United States Patent [19]

Ueyama

[11] **3,891,787**

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[54] **ELECTROSTATIC RECORDING MEMBER**

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[73] Assignee: **General Company Ltd.**, Tokyo, Japan

[22] Filed: **Dec. 3, 1973**

[21] Appl. No.: **421,143**

Related U.S. Application Data

[63] Continuation of Ser. No. 197,756, Nov. 11, 1971, abandoned.

[52] **U.S. Cl.** ..... **428/409**; 346/135; 428/323; 428/324; 428/328; 428/332; 428/336; 260/18 EP; 260/37 EP

[51] **Int. Cl.**..... **B32b 5/16**; B41m 5/00

[58] **Field of Search** 161/182, 162, 184, 268, 161/400, 265, 163; 101/401, 128.2, 128.3; 117/17.5, 36.7, 201; 346/135

[56] **References Cited**

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[57] **ABSTRACT**

An electrostatic recording member comprises a recording layer composed of a resin film component and an inorganic pigment or a metal soap dispersed therein, at least one member of the resin film component being selected from the group consisting of fatty acid modified epoxy resin ester, cellulose ester, cellulose ether and chlorinated rubber.

7 Claims, 1 Drawing Figure

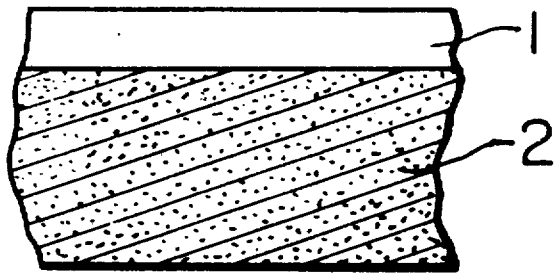


FIG. 1

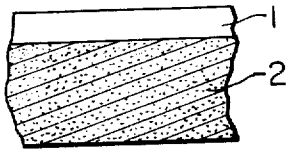
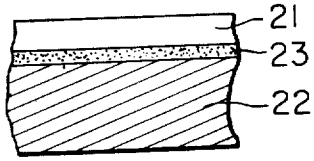


FIG. 2



INVENTOR.

BY

ELECTROSTATIC RECORDING MEMBER

This is a continuation of application Ser. No. 197,756, filed Nov. 11, 1971 and now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an electrostatic recording member, and more particularly to an electrostatic recording member having a recording layer of good inscribability, printability, and seal-affixing property.

2. Description of the Prior Art

In general, an electrostatic recording layer should have a surface resistivity higher than $10^{12}\Omega$ for the purpose of retaining electrostatic latent images, as shown, for example, in Japanese Patent Publication No. 24344/1963. Heretofore, the recording layer of conventional electrostatic member is composed of electrically insulating resin film and therefore, the surface of recording layer has lustre, and low inscribability by pencil, ball pen, and fountain pen, low printability and low seal-affixing property.

This invention relates to an electrostatic recording member free from the disadvantages of the conventional electrostatic recording members.

As resins for forming a recording layer, heretofore these have been generally used polymers of good charging property such as polyvinylacetate, polyvinylchloride, polyacrylic acid ester, polymethacrylic acid ester and the like. Accessability of recording layer film for ink has been improved by dispersing uniformly inorganic pigment or metal soap in the recording layer film to eliminate the surface lustre. However, such a dispersion of pigment in the resin results in lowering the surface resistivity to a value less than $10^{12}\Omega$ necessary for electrostatic recording and thereby, good recording is not obtained.

The present inventor has found that when inorganic pigment or metal soap is dispersed in a film forming resin such as fatty acid modified epoxy resin ester, cellulose ester and chlorinated rubber, the resulting recording lay has a surface resistivity not so lowered by incorporation of the pigment or metal soap, and good recording is obtained.

SUMMARY OF THE INVENTION

According to the present invention, the electrostatic recording member comprises a recording member composed of a resin film component and an inorganic pigment or a metal soap dispersed therein, at least one member of the resin film component being selected from the group consisting of fatty acid modified epoxy resin ester, cellulose ester, cellulose ether and chlorinated rubber.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows schematically an enlarged cross section of an embodiment of electrostatic recording member according to the present invention; and

FIG. 2 shows schematically an enlarged cross section of another embodiment of electrostatic recording member according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. 1 shows an electrostatic recording member composed of two layers, that is, a paper **2** and a recording layer **1** overlying the paper **2.** This recording layer is a resin film layer containing at least one of fatty acid modifying epoxy resin ester, cellulose ester, cellulose ether and chlorinated rubber, and an inorganic pigment or a metal soap is disposed therein.

