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PHOTOCONDUCTIVE ZINC OXIDE COATING COMPOSITIONS AND METHOD OF PRODUCING THEM

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ABSTRACT OF THE DISCLOSURE

Photoconductive zinc oxide, a powdered, friable, fusible, water-insoluble resin having a high electrical resistance, a blending agent, and water, as a coating composition, applied to a substrate and heated to fuse the resin and produce a photoconductive coating.

BACKGROUND OF THE INVENTION

This invention relates to photoconductive compositions containing zinc oxide as the photoconductive agent and to methods for producing these compositions.

Photoconductive zinc oxide is presently employed to produce aqueous electrophotographic coatings. The term "photoconductive zinc oxide" is used herein to mean a zinc oxide powder with photoconductive characteristics, with an average particle diameter of the magnitude of .20–.45 micron.

The present aqueous electrophotographic coatings in which photoconductive zinc oxide is used contain various latex emulsions or water soluble resins, or combinations of the two, with appropriate dispersing, wetting and sensitizing agents. The latex and resinous emulsions form, on drying, an electrically insulating binder for the photoconductive zinc oxide. Usually these aqueous photoconductive compositions are used to coat paper, which has been treated previously to produce a uniformly electrically conducting or semi-conducting substrate.

In the electrophotographic process, the photoconductive coating is given a uniform electrical charge, usually in the form of a corona discharge. It is then exposed to an image, usually reflex light from indicia to be copied, the light including wave lengths to which the photoconductive coating is sensitive.

This exposure in an image pattern causes a selective discharge of the surface voltage of the photoconductive surface in the discrete areas on which the light impinges, as a function of the amount of radiation received. The photoconductive surface, with its discrete areas of varying charge levels, is then either treated with a dry developer powder of opposite charge, or is exposed to a suspended colored pigment, capable of electrophoretic deposition, in a liquid of high electrical resistance. The terms "developers" and "toners" are used herein to refer to both types. The resulting deposited image powders or colored pigments are then fixed, usually by the application of heat, to form a permanent image.

It can be appreciated that a high initial maximum charge acceptance and a high gradient after exposure (i.e., good charge retention in the unexposed parts, discharge in exposed parts) are desirable. They are not, however,

the only criteria. Coatings commonly carry a so-called uninduced charge. A high uninduced charge which remains after exposure will nullify the good that a high maximum charge acceptance might promise. The uninduced charge, among other factors, may act differently with different developers, both dry and wet. When these factors cause poor results with particular developers, the condition is referred to in the art as "incompatibility."

The coatings and methods of coating known heretofore have suffered from several serious defects. The amount of photoconductive zinc oxide which can be dispersed in water within usable viscosities is limited. The addition of dispersing and wetting agents increases the amount of zinc oxide which can be added to water without increasing the viscosity to an impractical degree, but these agents are normally conductive, and very small amounts can reduce excessively the maximum charge acceptance of the coating. This problem is complicated by the fact that zinc oxide scavenges dispersing and wetting agents from emulsified resins, which either increases the viscosity of the coating or, if insufficient wetting and dispersing agent is present, causes a breakdown of the emulsified resin.

The resin emulsions used heretofore have also contained catalysts or emulsifying agents which tend greatly to reduce the maximum charge acceptance, to increase exposure time required, and to cause background on the electrophotographic prints.

In order to produce the required low viscosity and to prevent breakdown of the resin emulsions, an amount of surfactant is used in present aqueous electrophotographic coatings which causes foaming of the coating composition. When a foamy composition is applied to the substrate (paper, or in some instances metal), and the coating is dried, the coating surface is pocked with small depressions or pin holes.

The electrophotographic coatings of this type, known heretofore, have been difficult to dry, because the amount of solids consistent with the viscosity requirements for high speed coating, has been limited to approximately 50% of the aqueous compositions.

Additionally, some of the water-soluble resins tend to be unstable and some of them take up an excessive amount of moisture at high humidity so that the resistance of the coating drops to the point at which the coating can no longer hold a charge. Many of the present aqueous coating compositions also cause curling of coated sheets of paper, when the sheets are subjected to humidity changes.

One of the objects of this invention is to provide aqueous coating compositions which have a high solids content as compared with such compositions known before, which have a viscosity only slightly higher than that of water, which produce little or no foaming, which are easily dried, and which contain little conductive material.

Another object is to provide aqueous coating compositions containing water-insoluble resins which have very desirable electrical properties but which have heretofore been usable only in solvent-system coatings.

Another object of this invention is to provide such a coating composition which, when applied to a substrate and dried, produces at practically low drying temperatures a uniform coating which provides a high maximum charge acceptance, holds a charge well, and is less affected

by humidity changes and high humidity than coatings known heretofore.

