

[54] **SUPPORT PROVIDED WITH ANTISTATIC LAYER**

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[22] Filed: **Apr. 6, 1970**

[21] Appl. No.: **26,143**

[30] **Foreign Application Priority Data**

Apr. 8, 1969 France.....6910616
Dec. 23, 1969 France.....6944542

[52] **U.S. Cl.**.....**117/76 P, 96/87 A, 117/92, 117/138.8 F, 117/138.8 E, 117/138.8 UA, 117/138.8 UF, 117/144, 117/145, 117/168, 252/8.6**

[51] **Int. Cl.**.....**G03c 1/82, C09k 3/16**

[58] **Field of Search**..... 96/87 A; 117/139.5 CQ, 76 P, 92, 138.8 B; 106/177; 252/8.6

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[57] **ABSTRACT**

Compositions for coating onto polymeric surfaces such as photographic film supports to reduce static include alkali metal salts of alkylphosphoric acid esters, arylphosphoric acid esters or aralkylphosphoric acid esters. The alkyl chains of the phosphoric acid esters contain from about eight to 22 carbon atoms and the alkali metal has an atomic weight of at least 23, the preferred alkali metals being potassium, rubidium and cesium. The salts are applied to the polymeric surfaces from aqueous or organic solvent solutions which may contain a binder such as a polyvinyl acetal, cellulose esters and ethers, etc. The phosphoric acid salts have distinctive properties as antistatic agents compared to lower alkyl phosphate salts such as alkali metal arylphosphates; for example, they impart good static protection at low humidity and do not transfer to adjacent film surfaces so to interfere with coating of photographic emulsions thereon. They also function as film lubricants.

10 Claims, No Drawings

SUPPORT PROVIDED WITH ANTISTATIC LAYER

The present invention concerns antistatic compositions, usable in the preparation of antistatic layers, designed, in particular, for photographic and magnetic film products. In that which follows, the invention will generally be described by referring to photographic products, although it applies to all products involving the problems of electrostatic charges.

It is well known that numerous types of photographic film supports have a tendency to produce static electric charges during the winding or the unwinding of these films and that these electric charges do not dissipate easily, because the materials that are used as film supports are poor conductors of electricity. High potentials which are being created in this manner often discharge suddenly, in the course of manufacture or of use of the film by the user, which produces a flash of light and an undesirable recording of the discharge of static electricity on the photographic emulsion. In order to avoid this result, it was customary, in the prior art, to apply to the back of the film support, a conductive layer making it possible to facilitate the dissipation of static charges, thus making it possible to avoid the sudden charges and the light flashes which accompany them.

The antistatic layers usually consist of a binder wherein an organic or mineral organic conductive substance is dispersed, which makes it possible to render the surface of the support sufficiently conductive so as to make possible the flow of electrostatic charges. They are most often hygroscopic layers the effectiveness of which varies as a direct result of the degree of humidity in the air. Such antistatic layers are thus not suitable for low degrees of humidity, because they are then no longer sufficiently conductive. These hygroscopic layers are also not suitable for very high degrees of humidity, because they become sticky and hard to separate from the surface to which they adhere; the effort that is necessary to separate two superimposed windings create, sometimes, even higher charges than those which would appear without any antistatic layer.

In order to eliminate electrostatic phenomena, it was suggested in particular to use, as antistatic agents, mixtures such as described in French Pat. No. 1,089,923, which comprise two compounds, one of these compounds being selected from among the alkylphosphates of alkaline metals and alkaline metals, ammonium or amine cellulose sulfate salts or cellulose acetate sulfate salts, the other compound being a spreading agent selected from among the esters of higher fatty acids and polyalcohols. The alkyl groups of alkylphosphates consisted of lower alkyl groups, such as ethyl or amyl. There have also been described diester alkali or ammonium salts produced from orthophosphoric acid and lower aliphatic alcohols, such as described in French Pat. No. 1,282,354. There have also been described the ammonium or ethanolamine alkylsulfate and alkylphosphate salts, as described in French Pat. No. 1,435,826. Compound such as potassium amylphosphate and especially triethanolamine alkylphosphates have a good solubility in the usual organic solvents. However, when they are used on the photographic or cinematographic film supports, they are too sensitive to water and easily transfer to the opposite surface of the support with which they are in contact after winding in a roll and therefore cause a poor wettability of the photosensitive emulsion on this surface during its application. On the other hand, the organic salts, e.g. those of triethanolamine, have a damaging action on the photographic emulsions, such as a desensitization or fog-formation.

The present invention provides new antistatic compositions having no damaging action on the photosensitive layers of photographic and cinematographic films, and also usable for magnetic films, causing no adherence between the windings of the films and which are not deteriorated by heat or humidity, and which are, for the most part, self-lubricating.

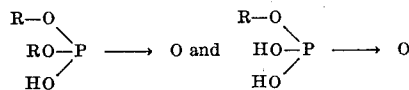
The antistatic compositions according to the invention, comprise as antistatic agent a salt of an alkali metal having an atomic weight at least equal to 23, of an organic mono- or di-ester of phosphoric acid in an aqueous or organic medium, characterized in that the organic ester is derived from an al-

kylphosphoric acid the alkyl group of which contains of from about eight to 22 carbon atoms or from an alkylarylphosphoric acid, or an arylphosphoric acid containing a comparable number of carbon atoms. That is, when an aryl group is present as in phenylphosphate, the six-carbon atom phenyl group imparts the desired properties. Similarly, with an aralkyl group such as benzyl or phenylethyl, the carbon chain can contain less than eight carbon atoms. Moreover, the compositions may contain a binder.

