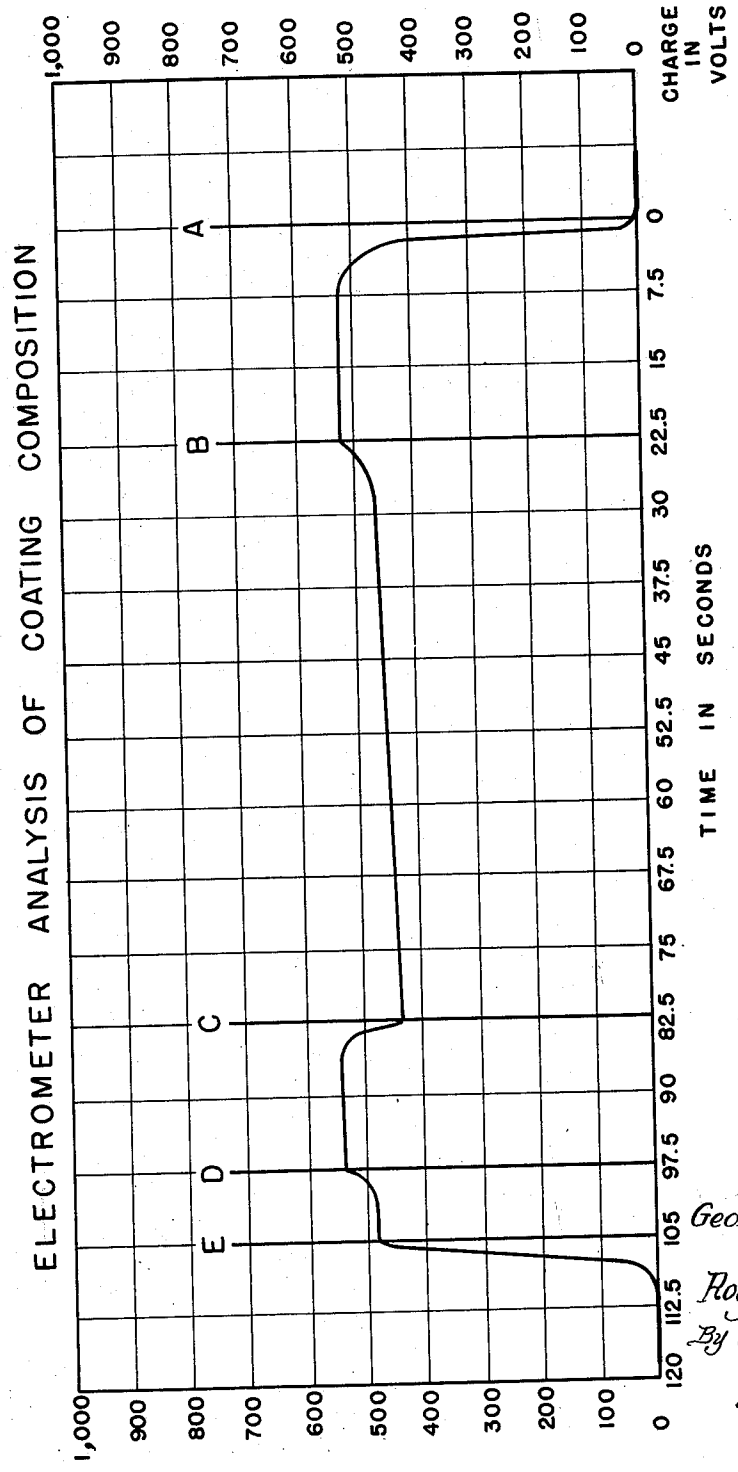
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COATING COMPOSITION FOR THE PRODUCTION OF ELECTROPHOTOGRAPHIC RECORDING ELEMENTS

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Inventors
George H. Tinker
and
Roger E. Burke
By Davis, Robertson, & Vandenburgh
Attys.

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COATING COMPOSITION FOR THE PRODUCTION OF ELECTROPHOTOGRAPHIC RECORDING ELEMENTS

George H. Tinker, Golf, and Roger E. Burke, Chicago, Ill., assignors to T. F. Washburn Company, Chicago, Ill., a corporation of Delaware

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This invention relates to the field of electrophotography, and more particularly refers to novel rapid-drying coating compositions for the production of electrophotographic recording elements, and to the products produced therefrom.