Still another object is to provide a method of making coatings, by which a photoconductive zinc oxide is inhibited from scavenging wetting or dispersing agent, and made receptive to homogeneous distribution with water-insoluble resin through an aqueous vehicle.

Still another object is to provide a method of incorporating addition agents such as dyes into a coating composition in such a way as to produce a coating with high maximum charge acceptance.

Other objects will become apparent to those skilled in the art in the light of the following description.

SUMMARY OF THE INVENTION

In accordance with this invention, generally stated, a photoconductive composition is provided which comprises a photoconductive zinc oxide, a finely divided hard, friable, water-insoluble resin, and a blending agent by which the zinc oxide and the water-insoluble resin are dispersed homogeneously through the coating composition in an aqueous vehicle.

The zinc oxide used should have a low dispersed water absorption value as measured by the method outlined below. The preferred coating compositions are made with photoconductive zinc oxides having dispersed water absorption values in the neighborhood of 235–275, although usable coatings can be produced with photoconductive zinc oxides with dispersed water absorption values within the range of 200–400, as indicated by the illustrative examples set out hereinafter.

The term blending agent as used in the specification and claims means a wetting agent which is either non-ionic or weakly ionic and a precoating material.

The wetting agent, which may be a single compound or several wetting or dispersing compositions, must be capable of wetting and dispersing both the zinc oxide and the water-insoluble resin. The precoating material functions to inhibit scavenging by and to improve the wetting and dispersing characteristics of the zinc oxide, and to improve the wetting and dispersing characteristics of the water-insoluble resin.

The water-insoluble resin has a high electrical resistance, is hard, friable, fusible and preferably has a ring and ball softening point of 50–120 degrees centigrade. Such resins with softening points up to 150 degrees centigrade can be used if the application of the coating admits of the use of high drying temperatures or if the coating is hot pressed at a temperature above 150 degrees centigrade. In general, it is desirable to dry the coating at about 115 degrees centigrade.

The use of the water-insoluble resin in the coatings and method of this invention provides the advantages of higher solids content, low frothing, high maximum charge acceptance, and ready drying and homogenous distribution suggested in the objects. Also, importantly, dyes and various other addition agents, such as plasticizers and sensitizers, which would ordinarily destroy the usefulness of a coating because of their conductivity or incompatibility, may be incorporated into the coating compositions without subjecting them to the agglomerating effects of the zinc oxide and without substantially reducing the compatibility and maximum charge acceptance of the coating, by incorporating them first into a melt of the friable resin, subsequently reducing the resin to a fine powder and incorporating the powder into the coating composition. The resultant coating is superior in color, brightness and effectiveness to coatings known heretofore.

The method of this invention includes steps of precoating photoconductive zinc oxide, and, in the preferred embodiment, incorporating addition agents into the water-insoluble resin by melting them together and then powdering the mixture.

In one illustrative embodiment of coating composition of this invention, a photoconductive zinc oxide is dispersed in an aqueous solution of gelatin and 1,4 butanediol. A small amount of a water soluble resin is introduced to the suspension, and powdered water-insoluble resin, of a fineness of about 65 mesh is added. The water-insoluble resin preferably constitutes the major non-volatile part of the binder. The constituents are milled together until a homogeneous composition is produced with a fineness of 6+ on the Hegman fineness gauge. It is foam free and contains 60–80% solids. It dries quickly after application to a substrate, and produces a homogeneous mass at a temperature of 115 degrees centigrade. The coating has superior electrical qualities even at low coating weights.

The blending agent of this illustrative embodiment illustrates the peculiarity of the coating composition of this invention. Neither gelatin nor 1,4 butanediol acts as a wetting agent or effective precoating agent; together, they serve both purposes. If sufficient gelatin is used, the amount of water soluble or emulsified resin can be greatly reduced, though the use of the resin to aid in the precoating is indicated even with the gelatin.

In another illustrative embodiment of coating composition of this invention, the same procedure is followed, except that the water-insoluble resin is first melted together with certain dyes, cooled, and ground to a fine powder before being added to the mixture of zinc oxide, water soluble resin and blending agent. By this method, a bright white sheet, with high maximum charge acceptance is produced. If effective quantities of the same dyes are added to the aqueous slurry, a totally unsatisfactory coating is attained, with maximum charge aceptance being less than a third as high.