FIG. **2** shows another embodiment of electrostatic recording member of this invention composed of three layers, that is, a support **22,** a low resistant layer **23** overlying the support **22,** and a recording layer **21** overlying the low resistant layer **23.**

It should be noted tht electrostatic recording members according to the present invention are not restricted to those as illustrated above.

Fatty acid modified epoxy resin esters used in this invention may be epoxy resins esterified with a drying oil fatty acid such as tung oil fatty acid, dehydrated castor oil fatty acid, linseed oil fatty acid and the like, a semi-drying oil fatty acid such as colza oil fatty acid and the like, or non-drying oil fatty acid such as castor oil fatty acid, cocoa-nut oil fatty acid and the like.

The fatty acid modified epoxy resin have preferably a degree of esterification ranging from 30 to 90%. Representative fatty acid modified epoxy resins are Beckosol P 786, 787, and 789 (trade names, supplied by Japan Reichhold Co. Ltd., they are castor oil fatty acid ester, cocoa-nut oil fatty acid ester, and linseed oil fatty acid ester, respectively).

Cellulose ester is a cellulose which hydroxy groups are esterified with a mineral acid such as nitric acid, sulfuric acid, and the like, or a fatty acid such as acetic acid, propionic acid, butyric acid and the like.

Represent cellulose esters are nitrocotton (supplied by Asahi Kasei, nitric acid ester), acetate cotton (supplied by Dainihon Celluloid, acetic acid ester), and Half-Second Butyrate Type EAB-381 (supplied by Eastman Chemical Products INC., acetic acid and butyric acid ester).

Cellulose ether is cellulose which hydroxy group is etherified. Representative cellulose ethers are alkyl ether such as methyl ether, ethyl ether and the like, aralkyl ether such as benzyl ether and the like. For example, there may be mentioned Metorose (trade name, supplied by Shinetsu Kagaku, methyl ether) and Ethocel (trade name, supplied by Dow Chemical Co.).

Chlorinated rubber is chlorinated natural rubber. For example, there may be mentioned Adeka Chlorinated Rubber (trade name, supplied by Asahi Denka Kogyo).

Representative inorganic pigments dispersed in the resin film are calcium carbonate, clay, titanium oxide, and mica. Representative metal soaps are barium stearate, calcium stearate, barium palmitate, and calcium palmitate. These examples of pigment are white pigments, but these may be used color pigments other than white pigment.

The results of experiment are shown in Table 1.

TABLE I

Film forming resin	Trade name (Supplier)	Surface resistivity of recording layer (ohm)
(1) Polyvinylchloride	Denka Vinyl 1000A (Denki Kagaku Kogyo)	7×10^{11}
(2) Polymethylmethacrylate	Acrynal No. 40 (Toei Kasei)	5×10^{11}
(3) Polyvinylacetate	Gosenyl T50 (Nihon Gosei)	8.5×10^{10}
(4) Polystyrene	Dialex (Mitsubishi Monsanto)	6×10^{10}
(5) Phenolic resin	Tamanol 1000 S (Arakawa Rinsan)	1.1×10^{11}
(6) Dehydrated castor oil epoxy resin ester	Beckosol P 786–50 (Japan Reichhold)	1.2×10^{13}
(7) Nitrocellulose	Nitrocotton H ¼ (Asahi Kasei)	2×10^{12}
(8) Cellulose acetate	Half-Second Butyrate EAB 381 (Eastman Chemical)	4×10^{12}
(9) Ethyl cellulose	Ethocel STP (Dow Chemical)	4.6×10^{12}
(10) Rubber chloride	Adeka Rubber Chloride No. 2 (Asahi Denka)	2.6×10^{12}

Note:
(1) Pigment employed was titanium oxide of rutile type.
(2) Thickness of coating of recording layer was about 5 microns.
(3) The ratio of resin to pigment was 1:1.
(4) The support was a base paper subjected to a resistance-lowering treatment as shown in Example 1.
(5) Electric resistance was measured by a dynamic condenser electrometer (supplied by Toshiba).
(6) Measurement was effected at 25°C at 60% R.H.

As pigment, titanium oxide of rutile type was employed, and the ratio of resin to pigment was 1:1. The experiment was made with respect to various resins. In Table 1, (1) polyvinylchloride, (2) polymethylmethacrylate and (3) polyvinylacetate have been generally used for electrostatic recording, but when pigment is dispersed in any of them, surface resistivity of the resulting recording layer is reduced to a great extent and becomes that of less than $10^{12}\Omega$. (4) Polystyrene and (5) phenolic resin have large volume resistivity and they are $10^{17} - 10^{19}\Omega$·cm and $10^{12} - 10^{13}\Omega$·cm, respectively. However, surface resistivity of layer of such resins in which pigment is dispersed is less than $10^{12}\Omega$.

