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3,707,402

METHOD OF MANUFACTURING ELECTRONIC RECORDING MATERIAL

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ABSTRACT OF THE DISCLOSURE

A method of manufacturing an electronic recording material, which comprises the step of forming on a support a recording layer or a photoconductive layer consisting of a highly insulating resin or a material composed of said highly insulating resin and a photoconductive substance contained therein, said resin being a resin emulsion of vinyl copolymers having an epoxide radical or a hydroxyl group.

BACKGROUND OF THE INVENTION**(a) Field of the invention**

The present invention relates to a method of manufacturing an improved electronic recording material for use in electrophotography.

(b) Description of the prior art

The electrophotographic material includes one prepared by forming a photoconductive layer consisting of a highly insulating resin containing a metallic oxide such as zinc oxide, titanium oxide and the like and one prepared by forming a recording layer consisting of a highly insulating resin only. The former is intended for developing the electrostatic latent image obtained by means of exposure through an original subsequent to impression of an electric charge by corona discharge on a photoconductive layer, while the latter is intended for developing the electrostatic latent image obtained by means of direct electrification of a recording layer like an original.

Inasmuch as the highly insulating resin to be employed for such electronic recording materials is required to function as a binder to firmly fix a photoconductive layer or a recording layer onto a support, such resins of a highly insulating property and which are soluble in organic solvents have hitherto been in general use. However, the foregoing electronic copying materials are prepared by coating the resinous binder dispersed in organic solvents on the support, so that costly equipment is necessary for preventing harm to humans and fires or explosions during vaporization of the organic solvent employed.

Viewed from the point that no such precautions would be necessary if the resinous binder is either water soluble or water dispersible, there have so far been proposed a variety of water soluble resins or water dispersible resins as the resinous binder. However, the electronic recording materials prepared by employing those resinous binders have such drawbacks that, the electrostatic properties of photoconductive layers are deficient as evidenced by the low potential charged at the time of corona discharge and the tremendous dark decay thereof when left in a dark place subsequent to electrification, whereas when a recording layer has been provided therefor through direct electrification, a change in humidity is apt to give rise to fogging because of the highly insulating resin employed for said recording layer.

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SUMMARY OF THE INVENTION

The present invention relates to a method of manufacturing an electronic recording material by employing polymers of vinyl emulsion having a bridge-making property in forming a photoconductive layer or a recording layer of said material.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is based on the findings resulting from examination of the electrostatic characteristics, image properties and so on of various electronic recording materials provided with a photoconductive layer or a recording layer formed on the support thereof, respectively, by means of varieties of water soluble resins and resinous emulsions obtained by emulsion polymerization. In other words, the present invention relates to a method of manufacturing an electronic recording material by means of forming, on a support such as paper and the like, a recording layer or a photoconductive layer comprising a highly insulating resin or a material composed of said highly insulating resin and a photoconductive substance contained therein, said method being characterized by the fact that the highly insulating resin employed therefor is a resin emulsion comprising any vinyl copolymers having an epoxide radical or a hydroxyl group at the end of a long chain molecule or vinyl copolymers containing carboxylic acid as well as said hydroxyl group bonded at the end of a long chain molecule. The electronic recording material according to the present invention has proved to be particularly superb in the weather-proofing property thereof.

