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[54] **ELECTROSTATIC RECORDING SHEET AND PROCESS FOR MAKING THE SAME**
22 Claims, 2 Drawing Figs.

[52] **U.S. Cl.** **117/221,** 117/201, 96/1.5
[51] **Int. Cl.** **G03g 5/10**
[50] **Field of Search** ..... 117/201, 37; 96/1 S

[56] **References Cited**
UNITED STATES PATENTS
3,097,964 7/1963 Stowell 117/155

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ABSTRACT: Improved electrostatic recording sheets (on paper, plastic films, metal plates, or the like), and a process for making the same is disclosed, wherein the substrate having an electrically conductive base sheet thereon is coated with a suspension of a resinous polymer having insulating or dielectric properties, dispersed in an organic solvent, which is substantially a nonsolvent for said polymer, whereby a dielectric or insulating electric-charge-retentive layer is formed on the surface of the electrically conductive base sheet, so that said dielectric layer contains solid polymeric particles of particular characteristics. The result of this process, and the product thereby formed, is a mat-finish surface, having both excellent electrostatic recording characteristics, and also capable of being written thereupon by conventional ink pens, lead pencils, ballpoint pens, or also being capable of receiving impressions made by conventional rubber stamps or printing processes.

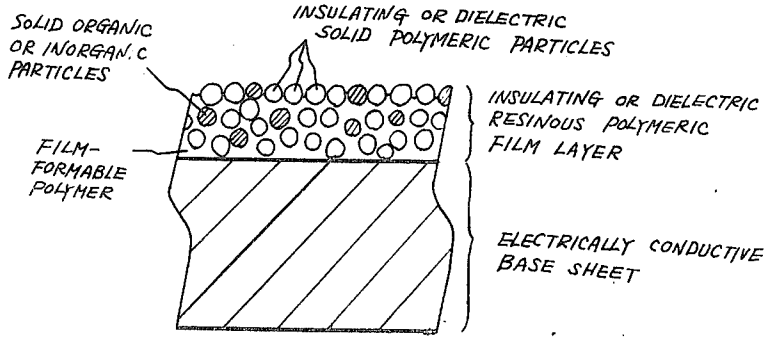


FIG 1

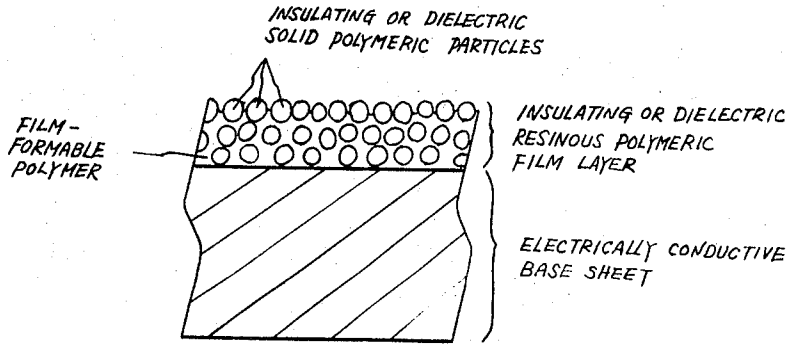
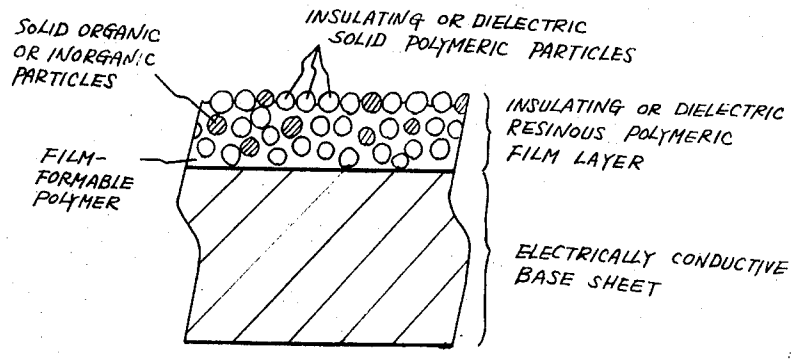


FIG 2



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ELECTROSTATIC RECORDING SHEET AND PROCESS FOR MAKING THE SAME

In general, electrostatic recording processes involve forming a latent image upon an electric-charge-retentive layer of an electrostatic recording (e.g., paper) sheet, having in its electrically conductive base a dielectric, or insulating, electric-charge-retentive layer capable of receiving and impressing an electric charge corresponding to an original pattern.

The thusly charged spots are then treated or developed with a visibly colored resinous powder which clings to the charged areas but which does not adhere to and is easily removed from the uncharged areas. The sheet thereafter is heated to fuse the colored powder to the spots to form a permanent visible image.

