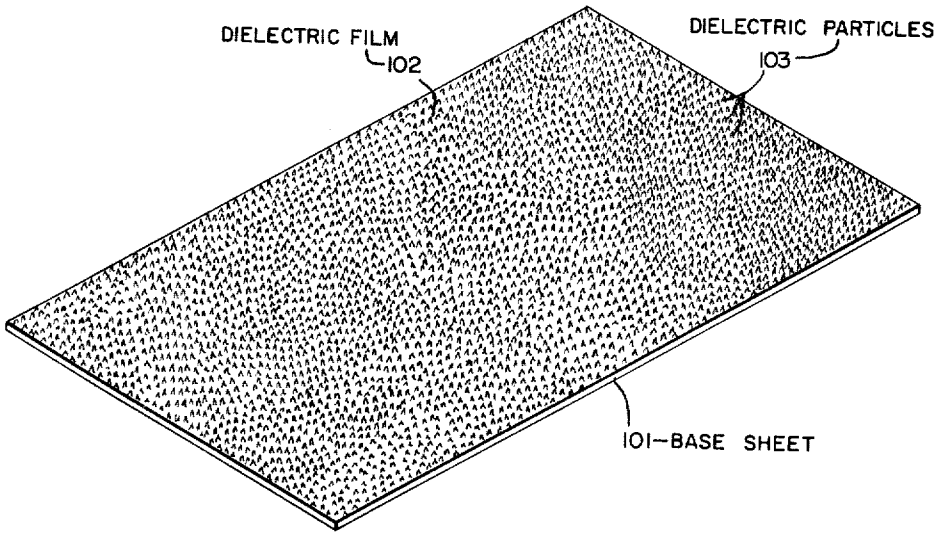
July 16, 1963 P. A. STOWELL 3,097,964

DIELECTRIC RECORDING MEDIUM

Filed June 30, 1959



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United States Patent Office 3,097,964 Patented July 16, 1963

3,097,964
DIELECTRIC RECORDING MEDIUM

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Filed June 30, 1959, Ser. No. 824,010
11 Claims. (Cl. 117—155)

This invention relates to media for electrostatic recording and to the production of such media.

In application for United States patent, Serial Number 443,646, now U.S. Patent No. 3,012,839, issued December 12, 1961, filed July 15, 1954, by Frank T. Innes and Herman Epstein, which application is assigned to the same assignee as this application, there is taught a process of electrostatic recording by the deposition of patterns of electric charges upon a dielectric surface employed as a recording medium. It is further taught to fix pigment particles, used to render such patterns of charges visible, by heating the dielectric medium sufficiently to render it soft or tacky and by applying force sufficient to partially embed the particles in the thus softened dielectric.

For reasons of economy and convenience, and in order that the recording medium may not appear too strange when compared with the conventional papers of more common business use, it is highly desirable that the dielectric medium take the form of a thin coating applied in some inexpensive manner to a surface of a paper base. In addition to receiving electrostatic printings, it is also desirable that the dielectric surface be suitable for the addition of notes, stamp marks, and similar markings applied by conventional means such as graphite pencils, fluid pen inks, the marking means employed in so-called "ball point" pens, and others. Since the electrostatic recording process is capable of very high-speed operation, there is a large usage of the recording medium, much of which is scrapped after it has served its purpose. Moreover, any human operator errors in recording in the wrong format or in selecting the wrong data for recording can produce large quantities of scrap material. It is therefore desirable that the dielectric coatings be of such nature that scrap may readily be converted into usable paper pulp. In order that the capacity of a unit surface of the dielectric to, e.g. a metal backing plate on which the coated paper might rest, may be uniform, it is desirable that the dielectric coating on the paper be uniform, not penetrating to various depths into the paper.