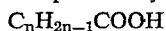
The resinous binder to be employed for the present invention includes, for instance, the resin emulsions of vinyl copolymers obtained by copolymerizing at least one member of the group consisting of glycidyl methacrylate, glycidyl acrylate, hydroxyethyl-methacrylate, 2-hydroxyethylacrylate, hydroxypropyl - methacrylate, hydroxypropylacrylate, 5-hydroxypentylvinyl ether and the like with at least one member selected from the group of unsaturated mono- and di-carboxylic acids such as acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, and at least one member selected from the group consisting of (1) acrylic esters and methacrylic esters such as ethyl acrylate, propyl acrylate, butyl acrylate, isobutyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, isobutyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate and cyclohexyl methacrylate, (2) vinyl aromatic monomers such as styrene, α -methylstyrene, p-methylstyrene, p-methoxystyrene, vinyl toluene, vinyl xylene, isopropyl styrene, ethyl vinylbenzene and divinylbenzene, (3) vinyl cyanides such as acrylonitrile, methacrylonitrile and vinylidene cyanide, (4) unsaturated amides from α,β -olefin such as acrylamide, methacrylamide, N- and N'-dimethylacrylamide, N- and N'-dipropylmethacrylamide, N-phenylacrylamide, N-methylolacrylamide and N-vinylpyrrolidone, (5) vinyl amines such as 2-vinylpyridine and 3-vinylpyridine, (6) vinyl halogenides such as vinyl chloride, vinyl bromide, vinyl fluoride, vinylidene chloride and vinylidene fluoride, (7) vinyl esters such as vinyl acetate and vinyl propionate by emulsion polymerization. A substance obtained by simultaneously copolymerizing a derivative of acrylic acid having β -hydroxyl radical with the foregoing monomers is applicable, and a substance obtained by mixing several prepared emulsion polymers to form a polymer blend is also applicable. Furthermore, a latex obtained by blending epoxide resin in the monomer at the time of emulsion polymerization may also be employed.

Concerning the emulsifier for the aforesaid resin emul-

sion to be employed in the present invention, it is required to have such properties as dispersibility for zinc oxide, water resisting property of the film formed thereby and capability of enhancing the efficiency of the electronic recording materials to be produced. As an emulsifier to meet said requirements, there can be used natural resins containing resin acid, synthetic resins containing acid radical such as carboxylic acid, aliphatic carboxylic acid, aromatic carboxylic acid, alicyclic carboxylic acid, or some substances obtained by salifying them with a volatile base are desirable, and, as occasion demands, a small amount of anionic or nonionic field activator may be added thereto.

As for said natural resin containing resin acid, it includes elemi, gurrjun, jalap, scammonium, bdellium, saganum, euphorbium, myrrhe, opopanax, guajak, tacamahac, galbanum, gamboge, olibanum, ammoniacum, asafetida, benzoin, sandarac, kawa kawa, a variety of balsams such as Canada balsam, Mecca balsam, true balsam, copaiba balsam and Peru balsam, a variety of dammars such as benak, dead dammar, melanty, chn, yan, panoun, and Papuan dammar, a variety of kopals such as kauri kopal, soft Manila kopal, hard manila kopal, Congo kopal, Benguela kopal, Angora kopal, Demerara kopal, Madagascar kopal, hard Bornea kopal and New Zealand hard kopal, a variety of rosin such as gum rosin, heterogeneous rosin, polymerized rosin, hydrogenated rosin, tall oil, rosin maleate, rosin oxide, hardened rosin and ester gum.

As for said aliphatic carboxylic acid, it includes the group of saturated monocarboxylic acids expressed by the general formula $C_nH_{2n+1}COOH$ and having 5 or more carbons, such as valeric acid, isovaleric acid, caproic acid, enanthic acid, pelargonic acid, caprylic acid, undecanoic acid, lauric acid and tridecanoic acid, the group of olefin monocarboxylic acids expressed by the general formula



and having 5 or more carbons, such as angelica acid, tiglic acid, 1-pentenoic acid, 2-hexenoic acid, 2-heptenoic acid, 2-octenoic acid, 2-nonenic acid, 4-tenenoic acid, linderic acid, elaidic acid and oleic acid, the group of acetylene monocarboxylic acids expressed by the general formula $C_nH_{2n+1}C\equiv C(CH_2)_mCOOH$ and having 5 or more carbons, such as ethylpropionic acid, n-propylpropionic acid and behenolic acid, the group of di- and triolefin monocarboxylic acids expressed by the general formulas $C_nH_{2n-3}COOH$ or $C_nH_{2n-5}COOH$ and having 5 or more carbons, such as 2,4-pentadienoic acid, 2,4-hexadienoic acid, lioic acid, elaeostearic acid, and linolenic acid, the group of saturated carboxylic acids expressed by the general formula $HOOC(CH_2)_nCOOR$ (wherein R is hydrogen or an alkyl radical) and having 4 or more carbons, such as succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid and azelaic acid and sebacic acid as well as monoesters of these acids, and also the group of hydroxycarboxylic acids having 5 or more carbons, such as 2-hydroxyvaleric acid, 2-hydroxycaproic acid, 2-hydroxyheptanoic acid, 2-hydroxycaprylic acid, 3-hydroxycaprylic acid and 3-hydroxyundecanoic acid.