It is known that the electric-charge-retentive layer of the electrostatic recording sheet may consist essentially of any kind of insulating or dielectric resin such as polyethylene, polyvinylacetal, silicone resin, polyvinylacetaldehyde, polyvinylacetate, vinylacetate-vinylchloride copolymer, vinylacetate-crotonic acid copolymer, acrylic acid ester-methacrylic acid ester copolymer, etc., and mixtures thereof. These insulating resins are commonly coated onto the surface of conductive sheet as a solution dissolved in a suitable organic solvent. The resulting product forms an electric-charge-retentive layer comprising a substantially continuous film of the insulating resin. As a result, the surface of said electric-charge-retentive layer is of a glossy nature presenting an appearance quite foreign in comparison with the conventional papers of more common business usage, such as letter bond. Further, the surface is so smooth and nonabsorbable for aqueous or nonaqueous ink that writing, stamping and printing cannot ordinarily be satisfactorily done. These disadvantages adversely affect the utility of the electrostatic recording paper sheets.

A number of improvements have so far been proposed in order to overcome or compensate for the above disadvantages. However, a practical, satisfactory product has not yet been obtained. Many so-called improvements introduce unexpected additional difficulties. For example, it has been proposed to include inorganic particles such as clay, titanium oxide, zinc oxide, barium sulphate, or organic particles such as pulverized cellulose, starches in the insulating resin component in order to reduce the gloss of electric-charge-retentive layer and to permit writing or marking to be more easily done. However, in such cases, comparatively large quantities of inorganic or organic particles have to be used to obtain a desirable effect, and this inevitably causes such disadvantages as reduction of the electrical resistivity and dielectric strength or an increase of moisture sensitivity of electric-charge-retentive layer, and also defacement of recording head of the duplicating equipment because of the excessive roughness of the said surface.

For another example, U.S. Pat. No. 3,097,964 discloses an electrostatic recording sheet formed with a rough surface by having partially embedded therein discrete sharp particles of average size of the order of less than a micron of a dielectric resin material. In such cases, the sharp particles of dielectric resin material are obtained by a mechanical pulverizing treatment such as ball-milling for a period of several hours, crushing the resin material into particles of average size of the order of less than a micron. Such treatments require much time and trouble, and if resin particles are to be obtained more effectively, this requires longer treatment in proportion to the desired effect, which results in the increased cost of the product. The sharp particles so obtained are also so irregular in shape as to tend to make the surface of electric-charge-retentive layer geometrically nonuniform or uneven.

We have also found that it is desirable that the surface of the electric-charge-retentive layer should be only moderately rough. If it is too smooth, or too rough, the threshold voltage between the electrode and the dielectric layer will then be too low, and a clear image will not be obtained. If the surface has excessive roughness in the electric-charge-retentive layer, mechanical adherence of the developer material may occur in uncharged areas, thereby causing background impressions or overall grayness of the sheet after the recording process. This also can give rise to obscure images as a result of too much recording "noise" due to nonuniformity of contact between the recording stylus and the dielectric layer.

The principal object of this invention is to provide a new electrostatic recording paper sheet superior to those hitherto known.

The first important object of the invention is to provide an electrostatic recording sheet having a very uniform roughened surface on which a clear image can still be recorded.

A second object is to provide an electrostatic recording sheet having a substantially mat-finished appearance similar to the commonly used business papers.

A third object is to provide an electrostatic recording sheet having good receptivity and retention for writing or marking.

A fourth object is to provide processes for the manufacture of the electrostatic recording paper sheet in a more effective manner.

Other objects or advantages of the invention will be understood by the following description.

In the case of polymerization of acrylonitrile using toluene as a solvent, the acrylonitrile monomer dissolved in the said solvent at the initial stage will gradually become polymerized into polymer material insoluble in the said solvent as the polymerization advances forming a dispersion in the solvent of the polymeric solid particles. The method of polymerization, under which one or more kinds of monomer are dissolved in suitable solvent and polymerized to polymeric solid particles as to which such solvent is a poor solvent, is known as a kind of so-called heterogeneous polymerization. The resulting polymeric particles are substantially fine and spherical polymeric solid particles.

We have now succeeded in obtaining an electrostatic recording paper sheet which meets the above-mentioned objects by including the above solid polymeric particles in the electric-charge-retentive layer.

As used hereinafter in this specification and the appended claims, the technical term "polymeric solid particles" should be understood as referring to the solid polymeric particles obtained as the result of the above-mentioned "heterogeneous" polymerizing process, except for particular cases wherein separate mention is made. Similarly, the phrase "heterogeneously polymerized polymeric solid particles" refers to the particularly formed particles.

As is illustrated in the accompanying drawings, the electrostatic recording sheet of this invention includes a layer of an electric-charge-retentive component substantially consisting of dielectric or insulating resinous polymer film on an electrically conductive base sheet. More particularly, said insulating resinous polymer film is composed at least partially of dielectric or insulating "polymeric solid particles" which are so adhered to the surface of the base sheet with the film-formable polymer as to make the same uniformly rough.