Other characteristics required are that differential expansion of the dielectric and the paper base, whether as a result of thermal stresses, changes in external humidity, or other causes shall not cause curling of the composite medium. Also, the medium must be sufficiently flexible so that it will not tend to flake or crack under the pressure of a writing instrument. Polyethylene, for example, may be applied as a dielectric coating by extruding it hot over the paper surface; but it tends to acquire stray surface charges from ordinary handling and produces curling of the paper. Coatings of copolymers of styrene and butadiene, and of styrene and acrylonitrile, and of vinyl chloride and vinyl acetate may be applied in (relatively expensive) organic solvents. None of these is writable by ordinary ink; and none is removable by any medium which is also suitable for pulping the paper base for scrap recovery.

One important object of my invention is thus to provide an inexpensive dielectric recording medium having a surface which is "writable," i.e. capable of being whitten upon by conventional pen and ink, by lead pencil, and other conventional writing means.

Another important object of my invention is to provide a dielectric recording medium having a writable surface, a dielectric coating of uniform thickness, and a paper base readily recoverable as pulp from the scrap medium.

Yet a further object of my invention is to provide a dielectric recording medium capable of being produced by simple processes performed on a paper base.

For these and other objects (which will become apparent to those skilled in the art in the course of the following detailed description and specification) I provide a liquid colloidal dispersion of a film-forming, lyophilic dielectric resin in which there are suspended small solid particles of other lyophobic dielectric material, the suspending liquid being such as to be readily absorbed by capillary attraction into the paper base; and I apply this suspension to a surface of suitable paper base material, whereby, upon drying, there is formed on the surface a thin uniform coating of the lyophilic dielectric material, roughened and made adrasive to graphite by small included aprticles of the lyophobic dielectric material. The term "lyophilic," meaning literally "fond of solution" refers to a material which apparently enters into colloidal dispersion as a result of forces between itself and the dispersing medium; and the term "lyophobic," meaning literally "solution hating," refers to a material which apparently can be suspended colloidally only as a result of forces between itself and some agent or substance, often ionic, other than the dispersing medium although simple Brownian movement and viscosity may suffice to retain temporarily suspended a sufficiently finely divided lyophobic material. When the suspending or dispersing medium (what would incorrectly be called the "solvent" in an incorrectly described "colloidal solution") evaporates from a dispersion of lyophilic material, the forces between the dispersing medium and the lyophilic material tend, apparently, to be converted into forces between different particles of lyophilic material, and thus such a material may form a continuous film, under suitable conditions. Since there are believed to be no such forces between particles of lyophobic suspensoid and the dispersing medium, the evaporation of the medium cannot produce such linking together of forces between particles of lyophobic material, and discrete lyophobic particles will remain, embedded (in the present instance) in a film of lyophilic material. For the special case of an aqueous dispersing medium, the term "hydrophilic" is the specific equivalent of "lyophilic" and the term "hydrophobic" is the specific substitute for "lyophobic."

For the better understanding and explanation of my invention, I have provided a figure of drawing, as follows:

The FIGURE represents a paper base coated with dielectric material, according to my invention.

For carrying out my invention, I have employed the following process. A vinyl acetate copolymer (of the group known as crotonic acid-vinyl acetate copolymers) having carboxyl and hydroxyl groups attached to a polyvinyl acetate molecule, and therefore dispersible in water containing free alkali and thus lyophilic may be ob-