As for said aromatic carboxylic acids or alicyclic carboxylic acid, the former includes the group of benzoic acids such as toluic acid, dimethyl benzoic acid and ethylbenzoic acid, the group of benzene-dicarboxylic acids such as phthalic acid, n-phthalic acid and terephthalic acid, the group of benzene-tricarboxylic acids such as hemimellitic acid, trimellitic acid and trimesic acid, the group of sulfocarboxylic acids such as orthosulfocarboxylic acid, meta-sulfocarboxylic acid and para-sulfocarboxylic acid, the group of alkylbenzene-sulfocarboxylic acids such as 2-methylbenzenesulfocarboxylic acid and 2- and 6-dimethylbenzenesulfocarboxylic acid, the group of hydroxycarboxylic acids such as hydroxybenzoic acid, methylsalicylic acid and 3-hydroxy-phthalic acid, the group of anthracenecarboxylic acids such as naphthoic acid, 2-methyl-1-naphthoic acid, 3-hydroxy-2-naphthoic acid and naphthalene-1,2-dicarboxylic acid, and further anthra-

cene-1-carboxylic acid and anthracene-1,2-dicarboxylic acid, while the latter viz. alicyclic carboxylic acid includes the group of cyclopropanecarboxylic acids such as 3- α -hydroxybenzyl-2-phenylcyclopropanecarboxylic acid, 3-benzoyl-2-phenylcyclopropanecarboxylic acid and dicyclopropane-1,1-dicarboxylic acid, the group of cyclobutanecarboxylic acid such as cyclobutanecarboxylic acid, 2-methylcyclobutanecarboxylic acid and cyclobutane-1,1-dicarboxylic acid, the group of cyclopentanecarboxylic acids such as methylcyclopentanecarboxylic acid, 1-isopropylether-2-methylcyclopentanecarboxylic acid, 1- and 2-cyclopentane-dicarboxylic acid, cyclopentane acetic acid, naphthenic acid and 1-hydroxypentanecarboxylic acid, the group of cyclohexanecarboxylic acids such as methylcyclohexanecarboxylic acid, cyclohexylpropanecarboxylic acid, 1-phenylcyclohexyl acetate and cyclohexenecarboxylic acid, the group of terpenes such as abietic acid, β -boswellic acid, quinovic acid, glycyrrhezoic acid, hederagenin oleanolic acid, pimaric acid, quillaic acid and ursolic acid, and the group of cholic acids such as bisnorcholic acid, chenodesoxycholic acid, cholic acid, dehydrocholic acid, glycocholic acid, hideoxychoalic acid, lithocholic acid and ursodioxycholic acid. As for the aforesaid anion field activator to be employed in combination with the foregoing acids or such substances as obtained by neutralizing said acids with a volatile base, it includes, for example, sodium stearate, potassium laurate, sodium laurate, 2-ethylhexylsodiumsulfate, triethylamine xylenesulfonate, diethylamine xylenesulfonate, triethanolamine alkylbenzenesulfonate, diethylamine alkylbenzenesulfonate and triethylamine alkylbenzenesulfonate.

The vinyl polymer latex obtained through an ordinary emulsion polymerization by employing the above-stated monomer composition and emulsifier has a pH value in the range of 1.5-3.5, but, due to neutralization by means of a volatile alkali aqueous solution such as ammonia, morpholine, cyclohexylamine, an aliphatic primary amine, e.g. methylamine, ethylamine, and isopropylamine, an aliphatic secondary amine, e.g. dimethylamine, diethylamine and dipropylamine, an aliphatic tertiary amine, e.g. trimethylamine, triethylamine and tri-isopropylamine, and alcoholamines, e.g. monoethanolamine, diethanolamine and triethanolamine, the acidic component of an emulsifier as well as the acidic component of a copolymer latex as stated above is neutralized by virtue of said volatile base, and, as a result, not to speak of the superb preservation stability and mechanical stability brought about thereby, the pigment dispersion effect is extremely improved, as has been confirmed.

