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[54] ELECTROSTATOGRAPHIC DEVELOPER CONTAINING UNCOATED GLASS-CERAMIC CARRIER PARTICLES

[75] Inventor: **Robert D. Fenity, deceased,** Webster, N.Y. by Nancy Fenity, executrix

[73] Assignee: **Xerox Corporation,** Stamford, Conn.

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[58] **Field of Search** 252/62.1

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Primary Examiner—George F. Lesmes
Assistant Examiner—J. P. Brammer
Attorney—James J. Ralabate, Albert A. Mahassel, Peter H. Kondo and Marn & Jangarathis

[57] **ABSTRACT**

Electrostatographic developer comprised of a toner and an uncoated carrier wherein the carrier comprises a crystalline phase dispersed in a glass matrix, and the crystalline phase is a Group IV metal oxide or a double oxide of tin, hafnium, germanium, zirconium or titanium and an alkaline earth metal or lead or cadmium. These carriers have the desirable properties generally associated with the coated carriers heretofore employed in the art, but unlike the coated carriers, are not prone to degradation and impactation and therefore have a longer useful life.

13 Claims, No Drawings

ELECTROSTATOGRAPHIC DEVELOPER CONTAINING UNCOATED GLASS-CERAMIC CARRIER PARTICLES

BACKGROUND OF THE INVENTION

This invention relates to electrostatography and more particularly to a new and improved composition and process for developing an electrostatic image.

Electrostatography is exemplified by the basic electrophotographic process taught by C. F. Carlson in U.S. Pat. No. 2,297,091, which involves placing a uniform electrostatic charge on a photoconductive insulating layer, exposing the layer to a light and shadow image to dissipate the charge on the areas of the layer exposed to the light and developing the resulting latent electrostatic image by depositing on the image a finely-divided electroscopic material referred to in the art as "toner". The toner is normally attracted to those areas of the layer which retain a charge, thereby forming a toner image corresponding to the latent electrostatic image, which may then be transferred to a support surface, such as paper. The transferred image is generally permanently affixed to the support surface by heating, although other suitable fixing means, such as solvent or overcoating treatment, may be substituted for the foregoing heat fixing step.

One method for applying the electroscopic material to a latent electrostatic image is the "cascade" process disclosed by L. E. Walkup in U.S. Pat. No. 2,618,551 and E. N. Wise in U.S. Pat. No. 2,618,552. In the cascade process, the developer is basically a two component system comprised of a finely-divided electroscopic material (toner) and a carrier. The carrier is generally comprised of a core material, such as glass or sand, and a triboelectric resinous coating with the toner particles being loosely held on the coating by triboelectric action. The carrier and toner are chosen so that the toner assumes a charge of an opposite polarity to the latent electrostatic image, whereby upon rolling or cascading the developer over the surface bearing the latent electrostatic image, the toner particles are attracted to he image being developed. Conversely, if the toner particles have a charge of identical polarity to the latent electrostatic image, the toner particles accumulate on the background portions.

In automatic xerographic equipment, it is conventional to employ a electrophotographic plate in the form of a cylindrical drum which is continuously rotated through a cycle of sequential operations including charging, exposure, developing, transfer and cleaning. The plate is usually charged with corona with positive polarity by means of a corona generating device of the type disclosed by L. E. Walkup in U.S. Pat. No. 2,777,957 which is connected to a suitable source of high potential and the charged plate is then exposed to a light and shadow image to dissipate the charge on the areas exposed to the light, thereby forming a latent electrostatic image. A developer comprised of toner loosely held on a coated carrier is conveyed from a reservoir to a point above the drum bearing the latent electrostatic image and is allowed to fall and roll by gravity over the image-bearing surface thereby forming a powder image. The carrier along with any unused toner is returned to the reservoir for recycle through the development system. After forming a powder image on the electrostatic image during the development step, the powder image is electrostatically transferred to a support surface by means of a corona generating device such as the corona device mentioned above. In automatic equipment employing a rotating drum, a support surface to which a powdered image is to be transferred is moved through the equipment at the same rate as the periphery of the drum and contacts the drum in the transfer position interposed between the drum surface and the corona generating device. Transfer is effected by the corona generating device which imparts an electrostatic charge to attract the powder image from the drum to the support surface. The polarity of charge required to effect image transfer is dependent upon the visual form of the original copy relative to the reproduction and the electroscopic characteristics of a developing material employed to effect development. For example, where a positive reproduction is to be made of a positive original, it is conventional to employ a positive polarity corona to effect transfer of a negatively charged toner image to the support surface. When a positive reproduction from a negative original is desired, it is conventional to employ a positively charged developing material which is repelled by the charged areas on the plate to the discharge areas thereon to form a positive image which may be transferred by negative polarity corona.

