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PROCESS OF ELECTROSTATIC PRINTING BY PROJECTING ELECTRICALLY PHOTOSENSITIVE PARTICLES THROUGH AN IMAGE-DEFINING SCREEN

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ABSTRACT OF THE DISCLOSURE

A process is provided for electrostatically printing an image upon a surface which comprises forming a layer of photoconductive material-containing, resin based, particles on a first charged surface. This surface is then illuminated with electromagnetic radiations. By forming a first potential between the first surface and an image-defining screen and a second potential between this screen and a second surface oppositely charged from the first surface, and by providing a potential of at least 20,000 volts per linear inch of separation between the screen and each of the surfaces. The particles on said first surface are projected through the image-defining area of the screen and onto the second surface to form an image thereon. To insure good adherence of the particles on the second surface, the second surface is shielded from electromagnetic radiation during the process.

This invention relates to a novel composition and process for the practice of electrophotographic decorating, especially electrostatic printing.

More particularly, this invention relates to an electrostatic decorating or printing process wherein a semi-electroconductive organic coating composition is transferred by means of an electric field from one surface to another surface.

Many electrostatic printing processes, as generally employed for printing and decorating, comprise moving by means of an electric field a decorative coating composition consisting of powder particles through the image-defining apertures of a screen or stencil to a printable or decorable surface. In addition, other printing techniques may be used wherein the image-forming powder is first transferred by means of an electric field through an image screen to an intermediate surface and then off-set from the intermediate surface to a printable or decorable surface. Such off-setting may be accomplished by means of a further electric field or by direct contact with the decorable surface.

In the practice of such electrostatic printing processes, various problems are typically encountered from the use of the decorative or image-forming powder particles. For example, if a powder particle is inherently non-electroconductive, it will not readily move in the electrostatic field. Accordingly, if the resistivity of a powder particle is very high, it may require precharging by corona techniques or by triboelectric means, in which event, the polarity of the electrical field must be oriented in accordance with the polarity of the charge on the particle. Furthermore, if a group of powder particles are given a triboelectric charge, the particles so charged tend to agglomerate at the image screen apertures resulting in a blocking of same. Moreover, the charged particles tend to adhere electrostatically when in immediate contact with other particles or surfaces.

Prior art teachings are available for rendering inherently non-electroconductive powder particles conductive. For example, various fillers have been added to the decorative powder particles to make them semiconductive. Typical of the fillers employed for this purpose are carbon black, silver and gold, all of which seriously limit the possible color range and shades of colors which can be obtained.

In addition, non-electroconductive particles have been rendered electroconductive by other methods including by way of example the treatment of the particles with selected organic compounds.

However, it has been found that such electroconductive particles are of limited use in some electric field processes particularly of the types described hereinbefore. For example, in the practice of such electric field process(es) the particles are charged at a first surface and repelled therefrom by means of the electric field. After passing through the image screen or stencil, the charged particles are attracted to the decorable surface (or an intermediate surface) which is charged opposite to the particle by means of an electric field. After the charged particle has contacted such surface, there is a tendency for the particle to acquire the same charge as this surface and consequently be repelled away from it. This repelling at the second surface results in a noticeable powder transfer loss.

In accordance with the practice of this invention, there is provided a novel photoconductive organic powder composition for use in a novel electric field decorating process whereby the aforementioned problems of the prior art are substantially eliminated.

More particularly, in accordance with this invention, there is provided solid particles of an organic composition containing effective amounts of a photoconductive material, the particles being electrically charged by an electric field and simultaneous illumination with appropriate electromagnetic radiation at a first charged surface and attracted to an oppositely charged second surface which is substantially free of electromagnetic radiation.

Electromagnetic radiation as used herein is defined as any appropriate radiation, visible or invisible, which will cause the photoconductive containing particles to become conductive so as to acquire an electric charge in an electric field. Such radiation includes not by way of limitation visible light, infra-red, ultra-violet, X-rays, gamma rays, and beta rays.

In the preparation of the photoconductive organic particles, an effective amount of at least one selected photoconductive material is suitably incorporated with an organic resin-based or resin-containing decorative composition.

The composition is preferably prepared from a resin having a melting range of about 100 to 200° C., sufficient brittleness to grind to less than 20 microns in average particle size, and a reasonable permanency of adhesion to the decorable surface.