The volatile base is easily evaporated by air heating at the time of forming a film. The aforesaid polymer latex contains quite a small amount or none of an intensively hydrophilic field activator and has excellent water-resisting qualities ascribable to a multiplied effect of natural resin acid, fatty acid, aromatic alicyclic-carboxylic acid, etc. having a large number of carbons, and especially has such an advantage that it can provide a film of a superb electric-insulating property which is hardly influenced by humidity.

Moreover, said resin emulsion, when employed as a binder to be dispersed in water together with a photoconductive substance and a sensitizer, exhibits an excellent dispersion effect, and, not only that, a sensitive layer formed by coating the resultant dispersion on the surface of a support and drying thereafter, can be provided with another excellent character. That is to say, the epoxide radical or hydroxyl group contained in a resinous binder gives rise to a bridge-making reaction with the acidic component of the copolymer or the carboxylic acid contained in an emulsifier during the hot-drying process at the time of forming a sensitive layer and easily forms reticulations among molecules or within molecules, to thereby bring about a superb weather-proofing property. For instance, a recording material according to the present invention can display such properties and copied

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images are by no means inferior to those obtained in an atmosphere of high humidity. This is presumably attributable to the fact that, owing to the reticulations of a resinous binder formed within a sensitive layer, it becomes difficult for the photoconductive substance to absorb the moisture of the atmosphere.

As mentioned above, the present invention relates to an electronic recording material comprising a support and a photoconductive layer or a recording layer formed on the surface of said support, and has been successful particularly in effecting a novel improvement of the above stated binders to thereby provide a sensitive layer with weather-proofing qualities so as to enhance the unsusceptibility of the electric resistance of said sensitive layer to the humidity of the atmosphere as required for an electrophotograph, and also in eliminating all such defects are attributable to those binders which used to be dissolved in organic solvents only, as in case of the electronic recording materials in the prior art.

The following is a further elucidation of the present invention with reference to specific embodiments thereof.

EXAMPLE 1

(A-resin emulsion)

As for the material in this case, 60 parts by weight of methylester acrylate, 20 parts by weight of ethyl-ester acrylate, 15 parts by weight of glycidyl methacrylate, 5 parts by weight of acrylic acid, 4 parts by weight of dammar, 0.1 part by weight of triethanolamine dodecylbenzenesulfonate, 0.3 part by weight of ammonium persulfate and 150 parts by weight of water were employed. Two-liter glass flask equipped with a stirrer, a counter-flow cooler, a raw material inlet and a thermometer, was installed in a hot-water bath, and into this flask were placed said monomers, dammar, dodecylbenzenesulfonate and water (exclusive of the quantity for use in dissolving ammonium persulfate). Then, nitrogen gas was introduced into the flask to replace the air therein, and the inner temperature of the flask was raised to 65–70° C. by slowly raising the temperature of the hot-water bath. Ammonium persulfate was divided into three doses, and each dose was introduced into the flask at an interval of one hour so as to control the temperature for reaction. The material thus mixed was subjected to a further intense stirring continuously for some time, and a resinous emulsion having 39.7% of solid matters and a pH value of 2.8 was obtained upon polymerization for 6 hours in all.

