

1

3,840,464

ELECTROSTATIC GLASS BEAD CARRIER MATERIAL

Jozef Leonard Van Engeland, St. Katelijne-Waver, Noel Jozef De Volder, Edegem, and Daniel Maurice Timmerman, Mortsels, Belgium, assignors to Agfa-Gevaert N.V., Mortsels, Belgium

No Drawing. Continuation-in-part of application Ser. No. 162,303, July 13, 1971. This application Dec. 29, 1971, Ser. No. 213,806

Claims priority, application Great Britain, Dec. 30, 1970, 61,855/70

Int. Cl. G03g 9/00

U.S. Cl. 252—62.1

7 Claims

ABSTRACT OF THE DISCLOSURE

A process is described for the manufacture of an improved electrostatic carrier material. Glass beads are treated with a solution of a trialkoxysilane or of an organic phosphor compound and the thus treated glass beads are enveloped with a layer of a polymer containing reactive hydrogen atoms, e.g. ethyl cellulose. For developing a latent electrostatic photographic image, the thus enveloped glass beads are mixed with a toner material and the mixture applied to a latent electrostatic image where the toner particles are attracted electrostatically.

The invention relates to the manufacture of an electrostatic carrier material, to the electrostatic carrier material thus obtained and to an electrostatic developer containing this carrier material, and is a continuation-in-part of application Ser. No. 162,303 filed July 13, 1971.

It is known to convert latent electrostatic images into visible images by means of a toner consisting of minute particles of a material, usually being a resin which mostly is coloured and which has specific triboelectric properties. Depending on the sign of the electrostatic charge the resin particles are either attracted and deposited on the charged areas of the latent image, or are repelled by the charged areas and deposited on the discharged places. Such an operation is called development of the latent electrostatic image. The latent image itself can be formed according to known techniques, e.g. by exposure of a uniformly electrostatically charged photoconducting surface containing zinc oxide, selenium, or an organic photoconductor as photoconductor.

For the development of the electrostatic images the toner is applied loosely to the latent electrostatic image where it is attracted electrostatically at the latent image areas. The most usual developing method is cascade development. According to this method the electrostatic toner is mixed with a granular carrier material, which may be electrically conductive or insulating, and which has particle diameters of about 0.3 to 1.5 mm. The granular carrier material is composed of glass or steel beads, either or not encased in a suitable envelope, which imparts the necessary triboelectric properties to the granular carrier material. Normally 1 part by weight of toner powder is mixed with about 100 parts by weight of granular carrier material.

The carrier particles, when brought in close contact with the powdery toner particles, obtain by frictional electrification a charge of a polarity opposed to that of the toner particles, so that the latter envelop the carrier particles. If a positive reproduction of an electrostatic image is desired, the carrier is chosen in such a way that the toner particles obtain a charge with a polarity opposite to that of the electrostatic charge. In order to obtain a negative copy the carrier can be chosen in such a way that the toner particles obtain a charge having the same polarity as that of the electrostatic image.

2

The carrier particles have to be large enough, larger anyway than the toner particles. They have such a shape, that they roll over the image-carrying surface. Preferably glass beads are used having a diameter of 0.6 to 0.8 mm. The toner particles are attracted by the charged areas of the surface and separated from the carrier particles, which in consequence of gravity continue their rolling motion.

Although simple glass beads may be used as electrostatic carrier material for the toner particles, the glass beads may be subjected to special pretreatments in order to improve the action of the carrier particles, especially at high relative humidities, e.g. at relative humidities of 65% or more.

If covered glass beads are used the covering layer thereof should have several properties. For instance, it should have a smooth surface, a high tensile strength, stable friction properties, a strong adhesion to the glass beads and a good solubility in common solvents.

According to the invention a process is provided for the manufacture of an improved electrostatic carrier material, which process comprises treating the glass beads with a solution of a trialkoxysilane or of an organic phosphor compound and enveloping the thus treated glass beads with a layer of a polymer containing reactive hydrogen atoms.