The insulating resinous polymer materials forming the electric-charge-retentive layer are homopolymers or copolymers, polymerized from monomers or their derivatives, such as vinylchloride, vinylacetate, vinylidenechloride, methylacrylate, ethylacrylate, buthylacrylate, 2-ethylhexylacrylate, methylmethacrylate, ethylmethacrylate, vinylmethyl ether, vinylethyl ether, vinylisobuthyl ether, ethylene, vinylpyrrolidone, styrene, cumarone, indene, acrylonitrile, butadiene and the like, and other polymers and cellulose derivatives such as nitrocellulose, celluloseacetate and polyamide, and mixtures of said polymers or cellulose derivatives. And particularly, the resinous polymers consist at least partially of polymeric solid particles or homopolymer or copolymer polymerized from above-mentioned monomers, their derivatives or other polymers. For example, the electric-charge-retentive layer may be a film, consisting of vinylidenechloride-methylmethacrylate copolymer, which is at least partially formed by

polymeric solid particles of vinylidenechloride-methylmethacrylate copolymer having a higher degree of polymerization. For another example, the electric-charge-retentive layer may be a film, consisting of isobuthylacrylate-methylmethacrylate-acrylonitrile copolymer and acrylonitrile polymer, at least partially formed by polymeric solid particles of acrylonitrile polymer.

The electrostatic recording sheets of this invention are made by coating onto an electrically conductive base sheet a suspension consisting essentially of an organic solvent, an insulating or dielectric resinous polymer having film-forming properties and soluble in such organic solvent and also the insulating or dielectric heterogeneously polymerized polymeric solid particles which are themselves at most partially soluble in said organic solvent (the organic solvent being so selected as to essentially be a "nonsolvent" for such particles). This suspension, as an example, may be obtained as follows. One or more kinds of monomers or their derivatives dissolved in a suitable organic solvent such as acetone, toluene, benzene, methyl, acetate, methyl ethyle ketone, methyl isobuthyl ketone, ethanol and the like is polymerized and at least a part of such polymer is deposited as polymeric solid particles by selecting a suitable solvent which is a poor solvent therefor. Or, as an example, one or more kinds of monomers or their derivatives in a solution formed by dissolving resinous polymer in a suitable organic solvent is deposited as polymeric solid particles with additional use of such "poor" solvent. These suspensions can additionally contain insulating resinous polymer soluble in said suspension, or also organic or inorganic particles.

As will be understood from the above, the suspension of this invention is essentially obtained by the aforementioned heterogeneous polymerization. And it will be understood also that the suspension satisfying the objects of this invention may be obtained according to a variety of modification by properly choosing such factors as the kinds and ratios of monomer, organic solvents, polymerizing conditions and degrees of polymerization, etc. Further, it will also be understood that this invention has the advantage of shortening the process of obtaining suspension compared with the aforementioned United States Patent since the polymeric solid particles can be obtained during polymerization. The above suspension is coated on the surface of the electrically conductive base sheet by conventional coating means such as by use of a roll-coater, air-knife coater, blade coater, etc. For the base sheet, paper, plastic film, metal plate, etc., can be used. Among these, paper can be most widely used in that it is cheaper and more convertible to useful products than any other materials.

In most cases, these base sheets are treated by electrically conductive materials such as inorganic salts, metal powders, surface active agents, polyelectrolytes and others. The suspension on the surface of the base sheet is then dried, the organic solvent is evaporated and polymeric solid particles are adhered on the surface of the base sheet along with film-formable insulating resinous polymer to form an electric-charge-retentive layer.

The characteristics and advantages of the invention are as follows:

The surface of the electric-charge-retentive layer of insulating resinous polymer has a substantially moderate rough surface which is formed by insulating polymeric solid particles. See schematic FIG. 1. The geometrical shape of this surface differs from the aforementioned United States Patent having a surface formed by sharp edge particles. The surface of this invention is extremely uniform since it is formed by fine and spherical polymeric solid particles. Therefore, this eliminates the root of the background development which often appears when developer mechanically adheres to uncharged areas during developing process. Further this invention permits a clearer image with less "noise" because of the uniformity of the contact between the recording stylus and insulating or dielectric layer. Still further, the surface of the invention substantially corresponds to the so-called mat-finish and presents a natural appearance similar to commonly used business paper. And, also, the surface is easy to write upon with lead pencil or ballpoint pen and also easy to stamp or mark with fluid pen ink because of the good receptivity and retention. These advantages are not accompanied in any way by the disadvantages of decreased electric resistivity or moisture sensitivity of the electric-charge-retentive layer, nor by increased defacement of the recording head, unlike surfaces obtained solely by the function of large amounts of conventional organic or inorganic particles contained in the insulating resin.