In one embodiment of this invention it is particularly contemplated using resin(s) which have reasonable permanency of adhesion to a glass or paper surface. Glass surface as used herein also includes glass surfaces which have been appropriately treated so as to increase the permanency of adhesion of specific resin(s) compositions thereto, e.g. such as organopolysiloxane resin-based glass decorative compositions as disclosed in copending U.S. patent application Ser. No. 578,137, filed Sept. 9, 1966 by Robert H. Kiel (Owens-Illinois File K–8974).

The resins and polymers suitable for use in the preparation of the decorative composition include commercially available resins such as polyvinyl chloride, polyacrylates, polyvinylidene chloride, polyethylene, polystyrene, copolymer vinyl acetate with ethylene, melamine formaldehyde resins, organopolysiloxane resins, aldehyde resins, ketone resins, and the polyamide-type resins. In addition

it is contemplated that other resins, non-commercial or commercial, may be used.

It is especially suitable to use polyamide resin(s) in the practice of this invention. Polyamide type resins are generally thought of as condensation products which contain recurring amide groups. Such resins may be formed by means well known in the art, for example by the condensation of diamines with diacids.

Examples of polyamides contemplated in the practice of this invention include not by way of limitation the condensation products of ethylenediamine and sebacic acid, propylenediamine and sebacic acid, tetramethylenediamine and adipic acid, tetramethylenediamine and suberic acid, pentamethylenediamine and malonic acid, pentamethylenediamine and octadecanedioic acid, hexamethylenediamine and adipic acid, octamethylenediamine and sebacic acid, decamethylenediamine and oxalic acid and the like.

Commercially available polyamide resins suitable in the practice of this invention include not by way of limitation polyamide resin Scope 30, which is the resinous derivative of diphenolic acid characterized by a softening temperature of 98° C. to 102° C., and acid value of 3.75 maximum, an amine value of 8.50 maximum, and a specific gravity of 0.99; the thermoplastic resins known commercially as Versalon, for example Versalon 1112 as characterized by a softening temperature of 105° C. to 115° C., a tensile strength of 1900 to 2100 pounds per square inch at 75° F., and a specific gravity of 0.955; and the commercially available polyamide resins known as Polymid 1144 characterized by an acid value of 3.4, an amine value of 4.8, a melting temperature of 99° C. to 104° C., and a specific gravity of 0.99; the polyamide resin Polymid 1155 with an acid value of 5, an amine number of 5, and a specific gravity of 0.98; the polyamide resin Polymid 1060 with an acid value of 4.0, an amine value of 1 to 2, a melting temperature of 112° C. to 113° C., and a specific gravity of 0.97; and the polyamide resin known commercially as Polymid 1074, characterized by an acid value of less than 6, an amine value of less than 6, a melting tempeatrure of 102° C. to 108° C., and a specific gravity of 0.98. Also, other polyamide thermoplastic resins may be used such as Versamid 900 with an amine value of 4, a specific gravity of 0.98, and a softening temperature of 180 to 190° C., and Versamid 950 with an amine value of 4, a specific gravity of 0.98, and a softening temperature of 90 to 100° C.

Scope is a registered trademark for resinous derivatives of diphenolic acid available from S. C. Johnson and Son, Inc., Racine, Wis. Technical bulletins are available which contain additional technical information including physical and chemical properties of the Scope resins and general procedures for preparation. Such bulletins include Technical Bulletins CD–20, Revision 2, issued June 1964, and CD–43, issued April 1963 by the Chemical Division of S. C. Johnson and Son, Inc.

Versalon is a registered trademark for polyamide resins available from General Mills, Inc., Chemical Division, Kankakee, Ill. Technical bulletins published by such company include CDS 4–63 and CDS 5–63, each having an effective date of Nov. 1, 1963, and such being revised on Feb. 1, 1965.

Versamid is a registered trademark for polyamide resins also available from General Mills, Inc., Kankakee, Ill. Technical bulletins published by such company include Versamid Specification Sheet 11, June 1, 1962.

For additional technical information on the General Mills polyamide resins, reference is made to U.S. Letters Patent 3,224,893, which is incorporated herein by reference.

Generally, the polyamide resins used herein will have an acid value of about 3 to 5, an amine value of about 1 to 8.5, and a specific gravity of about 0.92 to 0.99.

The polyamide based particles to be treated in accordance with this invention are generally prepared by intimately mixing the selected polyamide resin(s) with at least one inorganic and/or organic pigment(s).

