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3,681,070

ELECTROCONDUCTIVE LAYERS OF WATER INSOLUBLE COPOLYMERS OF STYRENE AND SULFONIC ACID OR SALTS FOR USE IN RECORDING MATERIALS

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No Drawing. Filed June 20, 1969, Ser. No. 835,258
Claims priority, application Great Britain, June 21, 1968, 29,801/68

Int. Cl. G03c 1/78; G03g 5/02
U.S. Cl. 96—1.5

9 Claims

ABSTRACT OF THE DISCLOSURE

An electroconductive layer for sheet material having a surface resistivity lower than 10^{11} ohms/sq. cm. and formed of a copolymer of styrene and styrene sulphonic acid or acid salt having a styrene sulphonic acid content within the range of about 17.5–35 mole percent.

The invention relates to electroconductive layers for use in recording materials.

Electroconductive products are used in all kinds of recording materials to carry off static charges. For instance, it is known that in normal photographic silver halide emulsion materials the usual synthetic film supports possess the property of being charged electrostatically, whereby the charged films strongly attract the surrounding dust and thereby become soiled at their surface. Moreover, latent discharge images on silver halide emulsions which are applied to such film supports become visible upon development. Such an electrostatic charging is caused by quickly moving the film support or light-sensitive photographic material during rolling or unrolling in the coating, cutting, or packing machines and by making the film run through the camera and the projector. It is also known that the static charging can be decreased by coating the synthetic resin support with a conductive auxiliary layer.

In other recording materials such as for use in electrostatic printing an electrostatic charge is imparted to paper or other dielectric supports in a predetermined pattern. The support is conductive or must be coated with a conductive layer. For instance, in an electrophotographic recording element a photoconductive layer stands in contact with an electroconductive layer or sheet, the latter being present for carrying off the electrostatic charges at the areas of the photoconductive layer undergoing an exposure to light rays.

In electrophotographic materials comprising an insulating layer whereon an electrostatic charge pattern is built up by image-wise or record-wise charging, e.g. by means of a modulated electron beam, the conductive element (support or layer) serves to apply a voltage thereon, thus enabling the formation of the electrostatic charge pattern applied to the insulating top layer.

Electroconductive layers for carrying off electrostatic charges may also be useful in recording elements wherein photosensitive semiconductor compounds are reversely activated by electromagnetic radiation and wherein the activated patterns provide irreversible images by an oxidation-reduction chemical process.

In the following description and claims the general term "recording material" is intended to include the materials used in all of the above described recording methods. In all these recording materials the surface resistivity of the electroconductive layer must not be higher

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than 10^{11} ohms per sq. cm. at 15% of relative humidity.

It would be very desirable to utilize in such recording materials products which are insoluble in water but which are electroconductive. For instance in photographic silver halide materials the electroconductive layer would not dissolve in one of the processing baths, but would remain present in the finished photographic material to prevent static charging and e.g. the attraction of dust on finished photographic images. In the electrophotographic and electrophotographic processes this is also of great importance. Indeed, in that case, the insulating layer or the photoconductive layer could be coated from an aqueous solution. This simplification would result in large economies.

There has been found now a class of electroconductive polymers that are insoluble in water and that are capable of being used for antistatic layers in the above described light-sensitive photographic recording materials, in an electroconductive layer in an electrophotographic, or in an electrophotographic recording element.

According to the invention a sheet or web-forming material of paper or synthetic polymers is provided, at least one side of which is coated with an electroconductive layer having a surface resistivity lower than 10^{11} ohms/sq. cm., said layer being formed mainly of a copolymer, which at normal temperatures is insoluble in water and comprises:

- (A) randomly distributed units deriving from at least one non-ionic hydrophobic monomer capable of yielding homopolymers insoluble in water, and
- (B) randomly distributed units deriving from highly ionisable hydrophilic acid monomers or salts thereof capable of forming water-soluble homopolymers.

As non-ionic, hydrophobic monomers capable of being polymerized into homopolymers, which are insoluble in water, use can be made of vinylaryl compounds and derivatives thereof, such as styrene, vinyl-naphthalene, vinyltoluene, 2,5-dimethylstyrene, p-, m-, and o-chlorostyrene, nitrostyrene, m- and p-styrene sulphonyl fluoride; further vinyl chloride, vinylidene chloride, vinylcarbazole; higher vinyl esters such as vinyl stearate; higher acrylic acid and methacrylic acid esters such as hexyl esters, octyl esters, stearyl esters; acrylonitrile, higher vinyl ethers such as vinyl nonyl ether, vinyl cetyl ether, vinyl trimethylnonyl ether and vinyl octadecyl ether.

