consisting of polystyrene and a copolymer of styrene and butadiene.

4. As a new article of manufacture a photographic film product exhibiting improved antistatic properties, said product being comprised of a film base selected from the group consisting of cellulose acetate, ethylene glycol polyterephthalate, polyundecanamid, and a copolymer of polyvinyl chloride which carries a photographic gelatin-silver emulsion layer on one surface thereof and on the other surface an antistatic layer having a thickness of from about 0.1 to 0.3 micron and being characterized in that it consists essentially of polystyrene.

5. As a new article of manufacture a photographic film product provided with static protection, said product being comprised of an ethylene glycol polyterephthalate film base which base carries a photographic gelatin-silver halide emulsion layer on one surface thereof and on the other surface an antistatic layer, said antistatic layer being characterized in that it is principally comprised of polystyrene and the thickness of the layer is of the order of 0.1 to 0.2 micron.

6. An article of manufacture in accordance with claim 1 wherein in addition to the styrene resinous material there is present a small amount of at least one lubricant layer selected from the group consisting of paraffins, waxes, stearic acid and glycerin oleate.

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