In order to effectively obtain said advantages of the invention, it is desirable to take the average size and second-order-transition-temperature of polymeric solid particles into consideration. For instance, polymeric solid particles may be obtained ranging from approximately 0.01 micron to hundreds of microns according to the polymerizing conditions. In the practice of this invention, best results are obtained by using polymeric solid particles with an average size of 0.1 to 25 microns to obtain an electric-charge-retentive layer having satisfactory recording characteristics.

The polymeric solid particles are formed, during polymerization, as independently suspended particles in the suspension. There can be the circumstance that such independent particles gather themselves into an aggregate. In such a case, it is easily possible to adjust these aggregates into a preferable size range as mentioned above through dispersing the same into independent polymeric solid particles by generating shear forces in the suspension with mechanical pulverizing treatments such as ball-milling and the like. In regard to the second-order-transition-temperature of the polymeric solid particles, if such is too low, for example, a decrease in optical density of image and the background will be caused during developing process, since discharge of static latent image will be accelerated when recording under higher temperature. Also, this could even badly affect the appearance of the mat-finish surface of the electric-charge-retentive layer. Under such strict conditions, the second-order-transition-temperature of polymeric solid particles should preferably be at least higher than 10° C., and more desirably it should be between 10° C. to 70° C.

The electric-charge-retentive layer usually has a surface resistivity ranging from about 10^{9}–10^{17} ohms centimeter. In order to apply a latent image onto the surface of the electric-charge-retentive layer, the method under which a tungsten or stainless steel recording stylus is practically used, whereby the electric charge is applied to the stylus in contact with the surface. And, when the electrostatic recording sheet passes through the recording head, this would inevitably contact with a part of the head. The most desirable characteristics for the surface of the electric-charge-retentive layer include the characteristics of being only slightly chargeable or chargeable to a polarity a little bit opposite to that of the latent image, when said layer is rubbed or passed across (in contact with) a recording stylus or other part of a recording head as mentioned above. This is desirable because, otherwise there is the possibility that a background impression will be obtained due to the fact that the developer may adhere to such background areas which are not otherwise intended to be "charged." If the electric-charge-retentive layer developed any strong electrostatic charge through rubbing contact with the said recording stylus or recording head, attachment of the developer to areas desired to be left uncharged, could undesirably occur. We have found the electric-charge-retentive layer with said desirable characteristics can be obtained when electric-charge-retentive layer of insulating resinous polymer substantially comprises a combination of monomer or their derivatives each of which has a different triboelectricity.

The electrostatic recording sheet of this invention can also have added into its insulating layer inorganic particles such as kaolin, clay, aluminum oxide, titanium dioxide, acid clay, silicagel, zinc oxide, barium sulfate, calcium carbonate or organic particles such as pulverized cellulose and starch. See schematic FIG. 2. The said addition may in certain cases

further improve characteristics of writability, printability, etc. as aforementioned. However, in such cases, a large quantity of the said particles need not and should not be added into the electric-charge-retentive layer. The quantity thereof is limited to below about 20 parts per 100 parts of insulating resinous polymer by weight, and preferably from about 3 parts to 10 parts. The above organic or inorganic particles are auxiliarily added for the purpose of giving additional improvement to the receptivity and retention of inks. Accordingly, it will be understood that the comparatively small addition of such particles does not affect the electric resistivity, dielectric strength or moisture sensitivity.

The following examples serve to illustrate further the invention although the invention is not limited to these examples. The amount of each example shows parts by weight.

EXAMPLE 1

Fifty parts of vinylidene chloride and 50 parts of methylmethacrylate were copolymerized using azobisisobutyronitrile as catalyst and toluene as solvent, and to obtain a colloidal suspension of polymeric solid particles of a part of said copolymer only partly soluble in toluene as said solvent. Said polymeric solid particles have an average size of about 0.3 micron and a second-order-transition-temperature of about 60° C. The suspension was then coated on the surface of conductive base paper of 55-micron thickness impregnated with polyvinylbenzyltrimethylammonium chloride and a dielectric film layer with the thickness of 5 microns was formed. The resulting product has a surface resistivity of 1.2×10^{13} ohms/centimeter at 20° C., 60 percent RH, and 100 voltages of direct current. When its surface was uniformly rubbed with tungsten wire, it was only slightly positively charged. A latent image was formed on such surface using a recording head coupled with mulistyli with the pitch of 6 lines per mm. under a pulse signal of −700 V, 10 microsecond, and developed with a positively charged developer to obtain a good image quite free of the background. The product has a substantially mat-finish surface and has an appearance similar to commonly used business paper being markable and writable with lead pencil or ballpoint pen.