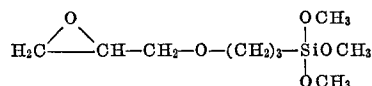
Before pretreatment of the glass beads according to the invention their surface is preferably degreased and cleaned e.g. with chromic acid. A great many methods can be used for chemically cleaning glass surfaces and in this connection there can be referred to L. Holland, "The Properties of Glass Surfaces," Chapman & Hall, London, 1964, Chapter 5, p. 290-347

After having been cleaned the glass beads are treated with a solution of a trialkoxysilane or of an organic phosphor compound.

If in the present description there is mention of treating the glass beads with a solution of a trialkoxysilane or of an organic phosphor compound, the invention is neither restricted by the fact that in this treatment a real layer of trialkoxysilane or of organic phosphor compound would be formed around the glass beads, nor that this treatment only would result in an activation of the glass surface, so that a better binding with the polymer layer applied thereto is brought about.

The treatment of the glass beads with trialkoxysilane or with an organic phosphor compound can be accomplished by merely rolling the beads in a solution of these compounds and then allowing the solvent to evaporate, or by treating the glass beads with the solution in a fluidized bed reactor either or not with heating of the mixture, or by exposing the glass beads, while in contact with the treating liquid, to a strong vibration. The treated pearls can be isolated from the treating bath i.e. by evaporation, by sieving, by centrifugation or according to other known techniques.

Suitable trialkoxysilanes are those described in our Belgian Patent Specification 741,820. Preferably a trialkoxysilane is used, which corresponds to the following structural formula:



In this case cyclohexane is suitable as the solvent for the trialkoxysilane.

The degreased and cleaned glass beads can be treated with a solution of an organic phosphor compound instead of a trialkoxysilane. Very interesting phosphor compounds are those described in United Kingdom Patent Specification 1,151,141, which are bivalent or trivalent metal salts

3

of a phosphorus oxyacid containing at least one organic group. Most preferred is zinc tridecyl phosphate.

The dried glass beads are then enveloped with a layer of a polymer comprising reactive hydrogen atoms. Suitable compounds for the covering layer are natural resins, thermoplastic resins and partially hardened thermosetting resins. Examples of natural resins are rubber, colophony and damar. These natural resins can also be modified as is the case in cellulose nitrate and ethyl cellulose. Examples of thermoplastic resins are polyethylene, polypropylene, polyvinyl resins such as polystyrene and copolymers of styrene, polyacrylate- and polymethacrylate esters, polyvinyl esters such as polyvinyl acetate, polyvinyl butyral, polyvinyl carbazole, polyvinyl ethers, polyamides, polyesters, polyurethanes, polycarbonates and mixtures thereof. Examples of thermosetting resins are phenol resins, amino resins, unsaturated polyester resins, epoxy resins and mixtures thereof.

The choice of the polymer depends, of course, on the triboelectrical properties desired in respect of the toner material used.

Further it is desirable that the polymers have satisfactory mechanical properties so that they can be processed in the electrophotographic apparatuses at a temperature that may be as high as 50° C. In order to obtain a good adhesion to the pretreated glass beads polymers are used preferably, which contain reactive hydrogen atoms. Especially suitable polymers are ethyl-cellulose, polystyrene, copolymers of styrene and n-butyl methacrylate, polyvinyl butyral, unsaturated polyesters and epoxy resins.

The enveloping with a polymer can be performed by rolling the beads in a solution of the polymer or by treating them with a solution of the polymer in a fluidised bed reactor.

All other methods known for treating the beads can be applied here too. Moreover, when a thermoplastic polymer is used the treated beads can be rolled in a melt of the polymer until a layer of polymer has deposited around the beads.

In certain conditions it may be advantageous to add a dye or pigment to the solution of the polymer, in order to realize in the electrostatic development a correct triboelectric adjustment in respect of the toner material.

As a result of the pretreatment with trialkoxysilane or with an organic phosphor compound, the polymer coating adheres very strongly to the glass beads. Moreover, even after thousands of copies the toner powder still adheres very well to the carrier beads. The treatment also reduces the fog in the toner image during continuous use.