The alkyl phosphoric acid esters of the invention containing eight to 22 carbon atoms in the alkyl group, straight or branch-chained, will be found to be generally superior, when they are used in antistatic layers, to similar esters, such as the ethyl or amyl phosphoric acid esters of the above patents. The esters of the invention show little tendency to transfer from the antistatic layer to adjacent surfaces such as a subbing layer on the opposite surface of the support on which they are coated and thus do not interfere with subsequent coating of a silver halide emulsion onto the subbing layer. In particular, the alkyl esters of 12, 14, 16 and 18 carbon atoms are exceptional in this respect in that they show no noticeable tendency to interfere with emulsion coating of the opposite surface of the support on which they are coated. The eight to 11 and 19 to 22 carbon atom alkyl phosphoric acid esters, although useful, show some tendency to interfere with the emulsion coatings. The cetyl phosphate salts are exceptionally useful because of low tendency to transfer to the adjacent surfaces. Moreover, the cetyl esters when used in antistatic layers also exhibit excellent lubricating properties for the photographic films comparable to waxes such as Carnauba wax. The eight to 22 to carbon alkyl esters are also advantageous, compared to similar lower alkyl esters such as amyl phosphate, since they have higher solubility in organic solvents which allow dispersion of the esters together with waxes or synthetic polymers in organic solvent or aqueous organic solvent coating compositions for coating on all types of photographic film supports, as illustrated in the examples below. From the examples it will be seen that certain compositions, e.g., alkyl phosphate - wax dispersions are very useful for coating film base such as linear polyester. Other coating systems containing, e.g., a mixture of alkyl phosphate and polymer such as "Butvar" are very useful for coating cellulose ester film bases.

It is unexpected that the esters having chain lengths of about eight to 22 carbon atoms should be so effective as antistatic agents. One skilled in the art knowing that the hydrophilic organic and inorganic compounds are usually the most effective antistatic agents would expect that after coating the antistatic layers from aqueous solution, the higher molecular weight aliphatic groups would orient at the air-water interface forming paraffin-like monolayers which would not give antistatic properties, contrary to the facts.

The phosphoric acid esters that are preferred for preparing the salts according to the invention appear to correspond to the following formulas:



wherein R represents a substituted or unsubstituted alkyl group, having eight to 22 carbon atoms. For example, R is the octyl, nonyl, decyl, undecylenic, dodecyl, tridecyl, tetradecyl, hexadecyl, octadecyl, etc. group. The R groups can be the same or different organic radicals.

R may also contain one or more substituted or unsubstituted benzene nuclei, joined or not joined directly to the phosphoric group, e.g.: phenyl, octylphenyl, etc.

The preparation of these acids produces a mixture of acids corresponding to the preceding formulas. One may use for the preparation of the salts of the present invention, the phosphoric acid mono- or di- esters alone or in a mixture.

The long alkyl chain or an aromatic radical reinforces the organophile character of the compounds, and thus conferring solubility in the usual solvents, decreases their sensitivity to

water, and by minimizing transfer of the compounds to adjacent surfaces reduces the defects related to wettability of the surfaces by the emulsions. These compounds, especially in the case of those having long alkyl chains, display lubricating properties similar to those of the usual waxes. On the other hand, being alkaline salts, their properties bring them closer to soaps and they are dispersible in water and have a dispersive power toward certain substances.

When compared, e.g., to an amine salt, their antistatic power is increased by the presence of the alkali metal ion, their damaging action to the photosensitive emulsions is nil and their resistance to hydrolysis is increased.

One may use, according to the invention, as alkali metals, sodium, potassium, rubidium, as well as cesium, because for the same alkylphosphate, the effectiveness increases from lithium, for which it is practically nil, to the sodium, potassium, rubidium and cesium salts. In order to measure the surface resistivity, at 30 percent and 50 percent relative humidity, of the salts of lithium, sodium, potassium, rubidium and cesium of alkylphosphoric acids, one applies separately and without binder, e.g., the salts of Li, Na, K, Rb and Cs of mono-octylphosphoric acid to a cellulose triacetate support using a solution having 1/100 mole of the salt per liter in a mixture of solvents containing 80 parts of methanol and 20 parts of 2-methoxyethanol. The results are indicated in the following table:

Salt Cation	Surface resistivity in GΩ. cm/cm	
	at 50% RH	at 30% RH
Li	>6000	>6000
Na	1.1	6000
K	0.23	1.5
Rb	0.13	1.7
Cs	0.25	1.6

One sees that the surface resistivity depends on the relative humidity and that unexpectedly it decreases from lithium to potassium to then become fairly constant for rubidium and cesium salts.