EXAMPLE 2

Fifty-five parts of vinylidene chloride, 40 parts of methylmethacrylate and 5 parts of acrylic acid were copolymerized using azobisisobutyronitrile as catalyst and mixture of toluene and ethylacetate at the ratio of 60 to 40 as solvent. A colloidal suspension of polymeric solid particles of a part of such copolymer was obtained. This suspension was redispersed by ball-milling for 20 minutes. These polymeric solid particles have an average size of about 3 microns or less and a second-order-transition-temperature of about 50° C. The suspension was then coated on the surface of conductive base paper to form a dielectric film layer of 5-micron thickness in the same manner of example 1. The product has a surface resistivity of 1.5×10^{13} ohms under 20° C., 60 percent RH and 100 voltages of direct current. Approximately the same results reported in example 1 are obtained by the present example.

EXAMPLE 3

Seventy parts of vinylidene-chloride and 30 parts of methylmethacrylate were copolymerized using azobisisobutyronitrile as catalyst and mixture of toluene and ethylacetate at the ratio of 80 to 20 as a solvent, to obtain a colloidal suspension of polymeric solid particles of a part of such copolymer, the solvent being essentially a nonsolvent therefor. These polymeric solid particles have an average size of about 0.5 micron and second-order-transition-temperature of about 70° C. The suspension was coated on the surface of conductive base paper of 50-micron thickness impregnated with lithium chloride and polyethylene glycol and a dielectric film layer with the thickness of 5 microns was formed. The resulting produce has a surface resistivity of 0.8×10^{14} ohms under 20° C., 60 percent RH and 100 voltages of direct current. When its surface was uniformly rubbed with tungsten wire, it was neutrally charged. A latent image was formed on such surface using a recording head coupled with multistyli with the pitch of 6 lines per mm. under pulse signal of −700 V, 10 microsecond, and developed with a positively charged developer to obtain a good image quite free of the background. Also the product has substantially a mat-finish surface and has an appearance similar to commonly used business paper, markable and writable with lead pencil or ballpoint pen.

EXAMPLE 4

Three parts of titanium dioxide with an average size of about 2 microns were added into the suspension of example 3 with 100 parts of polymer, to obtain an electric recording sheet in the same manner as shown in example 3. The product has a recording property substantially similar to the product of example 3, which is mat-finished and writable with lead pencil or ballpoint pen.

EXAMPLE 5

Sixty parts of vinylidenechloride and 40 parts of vinylchloride were copolymerized, using azobisisobutyronitrile as catalyst and a mixture of toluene and acetone at the rate of 50 to 50 as solvent, to obtain polymer solution of vinylidenechloride-vinylchloride copolymer.

Seventy parts of acrylonitrile for 100 parts of the above copolymer were polymerized in the above solution to obtain a suspension of polymeric solid particles of acrylonitrile polymer. The polymeric solid particles have average size of about 1 micron and second-order-transition-temperature of about 65° C. The suspension was then coated on the surface of conductive base paper similar to that shown in example 1, to form a dielectric film layer with the thickness of 5 microns. The resulting product has a surface resistivity of 1.0×10^{14} ohms under 20° C., 60 percent RH and 100 voltages of direct current. The surface of the product is substantially a mat-finish and easily writable and markable with ballpoint pen and lead pencil.

EXAMPLE 6

Twenty-five parts of styrene, 25 parts of methylmethacrylate and 50 parts of ethylacrylate were copolymerized using benzoyl peroxide as catalyst and toluene as solvent to obtain polymer solution of styrene-methylmethacrylate-ethylacrylate copolymer. Thirty parts of acrylonitrile for 70 parts of the above copolymer were polymerized in the above solution to obtain a suspension of polymeric solid particles of acrylonitrile polymer. The solution of 60 parts of methylacrylate and 40 parts methylmethacrylate copolymer dissolved in toluene was mixed with the above suspension in the solid weight ratio of 30 parts to 70 parts polymer in the suspension. The thus-obtained suspension was coated on the surface of polyester film with the thickness of 25 microns which had an aluminum layer evaporated in vacuum, to form a dielectric film layer with the thickness of 4 microns. Approximately the same results reported in example 5 are obtained by the present example.

EXAMPLE 7

Fifty parts of isobutylacrylate, 35 parts of methylmethacrylate and 15 parts of acrylonitrile were suspended in water and copolymerized in the suspended condition. The thus-obtained polymer was washed by water and dried and then dissolved in toluene. Ten parts of acrylonitrile for 90 parts of above copolymer were polymerized in the above solution to obtain a suspension of polymeric solid particles of acrylonitrile polymer. The polymeric solid particles have an average size of about 0.5 micron and second-order-transition-temperature of about 30° C. The suspension was coated on the surface of con-

ductive base paper similar to example 1 to form a dielectric film layer of 5 microns. The product so obtained has a surface resistivity of 1.5×10^{12} ohms under 20° C., 60 percent RH and 100 voltages of direct current. When its surface was uniformly rubbed with tungsten wire, it was neutrally charged. A latent image was formed on such film surface using a recording head coupled with multistyli with the pitch of 6 lines per mm. under pulse signal of −800 V, 5 microsecond and then developed with a positively charged developer to obtain a good image quite free of the background. The product has substantially a mat-finish surface and has an appearance similar to commonly used business paper and markable and writable with lead pencil or ballpoint pen.