As strongly ionisable hydrophilic acid monomers and salts thereof capable of being polymerised into water-soluble homopolymers use can be made of styrene m- and p-sulphonic acid and salts, vinylsulphonic acid and salts, vinylphosphonic acid and salts, p-vinylbenzyl phosphonic acid and salts, the salts of acrylic acid, methacrylic acid, and maleic acid.

Very interesting conductive polymeric materials are formed from copolymers of styrene and styrene-sulphonic acid or from copolymers of styrene sulphonyl fluorides and styrene-sulphonic acid, also from styrene and vinylsulphonic acid. The first copolymer can be prepared by partially sulphonating polystyrene, whereas the second can be formed by partially hydrolysing polystyrene sulphonyl fluorides.

The invention will be described hereinafter with respect to the electroconductive copolymer of styrene and styrene sulphonic acid. The characteristic features of the invention may, however, be applied to every combination of a hydrophobic monomer and of a hydrophilic monomer as indicated above and a few tests suffice for a person skilled in the art to establish the proportion of recurring units deriving from hydrophobic and hydrophilic monomers needed respectively in the copolymer.

It is known that the value of the surface resistivity of polystyrene-sulphonic acid is far below the limit indicated

above. However, since polystyrene-sulphonic acid is soluble in water, it cannot be used e.g. in electrophotographic recording elements, wherein the photoconductive layer is to be deposited on the electroconductive interlayer from aqueous solution or dispersion. Indeed, when coating the photoconductive layer from aqueous solution or dispersion, the polystyrene sulphonic acid layer will be partly dissolved and mixed with the photoconductive material, so that it is not possible any longer to retain an electric charge in the photoconductive material.

The copolymer of styrene and styrene sulphonic acid with a relatively low molar proportion of styrene-sulphonic acid can be prepared in different ways. For instance, styrene can be copolymerized according to known methods with the desired amount of styrene-sulphonic acid. Styrene can also be copolymerized with styrene sulphonyl fluoride, whereupon the sulphonyl fluoride groups of the resulting polymer can be hydrolysed to sulphonic acid groups.

The desired copolymer can also be prepared by sulphonation of polystyrene. The last method is particularly interesting because of its simplicity and cheaper feasibility. Various sulphonation methods are described in the literature. For instance, polystyrene can be sulphonated by using sulphuric acid, sulphur trioxide, or chlorosulphonic acid as the sulphonating agent. This method is quite successful for the preparation of sulphonated polystyrenes with a relatively high degree of sulphonation. However, when using free sulphur trioxide it is almost impossible to avoid cross-linking of polystyrene having a high molecular weight. Moreover, these water-soluble polystyrene sulphonic acids in their free acid form, will oxidize a paper support upon heating. Indeed, although the excess of sulphonating agent has been removed, e.g. by ion-exchange treatment, the resulting polymer solutions when applied to a paper support, would give a dark-brown hue to the paper upon heating, thus rendering the latter inappropriate for use in electrophotographic image recording processes.

Sulphonated polystyrenes can also be prepared by allowing to react polymerized styrene in an organic solvent, which is inert to sulphur trioxide, with a complex of sulphur trioxide and an organic compound, which is capable of coordinating with the sulphur trioxide without being chemically attacked thereby, the complex being capable of releasing sulphur trioxide at temperatures below 50° C. The organic compounds, which form the complex with the sulphur trioxide are typified by dioxan and bis(beta-chloroethyl)-ether. In consequence of the use of these complexes, cross-linking of the polystyrene is prevented. Furthermore, this method of sulphonating polystyrene has the additional advantage of sulphonating more easily to a predetermined degree.

The sulphonated polystyrenes used as electroconductive polymeric material according to the invention, though being insoluble in water, are soluble in alcohol. To a solution in alcohol very large quantities of water can be added without causing the dissolved polymer to precipitate. The electroconductivity of the polymers is proportional to the mole percent of styrene units, which have been sulphonated to styrene sulphonic acid units. The water-solubility and the electroconductivity of the polymer decrease with decreasing content of styrene sulphonic acid. Surprisingly, however, it was found that the decrease of electroconductivity did not proceed as fast as the decrease of the water-solubility, so that but a very narrow range could be determined, wherein the polymer lost its solubility in pure water at room temperature, but wherein the electroconductivity was still sufficiently high to permit the polymer to be used as electroconductive polymeric material in any image-recording element.