(B-resin emulsion)—comparative

Another resin emulsion was prepared in the same way as the foregoing A-resin emulsion, except that glycidyl methacrylate alone was omitted from the monomer components of the present emulsion. By employing 50 g. of the thus obtained resinous emulsion and adding thereto, respectively, 100 g. of photoconductive zinc oxide, 100 g. of water and 5 cc. of sensitizing dye (viz a methanol solution containing 1% of Bromophenol Blue, 0.5% of Fluorescein and 0.1% of Rose Bengal), and further adding a small amount of aqueous ammonia and dispersing the resultant mixture with a homomixer, electrophotographic sensitive liquids were prepared. Then, said sensitive liquid were respectively coated on the surfaces of an art paper, whose back had been processed for conductivity, to the extent that the weight of the sensitive layer, when dried, was 25 g./m.², and was dried. Thus obtained copying paper was measured of its electric charge by means of corona discharge according to the conventional method under such high temperature and humidity as 32° C. and 85% RH, respectively. The resultant surface electric potential (as expressed by V_s) 30 seconds after the impression of voltage (–6 kv.) was as shown in the following Table 1.

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TABLE 1

Copying paper	V_s/μ , 32° C.—85% RH.
Product A of this invention ..	59(V).
Product B for comparisons sake	20.

Further, when development was effected by means of wet-developing process or dry-developing process subsequent to impression of an electric charge and exposure according to the conventional method, product A of the present invention could bring about an image of good contrast if it was under a high temperature and humidity or under a normal temperature, whereas product B prepared for comparisons sake could hardly exhibit any image-formability.

EXAMPLE 2

(C-resin emulsion)

As for the material in this case, 50 parts by weight of styrene, 30 parts by weight of methyl-ester methacrylate, 18 parts by weight of hydroxypropylacrylate, 2 parts by weight of acrylic acid, 3 parts by weight of kauri kopal, 0.01 part by weight of dialkylsulfosuccinate, 0.2 part by weight of ammonium persulfate and 150 parts by weight of water were employed. Kauri kopal was first thoroughly dissolved in the monomers, and then all the material was put in the flask as the foregoing Example 1 to effect 7 hours polymerization under the reaction temperature of 70° C. The resultant resin emulsion contained 40% of solid matters and had a pH value of 2.6.

(D-resin emulsion)—comparative

Another resin emulsion was prepared in the same way as the foregoing C-resin emulsion, except that hydroxypropylacrylate alone was omitted from the monomer components of this emulsion. By applying an electrophotographic sensitive liquid prepared by employing the thus obtained resinous emulsion as in the case of Example 1, the electrification property of copying paper was measured. The result was as shown in the following Table 2.

TABLE 2

Copying paper	V_s/μ 32° C.—80% RH.	V_s/μ 25° C.—50% RH.
Product C of this invention	63(V).	65(V).
Product D for comparison's sake	18.	31.

Further, when development was effected by means of a wet-developing-type electrophotographic copying press, product C of the present invention could bring about an image of superior qualities whether it was under a normal temperature and humidity or a high temperature and humidity, whereas product D prepared for comparison's sake exhibited but an image of inferior contrast.

EXAMPLE 3

(E-resin emulsion)

In this case, by employing 45 parts by weight of ethyl-ester acrylate, 30 parts by weight of acrylonitrile, 10 parts by weight of 2-hydroxyethylacrylate, 2 parts by weight of acrylic acid, 13 parts by weight of abietic acid, 0.09 part by weight of dodecylbenzenesulfonic acid, 0.2 part by weight of ammonium persulfate, 150 parts by weight of water and 5 cc. of triethylamine, said abietic acid was salified. Then, all the material was brought in the flask for 5 hours' polymerization at a temperature of 70° C. The resultant resin emulsion contained 40.5% of solid matters and had a pH value of 8.5.

(F-resin emulsion)—comparative

This F-resin emulsion was prepared by means of emulsion polymerization of the same material as that of the foregoing E-resin emulsion except that 2-hydroxyethylacrylate and abietic acid were omitted from the monomers for the present emulsion. Subsequently, for the sake

of comparison, a layer of resin weighing 10 g./m.², when dried, was formed on the surface of an art paper, whose back had been processed for conductivity, by means as regards coating the resin emulsion alone with a rotary coating apparatus. Thus obtained resin layer was measured of its electrification property in the same way as in case of the copying paper of Example 1, under 32° C. and 80% RH. As a result, the electric charge of the insulating layer of E-resin emulsion under the present invention was 68(V)(V_s/μ), while F-resin emulsion prepared for use in comparison was 26(V)(V_s/μ), and when these emulsions were respectively employed for preparing an electrostatic recording paper, the insulating layer of E-resin emulsion under the present invention exhibited a marvelous image-formability even under a high temperature and humidity, whereas F-resin emulsion could produce but an image of low concentration.