The inorganic and organic pigments contemplated in the practice of this invention may be white or colored.

Typical inorganic pigments include (not by way of limitation) barium sulfate, white lead, calcium carbonate, chrome green, iron blues, lithopones, and oxides of metals or metalloids such as titanium, silicon, aluminum, lead, zirconium and chromium.

When the selected pigment is a metal oxide, it is especially desirable for it to be prepared by a vapor phase decomposition technique such as the vapor phase decomposition of a titanium halide in the presence of an oxidizing or hydrolyzing agent to produce titanium oxide, e.g. TiO_2. Rutile TiO_2 as distinguished from anatase is particularly suitable.

Organic pigments contemplated herein may be chemically classified as nitro, azo, diazo, nitroso, isonitroso, oxyketone, ketonimides, hydrazides, triphenylamines, azins, quinolines, acridine, indanthrene, and phthalocyanine colors. Examples of pigments include not by way of limitation anthosine, benzidine, yellow, eosine, rose bengal, Hansa yellow, lithol red, methyl red, and peacock blue.

The selected resin(s) and pigment(s) may be suitably mixed by stirring, blending, and/or melting together, and hot milling at a suitable temperature. The milled composition is cooled, usually to room temperature, and the resulting cooled mass is dry ground or pulverized to subsieve sizes, usually about 2 to 20 microns.

The resin-based powder particles may also be prepared by blending a selected resin(s) and pigment(s) on a hot mill and cooling the blend to a solidified, hardened mass. The mass is then mixed with an appropriate solvent compatible with the resin and the resulting mixture spray-dried to form finely-divided discrete powder particles.

Additional methods and details for preparing decorative particles consisting essentially of polyamide-based resin(s) in the absence or presence of pigment(s) are disclosed in copending U.S. Patent application Ser. No. 551,210, filed May 19, 1966 by Robert F. Rywalski and Ralph E. Trease now abandoned.

The selected photoconductive material may be incorporated with the decorative composition by any convenient dry and/or wet procedure including dry or wet blending. In addition such material may be added during the preparation of the composition, e.g. during the hot milling of the resin and pigment providing the milling temperature is below the decomposition or degradation temperature of the photoconductive material.

The photoconductive material is incorporated with the decorative composition in an amount sufficient to provide the dry, solid particles with an electroresistivity of about 10^{12} to 10^5 ohms-centimeter.

Typically the photoconductive material is added to the composition in an amount sufficient to provide about 5 to 75 percent by weight photoconductive material in the resulting dry solid particles, based on the total weight of the particles after the incorporation of the photoconductive material.

Photoconductive materials contemplated herein include both organic and inorganic materials.

Typical inorganic materials include zinc sulfide, cadmium sulfide, zinc selenide, cadmium selenide, zinc oxide, cadmium oxide, selenium, tellurium, alkaline earth halides including mixtures of same especially mixture of selenium with tellurium, zinc-cadmium selenides, and zinc-cadmium sulfides.

Additional photoconductive materials contemplated herein include organic polymers especially polymers with aromatic or heterocyclic chain units such as poly-N-vinylcarbazole, polyindene, poly - 4 - vinylbiphenyl, poly - 9-vinylanthracene, poly - 3 - vinylpyrene, poly - 2 - vinylquinoline, polyacenaphthylene, poly - 2 - vinylnaphthalene, polystyrene, polyvinylxylene, poly - 1 - vinylnaphthalene,

poly(3,3'-dimethyldiphenylene-4,4'), and various aromatic and heteroaromatic derivatives of polyacrylamide and polymethacrylamide.

Likewise, other organic photoconductive compounds containing aromatic or heterocyclic chain units may be used such as naphthalene, biphenyl, anthracene, phenanthrene, acenaphthene, acenaphthylene, chrysene, pyrene, 1,4-dimethoxybenzene, diphenylamine, 2,2'-dinaphthylamine, 2-phenylindole, carbazole, phenothiazine, 1,5-diethoxynaphthalene, 2,4 - bis (4'-diethylaminophenyl)-1,3,4 - triazole, 2,4-bis (4'-diethylaminophenyl)-1,3,4-oxidiazole, 1,5-dinitronaphthalene, phthalic anhydride, p-chloranil, 1,8-dinitronaphthalene, 1,5 - dichloronaphthalene, benzil, 1,4 - dibromonaphthalene, 9-acetylanthracene, pyrene - 3 - aldehyde, 1,2-benzoanthraquinone, and 2,4,5,7-tetranitrofluorenone.