EXAMPLE 8

Eighty-five parts of vinylidenechloride and 15 parts of 2-ethyl hexylacrylate were copolymerized using azobisisobutyronitrile as a catalyst and toluene as a solvent, to obtain a polymer solution of vinylidenechloride-2-ethylhexylacrylate copolymer. Thirty parts of acrylonitrile against 100 parts of above copolymer were polymerized in the above solution to obtain a suspension of polymeric solid particles of acrylonitrile polymer. The solution of methylacrylate-methylmethacrylate copolymer dissolved in the toluene was mixed with the above suspension in the solid weight ratio of 20 parts to 100 parts polymer in the suspension. And then, 5 parts of 2 micron natural pulverized cellulose pulp were added to 100 parts of all polymer in the mixture. The thus-obtained suspension was coated on the surface of conductive base paper similar to that of example 1 to form a dielectric film layer of 5 microns. The product so obtained has a mat-finish surface and has been clearly stamped by ink.

EXAMPLE 9

Seventeen parts of isobutylacrylate, 60 parts of methylmethacrylate, 18 parts of acrylonitrile and 5 parts of glycidilmethacrylate were copolymerized using azobisisobutyronitrile as catalyst and toluene as solvent to obtain a polymer solution of isobutylacrylate-methylmethacrylate-acrylonitrile-glycidilmethacrylate copolymer. Forty parts of acrylonitrile against 100 parts of the above copolymer were polymerized in the above solution to obtain a suspension of polymeric solid particles of acrylonitrile polymer. The solid particles have an average size of about 8 microns and second-order-transition-temperature of about 50° C. The solution of methylacrylate-methylmethacrylate copolymer dissolved in toluene was mixed with the above suspension in the solid weight ratio of 20 parts to 100 parts polymer in the suspension. The thus-obtained suspension was coated on the surface of conductive base paper similar to that of example 1 to form a dielectric film layer of 8 microns. The product thus obtained has a surface resistivity of 0.9×10^{14} ohms under 20° C., 60 percent RH and 100 voltages of direct current. A latent image was formed on such film surface using a recording head coupled with multistyli with the pitch of 6 lines per mm. under pulse signal of −800 V, 5 microsecond and developed with a positively charged developer to obtain a good image quite free of the background. The product has substantially a mat-finish surface and is easily writable by lead pencil or ballpoint pen.

EXAMPLE 10

Seventy parts of vinylidenechloride and 30 parts of methylmethacrylate were copolymerized using azobisisobutyronitrile as catalyst and toluene as solvent to obtain a polymer solution of vinylidenechloride-methylmethacrylate copolymer. Forty parts of acrylonitrile against 100 parts of the above copolymer were polymerized in the above solution to obtain a suspension of polymeric solid particles of acrylonitrile polymer. The solution of methylacrylate-methylmethacrylate copolymer dissolved in toluene was mixed with the above suspension in the solid weight ratio of 20 parts to 100 parts polymer in the suspension. And further, 5 parts of colloidal silica were added to 100 parts of all polymer in the mixture. The thus-obtained suspension was coated on the surface of polystyrene film of 30 microns to form a dielectric film layer of 5 microns. In such case, the polystyrene film has a thin coated layer composed of 8 parts of polyvinylbenzyltrimethylammonium chloride and 2 parts of polyvinylalcohol. The product so obtained has substantially a mat-finish surface and good recording and writing characteristics.

EXAMPLE 11

Thirty parts of butylacrylate, 65 parts of styrene and 5 parts of glycidilmethacrylate were copolymerized using azobisisobutyronitrile as a catalyst and ethylacetate as solvent to obtain a polymer solution of butylacrylate-styrene-glycidylmethacrylate copolymer. Twenty-five parts of acrylonitrile against 100 parts of the above copolymer were polymerized in the above solution to obtain a suspension of polymeric solid particles of acrylonitrile polymer. The solution of methylacrylate-methacrylate copolymer dissolved in toluene was mixed with the above suspension in the solid weight ratio of 40 parts to 100 parts polymer in the suspension. The above polymeric solid particles have an average size of about 0.1 micron and second-order-transition-temperature of about 70° C. The suspension so obtained was coated on the surface of conductive base similar to that of example 1 to form a dielectric film layer of 5 microns. The product thus obtained has a surface resistivity of 0.8×10^{13} ohms under 20° C., 60 percent RH and 100 voltages of direct current. When its surface was uniformly rubbed with tungsten wire, it was slightly positively charged. A latent image as formed on such film surface using a recording head coupled with multistyli with the pitch of 6 lines per mm. under pulse signal of −650 V, 50 microsecond and developed with a positively charged developer to obtain a clear image. The product has a substantially mat-finish surface and good writing characteristics.

EXAMPLE 12

Sixty parts of vinylidenechloride and 40 parts of methylmethacrylate were copolymerized using azobisisobutyronitrile as catalyst and toluene as solvent to obtain a polymer solution of vinylidenechloride-methylmethacrylate copolymer. Forty parts of acrylonitrile for 100 parts of the copolymer were polymerized in the above solution to obtain a suspension of polymeric solid particles of acrylonitrile polymer. The solution of 85 parts vinylchloride and 15 parts vinylacetate copolymer dissolved in methylethylketone was mixed with the above suspension in the solid weight ratio of 70 parts to 100 parts polymer in the suspension. The thus-obtained suspension was coated on the surface of conductive base paper similar to that of example 1 to form a dielectric film layer of 5 microns. The product thus obtained has excellent characteristics as shown in example 11.

It will be appreciated that in the practice of this invention, as disclosed and illustrated above, it is necessary that discrete, undissolved solid particles of the dielectric polymer be obtained in the suspension coated onto the base sheet. To this end, it is therefore important that the said dielectric polymer be substantially insoluble in the nonsolvent-vehicle employed for the coating purpose, although it is recognized that at lower levels of polymerization (low molecular weight polymers), the polymer may be substantially soluble. The point is that for the coating step at least the higher molecular weight fraction of the polymer molecules should remain substantially undissolved in the nonsolvent-vehicle so that a true suspension or dispersion of the fine polymer particles is obtained.

A person skilled in this art is thus able to select the kind of dielectric polymer material with which he desires to work and also a suitable nonsolvent system therefor, in accord with the foregoing principles to provide himself with the required suspension or dispersion. Similarly, he can select the degree of polymerization which he desires to use in a given instance of use of these inventive principles.

This invention is not confined to the use of particular non-solvent systems or particular dielectric polymers, nor particular degrees of polymerization. Rather, this invention resides in the discovery that if such materials are so selected as to provide the above-described suspension of the fine particles of the dielectric polymer, then the improved mat-finish surface or electrostatic recording paper or other sheet material can be obtained.

It will be further understood and appreciated that the important characteristics of the electrostatic recording sheets of this invention are that they possess a very high degree of uniformity of surface composition and recording dielectric properties. The surface must have the required "roughness" to permit marking by a pencil or ballpoint pen, etc., (a requirement of friction) but still be of a uniform microscopic dimensional structure so that there is substantial uniform contact of the stylus with the sheet. If an irregularly rough surface were provided, or if the surface is of a jagged roughness, contact of the stylus with the sheet will also be irregular. As a result, the image-forming voltage imposed on the sheet will vary, with production of "noise" and an inferior recording of the image.

This invention provides the desired recording sheets with the substantially spherical small polymer particles in the dielectric layer whereby a very uniform, and nonjagged, rough surface is obtained with the improved recording characteristics mentioned above.

It should also be understood that in the above examples the development of the latent image may be achieved through use of either a dry or a wet process, as are conventionally now used by the industry and in either case the advantages derived from practice of this invention are realized.

It will also be understood from the foregoing that at least a portion of the heterogeneously polymerized solid polymer particles of the insulating or dielectric polymer reside on the surface of the dielectric polymer film which is laid down as a coating on the electrically conductive substrate sheet, in order to produce the desired surface characteristics. Generally speaking, the thickness of this polymer film is of the order of about 1 micron to about 10 micron, though these dimensions are not critical, and may be thicker, e.g., as much as 25 micron (a thicker film is unnecessary). (The film thickness may be varied according to the electrostatic characteristics desired in the final product, depending also on the kind of polymer used, the nature of the substrate sheet, and the type of electrostatic reproduction to be used, all as are understood by those skilled in this art.) It is desirable for best characteristic in the final sheet product that the dielectric polymer particle size be so controlled that the ratio of the maximum dimension of the said particles to the nominal thickness of the film be within the range of from about 1:100 to about 1:1, it being further desirable to have at least a majority of the particles within a maximum deviation of 50 percent from the average maximum particle dimension and most preferably within 25 percent or still better, 10 percent deviation from said average maximum particle dimension.

In forming the film from the suspension of the heterogeneously polymerized solid polymer particles on the substrate sheet, it is, of course, important that there be sufficient particles present in the resulting film to provide the necessary surface characteristics and also important to have present enough soluble film-forming polymer material (dissolved in the solvent) to form a film of adequate strength and structural integrity. In the practice of this invention, therefore, the volume of the heterogeneous solid polymer particles in the film should be at least about 5 percent, but not more than about 90 percent of the total volume of the film. Better results are provided when the solid particles are within the range of about 10 percent to about 70 percent of the total film volume, and superior results are obtained in the range of about 25 percent to about 40 percent.