tained under the trade name "Gelva" from Shawinigan Resins Corporation, 644 Monsanto Avenue, Springfield 1, Mass. In an aqueous solution of ammonium hydroxide having a pH from 8.7 to 9.5, I disperse, colloidally, sufficient of such resin to produce a dispersion having, at room temperature, the viscosity of a moderately thin syrup. For Gelva type C–3–V–20, this requires a concentration of about twenty percent by weight of resin for a given weight of dispersion. Additional ammonium hydroxide must be added to adjust the pH to 8.5 to 8.7; it is presumed that the carboxyl groups are effective in promoting the dispersion of the resin, and that they cause the reduction of the pH; but this is merely a reasonable assumption. I have found it possible to render the final film opaque by dispersing, by ball milling, in the dispersion of lyophilic resin, a pigment such as titanium dioxide sold commercially by the Titanium Pigments Company of New York City, New York, under the name "Titanox RA 50." A weight of such pigment equal to one fourth the weight of the lyophilic resin sufficed to render the final film opaque. A mechanical dispersion of a different dielectric resin, which is insoluble and hydrophobic in aqueous solutions, is prepared by ball milling in methanol for several hours a styrene-alpha-methyl styrene copolymer, having a melting point of about 112 degrees centigrade. The ball milling is continued until the average particle size of the copolymer is below 1 micron. The concentration of the ball-milled dispersion is by weight about 25 percent of resin. To the colloidal ammoniacal dispersion of the vinyl acetate copolymer I add from 3 to 6 percent by weight of the ball-milled methanol dispersion of styrene copolymer, mixing the two thoroughly. A styrene-alpha-methyl styrene copolymer satisfactory for this purpose is sold by the Pennsylvania Industrial Chemical Corporation, 120 State Street, Clairton, Pennsylvania, under the trade designation of "Piccotex-112." It should be observed particularly that the vinyl acetate copolymer is insoluble in water, and non-hygroscopic; and, in accordance with a common property of colloidal dispersions, a dispersion of this material suffers a rapid increase in viscosity upon a relatively small withdrawal of suspending liquid. The styrene-alphamethyl styrene copolymer is reasonably hard, sufficiently friable that it may readily be reduced in size by ball-milling, and has good dielectric properties.

The mixed colloidal and mechanical suspension whose preparation has been described was applied to a paper base by painting, rolling, or dipping, with the following results. The paper absorbed the aqueous ammonia solution into its interior portion by capillary action, leaving at its surface a highly viscous colloid gel containing mechanically dispersed particles of styrene-alphamethyl styrene copolymer. Upon drying, the gel deposited a continuous, flexible uniform thin film of vinyl acetate copolymer whose surface has what may be called "tooth" from the presence of the harder particles of styrene-alphamethyl styrene copolymer, which render the surface capable of abrading the graphite of a pencil lead, and are believed to assist in the spreading of conventional writing ink over the surface, as was observed to occur. It is suspected that the hydrophilic carboxyl groups in the film render the film writable by fluid ink.

Pulping of paper scrap coated as here described may be accomplished by the use of a somewhat alkaline water medium, which will carry the resin in colloidal dispersion, as described in connection with the coating operation.

The figure represents the base sheet, paper base **101**, the dielectric film **102**, for example, a film copolymer, and the embedded particles of dielectric material **103**, for example, particles of styrene-butadiene copolymer.

Particular advantages accrue to my practice of employing a collodial aqueous dispersion of a resin which is actually insoluble in water, since the use of a weak aqueous ammonia solution is very economical; it facilitates recovery of scrap paper by pulping; it permits the coating of paper which has not been coated with clay to prevent internal penetration by coating agents. Such clay coating is required for the preparation of paper which is to be coated by immersion in ordinary solutions which can penetrate into the paper; but, as observed above, the colloidal dispersion can suffer capillary withdrawal of the suspending liquid without being itself drawn into the interior of the paper. (An analogous effect is observed in slipcasting of ceramics in plaster molds, but there the ceramic body is in primarily mechanical suspension.) Apart from the economy inherent in not having to clay coat paper stock, stock not coated is easeir, and thus cheaper, to slit.

It has been found that paper coated as here described does not tend to curl or roll. This is assumed to be caused by the facts that no external mechanical stress is applied during the drying process, when the coating is actually forming, that small adjustments to stress may take place readily until the coating is quite thoroughly dry, and that no large temperature changes are required for the coating or drying operations.

The coating produced has been found, as before mentioned, to be capable of receiving good records from lead pencils, fountain pens and inks, ball point pens, and rubber stamps. It does not show any marked tendency to develop spontaneously stray electric charges.