On the other hand, (6) dehydrated castor oil epoxy resin ester (fatty acid modified epoxy resin ester), (7) nitrocellulose, (8) cellulose acetate and butyrate (cellulose ester), (9) ethyl cellulose (cellulose ether) and (10) chlorinated rubber can retain fairly high resistance even when pigment is dispersed in a film of said resin and the surface resistivity is higher than $10^{12}\Omega$.

There is not yet fully understood the mechanism enabling to prevent lowering surface resistivity and retain substantially high resistance (surface resistivity higher than $10^{12}\Omega$) when pigment or metal soap is dispersed in a film of fatty acid modified epoxy resin, cellulose ester, cellulose ether or chlorinated rubber, but it is considered that adhesion between such resin and pigment or metal soap is good and thereby the surface of pigment is appropriately covered with the resin.

Amount of pigment or metal soap to be dispersed in the resin film as mentioned above may be appropriately selected. The ratio of pigment or metal soap to resin is preferably higher than 1:5. Inscribability, seal-affixing property and printability are remarkably improved and surface lustre is reduced to a great extent in the above-mentioned ratio range. However, when the amount of pigment is too much, there occur fog upon electrostatic recording, choking of writing instruments and peeling of recording layer. Therefore, most preferable ratio of pigment or metal soap to resin ranges from 1/1 to 1/5. When a fatty acid modified epoxy resin ester, cellulose ester, cellulose ether, or chlorinated rubber as employed in this invention is mixed with polyvinylchloride, acrylic acid ester or methacrylic acid ester used in conventional electrostatic recording and pigment or metal soap is dispersed and the resulting mixture is made into a film for recording layer, the recording layer has sufficiently high surface resistivity to give good recording and inscribability is improved to a great extent. These advantages can be sufficiently obtained when the amount of resin as used in this invention such as fatty acid modified epoxy resin ester and the like is at least 30% by weight on the basis of total amount of the resin mixture.

The following examples are given for illustrating the present invention, but should not construed as limiting the present invention. Parts in the following examples are by weight unless otherwise specified.

EXAMPLE 1

(Reference Example)

To a base paper of about 60 μ thick subjected to a resistance-lowering treatment and having surface resistivity of $10^9\ \Omega$ was applied the following formulation an dried to form a recording layer of about 5 μ thick.

Titanium oxide of rutile type R820 (trade name, supplied by Ishihara Sangyo)	10 parts
Denka Vinyl 1000A (trade name, supplied by Denki Kagaku Kogyo)	10 parts
Toluene	40 parts
MEK	40 parts

Surface resistivity of the resulting recording layer was $5 \times 10^{11}\ \Omega$ and any good recording was not obtained.

EXAMPLE 2

(Reference Example)

The procedure of Example 1 was repeated except that the following formulation was used in place of that of Example 1.

Calcium carbonate	15 parts
Acrynal No. 80 (trade name, supplied by Toei Kasei, polymethylmethacrylate)	35 parts
Toluene	100 parts

Surface resistivity of the resulting recording layer was 5×10^{11} Ω and any good recording was not obtained.

EXAMPLE 3

The procedure of Example 1 was repeated except that the following formulation was employed in place of that of Example 1.

Calcium carbonate	40 parts
Beckosol P 786–50 (trade name, supplied by Japan Reichhold K.K., 50% solution of dehydrated castor oil epoxy ester in xylene)	60 parts
Toluene	60 parts
Cobalt naphthenate	0.5 parts

Surface resistivity of the recording layer was 1×10^{14} Ω and good recording was obtained.

EXAMPLE 4

The procedure of Example 1 was followed except that the following formulation was used in place of that of Example 1.

Titanium oxide of rutile type R 820	20 parts
Beckosol P 786–50	40 parts
Toluene	40 parts
Cobalt naphthenate	0.5 parts

Surface resistivity of the resulting recording layer was 1.2×10^{13} Ω and good recording was obtained.

When the above mentioned formulation was directly applied to an aluminum foil of about 65 μ thick (two layer structure), the resulting recording layer also gave a surface resistivity similar to the above mentioned one.

EXAMPLE 5

Following the procedure of Example 1, the formulation as shown below was applied.

Lake Red RC (trade name, supplied by Dainihon Ink Co.)	2 parts
Titanium oxide of rutile type, R 820	5 parts
Beckosol P 786–50	20 parts
Toluene	30 parts
Cobalt naphthenate	0.5 parts

Surface resistivity of the resulting recording layer was 3×10^{12} Ω and good recording was obtained, in this case the recording paper was red.