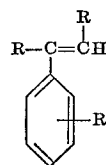
According to an alternative embodiment of the invention the glass beads can also be treated with a solution in which trialkoxysilane or organic phosphor compound are present together with the polymer.

For developing a latent electrostatic photographic image the glass beads, pretreated according to the process of the invention, are mixed with a known toner material, the finely divided particles of which are applied electrostatically to the carrier particles by frictional electrification. Suitable toner materials are described in the United Kingdom Patent Specifications 679,715, 686,466, 768,293, 893,332, 1,029,182, 1,179,095, and 1,210,665 and in the United States Patent Specifications 2,891,011, 2,892,794, 2,917,460, and 3,079,342 and in the United States Patent Reissue 25,136. A very suitable toner material is described in our United Kingdom Patent Application 61,855/70.

This toner material incorporates particles having a diameter between 1 and 30 microns of an intimate mixture of colouring material and of a mixture of resins (A), (B), and (C), wherein the proportion by weight of colouring material with respect to the resin mixture is not less than 5:95 and not more than 15:85 and wherein the resin mixture incorporates the following resins (A), (B), and (C) in proportions by weight of 40-60, 20-40, and 5-20

4

spectively, based on the aggregate weight of (A), (B), and (C), resin (A) being a polymer or copolymer comprising recurring units deriving from at least one styrene according to the formula:



wherein: R is hydrogen or methyl,

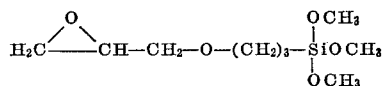
resin (B) being a polymer taken from the group consisting of homopolymers of butyl acrylate or methacrylate and copolymers of butyl acrylate or methacrylate with methyl acrylate or methacrylate containing up to 80% by weight of methyl acrylate or methacrylate, and resin (C) being a polymeric thermoplastic plasticizer selected from polyvinyl butyral, polyethylene, and co(vinyl acetate/ethylene).

In some cases the toner may include other materials than the colouring material and the mixture of resins as defined hereinbefore e.g. cleaning agents, ingredients modifying the free-flowing characteristics of the toner powder, anti-oxidants, and the like.

The following examples will serve to illustrate our invention.

EXAMPLE 1

Glass beads having a diameter of 0.6 to 0.8 mm. were degreased by treating them with chromic acid. After having been washed with distilled water until free of acid, the beads were dried with air at approximately 90° C. Subsequently they were rolled into a solution in cyclohexane of a trialkoxysilane according to the following structural formula:



A 1 vol. percent solution of the trialkoxysilane in cyclohexane was made and about 25 ml. of this solution was used per kg. of glass beads.

The beads were then dried in a hot air current of approximately 80° C. and rolled into a solution in tetrachloroethane of an azo dye and ethyl cellulose. Zapon fast yellow R (C.I. 18,690) sold by Badische Anilin- und Soda-Fabrik, Ludwigshafen/Rh., W. Germany, was used as azo dye. 1 kg. of glass beads, 0.5 g. of dye, 1 g. of ethylcellulose, and 25 ml. of solvent were used in the above treatment.

After approximately 30 min. of rolling in the solution the glass beads were dried in a hot air stream of about 80° C.

As a result of the pretreatment with the trialkoxysilane, the ethyl cellulose adhered very strongly to the glass beads.

To develop a latent electrostatic image, 100 g. of the thus treated glass beads were mixed with 1 g. of the toner material of the above mentioned United Kingdom Patent Application 61,855/70. The toner mixture was composed of:

5.2 parts by weight of resin A
2.8 parts by weight of resin B
1 part by weight of resin C
1 part by weight of carbon black.

Resin A was co(styrene/ α -methyl styrene/isobutyl methacrylate) (50:5:45% by weight), resin B was co(methyl methacrylate/n-butyl methacrylate) (39.61% by weight), resin C was polyvinyl butyral containing 20% by weight of vinyl alcohol groups and 2.5% by weight of vinyl acetate groups, and the carbon black was Spezial-

5

schwarz IV sold by Deutsche Gold- und Silberscheideanstalt, Frankfurt/M., W. Germany.