In this range, which was found to reach from 17.5 mole percent to 35 mole percent of styrene sulphonic acid depending on the molecular weight of the polystyrene used, the sulphonated polystyrene is not (or only partially)

soluble in water, though it is still soluble in mixtures of alcohol and large quantities of water.

The electroconductivity of the sulphonated polystyrenes is determined by measurement of their surface resistivity. A 10% solution of the polymer is applied therefor to a glass plate. The resulting layer is dried and conditioned at a specific relative humidity. The resistivity measurements are performed by means of a cell, both poles of which have a width of 0.5 cm. and are placed at a distance of 1 cm. between each other. For having a sufficient conductivity and allowing the use as an electroconductive layer in an image recording element, the surface resistivity should not exceed well defined limits, which themselves are influenced by the relative humidity degree. For instance, the surface resistivity at 15% of relative humidity must not be higher than 10^{11} ohms./sq. cm., whereas at 70% of relative humidity the surface resistivity must certainly not be higher than 10^8 ohms./sq. cm.

Polystyrene itself is insoluble in water. When it possesses a low polymerization degree, which means that the polystyrene is of low molecular weight, it suffices to sulphonate a relatively small number of recurring units to obtain a water-soluble polymer. With increasing molecular weight higher ratios of sulphonated recurring units are needed to obtain the same degree of water-solubility. The sulphonated polystyrenes, which are used as electroconductive polymers according to the invention, are necessarily insoluble in water. Accordingly, it is advisable to use sulphonated polystyrenes having the highest possible molecular weight. With high molecular weights the sulphonation degree whereon the electroconductivity of the polymer depends directly, can also be increased without reaching water-solubility.

Further, the sulphonated polystyrene must be soluble in some organic solvents or in mixtures of organic solvents and water, thus enabling the application as a coating composition on a support by spray, brush, roller, doctor blade, air brush, or wiping techniques. Examples of supports are paper, films of synthetic polymers such as films of cellulose acetate, films of polystyrene, and films of polyesters or of polycarbonates. If needed, the different supports may be provided previously with known subbing layers, whereon the electroconductive layer is coated afterwards.

The electroconductive sulphonated polystyrene also imparts electroconductivity when the paper base used as support is thoroughly soaked with a solution of the electroconductive polymeric material according to the invention. In the dried paper the electroconductive sulphonated polystyrene remains dispersed throughout the entire paper base. Electroconductivity may also be conferred to the paper base by adding a sufficient quantity of sulphonated polystyrene solution to the papermaking pulp.

When sulphonating polystyrene by making it react with a complex of sulphur trioxide and an organic compound such as dioxan in such proportions that between 17.5 and 35 mole percent of the styrene units in the polymer are converted into styrene sulphonic acid units, a copolymer is obtained, which is insoluble in water, but soluble in a mixture of alcohol and water. Upon coating an alcohol-water solution thereof on a paper or other support and drying, a layer of the sulphonated polystyrene is formed, which is also insoluble in water and remains undisturbed for instance when in the case of an electrophotographic recording element the photoconductive material is deposited thereon from an aqueous solution or dispersion, even when the latter is alkaline.

The insolubility in water of the copolymer is also of great importance in the case of photographic silver halide recording materials. Indeed, the electroconductive layer cannot be dissolved away in the processing baths and its antistatic properties are preserved in the finished photographic film material. The surrounding dust does not deposit any longer on such film material.

In an electroconductive layer according to the invention an amount of dry sulphonated polystyrene varying between 0.5 and 5 g./sq. m. of support will in general be sufficient. Also, when using paper as the support, care is to be taken that about 4% by weight of sulphonated polystyrene be present with respect to the dry solids weight of the paper support.

The invention is not restricted to the use in electroconductive layers of sulphonated homopolymers of styrene having a 17.5 to 35 mole percent content of styrene sulphonic acid units. Indeed, it is generally known that when using pure polystyrene for coating on paper, a very brittle material is obtained, which breaks very easily. This can be remedied by introducing in the polystyrene molecule a small number of plasticizing units e.g. approximately 5 mole percent of alkyl acrylate units. Practically speaking this results in the replacement of the original pure polystyrene by copolymers of styrene and alkyl acrylates. The same can be done in the present invention. Instead of sulphonating pure polystyrene, sulphonation is applied to a copolymer of styrene and alkyl acrylate or other plasticizing monomer. In this case there is also obtained a material, which is useful as electroconductive layer and which actually consists of a copolymer of styrene, styrene sulphonic acid, and alkyl acrylate or other plasticizing monomer.