The coated carriers presently employed in development compositions perform quite satisfactorily, but the time period over which such satisfactory performance can be expected is severely limited by two factors; namely, impactation or mechanical flow and degradation. The impactation or mechanical flow is caused by the continuous tumbling of the carrier in the development system, and as a result, toner particles adhere to the carrier surface. As the amount of toner adhering to the carrier surface increases, the triboelectric properties of the carrier material are changed and eventually such changes result in unsatisfactory reproduction. Similarly, continuous use of the carrier produces wear and chipping of the resinous coating, exposing the core material, and the use of such an exposed carrier results in print deletion and poor print quality.

The primary factors limiting the life of the carrier; i.e., impactation and degradation, are a direct result of the defects inherent in the use of a resinous coating. The resinous coatings, however, provide the properties required for an effective carrier; namely, low humidity sensitivity, good triboelectric qualities, and density. The low humidity sensitivity is required in order to prevent changes in the triboelectric properties of the carrier with changes in ambient conditions. The triboelectric qualities of the carrier are important in that the mutual electrification of the carrier and toner; i.e., their relative positions in the triboelectric series, is a determining factor in the overall quality of the resulting print. The density of the carrier is an important factor in preventing adherence of the carrier to the image bearing surface. Therefore, the limitations directly resulting from the use of a coated carrier are tolerated in order to provide the properties required for effective development.

SUMMARY OF THE INVENTION

An object of this invention is to provide an improved developer for developing a latent electrostatic image.

Another object of this invention is to provide for improved development of latent electrostatic images.

A further object of this invention is to provide an improved developer for developing latent electrostatic images which overcomes the aforementioned difficulties associated with the carrier material.

These and other objects of the invention should be more readily apparent from reading the following detailed description thereof.

The objects of this invention are broadly accomplished by providing an electrostatographic developer having a carrier which is comprised of a crystalline phase dispersed in a glass matrix with the crystalline material being either an oxide of a Group IV element or a double oxide of titanium, zirconium, tin, hafnium or germanium and an alkaline earth or lead. These materials possess the properties required for an effective electrostatographic developer carrier without the application of a resinous coating thereto and are therefore not as susceptible to degradation and/or mechanical flow as the coated carriers heretofore employed in the art.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with the invention, the uncoated carrier is comprised of a crystalline phase dispersed in a glassy matrix wherein the crystalline phase is comprised of one or more of the following: (1) crystalline oxides of Group IV metals, particularly zirconium dioxide, titanium dioxide, tin oxide, germanium oxide, hafnium oxide and lead oxide, with the oxides of germanium or hafnium generally being less preferred in that such oxides are very expensive; and (2) the crystalline double oxides of titanium, zirconium, tin, hafnium or germanium and either an alkaline earth, in particular calcium, strontium and barium; or lead or cadmium; in particular the titanates, zirconates and stannates of one or more of the alkaline earths, cadmium or lead, such as, lead titanate ($PbTiO_3$), lead zirconate ($PbZrO_3$), lead stannate ($PbSnO_3$), barium titanate ($BaTiO_3$), calcium titanate ($CaTiO_3$), barium zirconate ($BaZrO_3$), calcium zirconate ($CaZrO_3$), barium stannate ($BaSnO_3$), calcium stannate ($CaSnO_3$), barium strontium titanate ($BaSrTiO_3$), barium calcium titanate ($BaCaTiO_3$), cadmium zirconate ($CdZrO_3$), etc., and mixtures thereof, such as a solid solution of lead titanate and lead zirconate. These materials are commonly referred to in the art as semicrystalline ceramics or glass-ceramics.