With the use of potassium ion, the surface resistivities are practically constant, both at 50 percent and 30 percent relative humidity. The differences between the surface resistivities for 30 percent and 50 percent relative humidity are small for the potassium, cesium and rubidium. On the other hand, for sodium, this difference is very great since the surface resistivity for a 30 percent relative humidity reaches up to 6,000 GΩ. cm/cm, whereas it is only 1.10 GΩ. cm/cm for a 50 percent relative humidity.

From that which precedes, it appears that the salts which will produce the best conductive properties are, preferably, those of potassium, rubidium and cesium. On the other hand, the alkylphosphate salts in which the alkyl group contains of from 14 to 18 carbon atoms, generally give the most satisfactory combination of properties that are desired for forming film backings.

One may apply salts of alkylphosphoric acids or alkylaryl or arylphosphoric acids in an aqueous or organic medium, with or without binder. The solvents or dispersing agents usable according to the invention comprise the compounds which have, in particular, hydroxyl groups, such as water, alcohols, glycols, etc., such as methanol, ethanol, methyl monoether of glycol or 2-methoxyethanol, etc., or mixtures of these compounds. In the mixtures, the alcohols may be used in any proportion, but it is preferred to use mixtures containing, e.g., 80 percent of methanol and 20 percent of 2-methoxyethanol, although good results are obtained with other proportions. It is also possible to use mixtures of water and an alcohol, e.g., water and methanol, or other solvents, e.g., methylene chloride.

The use of a binder, although not indispensable, may prove in many cases beneficial. Among the usable binders, we may cite most of the cellulose derivatives: cellulose acetate, cellulose acetatebutyrate, cellulose ether phthalate, methylcellulose, hydroxyalkylmethylcellulose such as hydroxypropylmethylcellulose etc. Numerous vinyl derivatives are also usa-

ble such as acetals, e.g., polyvinyl butyrals such as the "Butvar B 76" product sold in the U.S.A. by Schawinigan Resins Corp., suitable for applications in an organic medium, as well as polyvinyl alcohol and other polymers and copolymers soluble in an aqueous medium. Natural binders such as, e.g., gelatin, casein, agar-agar, waxes etc., may also be suitable.

On the other hand, due to the dispersing power of these antistatic compounds, one may consider the use, as a binder, of substances which have no mutual solvent. Thus, the compositions appear in the state of dispersions. As examples of such dispersions, one may indicate:

1. Aqueous dispersions of a natural or synthetic waxy substance, such as Carnuba wax, in which the antistatic compounds then play the part of dispersing agent. 2. Dispersions of these salts effected in the midst of an aqueous emulsion of synthetic polymer or copolymer, particularly of an acrylic ester, acrylonitrile, vinylidene chloride and of an unsaturated acid, e.g., a terpolymer of methyl acrylate, vinylidene chloride and itaconic acid or a terpolymer of acrylonitrile, vinylidene chloride and acrylic acid.

The products containing the salts of the invention in antistatic layers have particularly high conductive properties. As a result, a sizeable quantity of these salts is not necessary for obtaining an efficient protection, usually 2 to 200 mg/m² suffice, which may be obtained from solutions containing of from 0.2 to 20 g per liter of antistatic compound by using coating means such as indicated hereinafter.

The quantities of binder that are used may vary. One may use proportions of a binder up to approximately 50 percent by weight with respect to the total weight of binder and salt of the phosphoric ester. One obtains particularly good results with approximately 30 percent by weight of binder with respect to the total weight of binder and salt.

The films according to the invention may have, as support, a film formed by one of the numerous customary film-forming substances. One may use, in particular, as supports, cellulose esters such as cellulose acetate, cellulose triacetate, cellulose acetate propionate, cellulose acetobutyrate, linear polyesters such as ethylene glycol polyterephthalate, polycarbonates, copolyesters of terephthalate and ethyleneglycol isophthalate and of 1,4-cyclohexane-dimethanol; a polyolefin such as polyethylene or polypropylene; polystyrene; and a vinyl polymer such as a copolymer of vinyl acetate and vinyl chloride, a copolymer of vinyl chloride modified by maleic anhydride or a polymer of vinyl fluoride. A paper support coated with polyester or a polyolefin such as polyethylene is also useful.

The supports carrying the antistatic layers of the invention can be coated with well-known emulsion layers for black-and-white or color photography, suitable subbing layers being employed to adhere the emulsion layers to the support. Ordinarily, the antistatic layer is coated on the surface of the film base opposite to the surface to be emulsion coated. However, the phosphoric acid ester can be coated under the emulsion layer. In the case of polymer-coated paper the esters are useful both for sizing the paper (as an internal antistat), prior to coating the polymer, or for coating the surface of the polymer-coated paper.

The coating processes include, in general, using a wetting cylinder immersed into the solution that is to be applied and an adjacent cylinder around which passes the support so spaced that a meniscus is obtained between the support and the wetting cylinder. However, other processes may be used such as a hopper-type coating, surface-tension coating with removal of the excess quantity done by means of an "air knife," coating by brush, etc.

The antistatic layers obtained from the compositions according to the invention may have a permanent or temporary character depending on the use that is intended for the treated films. In addition to the use of the antistatic compounds having a long alkyl chain or an aromatic radical chain having low sensitivity to water, when a binder is also used for adhering the compounds to the support the layers have a more permanent

character than in the case of short-chain compounds per se of the above prior art.