The composition of the electroconductive layer may also include stabilizing agents, plasticizers, dispersing agents, pigments, and known binders such as gelatin. Due care must be taken to avoid mutual precipitation of the sulphonated polystyrene and of said binder.

The invention has been described especially with respect to polystyrene, which has been sulphonated in a very narrow range. It is possible, however, to use other copolymers as well, provided that they are insoluble in water and that they can be rendered electroconductive by the introduction of a sufficient number of recurring units deriving from highly ionisable hydrophilic acid monomers or their salts as indicated above. Care must be taken, however, that the introduction in the copolymer of hydrophilic recurring units is only carried out to such a degree that the copolymer acquires a sufficient electroconductivity without losing its insolubility in pure water at room temperature.

Instead of partially sulphonating polystyrene, there can also be applied a partial hydrolysis to polystyrene sulphonylfluorides, wherein the sulphonylfluoride group is substituted on the benzene ring of the styrene units in para or meta position, the sulphonylfluoride group being hydrolysed to a sulphonic acid group. Here also an increasing hydrolysis range will impart an increased electroconductivity to the copolymer obtained. A few tests indicate, at which moment the copolymer becomes sufficiently conductive and still remains insoluble in water at normal temperatures.

When compared with many other copolymers as indicated above, the sulphonated polystyrene has the great advantage of having the lowest cost-price. Polystyrene itself is commercially available in great quantities at very low prices. When sulphonating polystyrene, the low cost-price only increases with approximately a factor 10. Other polymers are not prepared that easily and they are much more expensive.

When the electroconductive layer of the invention is to be used as an antistatic layer in a photographic silver halide recording material, the electroconductive layer is generally applied to the backside of the photographic film. It can, however, also be applied as an interlayer between the support and the light-sensitive emulsion layer or layers.

If the electroconductive layer is to be used in an electrophotographic recording material, a photoconductive coating is applied on top thereof. This coating is prepared by dispersing or dissolving the photoconductive substance or substances in an aqueous or organic solution of an insulating binder or in a solution of such insulating binder

in a mixture of an organic solvent and water, and by applying the dispersion or solution in the form of a layer to the electroconductive surface. Even if the photoconductive layer is applied from aqueous solution or dispersion, there is no fear that the electroconductive polymeric material would wholly or partly dissolve. Indeed, since the sulphonated polystyrene is insoluble in water, at the most a relatively low swelling of the electroconductive layer would occur, thus leaving upon drying of the aqueous dispersion or solution of photoconductive material, a recording layer having a quick and high chargeability and a high sensitivity.

The electrophotographic recording element prepared with the electroconductive copolymer of the present invention is flexible and possesses a very good mechanical strength. A very good adhesion exists between the paper support and the electroconductive layer.

The present invention makes an end to the difficulties in electrophotography, which hitherto were described in the literature with respect to the precise composition of a separation layer between a paper soaked with salts or a paper web covered with the formerly known electroconductive polymers and a photoconductive material applied from aqueous phase. Indeed, when using a copolymer of styrene and styrene sulphonic acid according to the invention in such a separation layer all the favourable characteristics of the present invention are utilised. Electrophotographic images are obtained, which only in respect of quality are dependent on the composition of the photoconductive layer and which are not disturbed anymore by unfavourable properties of formerly used electroconductive substances.

Another method related with the invention consists in applying a separation layer between the copolymer of styrene and styrene sulphonic acid and the photoconductive layer. Such separation layer consists of a binder and a photoconductive pigment layer, which cannot be attacked by sulphonic acid groups. Obviously, this method of is particularly advantageous, when the inorganic photoconductors in the main layer are liable to attack by sulphonic acid groups.

The sulphonation of polystyrene with complexes containing sulphur trioxide is described in the following preparations.

PREPARATIONS

(A) In a reaction flask provided with a stirrer, reflux condenser sealed with a calcium chloride tube, two dropping funnels, and a thermometer 2,250 ccs. of dichloroethane dried on calcium chloride and 238 g. of dioxan are mixed. While stirring at room temperature 180 g. of freshly distilled sulphur trioxide and 100 ccs. of dichloroethane dried on calcium chloride were added dropwise. The exothermic reaction is controlled by cooling on a water-bath so that a temperature of 25° C. is not exceeded. A dispersion of a complex of sulphur trioxide and dioxan (0.83/1. molar) in dichloroethane is obtained.