A glass ceramic body which includes as the crystalline phase a titanate and/or zirconate of one or more of the following elements: cadmium, lead, barium, strontium or calcium; in particular one or more of the following: lead titanate, lead zirconate, barium titanate, barium strontium titanate, barium zirconate, lead zirconate and cadmium zirconate, has been found to provide particularly good results. These oxides may be present in the crystalline phase by themselves or as mixtures, with the mixtures being either incompatible mixtures of the oxides and/or solid solutions thereof.

The semicrystalline ceramic body contains from about 5 percent to 70 percent of the hereinabove described Group IV metal oxides or double oxides and from about 30 percent to about 95 percent of a glass forming oxide, such as SiO_2, Al_2O_3, B_2O_3, P_2O_5 or mixtures thereof, with from about 5 percent to about 60 percent, and preferably from about 20 percent to about 40 percent of the body containing the hereinabove described Group IV metal oxides or double oxides as a crystalline phase uniformly dispersed in the glassy matrix, with all percentages being by volume on an oxide basis. The glass forming oxides and Group IV metal oxides and/or double oxides generally comprise from about 90 percent to about 100 percent of the total composition, by volume, with the remaining components, if any, being any of the wide variety of glass stabilizers or modifiers known in the art.

The semicrystalline ceramic bodies may be produced by forming a mixture of the constituent oxides which are to be crystallized with at least one glass forming oxide and melting the mixture for a period of time sufficient to produce a homogeneous melt, such melting generally being effected at temperatures above about 1,000°C, and generally at temperatures from about 1,000°C to about 1,500°C, followed by rapid cooling to produce a glass. The formation of such glasses is well known in the art and, therefore, no detailed description in this respect is deemed necessary for a full understanding of the invention.

The glass may then be treated to produce a size and shape desired for an electrostatographic carrier, in that the subsequent crystallization is effected at temperatures below the melting point of the glass. The glass is preferably formed into a spherical shape as generally known in the art, but it is to be understood that other shapes are within the spirit and scope of the invention, with such non-spherical shapes preferably having no sharp corners or edges to cause excessive scratching and wear of the surface bearing the latent electrostatic image. The glass particles are formed into a particle size of larger than about 30 microns, preferably from about 30 to about 1,000 microns in that such sizes enable the carrier produced from the glass to roll across a latent electrostatic image-bearing surface, without being retained by toner particles attracted to the image-bearing surface. It is to be understood, however, that other sizes and shapes may be employed, provided the carrier is capable of developing a latent-electrostatic image without requiring special means or measures for effecting removal of the carrier particles from the image bearing surface.

The glass particles are then heated to a temperature (below the melting temperature of the glass) and for a period of time at which the glass particles are formed into semicrystalline ceramic bodies. The temperatures and times required to produce the semicrystalline ceramic bodies vary with both the composition of the glass and the amount of crystallization desired, with increases in temperature and/or time increasing the degree of crystallization. In general, the glass is heated to temperatures from about 800°C to about 1,200°C, preferably from about 900°C to about 1,100°C, for a period of time to produce a degree of crystallization within the hereinabove described ranges; i.e., the time-temperature relationship is controlled to produce a semi-crystalline ceramic body in which the crystalline phase comprises from about 5 percent to about 60 percent, preferably from about 20 percent to about 40 percent, all by volume, of the body. The selection of a particular time-temperature relationship is deemed to be well within the scope of those skilled in the art from the teachings herein.

The semicrystalline ceramic body may also be produced from a commercial glass having the desired oxide composition or the desired oxide composition may be formed into a glass, as hereinabove described. Thus, for example, copending U.S. application Ser. No. 631,192, filed Apr. 7, 1967, is directed to glass electrostatographic developer carriers produced from homogeneous glass compositions containing oxides of silicon, oxides of barium and oxides of titanium and further including one or more oxides of lead, zirconium and calcium and such carriers may be treated in accordance with the invention to produce a two phase carrier comprised of a crystalline phase dispersed in a glassy matrix. A particularly good carrier may be produced from a glass composition, as disclosed in the aforementioned copending U.S. application, comprised of about 42% PbO, about 18.3% TiO_2, about 2.3% ZrO_2 and about 5.6% BaO, all by weight, with the remainder primarily being SiO_2, with the crystalline phase of the final product most likely being $PbTiO_3$, although the crystalline phase may also include one or more of the following: $PbZrO_3$, $BaTiO_3$, or solid solutions thereof.