As developed in the prior art, the electrostatic printing process generally comprises placing a uniform electrostatic charge on a recording element by any one of several disclosed methods, subjecting the recording element to light from an optical image to dissipate the charge selectively in such a manner as to produce an electrostatic image, and converting the electrostatic image into a permanent visual image.

In the particular form of electrostatic photography with which the present invention is concerned, the recording element comprises a multi-layer sheet. The first layer is a base layer generally having high electrical conductivity. Over the base layer is coated a second layer comprised of a resinous binder exhibiting high electrical resistivity in which are embedded particles of a photoconductive material. During processing, the base layer is normally maintained at ground potential and serves as an electron reservoir.

In utilizing the recording member for forming an electrophotographic image, an electrostatic charge is first applied to the photosensitive or photoconductive layer, in the absence of actinic illumination, by means of a charging device as, for example, a corona. The charge is retained even after the charging device is turned off as long as the charged surface is not exposed to light. The charged surface is then subjected to an actinic image of the object which is to be reproduced, forming a pattern of light and shadow on the surface of the photosensitive layer. Wherever it is illuminated by actinic radiation, the conductivity of the photoconductive layer increases in proportion to the intensity of the radiation. As a result, the electrostatic charge is dissipated selectively in proportion to the magnitude of the actinic radiation to which it is exposed in each area. An electrostatic latent image is thereby formed, the greatest surface charge density remaining in unexposed areas, and the least charge density remaining in the areas which receive the strongest actinic illumination.

The latent image is then rendered visible by development with "toners" containing electrostatically charged pigment particles. The toners may be applied to the image as air-borne clouds, as suspensions in insulating liquids of low dielectric constant, or as dry particles adhering to oppositely charged carrier particles of substantially larger size such as iron powder or glass beads. Dependent upon the relative polarity of the electrostatic latent image and the developing pigments, the pigment will adhere differently to the charged and discharge areas, thereby rendering them differentially visible. The pigment image may be then transferred by contact to a receiving sheet and affixed thereto, or alternatively, may be directly affixed to the photoconductive layer by drying, thermofusion, or by the action of solvent vapor. The methods of development are well known in the art and do not constitute a part of the present invention.

The base layer should preferably be of a material which is more conductive than the photoconductive layer.

The base layer is normally connected to ground potential during processing. Examples of base layers of this type are aluminum sheet and carbon filled paper. A non-conductive base material may be used if a relatively conductive interlayer is provided between the insulating base and the photoconductive layer. Examples of this type of base layer include glass plates treated with semi-conductive tin oxide, and dry paper overcoated with a vacuum-deposited aluminum film or a layer of a semi-conductive pigment in a suitable binder resin. If conductive interlayers of this type are used, they are normally connected to ground potential during processing.

The photoconductive layer is comprised of a photoconductive material embedded in a resinous binder. Although numerous photoconductive materials are known in the art such as cadmium sulfide, sulfur, anthracene, anthraquinone, lead iodide, cadmium selenide, and many others, zinc oxide is generally used commercially, since it is relatively inexpensive and exhibits excellent photoconductive properties.

The resinous binder must have certain properties in order to be suitable for use in the production of electrophotographic recording members. It must not be sensitive to normal air humidity or normal temperature ranges. It must be compatible with the photoconductive pigment employed. It must have the ability to accept a high initial electrostatic charge, and to retain the charge over a substantial period, in the absence of actinic illumination, after the charging device is turned off. It must exhibit good electrical conductivity in conjunction with the photoconductive pigment when subjected to actinic illumination. It must also exhibit flexibility and the ability to offer satisfactory adhesive properties with respect to a variety of substrates. Finally, the coating composition in which it is applied must have a sufficiently high drying speed to permit it to be used in high speed commercial paper coating technique.

A number of resinous materials have been disclosed which may be used as binders. Among them are the silicone resins, cellulose esters such as cellulose acetate, cellulose acetate butyrate, cellulose nitrate, cellulose ethers such as ethyl cellulose, and methyl cellulose. Other suitable materials are polyvinyl acetate, polystyrene, acrylics, and various waxes.

Coating compositions for use in the production of electrostatic recording members are generally prepared by dissolving a resin binder in a suitable organic solvent, and dispersing a photoconductive pigment such as zinc oxide into the solution. Many coatings have been disclosed in the art which produce photoconductive coatings having excellent properties. However, many of the coating compositions disclosed are very difficult to use with high speed commercial coating machines since they dry very slowly, and remain tacky for extended periods of time. In fact, the drying rates of many of the prior art compositions are so slow as to render them completely impractical for commercial use.