It will thus be appreciated that this invention may be practiced according to procedures other than those specifically illustrated in the examples set forth hereinabove, as will be apparent to those skilled in the art reading this specification.

What is claimed is:

1. An improved electrostatic recording sheet consisting essentially of an electrically conductive substrate sheet having a coating thereupon composed of an electric-charge-retentive layer of an insulating or dielectric resinous polymeric film, said film also containing a plurality of insulating or dielectric heterogeneously polymerized solid polymeric particles dispersed therein and also disposed at least in part on the exterior of said film to provide a surface of substantially uniform roughness, said thus-coated sheet being adapted for receiving latent images by an electrostatic recording process and also adapted to receive conventional hand-written markings by ballpoint pen, pencil, rubber ink stamp, and the like, the ratio of the maximum dimension of said particles to the nominal thickness of said film being in the range of from about 1:100 to about 1:1.

2. An electrostatic recording sheet as defined in claim 1 in which said insulating or dielectric heterogeneously polymerized polymeric solid particles have an average size in the range of from about 0.1 micron to about 25 microns.

3. An electrostatic recording sheet as defined in claim 1 wherein said film has a thickness of between about 1 and about 25 microns.

4. An electrostatic recording sheet as defined in claim 1 wherein the volume of said heterogeneously polymerized solid polymeric particles in said film is at least about 5 percent, and up to about 90 percent of the total volume of the film.

5. An electrostatic recording sheet as defined in claim 4 wherein said volume range is between about 10 percent and about 70 percent.

6. An electrostatic recording sheet as defined in claim 5 wherein said volume range is from about 25 to about 40 percent.

7. An electrostatic recording sheet as defined in claim 1 wherein at least a majority of said heterogeneously polymerized solid polymeric particles have a maximum deviation of about 50 percent from the average maximum particle dimension.

8. An electrostatic recording sheet as defined in claim 7 wherein said maximum deviation is at most about 25 percent.

9. An electrostatic recording sheet as defined in claim 8 wherein said maximum deviation is about 10 percent.

10. An electrostatic recording sheet as defined in claim 1 in which said insulating or dielectric polymeric solid particles have a second-order-transition-temperature in the range of from about 10° to 70° C.

11. An electrostatic recording sheet as defined in claim 1 in which said insulating or dielectric resinous polymer film further includes additional organic or inorganic particles in a weight ratio of from 3 to 20 parts of said particles to 100 parts of said insulating or dielectric polymer.

12. An electrostatic recording sheet as defined in claim 11 in which said additional inorganic particles are selected from the group consisting of kaolin, clay, aluminum oxide, titanium dioxide, acid clay, silicagel, zinc oxide, barium sulfate and calcium carbonate.

13. An electrostatic recording sheet as defined in claim 11 in which said additional organic particles are selected from the group consisting of pulverized cellulose pulp and starches.

14. An electrostatic recording sheet as defined in claim 11 wherein the size of said additional organic or inorganic particles is such that the ratio of the maximum dimension thereof to the nominal thickness of said film is within the range of about 1:100 to about 1:1.

15. A process for the production of an improved electrostatic recording sheet which comprises coating a surface of an electrically conductive substrate sheet with a suspension consisting essentially of an organic solvent, an insulating or dielectric polymer having film-forming properties dissolved in said solvent, and dispersed in said solvent solid particles of a heterogeneously polymerized insulating or dielectric solid

polymer material, substantially insoluble in said organic solvent, said suspension being obtained by polymerizing one or more monomers dissolved in an organic solvent into solid polymeric material which is at most slightly soluble in said organic solvent, and thereafter drying or curing the deposited film on said substrate sheet with evaporation of the said solvent.

16. A process according to claim **15** wherein said suspension additionally contains solid organic or inorganic particles in a weight ratio of from 3 to 20 parts of particles per 100 parts of said insulating or dielectric polymer.

17. The process according to claim **15** wherein the volume of said heterogeneously polymerized solid polymeric particles in said film is at least about 5 percent, and up to about 90 percent of the total volume of the film.

18. The process according to claim **17** wherein said volume ranges between about 10 to about 70 percent.

19. The process of claim **18** wherein said volume range is from about 25 to about 40 percent.

20. The process of claim **15** wherein at least a majority of said heterogeneously polymerized solid polymeric particles have a maximum deviation of from about 50 percent from the average maximum particle dimension.

21. The process according to claim **20** wherein said maximum deviation is at most about 25 percent.

22. The process according to claim **21** wherein said maximum deviation is about 10 percent.

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