EXAMPLE 4

(G-resin emulsion)

The material comprising 50 parts by weight of styrene, 45 parts by weight of butyl-ester acrylate, 5 parts by weight of acrylic acid, 4 parts by weight of oleic acid, 0.3 part by weight of diethylaminododecylbenzenesulfonate, 0.2 part by weight of ammonium persulfate and 150 parts by weight of water was put in the flask for 5 hours' polymerization at a temperature of 63° C. The resultant resin emulsion contained 41.3% of solid matters, and had a pH value of 2.6.

(H-resin emulsion)

The material comprising 50 parts by weight of styrene, 40 parts by weight of butyl-ester acrylate, 10 parts by weight of glycidyl methacrylate, 4 parts by weight of ammonium oleate, 0.2 part by weight of ammonium persulfate and 150 parts by weight of water was put in the flask for 4 hours' polymerization at a temperature of 68%. The resultant resin emulsion contained 40% of solid matters, and had a pH value of 7.7.

(I-resin emulsion)—comparative

Another resin emulsion was prepared by polymerization in the same way as the foregoing H-resin emulsion except that glycidyl methacrylate alone was omitted from the monomer components of this emulsion. A copying paper prepared by applying a blended emulsion comprising the foregoing G-resin emulsion and H-resin emulsion according to the present invention at the rate of 1:1 could produce a clear-cut image even under a high temperature and humidity, whereas a copying paper prepared by applying a blended emulsion comprising said G-resin emulsion and I-resin emulsion, which was intended for use in comparison, at the rate of 1:1 had a very poor image-formability under a high humidity.

EXAMPLE 5

(J-resin emulsion)

The material comprising 50 parts by weight of styrene, 35 parts by weight of ethyl-ester acrylate, 5 parts by weight of acrylic acid, 10 parts by weight of epoxide resin (Epikote 1001 manufactured by Shell International Chemicals Corp.), 1 g. of ammonium dodecylbenzenesulfonate 0.5 part by weight of ammonium persulfate and 150 parts by weight of water was put in the flask for 7 hours' polymerization at a temperature of 75° C. The resultant resin emulsion contained 40% of solid matters, and a pH value of 2.6.

(K-resin emulsion)—comparative

This resin emulsion was prepared by emulsion polymerization in the same way as J-resin emulsion above except that epoxide resin alone was omitted from the monomer components of this emulsion. When an electrophotographic sensitive liquid was prepared in accordance with Example 1 above and applied in preparing the copy-

ing paper, a copying paper obtained by employing J-resin emulsion under the present invention could bring about an excellent image under any circumstances, whereas a copying paper prepared by employing K-resin emulsion for the sake of comparison could hardly be of practical use.

EXAMPLE 6

(L-resin emulsion)

The material comprising 20 parts by weight of 2-ethylhexylester acrylate, 65 parts by weight of styrene, 10 parts by weight of methylester methacrylate, 6 parts by weight of glycidyl methacrylate, 1 part by weight of acrylic acid, 3 parts by weight of phthalic acid, 0.5 part by weight of triethanolamine palmitate, 0.2 part by weight of ammonium persulfate and 150 parts by weight of water was put in the flask for 5 hours polymerization at a temperature of 70° C. The resultant resin emulsion contained 40.5% of solid matters, and had a pH value of 4.0.

(M-resin emulsion)—comparative

This resin emulsion was prepared by polymerization in the same way as L-resin emulsion above except that glycidyl methacrylate alone was omitted from the monomer components of this emulsion.

(N-resin emulsion)—comparative

This emulsion was prepared by polymerization in the same way as the foregoing L-resin emulsion except that phthalic acid alone was omitted from the monomer components of this emulsion. For the sake of comparing said L, M and N resin emulsions with one another, a copying paper was respectively prepared by applying each of those electrophotographic sensitive liquids which were prepared by employing said resin emulsions respectively in accordance with Example 1. The property of each copying paper thus prepared was as shown in the following Table 3. It is evident that the impression of voltage on the copying paper according to the present invention is excellent.