The examples below are illustrative of various other embodiments. Their specific ingredients, proportions and ranges are illustrative, but not limitative. In them, for instance, the precoating agents used are Parez 613, water-soluble melamine-formaldehyde resin produced by American Cyanamid Co., and Firestone Butaprene XR–3104, styrene-butadiene homopolymer produced by Firestone Plastics Co. However, the precoating agent can also be a water-emplsified polyvinyl acetate resin such as Gelva S–55–L, produced by Shawinigan Resins Corp., a water-soluble acrylic resin or a water-soluble alkyd or some combination of these, among others.

The wetting agent of the blending agent is, as has been indicated, preferably non-ionic, although Tamol 850, a preferred wetting agent with Firestone XR–3104, is slightly anionic, and Nopcogen 14L, used under the circumstances of Example 12, is cationic. Tamol 850, sodium salt of polymeric carboxylic acid, is a product of Rohm & Haas. Nopcogen 14L is produced by Nopco Chemical Co. Another wetting agent particularly useful with polyvinyl acetate resin emulsions such as Gelva S–55–L is Daxad–11, polymerized sodium salt of alkyl naphthalene sulfonic acid. The only requirements for the wetting agent are that it be sufficiently non-conductive so that it does not seriously reduce the maximum charge acceptance and charge retention of the coating, and that it serve to wet both the zinc oxide and water-insoluble resin, in the presence of the precoating composition.

The required characteristics of the water-insoluble resins have already been described. In the examples, Piccotex–100, styrene homolog copolymer, completely saturated, produced by Pennsylvania Industrial Chemical Corp., and Neville R–7, coumarone-indene resin, produced by Neville Chemical Co. are used as the water-insoluble resins. Other illustrative examples of such resins are Piccopale–100 (low iodine number hydrocarbon resin), Piccolastic D–75 (pure polystyrene of low molecular weight) and Piccolastic D–100 (pure polystyrene of somewhat higher molecular weight than Piccolastic D–75), all produced by the Pennsylvania Industrial Chemical Corp. Other water-insoluble resins, such as

polyethylene and alkyds may be blended with the high molecular weight, hard, friable resins, as long as the resultant blend is friable to the extent that it can be finely powdered and meets the Ring and Ball softening point specification of 50° C. to 150° C. The term "water-insoluble resin" is used hereinafter to embrace blends or mixtures of water-insoluble resins as well as a single resin composition. As is indicated in the examples in the melting together of Piccotex–100 and paraffin, the water-insoluble resin may be plasticized to improve its flexibility. It can be appreciated that the plasticizer and other materials can be incorporated with the water-insoluble resin in the coating in other ways than by melting, such as by the use of solvents, or briquetting, depending upon the nature of the additive. In any event, after the resin and additive materials are intermixed, they must be hardened to friability.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the following examples the water absorption value of the zinc oxide is given in terms of the milliliters of water determined by the following test: 200 grams of the zinc oxide is weighed out. 150 ml. of water is put into an Osterizer (blender) and the Osterizer started at low speed (approximately 8000 r.p.m.). The zinc oxide is added slowly to the water in the blender until the slurry stops moving due to the formation of an air pocket around the blade. The air is released with a spatula, 10 ml. of water is added, and more zinc oxide is added until the slurry again stops moving. The process of releasing the air and adding 10 ml. increments of water is repeated until all the zinc oxide has been added to the blender. The resulting slurry must remain dispersed for 10 minutes without the formation of an air pocket. Otherwise, enough water is added to provide dispersion. The total amount of water required to achieve the final dispersion of all of the zinc oxide is the measure of the water absorption value. It can be accurate within ±10 ml. of water, but the range of error is given in the examples as ±15 ml.

Example 1

200 grams of photoconductive zinc oxide (AZO–ZZZ French Process Electrophotographic, dispersed water absorption 260±15 ml., American Zinc Sales Co., Columbus, Ohio) was slowly added to 100 ml. of 1⅓% gelatin distilled water solution containing 2 ml. of 1,4 butanediol at low speed in an Osterizer. The zinc oxide slurry was transferred to a steel milling jar, and 15 grams of water soluble Parez 613 (American Cyanamid Co., New York, N.Y. 10020) was stirred into the slurry. Twenty-two grams of water-insoluble Piccotex–100 resin and 3 grams of paraffin were melted together, cooled to room temperature, and powdered. This powdered resin was added to the zinc oxide slurry, and all of the constituents were then milled with 400 grams of ⅜ inch steel balls for one and one-half hours.

An aqueous electrophotographic coating was thus produced that was foam-free and contained 71.4% solids at a Stormer viscosity of 50 KU. The coating dried quickly and produced a homogeneous mass on treated paper substrate at a temperature of 115° C.