On the other hand, certain of these layers may be removed in the course of treatments which photographic and cinematographic films may undergo. This is made possible, e.g., by using a binder that is soluble in an alkaline medium, such as an acidic or water-soluble polymer, or a binder that is capable of being submitted to chemical modifications in the course of treatment to render it soluble in water, acid or alkaline solutions.

The previously described phosphoric ester compositions are of particular interest when they are used in the form of antistatic backing layers for photographic film supports. However, certain of these may be used as sub-layers of the emulsion. One may also use these antistatic layers as protective over-layers of the unexposed or developed emulsion. Certain other above-described compounds may likewise be incorporated in the surface layers of the photographic emulsion. Antistatic properties of the esters is also retained when they are placed in these layers.

The backings containing the long-chain phosphoric ester compounds are self-lubricating. The friction coefficients, measured in contact with tungsten carbide are low, in the range of 0.15 for 20 g to 100 g, for example, of applied weight.

The surface resistivities are much below the resistivity of an untreated test sample. For example, with potassium octadecylphosphate in an organic medium (methanol and 2-methoxyethanol) applied on a cellulose triacetate support, the surface resistivities, measured for a relative humidity of 50 percent and 30 percent, are equal to 9 GΩ. cm/cm and 270 GΩ. cm/cm, respectively, compared to resistivities above 60,000 GΩ. cm/cm in the case of an untreated test sample.

The antistatic layers of the invention, as mentioned previously, may be used for photographic and cinematographic films. Another field for the application of antistatic layers of the invention is the magnetic recording, wherein one uses magnetic bands to the backing of which, in particular, one may apply an antistatic layer in order to remove the charges, due, in particular, to the friction of the bands in the various machines in which they are apt to be used.

The preparation of the antistatic salts, that are used according to the invention, may be effected, e.g., for the salts of alkylphosphoric acids, as follows.

Preparation of the alkylphosphoric acids.

One establishes a light circulation of dry air in a three-neck flask provided with a stirrer and introduces 3 moles of the selected alcohol, anhydrous, and melted if it is solid at room temperature. One heats and, without surpassing 95° C, one introduces, in small quantities, one mole of phosphoric anhydride. After the emission of heat has stopped, the reaction mixture is kept between 90° and 95° C for approximately 6 hours, until complete disappearance of the anhydride.

Preparation of alkylphosphoric acid salts, in particular potassium salt.

In a flask provided with a stirrer, one introduces a sufficient amount of ethanol for dissolving the stoichiometric quantity of potassium hydroxide, in the form of pellets, necessary for the complete salt formation of the alkylphosphoric acid. The alcoholic solution is brought up to a temperature that is sufficient for dissolving the acid, either solid or liquid, that one introduces into the flask in small quantities while stirring. After the complete introduction of the acid, the temperature of the mixture is kept at 70° C and the stirring for a period of 10 minutes.

If the obtained product is solid, it is cooled down to from 15° to 20° C and the resulting salt is filtered on a Buchner funnel. The residual ethanol is then removed by means of drying in an oven at a temperature of from 80° to 85° C. If the salt obtained is liquid, the alcohol is distilled under vacuum.

The following examples illustrate the invention. In these examples, the antistatic layers are applied to cellulose triacetate or ethyleneglycol polyterephthalate supports. However, it is possible to apply them to other supports such as those cited previously.

Except as indicated below (Example 11) the mixed esters prepared as above were used. In Example 11 the monoocetyl ester had been isolated from the reaction mixture also containing the dioctyl ester.

In these examples, the surface resistivities are given in GΩ. cm/cm and the electrostatic fields in V/cm for endless bands turning on a system of metallic rollers connected to the ground.

The Examples 1 to 14 relate to applications, effected without binder, in an organic medium as well as in an aqueous medium with different alkaline salts, to a cellulose triacetate support (Examples 1 to 11) as well as on an ethyleneglycol polyterephthalate support (Examples 12 to 14).

EXAMPLE 1

A cellulose triacetate film is coated with a solution containing:

Potassium octadecylphosphate	0.4 g
Methanol	80 ml
2-methoxyethanol	20 ml

After drying, the properties of the product are compared with those of an untreated test sample. The results are indicated in Table I.

EXAMPLE 2

One applies to a cellulose triacetate support a coating solution comprising 0.4 g of potassium cetylphosphate, 80 ml of methanol and 20 ml of 2-methoxyethanol. The surface resistivities for 50 percent and 30 percent relative humidity are 4 GΩ. cm/cm and 230 GΩ. cm/cm, respectively.

EXAMPLE 3

The coating solution contains 0.4 g of potassium tetradecylphosphate, 80 ml of methanol and 20 ml of 2-methoxy ethanol and it is applied to a cellulose triacetate support. The results obtained are given in Table I.

EXAMPLE 4

The coating solution contains 0.4 g of potassium dodecylphosphate and 100 ml of ethanol and it is applied to a cellulose triacetate support. The surface resistivities, measured for 50 percent and 30 percent relative humidity, are 1.1 GΩ. cm/cm and 45 GΩ. cm/cm, respectively.