It is further contemplated that effective amounts of suitable dopants or activators may be used as required to photosensitize or activate the selected organic or inorganic material or to increase the photosensitivity thereof.

Suitable activators especially for the inorganic compounds include gold, silver, or copper.

Suitable dopants include not by way of limitation nitro compounds, cyano compounds, acids, carboxylic acid anhydrides, esters, halogen compounds, quinones, keto compounds, and aza compounds such as 1,3,5-trinitrobenzene, anthraquinone, 9,10-dichloroanthracene, 2,2'-dinaphthylamine, 2,4,7-trinitrofluorenone, picryl chloride, 3,5-dinitrosalicylic anhydride, 2,3,5 - triphenylpyrole, N-ethylcarbazole, hexamethylbenzene, dibenzofuran, tetracyanoethylene, dibromomaleic anhydride, hydrochloric acid, acetone dicarboxylic acid, cyanoacetic acid, chrysene-2,3, acetone dicarboxylic acid, tetraethyl ester, phthalic acid diesters, chloranil, bromanil, xanthone, benzil, and benzoin.

For additional photoconductive organic compounds and dopants, reference is made to pages 755 to 766, The Journal of Physical Chemistry, vol. 69, No. 3, March 1965, which is incorporated herein.

The selected photoconducting material (with or without dopants or activators) must be compatible with the organic decorating composition. Although it is preferred to select a photoconductor which is capable of being fused to the decorable surface, such is not necessary providing the photoconductor does not otherwise hinder the fusion of the resin-based decorating composition to such surface.

The selected photoconductor may perform a dual function depending upon the characteristics thereof. Thus selected inorganic photoconductors may be used as the pigment in the basic decorative composition.

Likewise, selected organic polymer photoconductors may be used in lieu of the base resin in the decorative composition providing the polymer has sufficient film forming characteristics, e.g. on the particular surface to be decorated.

In the specific practice of this invention, there is provided an electric potential between the first charged surface (upon which the photoconductor-containing powder particles are placed) and the printing stencil (or screen) with a separate potential between the stencil and the second charged surface (decorable or intermediate). Typically this is accomplished by connecting the stencil to ground.

If the second surface is intermediate and the powder particles are to be transferred therefrom to a decorable surface, there may be provided a third electric field potential between such intermediate and decorable surfaces.

In any event, the electric field potential between any two transfer points, e.g. first surface and stencil, stencil and second surface, or intermediate and decorable surfaces, must be sufficient to efficiently transfer the charged photoconductor-containing powder particles, e.g. at least about 20,000 volts per linear inch of separation between the two electrodes.

The particles may be supplied to the first charged electrode surface by any convenient method, batch or continuous.

Although the photoconductor-containing particles may be illuminated at the first electrode surface by any suitable electromagnetic radiation, the particles are most conveniently illuminated with light in the visible range. In any event, the illumination should be relatively uniform; that is, a large portion of the particles should be flooded with the radiation while in contact with the charged surface. However, the decorable or intermediate surface is shielded by any convenient means so as to prevent or substantially eliminate radiation from illuminating the particles, e.g. ambient light in the ordinary visible range.

Additional details for establishing and operating an electric field decorating process are set forth in the disclosure of U.S. patent application Ser. No. 393,817, filed Aug. 31, 1964, now U.S. Pat. No. 3,402,659 and U.S. patent application Ser. No. 434,819, filed Feb. 24, 1965, now U.S. Pat. No. 3,460,468, by William E. Johnson, which disclosures are incorporated herein by reference.

The hereinafter example illustrate one of the best modes contemplated by the inventors in the practice of this invention.

EXAMPLE

Polyamide-based powder particles are prepared by intimately mixing 50 grams of rutile TiO_2, 25 grams of Scope 30, 24.5 grams of Versalon 1112, and 0.5 grams of paraffin wax, and hot milling the mixture on a three roller mill at about 300° F. The sample is then cooled and pulverized to a fine powder (minus 200 mesh).

The resistivity of the sample is found to be about 10^{12} ohm-centimeter using a Keithly Electrometer technique. The activity of the sample is tested using a parallel plate test and found to be zero; that is, the sample particles are completely inactive.