After positive charging of a selenium drum and image-wise exposure to an original, the developing mixture of glass beads and toner material was cascaded over the latent electrostatic image. The powder image formed was then transferred to a paper support and fixed on this paper by heating.

After repeated use (approximately 15,000 copies) the adhesion of the toner material to the carrier particles was still good. The pretreatment of the glass beads with trialkoxysilane and ethyl-cellulose also reduced the fog in the toner images during continuous use. Moreover, the activity of the carrier particles at high relative humidities of 65% or more, had improved markedly.

EXAMPLE 2

The process of Example 1 was repeated with the difference that the ethylcellulose was replaced by a same amount of polystyrene and that methylene chloride was used as solvent.

As a result of the pretreatment with trialkoxysilane, the polystyrene coating adhered very strongly to the glass beads.

The same good results as in Example 1 were obtained when the thus treated glass beads were used together with the toner material described therein to develop a latent electrostatic image.

EXAMPLE 3

The process of Example 1 was repeated with the difference that the ethylcellulose was replaced by a same amount of polyvinyl butyral containing approximately 20% by weight of vinyl alcohol units and 2.5% by weight of vinyl acetate units, using methylene chloride as solvent.

As a result of the pretreatment with trialkoxysilane the polyvinyl butyral coating adhered strongly to the glass beads.

The same good results as in Example 1 were obtained when the thus treated glass beads were used together with the toner material described therein to develop a latent electrostatic image.

EXAMPLE 4

The process of Example 1 was repeated with the difference that after treatment of the glass beads with the trialkoxysilane and after drying in a hot air current of approximately 80° C., they were rolled in a solution, in acetone of Calco Oil Black and cellulose nitrate.

Calco Oil Black is the trade name of carbon black powder sold by Pylam Products Co., U.S.A.

The solution in acetone was prepared in the following way. 250 mg. of Calco Oil Black was dissolved in 50 ml. of acetone. The resulting solution was filtered. In a second flask 3 g. of cellulose nitrate were dissolved in 5 ml. of acetone and the carbon black solution was added thereto.

After approximately 30 min. of rolling in the solution the glass beads were dried in a hot air stream of about 80° C.

As a result of the pretreatment with trialkoxysilane the cellulose nitrate coating adhered strongly to the glass beads.

The same good results as in Example 1 were obtained when the thus treated glass beads were used together with the toner material described therein to develop a latent electrostatic image.

EXAMPLE 5

Glass beads having a diameter of 600-800 microns were degreased by treating them with chromic acid, and washed with distilled water until free of acid. Thereafter the beads were dried with air at approximately 90° C. Subsequently, the glass beads were rolled into a solution of zinc tridecylphosphate in diethyl ether. For 1 kg. of

6

glass beads 25 ml. of a 5% by weight solution of zinc tridecylphosphate in diethyl ether was used.

The glass beads were dried in air of approximately 80° C. and rolled for 30 min. in a ball-mill containing the following mixture:

Azo dye	-----g--	0.5
Ethyl cellulose	-----g--	1
Methylene chloride	-----ml--	22.5
1,2-dichloroethane	-----ml--	2.5

After drying in air of 80° C. glass beads were obtained, which were surrounded by a layer of ethyl cellulose and an azo dye.

100 g. of glass beads thus pretreated were mixed with 0.5 g. of toner mixture as described in Example 2 of our United Kingdom Patent Application 61,855/70 and used as a xerographic developer. The images formed after transfer to a paper support and thermofixation had an excellent quality, even after the production of more than 10,000 copies. Even then the adhesion of the ethyl cellulose layer to the glass beads was still excellent.

EXAMPLE 6

100 g. of glass beads pretreated as in Example 5 were mixed with 0.5 g. of a toner sold by the Nashua Corporation (Office Copy Division, Nashua, N.H., U.S.A.).

The images formed after transfer to a paper support and thermofixation had a good quality, even after the production of more than 10,000 copies. Even then the adhesion of the ethyl cellulose layer to the glass beads was still excellent.