EXAMPLES 5 and 6

One applies to cellulose triacetate supports, coating solutions containing, in a solvent mixture of 80 ml of methanol and 20 ml of 2-methoxyethanol, 0.4 g of rubidium cetylphosphate for the example 5, and 0.4 g of cesium cetylphosphate for the example 6.

EXAMPLES 7 and 8

In these two examples, the respective coating solutions are applied to triacetate supports. The coating solutions contain, the one, 0.4 g of rubidium octadecylphosphate, the other, 0.4 g of cesium octadecylphosphate, in 80 ml of methanol and 20 ml of 2-methoxyethanol.

EXAMPLE 9

One applies to a cellulose triacetate support, the following solution:

Potassium phenylphosphate	0.4 g
Methanol	90 ml
2-methoxyethanol	10 ml

EXAMPLE 10

One applies, in the above manner, to a cellulose triacetate support a solution similar to that of Example 9, but wherein

the potassium phenylphosphate is replaced by potassium octylphenylphosphate.

EXAMPLE 11

In a solvent mixture containing 80 ml of methanol and 20 ml of 2-methoxyethanol, one dissolves 1/1,000 of a mole of sodium monoethylphosphate. The obtained solution is applied to a cellulose triacetate support.

The results of Examples 1 to 11 are given in Table I.

TABLE I.—TESTS EFFECTED WITHOUT BINDER

Test number	Support	Surface resistivity in GΩ. cm./cm.		Electrostatic field in V./cm.		Coefficient of friction in contact with tungsten carbide under—	
		50% RH	30% RH	50% RH	30% RH	20 g.	100 g.
Untreated test sample	Cellulose triacetate	60,000	60,000	+1,320	+2,040	0.70	0.62
1	do.	9	270	0	+800	0.12	0.14
2	do.	4	230	0	+740	0.19	0.14
3	do.	1.6	340	0	+690	0.07	0.06
4	do.	1.1	45	0	+56	0.20	0.13
5	do.	0.80	10	0	0	0.17	-----
6	do.	1	5	0	0	0.16	-----
7	do.	0.95	18	0	+230	0.16	-----
8	do.	1	10	0	+50	0.16	-----
9	do.	5	6,000	0	+840	-----	0.80
10	do.	220	6,000	0	+235	-----	0.75
11	do.	1.10	6,000	0	+610	-----	-----
Untreated test sample	Polyester	60,000	60,000	+1,800	+1,600	0.30	0.28
12	do.	0.12	7.7	0	+155	0.24	0.12
13	do.	0.40	5	0	0	0.18	-----
14	do.	0.30	5	0	0	0.15	-----

EXAMPLE 12

The coating solution consists of 0.4 g potassium octadecylphosphate in 100 ml of water. It is applied to an ethyleneglycol polyterephthalate support. After drying, the surface resistivities and the electrical fields are measured for 30 percent and 50 percent relative humidity.

EXAMPLES 13 and 14

In these two Examples, the support is a polyester: ethyleneglycol polyterephthalate. The first coating solution contains 0.4 g of rubidium cetylphosphate, the second 0.4 g of cesium cetylphosphate in solution in 100 ml of water containing 0.08 g of saponine as spreading agent.

In the following Examples, 15 to 26, one uses compositions containing a polymer binder soluble either in an organic medium or in an aqueous medium, which is applied to a cellulose triacetate support (Examples 15 to 20) or to a polyester support (Examples 21 to 26). The results obtained: surface resistivities, electrostatic fields, friction coefficients, are shown in Table II.

EXAMPLE 15

One applies to a cellulose triacetate film support a coating solution containing 0.15 g of high-viscosity cellulose triacetate, supplied by Rhone-Poulenc and having a degree of acetylation of 60.5 at 61 percent expressed as acetic acid, 0.30 g of potassium octadecylphosphate, 50 ml of dichloromethane, 46.5 ml of methanol and 3.5 ml of distilled water.

The surface resistivity, for a 30 percent relative humidity, is 700 GΩ. cm/cm. The surface resistivity for a 50 percent relative humidity, is 34 GΩ. cm/cm.

EXAMPLE 16

In this example, the conductive layer that is applied is temporary and is completely removable with water after saponification in an alkaline bath.

One applies to cellulose triacetate support the following coating solution:

Potassium octadecylphosphate	0.25 g
Low-viscosity cellulose ether phthalate	0.25 g
Methanol	80 ml
2-methoxyethanol	20 ml

The surface resistivities for 50 percent and 30 percent relative humidity are 35 GΩ. cm/cm and 460 GΩ. cm/cm, respectively. The electrostatic fields, measured for 50 percent and 30 percent relative humidity, are 0 and 1,390 V/cm, respectively.

EXAMPLE 17

One applies to a cellulose triacetate support the following coating solution:

Potassium octadecylphosphate	0.25 g
Product Butvar B 76 (Polyvinyl Butyral sold by Shawinigan Resins Corp.)	0.1 g
Methanol	85 ml
2-methoxyethanol	15 ml

EXAMPLE 18

One applies to a cellulose triacetate support a conductive layer from a coating solution containing: 0.1 g of the cellulose triacetate, 0.3 g of potassium cetylphosphate, 50 ml of dichloromethane, 46.5 ml of methanol and 3.5 ml of distilled water. The results that are obtained are indicated in Table II.

EXAMPLE 19

One applies to a cellulose triacetate support a conductive layer from a coating solution containing 0.1 g of the product Butvar B-76, 0.25 g of potassium cetylphosphate, 85 ml of methanol and 15 ml of 2-methoxyethanol. The surface resistivity electrostatic field and friction co-efficient are given in Table II.

EXAMPLE 20

One applies to a cellulose triacetate support the following composition:

Methocel 90HG resin, 100 centipoises	0.2 g
Potassium cetylphosphate	0.4 g
Water	15 ml
Methylglycol	20 ml
Methanol	65 ml

EXAMPLE 21

The coating solution consists of 0.4 g potassium octadecylphosphate, 0.2 g of product Butvar B-76, 80 ml of methanol and 20 ml 2-methoxy-ethanol. It is applied to a

polyester (ethyleneglycol polyterephthalate) support. The results are given in Table II.

EXAMPLE 22

One applies to a polyester support the following composition:

Methocel 90HG resin, 100 centipoises	0.2 g
Potassium cetylphosphate	0.4 g
Water	100 ml

EXAMPLE 23

One applies to a polyester support the following composition:

Methocel 90HG resin, 100 centipoises	0.4 g
Potassium cetylphosphate	0.4 g
Water	100 ml

EXAMPLE 24

One applies to a polyester support the following composition:

Methocel 90HG resin, 100 centipoises	0.4 g
Potassium octadecylphosphate	0.4 g
Water	100 ml

EXAMPLE 25

One applies to a polyester support the following composition:

Methocel 90HG resin, 100 centipoises	0.2 g
Potassium octadecylphosphate	0.4 g
Resorcinol	1.5 g
Water	100 ml

EXAMPLE 26

The ethylene glycol polyterephthalate film is coated with a composition obtained by mixing:

A polymer latex with a 15% content in methacrylate, vinylidene chloride, itaconic acid (23-85-2)	0.5 g
Resorcinol	1.0 g
Saponine	0.25g
Water	98.25ml

To the surface of the coated and dried support, one applies the following antistatic composition:

Aqueous solution containing 10% of polyvinyl alcohol (acetyl content in the proximity of 2%)	5.0 g
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Aqueous solution containing 1% of Volan product (polyvinyl alcohol reticulating agent sold by DuPont) 2.0 g
25% cetylbetaine in water 0.04g
Polymethacrylate (small spherical balls) as a matting agent, 40% in water 0.05g
Potassium cetylphosphate 0.4 g
Water 92.51ml

TABLE II

[Application in aqueous or organic solution with a binder]

Example	Support	Binder	Surface resistivity G Ω . cm./cm.		Electrostatic field in V./cm.		Friction coefficient in contact with tungsten carbide under 100 g.
			50% R _H	30% R _H	50% R _H	30% R _H	
15	Triacetate	Cellulose triacetate	34	700	+150	+400	0.15
16	do	CEP-IV	35	460	0	+1390	0.15
17	do	Butvar B 76	9	340	0	+430	0.14
18	do	Cellulose triacetate	190	5500	+410	+1500	0.16
19	do	Butvar B 76	12	550	+62	+376	0.14
20	do	Methocel 90 HG	1.2	6.3	0	+254	0.14
21	Polyester	Butvar B 76	0.36	6	0	-79	0.28
22	do	Methocel 90 HG	6.2	13	0	+550	0.12
23	do	do	25	1600	0	+560	0.15
24	do	do	100	7000	+245	+780	0.17
25	do	do	2.3	110	0	+920	0.11
26	do	Polyvinyl alcohol	73	576	0	+600	0.14

In the following two examples 27 and 28, one uses gelatin as a binder (see results in Table III).

EXAMPLE 27

30 To the substrated surface of a cellulose triacetate support, one applies the following coating solution:

Gelatin	2 g
Potassium cetylphosphate	2 g
Water	100 ml

35 The solution is kept at 35° C and it is applied by means of surface-tension coating followed by "air knife" treatment under a pressure of 4.5mm Hg. As in the preceding examples, the surface resistivities, the electrostatic fields, as well as the friction coefficient are measured.

EXAMPLE 28

45 One operates as in Example 27, but the layer is treated with an "air knife" under a pressure of 6mm Hg.

TABLE III

Example	Surface resistivity in G Ω . cm./cm		Electrostatic field in V./cm.		Friction coefficient in contact with tungsten carbide under 100 g.
	50% R _H	30% R _H	50% R _H	30% R _H	
50 27	7.8	260	0	+324	0.08
55 28	28	470	0	+408	0.07

In the following Examples, the application of the conductive layer is effected in aqueous or dilute alcoholic emulsion. The antistatic agent is incorporated with an aqueous dispersion of copolymers. A particularly advantageous composition comprises a terpolymer of from approximately 10 to 15 percent by weight of alkyl acrylate, of from 80 to 89 percent of vinylidene chloride and of from 1.0 to 4.0 percent of itaconic acid. Similar results may be obtained if the alkyl acrylate is replaced with acrylonitrile and the itaconic acid with acrylic acid. Because of the intrinsic wettability properties of the alkaline salt of long-chain alkylphosphates, the use of a spreading agent is not necessary and the layer obtained is self-lubricating (Examples 29 to 34). The results obtained are indicated in Table IV.

70 Another equally advantageous solution consists in using an aqueous or dilute alcoholic dispersion of a waxy substance, e.g., Carnauba wax effected with the aid of the alkaline salts of alkylphosphates (Examples 35 to 44).

EXAMPLE 29

One prepares one liter of an aqueous dispersion containing 2 percent dry weight of a polymer latex containing methacrylate, vinylidene chloride, itaconic acid, the composition of which is as follows: 15 percent methacrylate, 83 percent vinylidene chloride and 2 percent itaconic acid.

At the same time, one prepares 1 liter of an aqueous dispersion containing 2 percent by weight of an approximately equimolecular mixture of potassium monocetyl and dicetylphosphates.

One mixes, under stirring, the two dispersions previously obtained. The final dispersion is applied to a cellulose triacetate support and it is dried for 5 minutes at 115° C.

EXAMPLE 30

One operates as in Example 29, but potassium octadecylphosphate is used in the place of potassium cetylphosphate.

EXAMPLE 31

One prepares the following mixture containing:

1 liter of a latex containing 2 percent dry terpolymer comprising, by weight, 15 percent acrylonitrile, 83% vinylidene chloride and 2 percent acrylic acid.

1 liter of an aqueous dispersion containing 2 percent of potassium cetylphosphate.

The mixture is applied to a cellulose triacetate support.

EXAMPLE 32

The following mixture is prepared containing:

1 liter of a latex containing 2 percent of dry polymer material comprising, by weight, 15 percent acrylonitrile, 83 percent vinylidene chloride and 2 percent acrylic acid.

1 liter of an aqueous dispersion containing 2 percent potassium octadecylphosphate.

The mixture is applied to a cellulose triacetate support.

EXAMPLES 33 and 34

One operates as in Examples 29 and 30, respectively, but the solution is applied to an ethyleneglycol polyterephthalate support.

TABLE IV

[Compositions containing a latex of a terpolymer and applied to a cellulose triacetate support]

Example	Measured at 50% RH		Measured at 30% RH		Friction coefficient
	Resistivity in G.Ω. cm./cm.	Field in V./cm.	Resistivity in G.Ω. cm./cm.	Field in V./cm.	
29	0.75	0	30	+108	0.19
30	0.95	0	45-280	+276	0.24
31	3.7	0	170	+560	0.15
32	7	0		+590	0.12
Ethyleneglycol polyterephthalate support					
33	0.72	0	14	+126	0.24
34	0.20	0	8.8	-126	0.28

EXAMPLE 35

With the aid of a stirrer, e.g., of the magneticbar type, one stirs a mixture consisting of 200 g of water at 60° C and 50 g of potassium octadecylphosphate, until a uniform dispersion is obtained. The temperature is then raised up to 90° C and the mixture is then poured into 30 g of the "fatty-grease" type of Carnauba wax, kept at the melted state under stirring (e.g., with a paddle-type stirrer or a planetary-motion type stirrer).

The obtained dispersion is diluted with distilled water until one obtains a concentration of a 0.5 percent phosphoric acid derivative.

This preparation is applied according to well-known techniques (transfer cylinder, surface-tension coating, air knife) to a cellulose triacetate photographic film support.

EXAMPLE 36

One applies, as previously, to a cellulose triacetate support a final dispersion containing 0.5 percent of phosphorous com-

pound in a 50/50 mixture of water/ethanol, but modifying the salt/wax relation in the following manner:

Potassium octadecylphosphate	25 g
Carnauba wax	6 g

In the Examples 37 to 40, the type of alkylphosphoric acid used is varied. The compositions that are indicated are primary (concentrated) dispersions which one dilutes for use with a 50/50 mixture of water-ethanol until it contains no more than 0.02 percent of the phosphorous compound; one applies them to a cellulose triacetate support.

EXAMPLE 37

Potassium dodecylphosphate	12.5 g
Carnauba wax	25 g
Water	200 g

EXAMPLE 38

Potassium tetradecyl phosphate	12.5 g
Carnauba wax	25 g
Water	200 g

EXAMPLE 39

Potassium cetylphosphate	12.5 g
Carnauba wax	25 g
Water	200 g

EXAMPLE 40

Potassium octadecylphosphate	12.5 g
Carnauba wax	25 g
Water	200 g

The values of surface resistivities of the electrostatic fields and of the friction coefficients are indicated in Table V.

In the above Examples, the ratio between the dispersing agent and the wax is

160% in example 35
400% in example 36
50% in examples 37 to 40,

but it is possible to have them vary within even greater limits. The maximum quantity of phosphoric derivative to be used with respect to the wax is limited only by the value of the friction coefficient that is desired, the minimum quantity being that which is indispensable for the preparation of the dispersion.

Good results are obtained with antistatic emulsifier/wax ratios from 0.1 to 4.

Entirely comparable results may be obtained when an ethyleneglycol polyterephthalate support is used.

EXAMPLES 41 to 44

One operates as in Examples 37 to 40, respectively, but, the solution is applied to an ethyleneglycol polyterephthalate support.

The results of the measures are indicated in Table V.