From a second funnel sealed with a calcium chloride tube a solution of 624 g. of polystyrene having a molecular weight of 246,000 in 3,300 ccs. of anhydrous dichloroethane is added in 5 minutes while stirring thoroughly.

The sulphonation is weakly exothermic. The temperature of the reaction medium is kept at 25° C. Subsequently the homogeneous solution is gradually heated to 30–35° C. At this temperature gelation occurs suddenly. The mixture is stirred thoroughly and heated to 45° C., thus yielding a white paste, which still needs stirring for 30 minutes between 45 and 50° C.

3 l. of n-hexane are added gradually whilst stirring. A white suspension forms, from which the sulphonated polystyrene can be isolated in a centrifugal drier. The brittle product is washed with distilled water, till the wash water contains no sulphuric acid any longer. Subsequently the product is dried.

The sulphonated polystyrene contains 29.5 mole percent of styrene sulphonic acid groups (product A).

(B)-(D) Polystyrene having a molecular weight of 246,000 is sulphonated according to the method described under (A), with the proviso, however, that the amounts of dioxan, sulphur trioxide, and polystyrene are modified. The following results are obtained.

Product	Dioxan ing.	Sulphur trioxide in g.	Polystyrene in g.	Total amount of dichloroethane in l.	Sulphonated polystyrene, mole percent of styrene sulphonic acid
B.....	222	168	624	6	21.5
C.....	264	192	624	6	23.3
D.....	317	240	624	6	32.6

(E) In a reaction flask fitted with a stirrer, reflux condenser sealed with a calcium chloride tube, 2 dropping funnels, and a thermometer 2.250 ccs. of dichloroethane (dried on calcium chloride), and 349 g. of anhydrous dioxan are mixed. 264 g. of freshly distilled sulphur trioxide and 150 ccs. of anhydrous dichloroethane are added whilst stirring at room temperature. The exothermic reaction is controlled by cooling on a water-bath so that a temperature of 25° C. is not exceeded. A dispersion of a complex of sulphur trioxide and dioxan in dichloroethane is obtained.

In a second funnel sealed with a calcium chloride tube a solution of 624 g. of polystyrene having a molecular weight of 246,000 in 3,300 ccs. of anhydrous dichloroethane is added in 5 minutes whilst thoroughly stirring.

The sulphonation is weakly exothermic and the temperature of the reaction medium is kept beneath 25° C. Subsequently, the mixture is heated gradually, till gelation occurs suddenly at 32° C. The stirring rate is increased and heating continued to 40° C. Since the sulphonation is weakly exothermic, the temperature rises to 47° C. upon stirring for 30 minutes.

An amount of 3 l. of n-hexane is added. The sulphonated polystyrene is filtered off. A white powder of sulphonated polystyrene containing 33 mole percent of styrene sulphonic acid (product E) is formed.

(F) The process of E is repeated, with the proviso, however, that the following amounts of reagents are used: 127 g. of dioxan, 96 g. of sulphur trioxide, 208 g. of polystyrene having a molecular weight of 246,000, and 1.5 l. of dichloroethane. A sulphonated polystyrene containing 34 mole percent of styrene sulphonic acid (product F) is obtained.

(G) In a 5 l. reaction flask fitted with a stirrer, a reflux condenser with calcium chloride tube, two dropping funnels and a thermometer, 415 ccs. of dichloroethane and 42.2 ccs. of dioxan are mixed.

32 g. of freshly distilled sulphur trioxide mixed with 25 ccs. of anhydrous dichloroethane are added to the homogeneous solution whilst stirring at room temperature. The reaction is exothermic but is controlled on a waterbath so that the temperature does not exceed 25° C.

A dispersion of a complex of sulphur trioxide and dioxan in dichloroethane is obtained.

From a second funnel sealed with a calcium chloride tube a solution in 560 ccs. of anhydrous dichloroethane of 104 g. of polystyrene having a molecular weight of 40,000 is added whilst thoroughly stirring in 5 minutes. By cooling on a water-bath the temperature is kept at 22° C., so that an homogeneous solution is obtained. This solution is gradually heated to 50° C., at which temperature gelation occurs after 10 minutes. The stirring rate is increased and continued for approximately 20 minutes. Whilst stirring 4.25 l. of ether are added, so that a white powder is formed. This powder is washed 4 times with 250 ml. of ether subsequently sucked off and dried in vacuo at room temperature.

The sulphonated polystyrene contains 18.9 mole percent of styrene sulphonic acid (product G).

In the first example hereinafter the surface resistivity of the different sulphonated polystyrenes according to

preparations A to G are measured. Examples 2 to 6 describe the application of electroconductive polymeric materials according to the invention in electrophotographic recording elements. They may also be used, however, in other electrographic processes. A survey of these different processes has been given by C. J. Claus in Photographic Science and Engineering, 7 (1963), pp. 5-13. The electroconductive polymers may be used in combination with coatings of various inorganic as well as organic photoconductive substances such as those described in the Belgian patent specification 587,300, the United Kingdom patent specifications 964,871, 964,873, 964,874, 964,875, 964,876, 964,877, 964,879, 970,937, 980,879 and 980,880, in the German patent specification 1,058,836, and in the Canadian patent specification 568,707. These photoconductive substances may be combined with insulating binder agents, known i.a. from the United States patent specifications 2,197,552, 2,297,691, 2,485,589, 2,551,582, and 2,599,542, from the United Kingdom patent specifications 566,278, 693,112 and 700,502, from the Belgian patent specifications 612,102, 711,376 and 714,257, the French patent specification 1,485,839, and the published Dutch patent application 6608814.

Suitable dispersing agents for dispersing photoconductive materials in an aqueous medium are described in the published Dutch patent application 6712156 and as is generally known the photoconductive substances can be spectrally sensitized as described in the published Dutch patent application 6717400 and in the Belgian patent specification 714,258.

Example 1

A paper web weighing 70 g./sq. m. which did not suffer very much from dimensional alterations when coming into contact with water, was coated with a 6 to 10% solution of a sulphonated polystyrene according to one of the preparations A to G. The solvent therefor was a mixture of water and methanol in a proportion of 95:5 by volume. The coating rate was such that upon drying 2 g. of sulphonated polystyrene were present per sq. m.

The resulting conductive paper web was preferably, though not necessarily, calendered at approximately 50° C. and a few kg./sq. cm.

Typical surface resistivities of such paper webs are given in the following table as a function of the sulphonation degree and of the relative humidity.

Sulphonated polystyrene	Molecular weight	Sulphonation degree in mole percent	Surface resistivity in 10 ⁸ ohms/sq. cm. at a relative humidity of—		
			15%	50%	70%
B.....	246,000	21.5	200,000	77	7
C.....	246,000	23.3	42,500	23.6	1.37
A.....	246,000	29.5	21,500	20	5.2
D.....	246,000	32.6	1,700	1.93	0.26
E.....	246,000	37.7	670	1.33	0.25
G.....	40,000	40.8	2,130	0.67	0.082

In the description it is stated that the upper limit of the sulphonation degree should be approximately 35 mole percent. From the above table it appears that the sulphonated polystyrenes E and G exceed this upper limit. The results prove that their surface resistivity is very low and that consequently their conductivity is very high. The disadvantage of these sulphonated polystyrenes E and G, however, is that they cannot be used as conductive polymer in a conductive layer according to the invention. Indeed, the solubility of these polymers in water is already too high. When a layer formed from these sulphonated polystyrenes is coated with a layer of photoconductive material from aqueous solution or dispersion, the danger exists that the sulphonated polystyrene dissolves partially and mixes with the photoconductive material, so that the chargeability of the latter is lost completely.

Example 2

A paper web prepared according to Example 1 with a layer of sulphonated polystyrene according to preparation

A (sulphonated up to 29.5 mole percent), was coated with the following composition:

566 ccs. of a 20% solution of poly-1,2-dihydro-2,2,4-trimethylquinoline in methylene chloride
266 ccs. of a 50% solution of a silicon resin in toluene
858 ccs. of methylene chloride.

This composition was coated on the electroconductive paper web, so that upon drying 2.5 g. remained per sq. m.

After dark adaption the layer was charged by means of a negative corona discharge, exposed to an incandescent bulb through a 0.3 wedge, developed electrophoretically, thereby yielding an image of the wedge with a maximum density, which was typical for highly conductive supports.

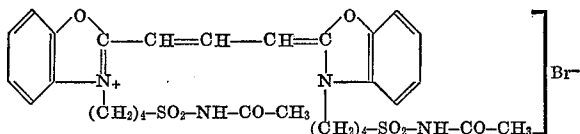
Example 3

The following composition was prepared:

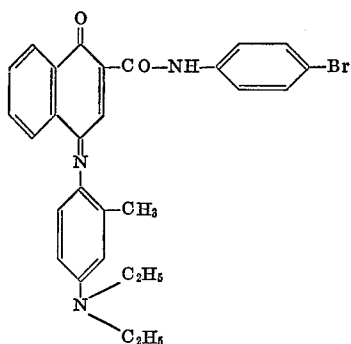
2,866 kg. of 1,2-dichloroethane,
0.615 kg. of a 40% solution of a copolymer of vinyl acetate and vinyl laurate (80:20 mole percent) in 1,2-dichloroethane
0.375 kg. of a 20% solution of a copolymer of vinyl chloride, vinyl acetate, and vinyl alcohol (91:3:6 mole percent) in 1,2-dichloroethane
0.180 kg. of a 20% solution of a copolymer of vinyl chloride, vinyl acetate, and maleic anhydride (90:8:2 mole percent) in 1,2-dichloroethane,
1 kg. of zinc oxide (French process).

This composition was treated once in a homogeniser at 250 kg./sq. cm. The following composition was then added thereto:

34 ccs. of a 10% solution of tetrachlorophthalic anhydride in ethanol
12 ccs. of a 10% solution of acid butyl phosphate in ethanol
13 ccs. of a 0.5% solution in diacetone alcohol of a dye according to the following structural formula:



44 ccs. of a 1% solution of bromophenol blue in methanol
8 ccs. of a 1% solution in 1,2-dichloroethane of a compound corresponding to the following structural formula:



This composition was coated at a rate of 20 g. of zinc oxide per sq. m. on a paper web prepared according to Example 1 (sulphonated polystyrene A). The resulting layer was dried and upon dark adaptation fed in a common commercial development apparatus for electrophotographic material. A sharp image, which entirely meets the presently set commercial standards, was obtained.

Example 4

The following composition was prepared:

750 ccs. of demineralised water

37.5 ccs. of a 10% solution of a copolymer of maleic anhydride and N-vinylpyrrolidone (40:60 mole percent) in a mixture of water and ammonia (9:1 by volume)
1000 g. of zinc oxide (French process).

The resulting composition was pumped through a sand-mill at a rate of approximately 30 l./h. A solution of 187 g. of copolymer of vinyl acetate and crotonic acid (94:6 mole percent) in a mixture of 750 ccs. of water and 7 ccs. of ammonia was added to the resulting dispersion. Then the following composition was added whilst stirring:

117.5 ccs. of a 10% solution of tetrachlorophthalic anhydride in a mixture of water and ammonia (750:7% by volume)

100 ccs. of a 0.5% solution of CI mordant red 5 (C.I. 14,290) in water

75 ccs. of a 0.5% solution of CI direct green 59 (C.I. 34,040) in water.

Stirring was continued till complete mixture. The resulting composition was coated on a paper web of Example 1 (sulphonated polystyrene A) at a rate of 25 g. of zinc oxide per sq. m. and dried. Upon dark adaptation the layer was fed in a commercial apparatus for development of electrophotographic recording material. An image with a high density and which was sharper than that on a paper not provided with such a conductive precoat, was obtained.

Example 5

5 g. of copolymer of styrene and styrene sulphonic acid having a molecular weight of 46,000 and containing 35 mole percent of styrene sulphonic acid was dissolved in a mixture of ethanol and water (90:10 by volume). This solution was neutralised with N/10 sodium hydroxide and diluted with acetone till concentrations of 0.5 and 1% by weight of copolymer were obtained.

The resulting solutions were coated on a cellulose triacetate film at a rate of 1 liter/40 sq. m. The dried films were cut in strips having a width of 35 mm. as is usual for photographic film. The other side of the film could be provided with one or more coatings and a gelatin silver halide emulsion layer according to known methods.

The relative humidity at 30% and 60% was measured in part of the film strips. The other part of film strips was treated in common photographic baths, e.g. developed for 5 minutes, fixed for 10 minutes, and rinsed for 1 hour. Upon drying the surface resistivity was measured at 30% and 60% of relative humidity.

The results of these measurements before and after treatment in the photographic baths, are listed in the following table.