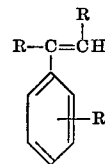
We claim:

1. Electrostatic carrier material consisting of glass beads contacted with a solution of a trialkoxysilane or of an organic phosphor compound which is a bivalent or trivalent metal salt of a phosphorus oxyacid containing at least one organic group, and coated with a continuous layer of polymer containing reactive hydrogen atoms.

2. A process of electrophotography wherein an electrostatic latent image is developed by means of a developer mixture incorporating a toner material and an electrostatic carrier material according to claim 1.

3. A process according to claim 2, wherein the said toner material is a mixture of particles having a diameter between 1 and 30 microns of an intimate mixture of colouring material and of a mixture of resins (A), (B) and (C), wherein the proportion by weight of colouring material in respect of the resin mixture is not less than 5:95 and not more than 15:85 and wherein the resin mixture incorporates the following resins (A), (B), and (C) in proportions by weight of 40-60, 20-40, and 5-20 respectively, based on the aggregate weight of (A), (B) and (C),

resin (A) being a polymer comprising recurring units deriving from at least one styrene according to the formula:



wherein R is hydrogen or methyl, resin (B) being a copolymer of 10 to 40% by weight of methyl methacrylate and 90 to 60% by weight of butyl methacrylate, and

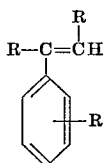
resin (C) being a polymer plasticizer selected from polyvinyl butyral, polyethylene, and co(vinyl acetate/ethylene).

4. A process according to claim 2, wherein the said toner material is a mixture of particles having a diameter between 1 and 30 microns of an intimate mixture of colouring material and of a mixture of resins (A), (B), and (C), wherein the proportion by weight of colouring

7

material in respect of the resin mixture is not less than 5:95 and not more than 15:85 and wherein the resin mixture incorporates the following resins (A), (B), and (C) in proportions by weight of 40-60, 20-40, and 5-20 respectively, based on the aggregate weight of (A), (B), and (C),

resin (A) being a polymer comprising recurring units deriving from at least one styrene according to the formula:



wherein R is hydrogen or methyl,

resin (B) being a polymer taken from the group consisting of homopolymers of butyl acrylate or methacrylate and copolymers of butyl acrylate or methacrylate with methyl acrylate or methacrylate containing up to 80% by weight of methyl acrylate or methacrylate, said resin (B), however, excluding copolymers of 10 to 40% by weight of methyl methacrylate and 90 to 60% by weight of butyl methacrylate, and

resin (C) being a polymer plasticizer selected from polyvinyl butyral, polyethylene, and co(vinyl acetate/ethylene).

5. A process according to claim 3 wherein the said toner material is formed from a mixture of 5.2 parts by weight of co(styrene/ α -methyl styrene/isobutyl meth-

8

acrylate) (50:5:45% by weight), 2.8 parts by weight of co(methyl methacrylate/n-butyl methacrylate) (39:61% by weight), 1 part by weight of polyvinyl butyral containing 20% by weight of vinyl alcohol groups and 2.5% by weight of vinyl acetate groups, and 1 part by weight of carbon black.

6. A carrier material according to claim 1 wherein said trialkoxysilane has a terminal epoxy group.

7. The carrier material according to claim 1 wherein the organic group of said phosphorus oxyacid salt is a long-chain saturated hydrocarbon group.

References Cited

UNITED STATES PATENTS

15	3,507,686	4/1970	Hagenbach	117—100 S
	2,618,551	11/1952	Walkup	252—62.1
	3,391,082	7/1968	Maclay	252—62.1
	3,526,533	9/1970	Jacknow et al.	117—100 B
	3,110,614	11/1963	De Vries	117—100 S
20	3,259,518	7/1966	Sterman	117—100 S

FOREIGN PATENTS

1,174,571 12/1969 England.

25 RONALD H. SMITH, Primary Examiner
J. L. GOODROW, Assistant Examiner

U.S. Cl. X.R.

30 96—1 LY; 117—17.5, 100