TABLE V

[Application of a waxy-substance emulsion cellulose triacetate support]

Ex.	Surface resistivity, in G.Ω. cm./cm. at—		Electrostatic fields in V/cm measured at—		Friction coefficient measured under a charge of—	
	30% RH	50% RH	30% RH	50% RH	20 g.	100 g.
35	30	1.6	+360	0	0.30	0.19
36	410	2.3	+510	0	0.28	0.18
37	370	5	-1300	0	0.25	0.22
38	350	50	-600	+230	0.17	0.16
39	400	70	-800	+113	0.20	0.18
40	100	10	-800	+110	0.23	0.17

Poly(ethyleneglycol terephthalate) support

Ex.	Surface resistivity in G.Ω. cm./cm. at 50% RH		Electrostatic fields in V/cm measured at 50% RH		Friction coefficient measured under a charge of—	
	50% RH	50% RH	50% RH	50% RH	20 g.	100 g.
41	300		+500		0.27	0.17
42	40		+90		0.17	0.16
43	100		+200		0.20	0.17
44		1,200		+226	0.28	0.21

TABLE VII

Tests Number	Supports	Surface resistivity in $G\Omega$ cm./cm.		Electrostatic fields in V/cm.		Friction coefficients under—	
		30% R _H	50% R _H	30% R _H	50% R _H	20 g.	100 g.
1	{ Astralon.....	100	43	+640	0	0.15	0.14
	{ Untreated control.....	>60,000	>60,000	-3,400	-3,900	0.35	0.42
2	{ Teslar.....	29	12	+450	0	0.20	0.17
	{ Untreated control.....	>60,000	>60,000	-4,800	-4,000	0.57	0.52
3	{ Paper plus polyethylene treated by corona discharge.....	470	12	+160	0	0.20	0.19
	{ Untreated control.....	>60,000	>60,000	-890	-710	0.19	0.20
4	{ Paper plus polyethylene treated by corona discharge.....	400	24	-310	-70	0.19	0.20
	{ Untreated control.....	>60,000	>60,000	-1,060	-350	0.52	0.50

EXAMPLE 45

One applies the following cetylphosphate composition in 15 aqueous solution with Carnauba wax in a 4 to 1 ratio:

Potassium cetylphosphate	0.4 g
Carnauba wax	0.1 g
Distilled water	80 g
Ethanol	19.28 g
"Antarox CO 436" (wetting agent sold by General Aniline & Film Corp.)	0.22 g

to two supports:

1. Diphenylpropane polycarbonate sold by Bayer,
2. Stretched polystyrene sold by Plax Corp.

by means of surface tension coating followed by air knife treatment.

The following results were obtained:

TABLE VI

Tests Number	Supports	Surface resistivity in $G\Omega$ cm./cm.		Electrostatic fields in V./cm.		Friction coefficients under—	
		30% R _H	50% R _H	30% R _H	50% R _H	20 g.	100 g.
1	{ Polycarbonate.....	37	6.7	+710	0	0.20	0.17
	{ Untreated control.....	>60,000	>60,000	+3,120	-742	0.80	0.80
2	{ Polystyrene.....	19	5.5	+474	0	0.17	0.14
	{ Untreated control.....	>60,000	>60,000	-336	-292	0.68	0.64

EXAMPLE 46

In the following example, one uses the aqueous dispersion of potassium cetylphosphate and Carnauba wax in the 4 to 1 ratio:

	Grams
Potassium cetylphosphate.....	0.4
Carnauba wax.....	0.1
Distilled water.....	99.28
Antarox CO 436.....	0.22

This dispersion is applied by means of the previously described methods to the following materials:

1. Astralon: vinyl chloride copolymer modified with maleic anhydride, sold by Dynamit Aktiengesellschaft Vormalis Alfred Nobel & Co.

2. Teslar (vinyl polyfluoride) sold by E.I. du Pont de Nemours.

3. Paper for photographic use coated with a polyethylene layer previously treated by corona discharge.

4. Paper for photographic use coated with a polyethylene layer, but which has not been submitted to corona discharge.

After treatment of these various supports, the following results are obtained:

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

We claim:

1. A polymeric photographic film support provided with a layer containing an antistatic agent consisting of a potassium, rubidium or cesium salt of an alkylphosphoric acid ester, the alkyl group of which contains from about eight to 22 carbon atoms.

2. A polymeric photographic support according to claim 1 wherein the antistatic layer also contains a polymeric binder.

3. A polymeric photographic support according to claim 1 wherein the antistatic layer also contains a wax.

4. The product according to claim 1 wherein the support is a

linear polyester, polyolefin, polycarbonate, polystyrene, vinyl polymer or copolymer support, or a paper coated with said polymers.

5. The product according to claim 4 wherein both the antistatic agent and a wax are present in the antistatic layer.

6. The product according to claim 4 wherein both the antistatic agent and a polymeric binder are present in the antistatic layer.

7. The product according to claim 1 wherein the support is a cellulose organic acid ester film support.

8. The product according to claim 1, wherein the support is a synthetic polyester film support.

9. The product according to claim 1, wherein the support is a paper coated with a polyolefin.

10. The product according to claim 1 wherein the alkyl group of the alkylphosphoric acid ester contains 12, 14, 16 or 18 carbon atoms.

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