Similarly, the glass-ceramic carrier may be produced by forming a glass from the Group IV metal oxides and/or double oxides, such glass being formed, as hereinabove described, by combining the Group IV metal oxide or double oxide with a glass forming oxide and then recrystallizing the glass below its melting point. As disclosed in copending U.S. application Ser. No. 104,498 filed concurrently herewith, the Group IV metal oxides and double oxides are effective electrostatographic developer carriers, but not all of these compounds may be thermally spherodized. Thus, in accordance with the present invention, such compounds or their constituent oxides may be formed into a glass, thermally spherodized and then recrystallized, thereby maintaining the spherical shape and providing the desired crystalline phase imbedded in a glassy matrix.

The glass-ceramic electrostatographic developer carriers of the invention have properties which not only vary with the constituents thereof, but also with the degree of crystallization in the final product. Thus, for example, for a given composition an increase in the amount of crystalline phase in the final product results in a slight increase in density and an increase in the specific charge. It should be readily apparent that the ability to effect changes in the properties of the carrier, without modification of the composition thereof, would permit the production of a single carrier composition for a wide variety of applications; for example, a multiplicity of electrophotographic machines with the properties of the carrier being adapted to a particular machine by a simple heat treatment.

The uncoated carrier materials of the invention are employed in an electrostatographic developer composition by loosely coating any suitable pigmented or dyed electroscopic toner material thereon, the toner material being affixed to the carrier by electrostatic attraction. Typical toner materials include: gum copal, gum sandarac, rosin, cumaroneindene resin, asphaltum, gilsonite, phenol-formaldehyde resins, resin-modified phenol-formaldehyde resins, methacrylic resins, polystyrene resins, polypropylene resins, epoxy resins, polyethylene resins and mixtures thereof. The particular toner material to be employed obviously depends upon the separation of the toner particles from the treated carrier beads in the triboelectric series. Among the U.S. Patents describing electroscopic toner compositions are No. 2,659,670 to Copley; No. 2,753,308 to Landrigan; No. 3,079,342 to Insalaco; Reissue No. 25,136 to Carlson and No. 2,788,288 to Rheinfrank et al. These toners generally have an average particle diameter from about 1 to about 30 microns.

The degree of contrast or other photographic qualities of the finished image produced with the electrostatographic developer compositions of the invention may be varied by changing the relative proportions of toner and carrier material and the choice of optimum proportions is deemed to be within the scope of those skilled in the art. In general, however, the developer compositions of the invention have carrier to toner weight ratios of from about 25:1 to about 1,000:1, preferably from about 75:1 to about 100:1, to produce a dense readily transferable image.

The invention will be further described with reference to the following examples, but it is to be understood that the scope of the invention is not to be limited thereby. The glass compositions are specified in cationic mol percent, on the oxide basis, unless otherwise indicated.

EXAMPLE I

Glass having a composition of approximately 42.0% PbO, 5.6% BaO, 18.3% TiO_2 and 31.8% SiO_2, all by weight, in bead form of 20–40 mesh, is heated in a kiln at 1,600°F. for about 3 hours to produce a glass-ceramic body having a crystalline phase uniformly dispersed in the glassy matrix. The crystalline phase includes $PbTiO_3$ and $BaTiO_3$.

A developer is prepared using the uncoated glass-ceramic as the carrier and a toner comprising a styrene-n-butyl methacrylate copolymer, polyvinyl butyral and carbon black which is produced as disclosed in Example I of U.S. Pat. No. 3,079,324 to Insalaco, the developer composition having 0.6 percent, by weight, of the toner.

The developer is used to develop a latent electrostatic image formed on a flat selenium plate charged to 700 volts. The image is transferred using 700 volts, and after fusing, the prints are examined.

The prints are of good quality, and the carrier does not stick to either the plate or print.