The superior electrical qualities of this aqueous electrophotographic recording coating composition are illustrated in Table II, which follows Example 14, when compared to control coatings that do not contain the powdered water-insoluble resin.

Example 2

200 grams of photoconductive zinc oxide of Example 1 was slowly added to 100 ml. distilled water containing 1 ml. of Tamol 850 (Rohm & Haas, Philadelphia, Pa.) dispersing and wetting agent while stirring at slow speed in an Osterizer. The zinc oxide slurry was transferred to a steel milling jar and 15 grams of Parez 613 and then 50 grams of Firestone resin emulsion XR–3104 (48.5% solids) were stirred by hand into the zinc oxide slurry. Ten grams of powdered Piccotex–100 (R. & B., softening point, 100° C.) was added to the mixture, and all the constituents were milled for one and one-half hours with 400 grams of ⅜ inch steel balls.

An aqueous electrophotographic coating was thus produced that was foam free, dried quickly, and contained 66.3% solids at a Stormer viscosity of 50 KU. When the coating was applied to a treated paper substrate, it had excellent flexure.

The superior electrical qualities of this aqueous electrophotographic recording coating composition are illustrated in Table I when compared to control coatings that do not contain the powdered water-insoluble resin.

Example 3

Distilled water	ml..	100
Tamol 850	ml..	1
Zinc oxide (AZO–ZZZ French Process electrophotographic, dispersed water absorption 260±15 ml.)	grams..	200
Parez 613	do....	15
Firestone resin emulsion XR–3104 (48.5% solids)	grams..	50
Piccotex-100	do....	10

This example differs from Example 2 in that all the constituents were put into a steel milling jar, and the coating of the zinc oxide particles and the milling of the water-insoluble resin were carried out at the same time. The constituents were milled for one and one-half hours, and the coating was applied to a treated paper substrate.

The results with the coating composition of Example 3 were the same as Example 2, except for a slight reduction in electrical characteristics. The superior qualities of the coating composition of this example over the control coatings are illustrated in Table II.

Example 3 illustrates the advantage of the precoating of the zinc oxide particles before the water-insoluble resin is added.

Example 4

This example differs from Example 1 only in the water-insoluble resin employed. The water-insoluble resin of this aqueous coating composition was Neville R–7, a coumarone-indene resin with an R. & B. softening point of 108–112° C.

The resin blend of this composition was found to have a different compatibility with commercial developers than the blend of Example 1.

The superior electrical qualities of this aqueous recording coating composition are illustrated in Table I.

Example 5

200 grams of photoconductive zinc oxide (AZO–ZZZ French Process Electrophotographic, dispersed water absorption of 250±15 ml.) was slowly added to 70 ml. of 1⅓% gelatin distilled water solution containing 2 ml. of 1,4 butanediol and 1 ml. of Tamol 850 at low speed in an Osterizer. The zinc oxide slurry was transferred to a steel milling jar, and 15 grams of Parez 613 was stirred into the slurry. Twenty-two grams of water-insoluble Piccotex–100 and 3 grams of paraffin were melted together, cooled to room temperature, and powdered. The powder was added to the zinc oxide slurry and all of the constitu-

ents were then milled with 400 grams of ⅜ inch steel balls for one and one-half hours.

An aqueous electrophotographic coating was thus produced that was foam free, containing 78.1% solids at a Stormer viscosity of 88 KU. This coating, with its very low water content, dried very quickly and produced a homogeneous mass on application to treated paper substrate and driving at a temperature of 115° C. The recording members produced from the coating composition had superior electrical qualities and made it possible to produce quality prints at low coating weights.

The superior electrical qualities of this aqueous electrophotographic recording coating composition are illustrated in Table II when compared with control coatings which do not contain the powdered water-insoluble resin.

Example 6

200 grams of photoconductive zinc oxide of the type used in Example 1 was slowly added to 100 ml. of 1⅓% gelatin distilled water solution containing 2 ml. of 1,4 butanediol at low speed in an Osterizer. The zinc oxide slurry was transferred to a steel milling jar, and 25 grams of powdered water-insoluble Piccotex–100 was added to the slurry. All of the constituents were then milled with 400 grams of ⅜ inch steel balls for one hour.

An aqueous electrophotographic coating was thus produced that was foam free and contained 70.1% solids at a Stormer viscosity of 50 KU. When applied to treated paper substrate, the coating dried quickly when brought to a temperature of 115° C. but did not become a homogeneous mass that completely covered the zinc oxide particles. The photoconductive properties of the coating as measured by the electrical tests were very poor (Table II, Example 6*a*). On further heating of the coated paper substrate for four seconds at a temperature of 163° C., the electrical properties of the recording member were greatly increased, and good electrophotographic prints could be made (Table II, Example 6*b*).