It is an object of the invention to provide a resinous coating composition from which coatings may be produced having excellent electrophotographic properties.

It is a further object to provide such resinous coating compositions having rapid-drying properties.

It is a further object to provide a coating composition containing zinc oxide pigment having rapid-drying properties, and which composition may be used with high speed processing equipment to produce electrophotographic recording members having improved properties.

Other objects and advantages of the invention will become more apparent from the following description and drawing in which:

FIG. 1 is a graph based on data obtained from a test,

by means of a "Spinner Electrometer" of a recording member prepared according to the invention.

According to the invention, a rapid-drying resinous coating composition may be provided by first reacting together an epoxy resin, a higher fatty acid containing rosin, and an ethylenically-unsaturated polymerizable monomer. The resulting reaction product is then combined with an organic solvent to form a coating composition which may be coated on a suitable surface and rapidly dried to form a highly electrically resistive coating. It has been further found that when a photoconductive pigment such as zinc oxide is incorporated into the coating composition of the invention the composition may be coated on a suitable base and rapidly dried to form electrophotographic recording members having excellent properties.

The epoxy resins suitable for use in preparing the coating compositions of the invention are generally the polyglycidyl polyethers of polyhydric phenols. The preferred and also the most common of the epoxy resins are the polyglycidyl polyethers of Bisphenol A, 4,4'-isopropylidenediphenol. The resin should have an average molecular weight in the range of from about 1000 to about 3000. A molecular weight in the range of from 2000 to 2500 is preferred.

The esterifying compound should be capable of reacting with the epoxy resin to form an epoxy-ester composition having good electrical properties. Suitable compounds are higher fatty acids containing rosin in an amount from about 4% to about 35% by weight. The rosin may be either rosin itself or the various rosin acids comprising the isomeric forms of abietic acid and other tricyclic diterpenes to be found in numerous grades and sources of naturally occurring rosin. Tall oil which has not been completely refined and therefore still retains its rosin is the preferred rosin-containing higher fatty acid. Tall oil containing about 28% rosin has been found to be optimum. The rosin acids occurring in unrefined tall oil are believed to comprise isomeric mixtures of tricyclic diterpenes such as 1,2,3,4-tetrahydro-6-isopropyl-1-dimethyl-propyl-2-naphthaleneacetic acid.

Other higher fatty acids such as oleic acid, linoleic acid, and acids derived from soya bean oil and linseed oil may be used in conjunction with wood or gum rosins.

The esterification reaction may be promoted by adding suitable catalysts such as lithium oxide, calcium oxide, or zinc naphthenate.

In order to increase the drying rate of the coating composition, an ethylenically-unsaturated polymerizable monomer is added to the reaction mixture prior to the esterification of the epoxy resin. The amount of the monomer should be from about 10% to about 40% based on total weight of the rosin-containing oil component. Amounts greater than 40% may have a deleterious effect on the electrical properties of the coating. The optimum amount is about 20%.

Among the monomers which are suitable are vinyl toluene, styrene, methyl methacrylate, divinyl benzene and 2-ethyl hexyl acrylate.

A polymerization catalyst such as ditertiarybutyl peroxide may be added in order to promote the reaction of the monomer with the epoxy-ester resin. However, the use of such a catalyst may have a tendency to cause undue gelation of the product. For most applications a catalyst need not be utilized.

The drying rate of the present coating compositions may be further improved by decreasing the oil length of the epoxy-ester resin, that is, increasing the proportion of the epoxy resin to the total of the epoxy resin and the rosin-containing fatty acid.

The proportion by weight of the epoxy resin to the total of the epoxy resin and the rosin-containing fatty acid should be from about 60% to about 80%, with optimum drying properties being obtained in the range of 70% to 80%.

The esterification reaction should be carried to the point where the acid number of the finished product is from about 2 to about 20, with a preferred range of from 8 to 10. Reaction to a higher acid number results in a coating which has a higher charge acceptance, but a reduced light sensitivity.

The following examples illustrate the preparation of coating compositions according to the invention.