The coating process described has the advantage over hot lamination, described with polyethylene coatings, of being capable of performance at much higher speeds, with somewhat simpler equipment.

In the exemplification described, it also enjoys the advantage over other possible coatings of requiring only non-inflammable, very inexpensive, and non-toxic solvents, which need not be recovered after use because of their cheapness and harmlessness. However, if the use of a recoverable solvent is desirable, for some particular requirements, there is no objection to such practice of the invention always provided that suitable lyophobic and suitable lyophilic materials are available. To permit writing by a given fluid ink, the film-forming resin employed should be lyophilic toward such ink.

If, on the other hand, even the methanol employed in the process above described is objectionable for any reason, water alone may be employed as a suspending medium. I have prepared satisfactory coatings employing only aqueous media, as follows. A styrene resin, such as those of the Dow Chemical Company, Midland, Michigan, trade designation PS–2 or PS–3, may be suspended conveniently by ball milling it in a small quantity of an aqueous suspension of the "Gelva" type resin with the pH adjusted to 8.5 to 8.7. A concentration of ten percent of the "Gelva" resin for a given weight of dispersion is satisfactory for suspending about fifty percent, by weight of dispersion, of the styrene resin (which is hydrophobic in the suspension of "Gelva" type resin). The concentrated suspension of the styrene resin may then be diluted by addition to a further alkaline aqueous suspension of "Gelva" type resin to produce final concentrations, by weight of suspension, of twenty percent of "Gelva" type resin and of two percent of styrene resin. Thus, in the final film the proportion of styrene resin to "Gelva" type resin is one to ten. I found this a satisfactory ratio, although it is obvious to one skilled in the art that wide variations in this ratio are permissible. Since there is a tendency for some suspensions to form when ball-milled, it is desirable to add antifoaming agents to any suspensions in which foaming is troublesome. The production of antifoaming agents is a flourishing part of the chemical industry, and abundant information is available on the selection and use of such agents. For example, the product sold under the commercial name of "Foamex" by the Glyco Products Corporation, Empire State Building, New York City, New York, was satisfactory in suppressing foaming in the completely aqueous suspension described

in the immediately preceding portions of this paragraph. However, the use of antifoaming agents is a convenience to my invention rather than an absolute necessity; and is an expedient well known in the manufacturing art.

Since the process of suspending and then removing from suspension is purely physical rather than chemical, no reactions being involved, it is possible to employ the same resin as the lyophobic material with one suspending medium and as the lyophilic material with a different suspending medium. Thus it is possible to use polyvinyl acetate in colloidal suspension in methanol as the film-forming lyophilic resin, with methyl or ethyl methacrylate (or a mixture of both) as the lyophobic resin. Similarly, an aqueous colloidal suspension of vinyl acetate copolymer may employ methyl methacrylate or ethyl methacrylate as the hydrophobic material. However, with acetone as the medium, methyl methacrylate or ethyl methacrylate becomes a lyophilic film-forming resin and could employ epoxy resin as a lyophobic substance. A practical limitation on the use of one material in two roles, however, is the difference in desired physical properties, since the lyophilic film is preferably more flexible than is consistent with the hardness desired in a lyophobic material. The very complex stereochemistry of organic resins provides an extremely large number of possible resin formulations which can probably never be exhaustively catalogued (except possibly by automatic means). A reference on this general problem is "Polyesters and Their Applications," by Bjorksten Research Laboratories, Incorporated, of Madison, Wisconsin, published in 1956 by the Reinhold Publishing Corporation of New York City, New York. Chapter VIII of this book is entitled "Tailor-Making Polyesters" and describes the various means for varying the properties of a resin in a given desired manner. A paragraph on page 162 of the reference is entitled "Water Sensitivity" and discusses means to make resins water-soluble, the term "soluble" being employed in the colloquial and trade sense of hydrophilically suspensible. In page 314 through 343 of the reference there are listed 300 United States patents on the manufacture of resins; the number supports the preceding observations on the number of possible resin formulations.

Following in a columnar list of usable combinations of a medium, a lyophilic resin, an a lyophobic resin. Quantities are not given because the practicable concentrations are those producing suitable viscosities of suspension; and the characteristics of resins of given chemical composition are sufficiently variable as a function of manufacturing and other parameters so that it is necessary to experiment to an extent to produce optimum concentrations. The concentrations and viscosity indications previously recited are adequate for initial points. The following five combinations were selected on the basis of known lyophobic or lyophilic characteristics in the medium concerned, and on the basis of high resistivity, and were found to produce satisfactory paper coatings of the predicted properties.

Medium	Lyophilic Film-Forming Resin	Lyophobic Resin
Water plus ammonium hydroxide.	Crotonic acid-vinyl acetate copolymer.	Styrene copolymer.
Do	do	Epoxy resin.
Methanol	do	Styrene copolymer.
Do	do	Epoxy resin.
Do	Polyvinyl acetaldehyde.	Do.

Other combinations having suitable characteristics for this use are the following:

Medium	Lyophilic Film-Forming Resin	Lyophobic Resin
Water plus ammonium hydroxide.	Crotonic acid-vinyl acetate copolymer.	Poly-methacrylate.
Methanol	do	Do.
Do	do	Urea formaldehyde polymer.
Do	Polyvinyl acetate	Styrene copolymer.
Do	do	Poly-methacrylate.
Do	do	Epoxy.
Do	do	Urea formaldehyde polymer.
Do	Polyvinyl acetaldehyde.	Styrene copolymer.
Do	do	Poly-methacrylate.
Do	do	Urea formaldehyde polymer.
Acetone	Crotonic acid-vinyl acetate copolymer.	Epoxy.
Do	do	Urea formaldehyde polymer.
Do	Polyvinyl acetate	Epoxy.
Do	do	Urea formaldehyde polymer.
Do	Polyvinyl acetaldehyde.	Epoxy.
Do	do	Urea formaldehyde polymer
Do	Vinylidene chloride copolymer.	Epoxy.
Do	do	Urea formaldehyde polymer.
Do	Vinyl chloride-vinylidene chloride copolymer.	Epoxy.
Do	do	Urea formaldehyde polymer.

Trade names of some typical resins, and the suppliers producing them under such trade names are listed here. The same materials may be available under other names from other suppliers. Purpose of the listing is primarily to record the present commercial availability of these materials.

Resin	Trade Name	Supplier
Crotonic acid-vinyl acetate copolymer.	Gelva C-3	Shawinigan Resins Corporation, Springfield 1, Massachusetts.
Polyvinyl acetate	Gelva	Shawinigan Resins Corporation.
Polyvinyl acetaldehyde	Alvar	Shawinigan Products Corp., Empire State Bldg., 350 Fifth Ave., New York City 1, New York.
Vinylidene chloride copolymer.	Saran	Dow Chemical Company, 1000 Main Street, Midland, Michigan.
Vinyl chloride-vinylidene chloride copolymer.	Experimental Resin X-2716.	Dow Chemical Company.
Polyvinyl acetal-butyral	Butvar	Shawinigan Resins Corporation.
Polyvinyl acetal-formal	Formvar	Do.
Styrene copolymer	Piccotex	Pennsylvania Industrial Chemical Corporation, Clairton, Pa.
Polymethyl methacrylate	Lucite	E. I. du Pont de Nemours & Co., Inc., Wilmington 98, Delaware.
Polyethyl-methyl methacrylate.	Plexiglas	Rohm & Haas Co.
Urea formaldehyde polymer.	Beetle	American Cyanamid Company, 30 Rockefeller Plaza, New York City 20, N.Y.
Epoxy	Epon	Shell Chemical Corporation, 380 Madison Ave., New York City, N.Y.

What is claimed is:

1. An information recording medium comprising a film coating of crotonic acid-vinyl acetate copolymer containing at least partially embedded particles of styrene-alpha-methyl styrene copolymer having sharp edges of average size of the order of less than a micron and further comprising a paper base.

2. A dielectric recording medium comprising a flexible absorbent base sheet which has on one side a substantially continuous electric-charge-retentive coating of non-hygroscopic dielectric material, said coating having partially

embedded therein discrete sharp particles of average size of the order of less than a micron of a second electric-charge-retentive dielectric resin material and being physically harder than the material of said coating.

3. As a dielectric electrostatic recording medium, a flexible absorbent base sheet covered on one surface by a substantially continuous electric-charge-retentive film of flexible dielectric resin, said film having partially embedded therein mechanically sharp hydrophobic particles of average size of the order of less than a micron of a different resin harder than the resin of the film.

4. As a dielectric recording medium, a flexible porous base sheet covered on one surface but negligibly impregnated by a substantially continuous flexible electric-charge-retentive film of dielectric resin which has partially embedded therein resin particles of average size of the order of less than a micron of electric-charge-retentive dielectric abrasive to graphite.

5. An electrostatically printable recording medium comprising a flexible porous base sheet bearing on one side thereof a flexible substantially continuous electric-charge-retentive film of a first dielectric resin lyophilic in alkaline water solution, in which said film there are embedded electric-charge-retentive particles of average size of the order of less than a micron of a second dielectric resin lyophobic in alkaline water solution, said resinous particles being sharp edged and physically more resistant to abrasion than the said film.

6. An electrostatically printable medium comprising a flexible porous base sheet bearing on one side thereof a flexible substantially continuous electric-charge-retentive film formed of a first dielectric resin lyophilic in alkaline water solution and containing an opacifying pigment, said film having partially embedded electric-charge-retentive particles of average size of the order of less than a micron of second dielectric resin lyophobic in alkaline water solution, said resinous particles having sharp edges and being harder than the film.

7. An information recording medium comprising a sheet base of otherwise uncoated absorbent paper which bears upon one side thereof a continuous film coating of crotonic acid-vinyl acetate copolymer containing partially embedded therein sharp-edged, non-conductive particles of average size of the order of less than a micron of styrene-alphamethyl styrene copolymer and containing particles of concentration below that for conductivity of titanium dioxide pigment.

8. An electrostatically printable information recording medium comprising a sheet base of otherwise uncoated absorbent paper which bears upon one side thereof a film coating of crotonic acid-vinyl acetate copolymer containing partially embedded therein non-conductive sharp-edged particles of average size of the order of less than a micron of styrene-alphamethyl styrene copolymer and containing particles of pigment, the concentration of particles of pigment being sufficient to render the film opaque and insufficient to cause conductivity.

9. A dielectric recording medium comprising a flexible absorbent base sheet, said sheet having on one side a substantially continuous, electric-charge-retentive coating of non-hygroscopic dielectric material, said dielectric material selected from the group consisting of crotonic acid-vinyl acetate copolymer, polyvinyl acetaldehyde, polyvinyl acetate, vinylidene chloride copolymer, and copolymer vinyl chloride-vinylidene chloride, said coating having partially embedded therein discrete sharp particles of average size of the order of less than a micron of a second electric-charge-retentive dielectric resin material physically harder than the material of said coating.

10. The recording medium of claim 9 wherein said second electric-charge-retentive dielectric resin material is selected from the group consisting of styrene copolymer, cured epoxy resin, polymethacrylate and urea formaldehyde polymer.

11. A dielectric recording medium comprising a flexible absorbent base sheet, said sheet having on one side a substantially continuous, electric-charge-retentive coating of non-hygroscopic dielectric material, said coating having partially embedded therein discrete sharp particles of average size of the order of less than a micron of a second electric-charge-retentive dielectric material physically harder than the material of said coating, said physically harder dielectric material particles being selected from the group consisting of styrene copolymer, cured epoxy resin, poly-methacrylate, and urea formaldehyde polymer.

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