TABLE 3

Copying paper	V _s /μ, 32° C.—90% RH.
Product employing L-resin emulsion under the present invention	55(V).
Product employing M-resin emulsion for comparisons sake	5.
Product employing N-resin emulsion for comparisons sake	40.

What we claim is:

1. A process for preparing a dielectric recording material comprising a support having an insulating layer on one surface thereof, comprising the steps of:

preparing a water-emulsified resinous material by subjecting to emulsion polymerization a reaction mixture consisting essentially of water having dispersed or dissolved therein

- (1) at least one monomer selected from the group consisting of glycidyl methacrylate, glycidyl acrylate, hydroxyethyl methacrylate, 2-hydroxyethylacrylate, hydroxypropyl methacrylate, hydroxypropyl acrylate and 5-hydroxy pentylvinyl ether,
- (2) at least one monomer selected from the group consisting of acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid and fumaric acid,
- (3) at least one monomer selected from the group consisting of acrylic esters, methacrylic esters, vinyl aromatic monomers, vinyl cyanides, α,β ethylenically unsaturated amides, vinyl amines and vinyl halides, and

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(4) at least one acidic compound selected from the group consisting of aliphatic carboxylic acids, aromatic carboxylic acids, alicyclic carboxylic acids and natural resins containing resin acid, coating onto one surface of a support the reaction product of said emulsion polymerization and consisting of said water-emulsified resinous material, and then drying the coating thereby forming an insulating layer on said support.

2. A process according to claim 1, in which said reaction mixture further contains a surface active agent selected from the group consisting of sodium stearate, potassium laurate, sodium laurate, 2-ethylhexylsodiumsulfate, triethylaminexylenesulfonate, diethylamine xylenesulfonate, triethanolaminealkylbenzenesulfonate, diethylamine alkylbenzenesulfonate, triethylamine alkylbenzenesulfonate, dialkylsulfosuccinate, dodecylbenzene sulfonic acid, triethanolamine palmitate and ammonium dodecylbenzene sulfonate.

3. A process for preparing an electrophotographic copying material comprising an electroconductive support having a photoconductive layer on one surface thereof, comprising the steps of:

preparing a water-emulsified resinous binder by subjecting to emulsion polymerization to a reaction mixture consisting essentially of water having dispersed or dissolved therein

(1) at least one monomer selected from the group consisting of glycidyl methacrylate, glycidyl acrylate, hydroxyethyl methacrylate, 2-hydroxyethylacrylate, hydroxypropyl methacrylate, hydroxypropyl acrylate and 5-hydroxy pentylvinyl ether,

(2) at least one monomer selected from the group consisting of acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid and fumaric acid,

(3) at least one monomer selected from the group consisting of acrylic esters, methacrylic esters,

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vinyl aromatic monomers, vinyl cyanides, α,β ethylenically unsaturated amides, vinyl amines and vinyl halides, and

(4) at least one acidic compound selected from the group consisting of aliphatic carboxylic acids, aromatic carboxylic acids, alicyclic carboxylic acids and natural resins containing resin acid,

dispersing an inorganic photoconductive substance into the reaction product of said emulsion polymerization and consisting of said water-emulsified resinous binder,

coating the resultant dispersion onto the surface of said support; and

then drying the coating thereby forming a photoconductive layer on said support.

4. A process according to claim 3 in which said reaction mixture further contains a surface active agent selected from the group consisting of sodium stearate, potassium laurate, sodium laurate, 2-ethylhexylsodiumsulfate, triethylaminexylenesulfonate, diethylamine xylenesulfonate, triethanolamine alkylbenzenesulfonate, diethylamine alkylbenzenesulfonate, triethylamine alkylbenzenesulfonate, dialkylsulfosuccinate, dodecylbenzene sulfonic acid, triethanolamine palmitate and ammonium dodecylbenzene sulfonate.

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