EXAMPLE 1

The following three separate reactant groups were first prepared:

Ingredients		Parts by Weight
Group A	Epon 1007 [1]	1,153.4
Group B	Shuco 300 [2]	869.8
	Triphenyl phosphite	1.6
	Zinc naphthenate	10.1
Group C	Vinyl toluene	202.5
	Ditertiarybutyl peroxide	2.0

[1] Polyglycidyl polyether of Bisphenol A having a molecular weight of 4000–5000.
[2] Tall oil containing 28% rosin.

The ingredients of group A were heated under xylene reflux to 390°–420° F. Those of group B were then added to the reaction mixture over a one hour period. The temperature was raised slowly to 420°–435° F. and held until an acid number of 18–20 had been obtained. The temperature was then lowered to 325°–335° F. and ingredient group C was added over a 30 minute period. Subsequently, the temperature was slowly raised to 465°–475° F., and held until the reaction was complete. The reaction product exhibited the following properties:

Acid number	7–9.
Total solids in xylene	60–65%.
Viscosity	Z4–Z6 Holdt-Gardner.
Color	H-G.

EXAMPLE 2

Preparation of coating composition having an epoxy-ester resin of shorter oil length than that of Example 1.

The following three separate reactive groups were prepared:

Ingredients		Parts by Weight
Group A	Epon 1007	1,125
Group B	Shuco 300	580
	Triphenyl phosphite	6
Group C	Vinyl toluene	116

The epoxy resin (A) was charged to a reaction flask with a reflux solvent (xylene) and heated to 390° F. The B component was slowly added over a 30 minute period. The temperature was then raised to 480° F. and held until an acid number of 15 was obtained. The temperature was then lowered to 325–335° F. and vinyl toluene added over a 30 minute period. Subsequently, the temperature was raised slowly to 465–475° F., and held until the reaction was complete. The reaction product exhibited the following properties:

Acid number	14.
Viscosity	Z–3.
Color	5.
Solids	70% in xylene.

Zinc oxide pigment may be dispersed in the coating compositions by any suitable means. An amount of resinous binder must be used which is sufficient to cause the particles of the pigment to adhere to each other and to the base, without unduly insulating the particles from each other during the conductive period. The coating composition, including the binder and pigment, is coated and dried on the base as a film having a thickness of the order of about one thousandth of an inch. It has been found that a ratio of pigment to resin by weight of 1:1

is required. The upper limit of the pigment to resin ratio is determined by the abiiity of the resin to bind the pigment to the base and to itself sufficiently so that it does not flake off. A practical upper limit of pigment to resin ratio is about 20:1 by weight. A preferred ratio range is from 2:1 to 9:1 with an optimum ratio being 4:1.

EXAMPLE 3

Preparation of an Electrophotographic Recording Member

The product obtained in Example 1 was adjusted to a 50% solids content in xylene. Zinc oxide was then blended into the solution utilizing a pigment to dry resin ratio of 3:1. The mixture was adjusted to a solids content of about 80%. Because of the high viscosity of the mixture prior to milling, xylene may be added, if necessary, until a desirable milling consistency is obtained. The premixed material was then put through a roller mill to obtain the proper degree of blending, and diluted to 40% total solids in xylene.

The coating composition thus produced was drawn down with a standard number 20 rod over an aluminum-coated paper sheet. It was dried for 2 to 4 minutes with heated forced air (180° F., 1200 LF/M). The recording member was then ready for use.

Evaluation of the recording member prepared in the examples above was made by means of an instrument termed a "Spinner Electrometer." This is a device which was designed to yield quantitative data with regard to the electrical properties of electrophotographic recording media. Particularly, the following properties are measurable by the instrument.

(1) Initial charge acceptance.
(2) Charge retention in darkness.
(3) Charge decay upon illumination.

In performing the testing on the electrometer, a disc cut from the sample to be tested is placed on a rotating table, and the table is rotated in turn past charging, illumination, and measuring stations. Equal areas are scanned in rapid alternation through three windows in a nearly coplanar grounded metal plate by a probe. As each window rotates over the probe, the electrostatic field from the charge on the paper induces a voltage on the probe. As the window rotates further, the probe faces the grounded metal plate and returns to ground potential. Due to the symmetry of the windows which are cut in the turntable, the voltage appearing on the probe, rather than being in the form of a series of sharp pulses, appears in an approximately sinusoidal wave form. The signal may either be viewed directly on an oscilloscope, or may be amplified and rectified to produce a D.C. current which in turn actuates a recorder.