Example 7

200 grams of photoconductive zinc oxide (AZO–ZZZ French Process Electrophotographic, dispersed water absorption value of 350±15 ml.) was slowly added to 100 ml. distilled water containing 1 ml. of Tamol 850 while stirring at slow speed in an Osterizer. The zinc oxide slurry was transferred to a steel milling jar and 15 grams of Parez 613 and then 20 grams of Firestone resin emulsion XR–3104 (48.5% solids) were stirred by hand into the zinc oxide slurry. Fifteen grams of powdered Piccotex–100 was added to the mixture, and all of the constituents were milled for one and one-half hours with 400 grams of steel balls.

An aqueous electrophotographic coating was thus produced that was foam-free, dried quickly, and contained 68.6% solids at a Stormer viscosity of 50 KU. The coating dried quickly and produced a homogeneous mass on treated paper substrate at a temperature of 115° C. When the coating was applied at a weight of 16 pounds per 3000 square feet of treated paper substrate, the recording members had superior electrical qualities, as shown in Table II.

Example 8

200 grams of photoconductive zinc oxide (AZO–ZZZ French Process Electrophotographic, dispersed water absorption 250±15 ml.) was slowly added to 100 ml. of 1⅓% gelatin-distilled water solution containing 2 ml. 1,4 butanediol, 1 ml. Tamol 850, 0.1 gram thiosinamine, 0.025 gram methylene green and 0.025 gram rose bengal at low speed in an Osterizer. The zinc oxide slurry was transferred to a steel milling jar and 15 grams of Parez 613 was stirred by hand into the slurry. Twenty-two grams of water-insoluble Piccotex–100 resin and 3 grams of paraffin were melted together, cooled to room temperature, and powdered. This powdered resin was added to the zinc oxide slurry, and all of the constituents were then milled with 400 grams of ⅜ inch steel balls for one and one-half hours.

An aqueous electrophotographic coating was thus produced containing 71.4% solids at a Stormer viscosity of 60 KU. The coating dried quickly and produced a homogeneous mass on treated paper substrate at a temperature of 115° C.

The electrical qualities of this aqueous electrophotographic recording coating composition are very poor when the sensitizing dyes are dissolved in the water. The electrical qualities are illustrated in Table II and can be compared with Example 9, in which the dyes were solubilized in the water-insoluble resin.

Example 9

200 grams of photoconductive zinc oxide (AZO–ZZZ French Process Electrophotographic, dispersed water absorption 250±15 ml.) was slowly added to 100 ml. of 1⅓% gelatin-distilled water solution containing 2 ml. of 1,4 butanediol and 1 ml. Tamol 850 at low speed in an Osterizer. The zinc oxide slurry was transferred to a steel milling jar, and 15 grams of water soluble Parez 613 was stirred by hand into the slurry. Twenty-two grams of water-insoluble Piccotex–100 resin, 3 grams of paraffin, 0.1 gram thiosinamine, 0.025 gram methylene green and 0.025 gram of rose bengal were melted together, solubilizing the sensitizing dyes. The constituents were then cooled to room temperature and powdered. This powdered resinous mixture was added to the zinc oxide slurry, and all of the constituents were then milled with 400 grams of ⅜ inch steel balls for one and one-half hours.

An aqueous electrophotographic coating was thus produced containing 71.4% solids at a Stormer viscosity of 60 KU. The coating dried quickly and produced a homogeneous mass on treated paper substrate at a temperature of 115° C.

The superior electrical qualities of this aqueous electrophotographic coating composition as compared to Example 8, with sensitizing dyes dissolved in the water, are illustrated in Table II.

Test results shown in Table I, which follows, verify that the color of the coating produced in Example 8 is not as white and attractive as the coating produced in Example 9.

TABLE I

	Coating of Example 8	Coating o Example 9
Hunter multi-purpose reflectometer brightness test		
Amber filter	73.0	79.5
Blue filter	72.7	78.2
Green filter	74.2	79.2
Yellow saturation	0.041	0.164

Example 10

200 grams of photoconductive zinc oxide, AZO–ZZZ French Process Electrophotographic, dispersed water absorption 260±15 ml., was slowly added to 140 ml. of 1% gelatin-distilled water solution containing 2 ml. of 1,4 butanediol at low speed in an Osterizer. The zinc oxide slurry was transferred to a steel milling jar, and 30 grams of Darex Everflex BG (50.0% solids) vinyl acetate copolymer resin emulsion (Dewey and Almy Chemical Division of W. R. Grace Co.) were stirred into the slurry. Twenty-two grams of water-insoluble Piccotex–100 and 3 grams of paraffin were melted together, cooled to room temperature, and powdered. This powdered resin was added to the zinc oxide slurry, and all the constituents were then milled with 400 grams of ⅜ inch steel balls for one and one-half hours.

An aqueous electrophotographic coating was thus produced containing 60.9% solids at a Stormer viscosity of 56 KU. The coating dried quickly and produced a homogeneous mass on treated paper substrate at a temperature of 115° C.

The superior electrical qualities of this aqueous electrophotographic recording coating composition are illustrated in Table I when compared with control coatings which do not contain the powdered water-insoluble resin.

Example 11

200 grams of photoconductive zinc oxide, AZO–ZZZ French Process Electrophotographic, dispersed water absorption 260±15 ml., was slowly added to 100 ml. of distilled water containing 1 ml. of Tamol 850 dispersing and wetting agent while stirring at slow speed in an Osterizer. The zinc oxide slurry was transferred to a steel milling jar and 15 grams of Parez 613 and then 50 grams of Firestone resin emulsion XR–3104 (48.5% solids) were stirred by hand into the zinc oxide slurry. Eight and eight-tenths (8.8) grams of water insoluble Piccotex–100 resin and one and two-tenths (1.2) grams of paraffin were melted together, cooled to room temperature, and powdered. This powdered resin was added to the zinc oxide slurry, and all the constituents were then milled with 400 grams of ⅜ inch steel balls for one and one-half hours.

An aqueous electrophotographic coating was thus produced that was foam free, dried quickly, and contained 66.3% solids at a Stormer viscosity of 50 KU. When the coating was applied to a treated paper substrate it had excellent flexure. The coating was applied at a weight of 13.0 pounds per 3000 square feet of substrate.

The superior electrical qualities of this aqueous electrophotographic recording coating composition are further illustrated in Table I when compared to control coatings that do not contain the powdered water-insoluble resin.

Example 12

200 grams of photoconductive zinc oxide, AZO–ZZZ French Process Electrophotographic, dispersed water absorption value of 260±15 ml., was slowly added to 100 ml. of distilled water containing 0.5 gram of cationic surfactant, Nopcogen 14L, and 1 ml. Tamol 850 at low speed in an Osterizer. The zinc oxide slurry was transferred to a steel milling jar. Twenty-two grams of water-insoluble Piccotex–100 resin and 3 grams of paraffin were melted together, cooled to room temperature and powdered. This powdered resin was added to the zinc oxide slurry, and after milling for one and one-half hours with 400 grams of ⅜ inch steel balls, formed a coating composition with a fineness of 6+ on the Hegman gauge.

An aqueous electrophotographic coating was thus produced that was foam free, containing 69.3% solids at a Stormer viscosity of less than 50 KU. The coating was dried quickly at 115° C. and then the temperature was raised to 163° C. for four seconds, which produced a flexible homogeneous mass on treated paper substrate.

The electrical qualities of this aqueous recording coating composition are illustrate in Table II.

When 1 ml. Tamol 850 was used with no Nopcogen 14L, the Piccotex–100 was not wetted, and floated out of the slurry.

Example 12 illustrates the necessity for a precoating agent. When the cationic surfactant is used, the electrical properties of the coating are adversely affected. When a precoating composition is used, a non-ionic or slightly anionic surfactant is effective to wet both the zinc oxide and the resin.

Example 13

200 grams of photoconductive zinc oxide, AZO–ZZZ French Process Electrophotographic, dispersed water absorption value of 350±15 ml. was slowly added to 100 ml. distilled water with additions of Tamol 850 one drop at a time to prevent thickening of the slurry. It was established that 0.9 ml. of Tamol 850 was the minimum amount of wetting surfactant that could be used with the zinc oxide at a 350 ml. dispersed water absorption value. The zinc oxide slurry was transferred to a steel milling jar and 15 grams of Parez 613 was stirred by hand into the zinc oxide slurry. Twenty-two grams of water-insoluble Piccotex–100 resin and 3 grams of paraffin were melted together, cooled to room temperature, and powdered. This powdered resin was added to the zinc oxide slurry, and all the constituents were then milled with 400 grams of ⅜ inch steel balls for one and one-half hours.

An aqueous electrophotographic coating was thus produced that was foam free and contained 70.7% solids at a Stormer viscosity of 60 KU. The coating dried quickly and produced a homogeneous mass on treated paper substrate at a temperature of 115° C.

The electrical qualities of this aqueous electrophotographic recording coating composition are illustrated in Table II and should be compared to Example 14 to show the effect on electrical qualities when it is necessary to use larger quantities of surfactant with zinc oxides of higher dispersed water absorption values.

Example 14

200 grams of photoconductive zinc oxide, AZO–ZZZ French Process Electrophotographic, dispersed water absorption value of 260±15 ml. was slowly added to 100 ml. distilled water with additions of Tamol 850 one drop at a time to prevent thickening of the slurry. It was established that 0.6 ml. of Tamol 850 was the minimum amount of wetting surfactant that could be used with the zinc oxide at a 260 ml. dispersed water absorption value. The zinc oxide slurry was transferred to a steel milling jar and 15 grams of Parez 613 was stirred by hand into the zinc oxide slurry. Twenty-two grams of water-insoluble Piccotex–100 and 3 grams of paraffin were melted together, cooled to room temperature, and powdered. This powdered resin was added to the zinc oxide slurry, and all the constituents were then milled with 400 grams of ⅜ inch steel balls for one and one-half hours.

An aqueous electrophotographic coating was thus produced that was foam free and contained 70.7% solids at a Stormer viscosity of 60 KU. The coating dried quickly and produced a homogeneous mass on treated paper substrate at a temperature of 115° C.

The superior electrical qualities of this aqueous electrophotographic coating containing a minimum of surfactant with a lower dispersed water absorption zinc oxide are illustrated in Table II when compared to Example 13 with a zinc oxide of higher dispersed water absorption.

TABLE II.—PHOTOCONDUCTIVE PROPERTIES AS MEASURED BY ELECTRICAL TESTS RECORDING MEMBERS NEGATIVE CORONA CHARGED AQUEOUS ELECTROPHOTO GRAPHIC COATINGS APPLIED TO TREATED PAPER SUBSTRATE

Test	Maximum charge acceptance	Volts end of 20 sec. dark decay	Volts end of 1 sec. light	Residual volts	Coating weight, lbs./ 3,000 sq. ft.	Print quality
Control-A [2]	140	40	20	15	24.0	Very poor.
Control-B [3]	260	120	75	15	26.5	Do.
Example 1	970	680	260	50	22.0	Very good.
Example 2	590	490	230	20	21.5	Excellent.
Example 3	500	440	220	35	21.0	Very good.
Example 4	860	670	270	40	21.0	Do.
Example 5	860	675	320	35	24.0	Do.
Example 6a [4]	54	25	20	20	23.0	None.
Example 6b [5]	570	320	170	40	23.0	Good.
Example 7	640	540	270	35	16.0	Very good.
Example 8	265	110	60	15	24.0	Poor.
Example 9	905	720	320	10	29.0	Good.
Example 10	570	335	185	70	15.5	Spotty-toner incomp.
Example 11	520	460	220	40	13.0	Very good.
Example 12	390	180	60	20	15.5	Poor-toner incomp.
Example 13	550	420	190	35	18.5	Very good.
Example 14	730	620	320	35	19.5	Do.

[1] The normal criteria for measuring the electrical properties include maximum charge acceptance, dark and light decay and residual voltage. A use test is then made by actually making a contact print on the recording member or by making a print in a commercial machine. Normally the prepared electrophotographic coating is drawn down with a wire-wound ¼" diameter rod on a standard treated paper substrate at the desired coating weight. After drying, the coated sheets are put into a humidity cabinet and conditioned overnight at a relative humidity of 50% and a temperature of 27° C. After conditioning, the coated sheets are dark adapted for at least one hour. The electrical tests are then made in a dark room at 50% R.H. and 27° C. The coated sheet is charged for one minute at 40 microamperes ± 5 microamperes with a negative corona discharge operating at six to ten thousand volts. Immediately after charging the coated sheet a standardized probe attached to a Keithley 610 electrometer and recording device is placed on the coated sheet. The surface voltage immediately registered by the Keithley electrometer is known as maximum charge acceptance. The coated sheet is allowed to discharge for twenty seconds in the dark. This voltage recorded at the end of twenty seconds is known as the voltage after twenty seconds dark decay. A light is then turned on (150 ft. candles at the coated surface), and the voltage recorded after one second of light is known as the light decay voltage. The light continues to discharge the surface voltage, and the residual voltage is recorded as point where a tangent intersects the straight part of the light decay curve. Several thousand of these electrophotographic electrical tests have been made on a wide variety of coatings; the tests can easily be duplicated by different operators at ± 10 volts.

[2] Produced by the same method and procedures as in Example 1 except that no powdered water-insoluble resin was used and the total amount of resin was made equivalent to Example 1 by increasing the amount of Parez 613.

[3] Produced by the same method and procedures as in Example 2 except that no powdered water-insoluble resin was used and the total amount of resin was made equivalent to Example 2 by increasing the amount of Firestone resin emulsion XR-3104.

[4] Coated recording member dried to 115° C.

[5] Coated recording member given further heating for four seconds at 163° C.

With the use of the coating composition of this invention, the coating weight, which, with present commercial compositions, is approximately 24 pounds per 3000 square feet, can be reduced below 15 pounds to produce a recording member which still has adequate maximum charge acceptance and excellent print quality.

Numerous variations in the coating composition of this invention, the coatings resulting from the use of the composition, and the method of producing the compositions and coatings, within the scope of the appended claims will occur to those skilled in the art in the light of the foregoing disclosure. It is to be understood, for example, that the companies which produce electrophotographic recording machines will require various addition agents and particular characteristics for the coating, to make the coating compatible with the particular developer or toner used by each company. It is for this reason that the resin blend of Example 4, for instance, was said to have a different compatibility than the blend of Example 1. This compatibility may be better for some types of developers than the blend of Example 1, and poorer with certain other developers. Numerous other blending agents and water-insoluble resin will suggest themselves to those skilled in the art, for these particular applications.

Having thus described the invention, what is claimed and desired to be secured by Letters Patent is:

1. A coating composition comprising photoconductive zinc oxide, a powdered, friable, fusible, water-insoluble resin having high electrical resistance, a blending agent and water, said zinc oxide and insoluble, powdered resin being distributed substantially uniformly through said composition.

2. The coating composition of claim 1 wherein the blending agent comprises gelatin and 1,4-butanediol.

3. The composition of claim 1 in which the weight of total liquid water is less than 90% of the weight of the zinc oxide.

4. The composition of claim 1 in which the photoconductive zinc oxide in the dispersed state has a water absorption value of 200 to 400 ml.

5. The composition of claim 1 in which the water-insoluble resin has a Ring and Ball softening point of from 50° C. to 150° C.

6. The composition of claim 1 in which paraffin and the water-insoluble resin are intermixed, hardened to friability, and then powdered.

7. The composition of claim 1 wherein dye is incorporated into the water-insoluble resin and the resin is thereafter powdered.

8. An electrophotographic coating composition comprising photoconductive zinc oxide; wetting agent taken from the group consisting of sodium salt of polymeric carboxylic acid, polymerized sodium salt of alkyl naphthalene sulfonic acid and 1,4-butanediol and gelatin; precoating composition taken from the group consisting of gelatin, styrene-butadiene emulsion, water soluble acrylic resin, water soluble melamine-formaldehyde resin, water soluble alkyd resin and water-emulsified polyvinyl acetate resin; and a water insoluble, friable, finely divided resin with a Ring and Ball softening point between 50° C. and 120° C. taken from the group consisting of styrene homolog copolymer (completely saturated), coumarone-indene resin, low iodine number hydrocarbon resin and pure polystyrene of low molecular weight.

9. A coating, on a substrate, said coating comprising a substantially uniform distribution of photoconductive zinc oxide and blending agent in a thermally fused matrix of water-insoluble resin binder, said coating being formed by applying to said substrate a coating composition comprising photoconductive zinc oxide, blending agent, and powdered water-insoluble resin having a Ring and Ball softening point in the range of 50° C. to 150° C., drying the said coating composition on said substrate, and heating the said coating composition to a temperature at which the water-insoluble resin fuses.

10. The coating of claim 9 wherein the water-insoluble resin is plasticized with paraffin.

11. A method of making an electrophotographic coating composition comprising dispersing photoconductive zinc oxide in water containing blending agent, thereafter adding powdered, water-insoluble resin having a Ring and Ball softening point of 50 to 150° C. and distributing the ingredients substantially uniformly through the resultant slurry.

12. The method of claim 11 in which the weight of the total liquid water used does not exceed 90% of the weight of the zinc oxide used.

13. The method of claim 11 in which the ratio of zinc oxide to total binders is at least 4 to 1 but not more than 10 to 1.

14. The method of claim 11 with the further intermediate steps of melting together at least one addition agent taken from the group consisting of dyes, plasticizers, and sensitizers, and the water-insoluble resin, cooling the melt, and grinding the cooled melt to a powder before adding the powder to the slurry.

15. The method of producing a photoconductive coating comprising applying to a substrate a coating composition comprising photoconductive zinc oxide, blending agent, and powdered water insoluble resin having a Ring and Ball softening point in the range of 50 to 150° C., drying the said coating composition on the substrate, and heating the coating composition to a temperature at which the water insoluble resin fuses.

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