	Surface resistivity (10 ¹⁰ ohms/sq. cm.)			
	30% RH		60% RH	
	Before processing	After processing	Before processing	After processing
Concentration of polymer in the coating composition in weight percent:				
0.5	1.2	150	0.008	0.34
1	0.083	32	0.0012	0.09
Triacetate film without antistatic layer	> 500	> 500	> 500	> 500

Example 6

Two copolymers of styrene and styrene sulphonic acid having a molecular weight of approximately 46,000 but having a styrene sulphonic acid content of 30 and 35 mole percent respectively were dissolved in the same way as in Example 5. The solutions were also adjusted to a concentration of 1% by weight of copolymer with acetone.

On a biaxially oriented polyethylene terephthalate film a subbing layer of a copolymer of vinylidene chloride, N-tert.-butylacrylamide, n-butyl acrylate, and N-vinylpyrrolidone (70:23:3:4% by weight) was coated as de-

scribed in the Belgian patent specification 721,469. The solutions of the copolymer of styrene and styrene sulphonic acid were coated thereon at a rate of approximately 1 l. per sq. m. Analogously to Example 5 the surface resistivity at 60% of relative humidity was measured before and after processing in photographic baths. The following results were attained:

	Surface resistivity (10^{10} ohms/sq. cm.) at 60% RH	
	Before processing	After processing
Copolymer styrene/styrene sulphonic acid in mole percent:		
70:30.....	0.0012	0.085
65:35.....	0.0004	32
Polyethylene terephthalate film without antistatic layer.....	> 500	> 500

We claim:

1. Electrographic recording material comprising a support of paper or synthetic polymer, an electroconductive layer coated on at least one side of said support and having a maximum surface resistivity measured at 15% relative humidity lower than 10^{11} ohms/sq. cm., said electroconductive layer being formed mainly of a copolymer of styrene and styrene sulphonic acid or acid salt having a styrene sulphonic acid content of at least about 17.5 and up to about 35 mole percent and sufficient to impart said maximum surface resistivity to said layer but insufficient to render said copolymer substantially water-soluble at room temperature, said electroconductive layer being coated on said support from an aqueous alcoholic medium, and an exterior photoconductive or insulating recording layer coated from an aqueous or organic solvent medium in which said copolymer is insoluble.

2. A sheet or web-forming material according to claim 1, wherein the copolymer of styrene and styrene sulphonic acid is formed by reacting polystyrene in an organic solvent, which is inert to sulphur trioxide, with a complex of sulphur trioxide and an organic compound capable of coordinating with the sulphur trioxide without being chemically attacked thereby, said complex releasing sulphur trioxide at temperatures below 50°C .

3. A sheet or web-forming material according to claim 2, wherein the organic compound capable of coordinating with sulphur trioxide is dioxan or bis(β -chloroethyl)ether.

4. A sheet or web-forming material according to claim 1, wherein a photoconductive layer is applied to the electroconductive layer to form an electrographic recording element.

5. A sheet or web-forming material according to claim 1, wherein an insulating layer is applied to the electroconductive layer to form an electrographic recording material.

6. A sheet or web-forming material according to claim 1, wherein the electroconductive layer is formed from 0.5 to 5 g. of said copolymer on a dry weight basis per sq. m.

7. A sheet or web-forming material according to claim 1, wherein the copolymer of styrene and styrene sulphonic acid also comprises up to 5 mole percent of recurring units deriving from alkyl acrylates.

8. Photographic recording material comprising a support of paper or synthetic polymer, an electroconductive layer coated on at least one side of said support and having a maximum surface resistivity measured at 15% relative humidity lower than 10^{11} ohms/sq. cm., said electroconductive layer being formed mainly of a copolymer of styrene and styrene sulphonic acid or acid salt having a styrene sulphonic acid content of at least about 17.5 and up to about 35 mole percent and sufficient to impart said maximum surface resistivity to said layer but insufficient to render said copolymer substantially water-soluble at room temperature, said electroconductive layer being coated on said support from an aqueous alcoholic medium, and an exterior light sensitive gelatin silver halide recording layer coated from an aqueous medium in which said copolymer is insoluble.

9. A sheet or web-forming material according to claim 8, wherein a light-sensitive gelatin silver halide emulsion is applied to the side of the support opposite to the electroconductive layer to form a photographic recording element.

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U.S. Cl. X.R.

96—87 A, 1.7; 117—201, 215, 218, 72, 76 P, 155 UA, 166, 76 F; 260—79.3 M, DIG 17; 162—138