Prior to carrying out the testing procedure, a disk was cut from the recording member prepared according to the invention in Example 3 above, using a Spinner disc pattern. The disc was placed on the turntable of the instrument and subjected to the testing procedure described above. The results of the test are shown in the graph of FIG. 1 of the drawing.

In carrying out the test, a corona discharge of about 7000 volts was first applied to the recording member. In FIG. 1 the point A represents the charge on the recording member when the corona was first applied. As can be seen, the charge on the recording member rose rapidly and approached a more or less constant maximum at point B. The value of the charge reached at the point B is termed the charge acceptance. At point B the corona discharge was removed and the charged member permitted to remain in darkness. The degree of discharge between point B and point C indicates the property of "dark resistivity." Dark resistivity is determined by the rate at which the charge tends to decrease towards ground potential. The dark resistivity is inversely proportional to the rate of change of the charge from B to C.

The member was then recharged for sixteen seconds, between C and D, the corona turned off at D, and the member allowed to rotate in the dark for about 8 seconds. At point E the member was illuminated, and the charge dissipated to zero. The rate at which the paper looses its charge under illumination is indicative of its "light conductivity." A paper which looses its charge readily under illumination is said to be highly photoconductive. Conversely, a paper which looses its charge slowly is said to have poor illuminated conductivity.

In order to be suitable for use in the electrophotographic recording process, a coated sheet must have high charge acceptance, high dark resistivity, and high conductivity when illuminated.

As can be seen in the graph, the recording member tested had a charge acceptance of about 530 volts, a charge retention at the end of 60 seconds of about 430 volts, and exhibited a sufficiently high conductivity under illumination to dissipate the charge from about 480 volts to zero in less than 7.5 seconds. These properties are indicative of an excellent electrophotographic recording member.

An evaluation of the rapid-drying properties of coating compositions containing ethylenically-unsaturated monomers according to the invention was made as follows:

Two coating compositions were first prepared. The first composition was prepared according to the invention as described in Example 1. Zinc oxide pigment was then blended into the solution in the manner described in Example 3, utilizing a pigment to dry resin ratio of 3:1 by weight. After proper blending, the composition was diluted with xylene to a 40% total solids content.

The second composition was prepared from an epoxy-ester resin formulation identical to that of Example 1 except that the vinyl toluene monomer was omitted as well as the ditertiary butyl peroxide catalyst. The identical esterification process was used as in Example 1, and the resulting epoxy-ester resin was blended with zinc oxide pigment in a ratio of 3:1 and diluted to 40% total solids in xylene, in the same manner as the first composition.

To obtain a measure of the relative drying speeds, both compositions were coated on a paper sheet to form a film when dry of two mils thickness. The coated sheets were placed in a drying enclosure, and air was passed therethrough at a rate of 1200 linear feet per minute, at a temperature of 140° F. At intervals the coated papers were removed and cotton pads were placed over the film and weighted to a pressure of 3.5 lbs./sq. in. Where the coatings were still sufficiently sticky as to cause the pad to adhere thereto when the force was removed, the condition was termed "tacky." Where the pad fell off the film as the sheet was turned over, but small fibers from the pad still adhered to the film, as observed under the microscope, the condition was termed "slightly tacky." Where, upon overturning the paper, the pad fell off and no fibers could be detected on the film upon microscopic observation, the condition was termed "no tack."

The following chart indicates the results obtained from the tests as described:

Drying time, seconds	Composition of claim 1 containing vinyltoluene	Composition of Example 1 with vinyltoluene omitted
30	Slight tack	Tacky.
60	Very slight tack	Do.
120	No tack	Do.
240	do	Slight tack.
480	do	No tack.

The results of the tests indicate that the coating composition of the invention containing an ethylenically-unsaturated polymerizable monomer dries from 3 to 4 times as rapidly as that of a similar resin composition, but containing no such monomer.

We claim:

1. A rapid-drying coating composition in the form of an

organic solution for the production of electrophotographic recording members, said composition being comprised of:

(A) the esterification product of

(1) a polyglycidyl polyether of a polyhydric phenol,

(2) a higher fatty acid containing rosin, and

(3) a vinyl ethylenically-unsaturated polymerizable monomer;

(B) an organic solvent for said esterification product; and

(C) a photoconductive pigment.

2. A coating composition according to claim 1 wherein said monomer is present in an amount from about 10% to about 40% by weight of said higher fatty acid containing rosin.

3. A coating composition according to claim 1 wherein said monomer is vinyl toluene.

4. A coating composition according to claim 1 wherein said monomer is styrene.

5. A coating composition according to claim 1 wherein said monomer is methyl methacrylate.

6. A coating composition according to claim 1 wherein said monomer is divinyl benzene.

7. A coating composition according to claim 1 wherein said monomer is 2-ethyl hexyl acrylate.

8. A rapid-drying coating composition in the form of an organic solution for the production of electrophotographic recording members, said composition being comprised of:

(A) the esterification product of

(1) a polyglycidyl polyether of Bisphenol A,

(2) a higher fatty acid containing rosin, and

(3) a vinyl ethylenically-unsaturated polymerizable monomer;

(B) an organic solvent for said esterification product; and

(C) a photoconductive pigment.

9. A rapid-drying coating composition in the form of an organic solution for the production of electrophotographic recording members, said composition being comprised of:

(A) the esterification product of

(1) a polyglycidyl polyether of Bisphenol A,

(2) tall oil containing from about 4% to about 35% rosin, and

(3) a vinyl ethylenically-unsaturated polymerizable monomer;

(B) an organic solvent for said esterification product; and

(C) a photoconductive pigment.

10. A coating composition according to claim 9 wherein said monomer is present in an amount from about 10% to about 40% by weight of said higher fatty acid containing rosin.

11. A coating composition according to claim 9 wherein the molecular weight of said polyglycidyl polyether is from about 1000 to about 3000.

12. A rapid-drying coating composition in the form of an organic solution for the production of electrophotographic recording members, said composition being comprised of:

(A) the esterification product of

(1) a polyglycidyl polyether of Bisphenol A,

(2) tall oil containing about 28% rosin, and

(3) a vinyl ethylenically-unsaturated polymerizable monomer;

(B) an organic solvent for said esterification product; and

(C) a photoconductive pigment.

13. A rapid-drying coating composition in the form of an organic solution for the production of electrophotographic recording members, said composition being comprised of:

(A) the esterification product of

(1) a polyglycidyl polyether of Bisphenol A,

(2) tall oil containing from about 4% to about 35% by weight rosin, and

(3) a vinyl ethylenically-unsaturated polymerizable monomer in an amount from about 10% to about 40% by weight based on the total weight of said tall oil and rosin;

(B) an organic solvent for said esterification product; and

(C) a photoconductive pigment.

14. An electrophotographic recording member comprising a base and having a photoconductive coating on said base comprised of:

(A) the esterification product of

(1) a polyglycidyl polyether of a polyhydric phenol,

(2) a higher fatty acid containing rosin, and

(3) a vinyl ethylenically-unsaturated polymerizable monomer; and

(B) a photoconductive pigment.

15. An electrophotographic recording member comprising a base and having a photoconductive coating on said base comprised of:

(A) the esterification product of

(1) a polyglycidyl polyether of Bisphenol A,

(2) tall oil containing from about 4% to about 35% rosin, and

(3) vinyl toluene; and

(B) zinc oxide.

16. An electrophotographic recording member according to claim 15 wherein the ratio of zinc oxide to said esterification product by weight is from about 1:1 to about 20:1.

17. An electrophotographic recording member according to claim 15 wherein the ratio by weight of zinc oxide to said esterification product is about 4:1.

18. A method for forming a visual image on an electrophotographic recording member which comprises producing an electrostatic charge on said recording member, exposing the charged recording member to a light image to form an electrostatic image, and treating said electrostatic image with a toner containing charged pigment particles to form a visual image, said recording member comprising a base having a coating thereon comprised of:

(A) the esterification product of

(1) a polyglycidyl polyether of a polyhydric phenol,

(2) a higher fatty acid containing rosin, and

(3) a vinyl ethylenically-unsaturated polymerizable monomer; and

(B) a photoconductive pigment.

19. A method for forming a visual image on an electrophotographic recording member which comprises producing an electrostatic charge on said recording member, exposing the charged recording member to a light image to form an electrostatic image, and treating said electrostatic image with a toner containing charged pigment particles to form a visual image, said recording member comprising a base having a coating thereon comprised of:

(A) the esterification product of

(1) a polyglycidyl polyether of Bisphenol A,

(2) tall oil containing from about 4% to about 35% rosin, and

(3) vinyl toluene in an amount from about 10% to about 40% by weight of said tall oil and rosin; and

(B) zinc oxide.

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