EXAMPLE 6

The procedure of Example 1 was repeated by using the following formulation in place of that of Example 1.

Barium stearate	10 parts
Beckosol P 786–50	20 parts
Toluene	50 parts
Cobalt naphthenate	0.5 parts

Surface resistivity of the resulting recording layer was 4×10^{13} Ω and good recording was obtained.

EXAMPLE 7

The procedure of Example 1 was repeated except that the following formulation was used in place of that in Example 1.

Titanium oxide of rutile type, R820	10 parts
Half-second Butyrate (supplied by Eastman Chemical Products, cellulose acetate and butyrate)	10 parts
Ethyl acetate	50 parts

Surface resistivity of the resulting recording layer was 4×10^{12} Ω and good recording was obtained.

EXAMPLE 8

The procedure of Example 1 was repeated except that the following formulation was employed in place of that in Example 1.

Titanium oxide of rutile type, R820	20 parts
Ethocel STP (trade name, supplied by Dow Chemical, ethyl cellulose)	20 parts
Methanol	60 parts

Surface resistivity of the recording layer was 4.6×10^{12} Ω and good recording was obtained.

EXAMPLE 9

The procedure of Example 1 was repeated except that the following formulation was employed.

Titanium oxide of rutile type, R820	20 parts
Adeka Chlorinated Rubber No. 2 (trade name, supplied by Asahi Denki)	20 parts
Toluene	60 parts

Surface resistivity of the recording layer was 2.6×10^{12} Ω and good recording was obtained.

EXAMPLE 10

The procedure of Example 1 was repeated except that the following formulation was used in place of that in Example 1.

Titanium oxide of rutile type, R820	50 parts
Beckosol P 786–50	15 parts
Acrynal No. 80 (trade name, supplied by Toei Kasei, Methyl methacrylate)	35 parts
Toluene	150 parts
Cobalt naphthenate	0.5 parts

Surface resistivity of the recording layer was 4×10^{12} Ω and good recording was obtained.

EXAMPLE 11

The procedure of Example 1 was repeated except that the following formulation was employed in place of that in Example 1.

Calcium carbonate	8 parts
Beckosol P 786-50	15 parts
Acrynal No. 80	12 parts
Toluene	25 parts
Cobalt naphthenate	0.5 parts

Surface resistivity of the recording layer was 7.0×10^{13} Ω and good recording was obtained.

According to the present invention, an electrostatic recording member of good inscribability, printability and seal-affixing property is obtained without deteriorating the recording characteristics. When the support is paper, the resulting electrostatic recording paper is almost the same as usual paper with respect to appearance, inscribability, printability and seal-affixing property.

I claim:

1. An electrostatic recording member which comprises an electrically low resistant substrate having a recording layer thereon which consists essentially of an inorganic pigment or a metal soap dispersed in a resin film which is composed of at least 30% by weight, based on the weight of the resin film, of a fatty acid modified epoxy resin ester having a degree of esterification of from 30% to 90% and up to 70% by weight of a member selected from the group consisting of polyvinyl chloride and polymers of acrylic acid esters and methacrylic acid esters, wherein the surface resistivity of the recording layer is at least about 10^{12} ohm-cm.

2. An electrostatic recording member according to claim 1 in which the inorganic pigment is selected from the group consisting of calcium carbonate, clay, titanium oxide and mica.

3. An electrostatic recording member according to claim 1 in which the metal soap is selected from the group consisting of barium stearate, calcium stearate, barium palmitate, and calcium palmitate.

4. An electrostatic recording member according to claim 1 in which the fatty acid modified epoxy resin ester is selected from the group consisting of epoxy resins esterified with a drying oil fatty acid, semidrying oil fatty acid or non-drying oil fatty acid.

5. An electrostatic recording member according to claim 1, in which the weight ratio of the inorganic pigment or the metal soap to the resin film is about 1:1 to 1:5.

6. An electrostatic recording member according to claim 1, in which the surface resistivity of the electrically low resistent substrate is less than about 10^{9} ohm. cm.

7. An electrostatic recording member according to claim 1, wherein said resin film is composed entirely of said fatty acid modified epoxy resin ester.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,891,787 Dated June 24, 1975

Inventor(s) SEIZI UEYAMA

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 2, line 7, after "recording layer" insert --1--;

line 17, "tht" should be --that--;

Col. 3, line 52, after "resin" insert --ester--;

Col. 4, line 49, "an" should be --and--;

Claim 1, Col. 8, line 3, "ohm-cm." should be --ohms--;

Claim 6, Col. 8, lines 22 and 23, "ohm.cm." should be --ohms--;

Signed and Sealed this

twenty-seventh Day of *January 1976*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks