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ELECTROPHOTOGRAPHIC COMPOSITION COMPRISING ZINC OXIDE AND A METALLIC NAPHTHENATE

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ABSTRACT OF THE DISCLOSURE

The electrical properties of an acrylic resin employed as a binder in a photoconductive coating composition are improved by the inclusion of an adjuvant amount of an active metallic drier, particularly exemplary of which are cobalt and zinc naphthenate.

The present invention relates to electrophotography. In one aspect, the present invention relates to the use of large amounts of metallic driers (e.g. cobalt naphthenate) in conjunction with non-oxidizing acrylic resins as binders for zinc oxide in manufacturing coated copy paper. In still another aspect, the present invention relates to the use of such coated copy paper in direct electrophotographic processes.

Electrophotography is one of several terms used to describe a reproduction or image transfer process utilizing electrical and light stimulation of conductive materials. Some common terms for commercial processes based on this technique are Electrofax, electrostatography, electrophotography, xerography, and electrographic recording. These processes all employ electromagnetic radiation and a photo-responsive member to obtain, on exposure to light, a latent electrostatic image on the photo-responsive member. Ordinarily, this latent electrostatic image is then converted into a positive image. Such techniques are used in commercial off-set printing, computer readout, film developing, map making, long-distance copying, recording, office copying, and the like.

There are two general types of electrophotography which have been commercially successful in the office and industrial copying field. These types, although using the same basic principles, differ in the type of photo-responsive member employed. These two types of electrophotography are the "direct process" and the "transfer process." This invention is concerned with the direct process, only.

In the transfer process, a latent image is first produced on a selenium-coated aluminum drum. This image is then transferred to a sheet of ordinary paper (i.e. paper which may be coated, but which is not coated with a photoconductor).

The direct process utilizes the same principles as the transfer process, except that a selenium-coated drum is not used. Instead, the image is directly produced on, for example, paper. The basis for this technique is the use of coated paper or the like containing, on the surface thereof, a finely-divided photoconductive material. Typically, zinc oxide is employed as the photoconductive material and is bonded to the paper by the use of some suitable organic binder. Often, dyes are used to sensitize the zinc oxide.

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The electrical conductivity of zinc oxide shows a significant increase when subjected to light. Consequently, the zinc oxide will lose any previously applied electrical charge when exposed to light.

The direct process operates as follows:

(1) The coated paper is made light sensitive by placing a uniform electrostatic charge on the coated surface in the dark by means of a high voltage corona discharge, e.g. 4000 to 6000 volts. The coated paper is not sensitive to light until properly charged.

(2) A latent image is produced on the paper by projecting an object image onto the paper, typically employing white light in the visible range. The original electrostatic charge carried by the paper is dissipated in all areas exposed to light and is retained in the shadowed areas, thus forming a latent electrical image on the paper.

(3) The latent image is then developed using liquid or dry toners. In the dry method, the toner (consisting of pigmented resin and ferromagnetic particles, e.g. iron filings) is applied to the paper by a magnetic brush. As the brush moves across the paper, the charged toner is attracted to the charges of opposite polarity on the paper. In the liquid method, the pigmented resin particles are suspended in an organic liquid such as odorless mineral spirits. This liquid is then brought in contact with the paper.

(4) Two methods are utilized to permanently fix the image to the paper. With the dry toner system, the image is fixed by heat (below the charring temperature of the paper) which fuses the toner to the coated paper. Fixing the image in the liquid toner system is accomplished by heat and solvent evaporation.

Multi-color copying can be performed by re-charging the coated copy paper for each new color and utilizing the proper color of toner. This technique is currently applied in map copying.

The effectiveness of any direct electrophotographic process depends, to a large extent, upon the electrical properties exhibited by the coated copy paper. In order for coated copy paper to provide pleasing, clear, legible copies, the coated copy paper should quickly accept a maximum electrostatic charge, should not allow the electrostatic charge on the paper to be significantly dissipated in the dark before the charged photoconductive coating is exposed to light, and should not interfere with the rapid dissipation of the electrostatic charge when the coated paper is exposed to light. Desirably, the coated paper should not accept or retain any appreciable residual voltage in the areas exposed to light. Although many organic binders are available which will effectively bond a finely-divided photoconductor (e.g. finely-divided zinc oxide) to the surface of paper, many such binders are unsuited for use in manufacturing coated copy paper because of their poor electrical characteristics.

We have now discovered that it is possible to improve or enhance the electrical properties of non-oxidizing acrylic resins when used as zinc oxide binders for coated copy paper by adding to the non-oxidizing acrylic resins significant amounts of metallic driers of the type used to harden oxidizing resins (e.g. used harden oil-modified alkyd resins). The benefits which accompany the use of metallic driers in combination with non-oxidizing acrylic resins is unexpected.

In the case of oxidizing resins, metallic driers (e.g. the various metallic naphthenates) have been used to increase

the speed at which the binder hardens during the manufacture of coated copy paper. When used with oxidizing resins (e.g. oil-modified alkyd resins and oil-modified silicone resins), cobalt naphthenate is commonly used as a hardener at a level of about 0.05% active metal based on the weight of the resin. Although larger amounts of driers can be used, their use is generally unnecessary and uneconomical. In contra-distinction, we have found that if significantly greater amounts of metallic driers are used one obtains significant improvements in the electrical properties of the coated copy paper. Unlike the prior art, we do not use the metallic driers as hardeners to increase the speed at which the binders harden during the manufacture of coated copy paper. In fact, no noticeable improvement in the rate of hardening is usually noted in the ordinary practice of our invention because we employ nonoxidizing acrylic resins. Instead, when used according to our invention in conjunction with non-oxidizing acrylic resins, metallic driers result in improvements in the coated copy paper as measured in terms of charge acceptance and/or light decay rate or light decay time.

As used herein, the term "bonding composition" means a solvent solution or emulsion of a hardenable or polymerizable binder which, when mixed with a suitable photoconductor (e.g. zinc oxide) and applied to a surface of a suitable substrate (e.g. paper), can be hardened or cured to firmly bond and position the photoconductor to the surface of the substrate. Frequently, bonding compositions are sold as articles of commerce to manufacturers of, for example, coated copy paper. Such bonding compositions can optionally contain various additives, dyes, emulsifiers, stabilizers, etc. Often, the curable binder will be a resinous polymer or copolymer, optionally mixed with a suitable cross-linking agent (e.g. an aminoplast resin).

As used herein, the term "coating composition" means a bonding composition to which has been added a suitable photoconductor (e.g. finely-divided zinc oxide). Optionally, such coating compositions can contain sensitizing dyes, catalysts, etc.

As used herein, the term "oxidizing" means a resin or binder which hardens or solidifies by reaction or polymerization with oxygen of the air. Metallic driers are commonly used to accelerate this reaction, thereby producing a "hardening" effect.

The metallic driers which are useful in the present invention are those metallic driers commonly used to accelerate the hardening of oxidizing resins (e.g. oil-modified alkyd resins). Suitable metallic driers include the rare earth driers, metallic octoates, metallic naphthenates, etc. Metal naphthenates are especially useful in practicing the present invention. Thus, zinc naphthenate, manganese naphthenate, lead naphthenate, calcium naphthenate, cobalt naphthenate, and the like, are effective in the practice of the present invention. Of the various metallic naphthenates, cobalt naphthenate and zinc naphthenate are especially preferred. Zinc naphthenate is particularly useful since it does not impart color to the organic binders as does cobalt naphthenate (the latter imparts a strong purple color to the binder).

The amount of metallic drier to be used in conjunction with the non-oxidizing acrylic resin will be from 0.05X-1X weight percent of active metal (present in the drier) based on the weight of the polymerizable or hardenable organic binder in the bonding or coating composition (i.e. based on the non-volatile binder content, thus ignoring any consideration of solvent). More usually, the amount of drier used will be within the range of 0.1X-0.7X weight percent on the same basis. An especially useful amount is from 0.2X-0.5X weight percent, e.g. about 0.3X weight percent. The term X is defined for purposes of this disclosure as the atomic weight of the active metal ion present in the metallic drier divided by 58.94 (the atomic weight of cobalt). Thus, for cobalt driers, the term X equals 1.

The resins or binders which can be benefitted by the practice of the present invention are the non-oxidizing acrylic resins. Although these non-oxidizing acrylic resins can be used as the only organic binder in the bonding and coating compositions, it is sometimes desirable to use blends of such non-oxidizing acrylic resins with other organic binders including those of the oxidizing type (e.g. alkyd resins, butadiene/styrene copolymers, Buton 100, etc.). Such mixtures should contain at least 25 weight percent of the non-oxidizing acrylic resins (based on the total weight of the mixture of organic binders). More preferably, the non-oxidizing acrylic resins will account for at least 35 weight percent of the mixture or organic binders. Mixtures of organic binders which contain at least about 50 weight percent of the non-oxidizing acrylic resins are particularly useful in the production of coated copy paper.

Suitable non-oxidizing acrylic resins can be prepared by polymerizing or copolymerizing various acrylic monomers with or without the additional use of monomers other than acrylic monomers. Thus, suitable non-oxidizing acrylic polymers can be prepared by polymerizing or copolymerizing acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid, citraconic acid, crotonic acid, methyl methacrylate, butyl acrylate, hydroxypropyl acrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, acrylonitrile, styrene, o-chlorostyrene, vinyl toluene, alpha-methyl styrene, and the like. Polymers and copolymers can be prepared from these monomers by conventional polymerization techniques as shown in, for example, U.S. Pats. 2,681,897, 3,082,184, and 3,198,850.

A particularly useful non-oxidizing acrylic polymer which gives outstanding physical and electrical properties when used as a binder even in the wet toner process, is a copolymer containing (1) from 1-30% by weight (preferably 10-20% by weight) of a hydroxyalkyl acrylate or methacrylate, or mixture thereof, (2) from 1-15% by weight (preferably 1-5% by weight) or a copolymerizable alpha, beta-unsaturated carboxylic acid or mixture thereof, and (3) the balance to make 100% of one or more copolymerizable mono-ethylenically unsaturated vinyl monomers which are devoid of hydroxyl and carboxyl groups (e.g. styrene or C₁-C₄ alkyl acrylate). These various non-oxidizing acrylic copolymers can be used as binders both with and without cross-linking agents such as the various aminoplasts (e.g. a melamine formaldehyde resin) or phenolic resins (e.g. phenol-formaldehyde resin).

The metallic driers can be added to the non-oxidizing acrylic resins at any time before the resins are used to coat, for example, paper. Frequently, it will be convenient to add the metallic drier to a solution of emulsion of the non-oxidizing acrylic resin almost immediately after preparation of the copolymer and as part of the original process of manufacturing the bonding composition. If the acrylic resin is to be blended with other resins, the metallic drier can be added at or about the time such blending is accomplished.

In preparing coating compositions for application to a substrate (e.g. paper) a photoconductive material is dispersed in a bonding composition (which can optionally contain the metallic drier) by suitable grinding techniques. Suitable photoconductive materials are zinc oxide, zinc sulfide, silver chloride, mercuric sulfide, as well as other photoconductive materials known to the art. Zinc oxide is the preferred photoconductor. The zinc oxide is usually dispersed at a concentration of 4-16 parts by weight of zinc oxide per one part of organic binder. If a cross-linking resin is to be used as part of the organic binder, it can be added at this time if it is not already present in the bonding composition. Preferably, the zinc oxide is dispersed or mixed at a level of 6 to 12 parts by weight of zinc oxide per one part of organic binder (e.g.

the weight of acrylic copolymer plus cross-linking resin), and more preferably 8-10 parts by weight of zinc oxide per one part of organic binder (on a non-volatile basis).

If an emulsion copolymer is utilized as a binder, the zinc oxide can first be dispersed in a suitable dispersing aid. Then, this dispersant mixture can be diluted with the copolymeric emulsion in a manner conventional to the art of pigment dispersion.

In any case, the final coating compositions will usually have a solids content (i.e. non-volatile content) of from 40-70%, preferably 50-60% (the remainder being solvent and/or water).

In order to render the dry, cured photoconductive coatings more receptive to a charge and a photoconductive effect, suitable dyes such as rose bengal, methylene blue, rhodamine B, dibromo-fluorescein, and various cyanine dyes can be included in the bonding or coating compositions. Usually a mixture of dyes is added, incorporating complementary colors so that the dried coatings have a pleasing, off-white appearance. These techniques and others similar to the art of electro-photographic binder compositions can be applied to the coating compositions of this invention.

The coating compositions, containing the zinc oxide, metallic driers, the non-oxidizing acrylic resins, solvent or water, and optionally other resins and cross-linking agents, are then applied to a suitable substrate (usually paper, although metal, foil, etc., can be used) in any suitable fashion such as by brushing, spraying, dipping, roller coating, or the like to give a coated paper having an average of from 5-50 pounds, e.g. 8-30 pounds of deposited dry coating per 3000 square feet of coated paper surface. Optionally, the paper can first be given a conductive pre-treatment as known in the art. As appropriate, the wet coated paper can be air dried or cured at room temperature or dried by baking, e.g. baked at 200°-350° F. The preferred drying temperature will depend on whether or not an aminoplast or phenolic resin is present. Without an aminoplast or phenolic resin, a curing temperature in the range of 75°-250° F., e.g. 100°-150° F. will ordinarily be used. In the presence of an aminoplast or phenolic resin, higher temperatures are usually required to obtain maximum benefits. The addition of small portions (0.1 to 1%) of an acidic catalyst such as toluene sulfonic acid or phthalic acid serves to lower the temperature required for proper curing.

The present invention will be further understood by reference to the following specific examples. Unless otherwise indicated, all parts and percentages are by weight.

EXAMPLES 1-5

In Examples 1-5, various bonding compositions were prepared as follows:

9.2 parts of methyl methacrylate, 15.3 parts of styrene, 11.5 parts of n-butyl methacrylate, 11.5 parts of n-butyl acrylate, and 21.6 parts of a commercially available xylene solution (from Rohm & Haas) containing 40% of hydroxypropyl methacrylate and 6% of methacrylic acid were mixed together. 0.7 part of azo-bis-isobutyronitrile was then added to the previous mixture. The resulting mixture was sparged with nitrogen and then added dropwise during a 2½ hour period at 250° F. to a mixture of 21.3 parts of xylene and 5.8 parts of n-butanol contained in a 2-liter, three-necked, glass flask equipped with an agitator, condenser, nitrogen inlet, thermometer, and addition tube. During this addition, the xylene/n-butanol solution was agitated. Two hours after the monomer addition was complete, 0.05 part of di-t-butyl peroxide were added as a booster catalyst. The reaction mixture was further heated at 250° F. until the non-volatile (NV) content was 59-61% and the viscosity was 40-80 stokes. The resulting mixture was then cooled and metallic drier

In Example 1, the metallic drier was cobalt naphthenate (2.9 parts of a 6% active metal cobalt naphthenate solution) and sufficient drier was used to give 0.3% of cobalt metal based on the weight of binder.

In Example 2, the metallic drier was lead naphthenate (using a 24% active metal lead naphthenate solution) at a level of 0.3% active metal based on the weight of binder.

In Example 3, the metallic drier was manganese naphthenate (using a 6% active metal manganese naphthenate solution) at a level of 0.3% active metal based on the weight of binder.

In Example 4, the metallic binder was calcium naphthenate (using a 4% active metal calcium naphthenate solution) at a level of 0.3% active metal based on the weight of binder.

In Example 5, the metallic drier was zinc naphthenate (using an 8% active metal zinc naphthenate solution) at a level of 0.3% active metal based on the weight of binder.

For purposes of comparison, a bonding composition was prepared by following Example 1, omitting only the metallic drier. This composition is identified as "Control A."

EXAMPLES 6-10

In the following examples, various coating compositions were prepared by dispersing zinc oxide and various dyes into the bonding compositions of Examples 1-5 by the following procedure:

Sufficient zinc oxide (American Zinc Sales AZO-ZZZ-661) was added to the bonding compositions to give weight ratios of zinc oxide to binder of about 8:1 based on the non-volatile weight of the binder. The zinc oxide was dispersed in the bonding compositions by agitation for 5 minutes in a Hamilton-Beach mixer. The dispersions were then diluted with toluene to a 58% concentration of zinc oxide and resin (i.e. 42% solvent).

Next, a sufficient amount of the following mixture of commercially available dyes was added to provide a level of 100 p.p.m. of dye solids based on the weight of zinc oxide. The purpose of adding the dyes was to sensitize the zinc oxide/resin mixture.

- (a) four drops of a 1% solution in methanol of Auramine O conc. (Allied Chemical)
- (b) 68 drops of sodium fluorescein (1% solution in methanol)
- (c) 22 drops of Brom Phenol Blue (Eastman (1% solution in methanol)
- (d) 40 drops of Alizarine Cyanine Green GWA (Gen. Aniline & Film) (1% solution in methanol).

The resulting coating compositions were then applied to paper using a No. 22 coating rod for this purpose. This deposits about 15-18 pounds of drying coating per 3000 square feet of coated paper surface. The wet, coated sheets were baked at 120° F. for one minute. Then the dry, tack-free coated sheets were allowed to stand in the dark for 16-24 hours at a humidity of 50% and 77° F.

For purpose of comparison, the procedure was repeated using the bonding composition previously identified as "Control A." The resulting coated paper sheets are identified as "Control B."

The coated sheets of Examples 6-10 were then processed through a commercial Electrofax copy machine utilizing a liquid toner. Excellent copies having high spectral response and excellent contrast were obtained.

In addition, the coated sheets (including Control C) were exposed to a commercial corona discharge unit (a transformer output of 1200 volts) and placed beneath a calibrated static detector probe. The probe was wired to a Keithley Model 610B electrostatic meter connected to an Esterline-Angus Recorder. The coated sheets were

then exposed to light. The following electrical results were obtained:

TABLE I

Coated paper	Bonding composition	Metallic drier	Charge ¹ acceptance (volts)	Dark decay (volts)	Light ³ decay time (seconds)	Residual ⁴ charge (volts)
Control B.....	Control A.....	None.....	380	20	7	20
Exam. 6.....	Exam. 1.....	Cobalt.....	470	10	4	15
Exam. 7.....	Exam. 2.....	Lead.....	360	20	3 1/4	5
Exam. 8.....	Exam. 3.....	Manganese.....	485	15	4	10
Exam. 9.....	Exam. 4.....	Calcium.....	390	30	2 1/2	10
Exam. 10.....	Exam. 5.....	Zinc.....	420	20	3 1/2	10

¹ Charge acceptance is the voltage from the base line to the maximum absorption of voltage.

² Dark decay is the voltage drop in darkness over a 4.5 second period from the maximum charge acceptance to the start of the light decay.

³ Light decay is the time required for the static charge (i.e. the accepted charge) to be dissipated to 50 volts:

⁴ The residual voltage is the amount of static charge which is not dissipated.

Although the light decay times of Examples 7-11 vary, the light decay rates for most of the examples are nearly the same. Zinc naphthenate gave the whitest coating.

In addition to giving excellent image quality, the coatings on the copy paper (i.e. the coated paper sheets of Examples 6-10) exhibited excellent adhesion and outstanding mar resistance. The coated sheets also displayed unusual pre-fogging properties in that light exposure immediately prior to charge acceptance did not affect the amount of charge acceptance. Most important was the ability of the coated sheets to provide copies of excellent contrast, image density, and spectral response especially at the low coating weights.

EXAMPLE 11

A mixed bonding composition was prepared by blending the bonding composition of Example 5 with a solvent solution of a commercially available oxidizing resin (AROPOL 832, a styrenated polyester resin sold by Archer-Daniels-Midland Co. of Minneapolis, Minn.) in a weight ratio of 25:75 (based on the weight of resin solids, only).

For purposes of comparison, a similar mixed bonding composition was prepared as shown for Example 11 using the bonding composition previously identified as Control A in lieu of the bonding composition of Example 1. This mixed bonding composition is identified as Control C.

EXAMPLE 12

In this example, a coating composition was prepared from the bonding composition of Example 11 and used to coat paper, following the procedures of Examples 6-10. For purposes of comparison, coated paper was also prepared in the same manner using a coating composition based on the mixed bonding composition previously identified as Control C. This coated paper is identified as Control D. The following electrical results were obtained using the test methods and equipment of Examples 6-10.

TABLE II

Coated paper	Metallic drier	Charge acceptance (volts)	Dark decay (volts)	Light decay time (sec.)	Residual charge (volts)
Control D.....	None.....	340	40	4 3/4	5
Exam. 12.....	Zinc.....	345	35	3 3/4	5

From Table II, it can be seen that the presence of a metallic drier (i.e. zinc naphthenate) increased the charge acceptance, reduced the dark decay, and decreased the light decay time. Note that these beneficial results were obtained using only 0.075% zinc naphthenate based on the weight of a mixed organic binder containing only 25% of a non-oxidizing acrylic resin. The prints obtained with the paper of Example 12 were of better quality than those of Control D.

EXAMPLE 13

A coating composition was prepared and paper was coated by following the procedures used in Examples 6-10. In this example (i.e. Example 13), the bonding composition used to prepare the coating composition was a

commercially available solution of a non-oxidizing acrylic resin (Acryloid B-72, a product of Rohm & Haas) to

which has been added a sufficient amount of a standard 6% cobalt naphthenate solution to provide 0.3% cobalt metal based on the non-volatile content of the solution of non-oxidizing acrylic resin.

For purposes of comparison, the procedure of this example was repeated, omitting only the use of cobalt naphthenate. This paper is identified as Control E. The electrical results obtained using the test methods and equipment of Examples 6-10 are shown in Table III, which follows.

TABLE III

Coated paper	Metallic drier	Charge acceptance (volts)	Dark decay (volts)	Light decay time (sec.)	Residual charge (volt)
Control E.....	None.....	120	40	1	0
Exam. 13.....	Cobalt.....	360	30	5	5

From the data contained in Table III, it can be seen that a major increase in charge acceptance resulted from the use of cobalt naphthenate. This change is quite significant and print quality was substantially improved over that of Control E when the paper was used in a SCM Model 44 copying machine.

Enhanced electrical properties similar to those obtained in Examples 6-10, 12 and 13 can be obtained using other substrates (e.g. plastic film, foil, etc.) instead of paper, other non-oxidizing acrylic resins, and other metallic driers (e.g. rare earth driers).

Although the present invention has been described with a certain degree of particularity, it is not intended that the invention be limited to the specific materials and specific proportions which have been given for the sake of illustration. Numerous modifications and variations will appear obvious to one skilled in the art.

What is claimed is:

1. An electrophotographic coating composition comprising one part by weight as the binder resin of a copolymer of (1) from 1 to 30% by weight of a hydroxyalkyl acrylate or a hydroxyalkyl methacrylate, (2) from 1 to 15% by weight of an α,β -ethylenically unsaturated carboxylic acid, and (3) the balance to make 100% of a vinyl monomer devoid of hydroxyl and carboxyl groups, said binder resin containing uniformly dispersed therein from 4 to 10 parts by weight of zinc oxide and a metallic compound selected from the group consisting of cobalt naphthenate, manganese naphthenate, lead naphthenate, calcium naphthenate, and zinc naphthenate, said compound being present in an amount so as to provide from 0.05X-1X% by weight active metal based on the weight of said binder, where X represents the atomic weight of the active metal present in the metal compound divided by 58.94.

2. A coating composition in accordance with claim 1 wherein said metallic compound is cobalt naphthenate.

3. A coating composition in accordance with claim 2 wherein zinc oxide is present in the amount of from 6 to 10 parts per part of said binder resin.

4. A coating composition in accordance with claim 1 wherein said metallic compound is zinc naphthenate.

5. A coating composition in accordance with claim 4 wherein said zinc oxide is present in the amount of from 6 to 12 parts by weight per part of said acrylic resin.

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