In the Keithly Electrometer technique contemplated herein, the powder to be measured is poured into a cylindrical glass container of electrical insulating composition to form an unpacked cylindrical body of known cross-sectional area and axial length. The unpacked powder is then compressed by reducing its axial length by a known amount and the electrical resistance of the packed cylindrical powder body is then measured by applying an electrical potential across its axial length. In this example the measurements are made by means of a Keithly Electrometer Model 610A.

The parallel plate test consists essentially of two parallel conductive surfaces generally separated by about a one-fourth inch air gap. A potential is applied across the plates forming an electrical field. When a powder is placed in this field, the powder is attracted to the plate possessing the opposite polarity. At this latter plate the charge of the particle is reversed and the particle then moves toward the original plate. This parallel plate test indicates activity in an electrical field..

A sixty (60) gram sample of the prepared polyamide-based powder is ball milled for thirty (30) minutes with sixty (60) grams of a photoconductor (ortho chloranil).

The resulting photoconductor-containing powder is found to have a resistivity of at least 10^{11} ohm-centimeter when flooded with visible light with substantial increase in parallel plate activity.

The powder is placed on the electrically charged surface of a first flat plate electrode positioned about one-eighth (⅛) of an inch from a printing stencil. The stencil is connected to ground. The potential between the first plate and the stencil is 3000 volts.

The powder is uniformly radiated with visible light such that the powder becomes conductive and acquires the charge of the first surface.

The charged powder is propelled from the first surface through the stencil and onto the surface of a corrugated paper structure charged opposite to that of the powder. The potential between the surface of the corru-

gated surface and the stencil is 3000 volts. The linear distance between the stencil and corrugated structure is about one-eighth (⅛) of an inch. The corrugated surface is shielded to substantially eliminate visible light and other electromagnetic radiation from the powder.

The corrugated structure is heated to about 150° C. for about one to two minutes for fusing of the powder to the surface.

Alhough this invention has been illustrated with specific embodiments and details, it will be apparent to those skilled in the art that obvious modifications can be made within the scope and spirit of this invention.

We claim:

1. An electrostatic image forming process which comprises establishing a first electric potential between a first charged surface and an image-defining stencil, and a second electric potential between the stencil and a second surface charged opposite to said first surface, providing photoconductor-containing, organic resin based, decorative particles in contact with the first charged surface, substantially uniformly illuminating said particles on said first charged surface with electromagnetic radiation, shielding said second oppositely charged surface such that said surface is maintained substantially free of electromagnetic radiation throughout said process, electrostatically propelling the resulting charged particles through the image defining area of said stencil and into contact with said second shielded oppositely charged surface to thereby form an image on said second surface.

2. The process of claim **1** which includes the further step of establishing an electric potential between said second surface and an oppositely charged third decorable surface and electrostatically transferring said particles from said second surface to said third surface.

3. The process of claim **1** wherein said organic resin is a polyamide.

4. The process of claim **1** wherein the potential for each surface is at least 20,000 volts per linear inch of separation between the respective surface and the stencil.

5. The process according to claim **1** wherein said particles are polyamide-resin based and contain 5 to 75 percent by weight photoconductor, based on the total weight of the particles and said photoconductor is selected from the group consisting of: poly-N-vinylcarbazole, polyindene, poly-4-vinylbiphenyl, poly-9-vinylanthracene, poly-3-vinylpyrene, poly-2-vinylquinoline, polyacenaphthylene, poly-2 - vinylnaphthalene, polystyrene, polyvinylxylene, poly-1-vinylnaphthalene, poly(3,3'-dimethyldiphenylene-4,4'), aromatic and heteroaromatic derivatives of polyacrylamide and polymethylacrylamide, naphthalene, biphenyl, phenanthrene, acenaphthene, acenaphthylene, chrysene, pyrene, 1,4-dimethoxybenzene, diphenylamine, 2,2' - dinaphthylamine, 2-phenylindole, carbazole, phenothiazine, 1,5-diethoxynaphthalene, 2,4-bis(4'diethylaminophenyl)-1,3,4 - triazole, 2,4 - bis(4'-diethylaminophenyl)-1,3,4-oxidiazole, 1,5-dinitronaphthalene, phthalic anhydride, p-chloranil, 1,8-dinitronaphthalene, 1,5 - dichloronaphthalene, benzil, 1,4-dibromonaphthalene, 9-acetylanthracene, pyrene-3-aldehyde, 1,2-benzoanthraquinone, and 2,4,5,7-tetranitrofluorenone.

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