EXAMPLE II

Glass which is produced by rapid cooling of a melt having a composition of approximately 32.9% BaO, 26.6% TiO_2, 31.7% B_2O_3 and 8.8% CaO, in bead form of 20–40 mesh,is heated in a kiln at 850°C for about 2.5 hours to produce a glass-ceramic body having a crystalline phase uniformly dispersed in the glassy matrix. The crystalline phase includes $BaTiO_3$ and probably some $BaCaTiO_3$.

A developer is prepared using the uncoated glass-ceramic as the carrier and a toner comprising a styrene-n-butyl methacrylate copolymer, polyvinyl butyral and carbon black which is produced as disclosed in Example I of U.S. Pat. No. 3,079,324 to Insalaco, the developer composition having 0.6 percent, by weight, of the toner.

The developer is used to develop a latent electrostatic image formed on a flat selenium plate charged to 700 volts. The image is transferred using 700 volts, and after fusing, the prints are examined.

The prints are of good quality, and the carrier does not stick to either the plate or print.

EXAMPLE III

Glass which is produced by rapid cooling of a melt having a composition of approximately 28.1% BaO, 28.1% TiO_2, 29.2% P_2O_5 and 14.6% CaO, in bead form of 20–40 mesh, is heated in a kiln at 1,000°C for about 2.5 hours to produce a glass-ceramic body having a crystalline phase uniformly dispersed in the glassy matrix. The crystalline phase includes $BaTiO_3$ and some $BaCaTiO_3$.

A developer is prepared using the uncoated glass-ceramic as the carrier and a toner comprising a styrene-n-butyl methacrylate copolymer, polyvinyl butyral and carbon black which is produced as disclosed in Example I of U.S. Pat. No. 3,079,324 to Insalaco, the developer composition having 0.6 percent, by weight, of the toner.

The developer is used to develop a latent electrostatic image formed on a flat selenium plate charged to 700 volts. The image is transferred using 700 volts, and after fusing, the prints are examined.

The prints are of good quality, and the carrier does not stick to either the plate or print.

EXAMPLE IV

Glass which is produced by rapid cooling of a melt having a composition of approximately 29.1% B_2O_3, 31.8% BaO, 31.8% TiO_2 and 7.3% SrO, in bead form of 20–40 mesh, is heated in a kiln at 850°C for about 2.5 hours to produce a glass-ceramic body having a crystalline phase uniformly dispersed in the glassy matrix. The crystalline phase includes $BaTiO_3$ and some $BaSrTiO_3$.

A developer is prepared using the uncoated glass-ceramic as the carrier and a toner comprising a styrene-n-butyl methacrylate copolymer, polyvinyl butyral and carbon black which is produced as disclosed in Example I of U.S. Pat. No. 3,079,324 to Insalaco, the developer composition having a 0.6 percent, by weight, of the toner.

The developer is used to develop a latent electrostatic image formed on a flat selenium plate charged to 700 volts. The image is transferred using 700 volts, and after fusing, the prints are examined.

The prints are of good quality, and the carrier does not stick to either the plate or print.

EXAMPLE V

Glass which is produced by rapid cooling of a melt having a composition of approximately 18.4% B_2O_3, 31.6% BaO, 31.6% TiO_2 and 18.4% Al_2O_3, in bead form of 20–40 mesh, is heated in a kiln at 850°C for about 2.5 hours to produce a glass-ceramic body having a crystalline phase uniformly dispersed in the glassy matrix. The crystalline phase includes $BaTiO_3$.

A developer is prepared using the uncoated glass-ceramic as the carrier and a toner comprising a styrene-n-butyl methacrylate copolymer, polyvinyl butyral and carbon black which is produced as disclosed in Example I of U.S. Pat. No. 3,079,324 to Insalaco, the developer composition having 0.6 percent, by weight, of the toner.

The developer is used to develop a latent electrostatic image formed on a flat selenium plate charged to 700 volts. The image is transferred using 700 volts, and after fusing, the prints are examined.

The prints are of good quality, and the carrier does not stick to either the plate or print.

EXAMPLE VI

Glass which is produced by rapid cooling of a melt having a composition of approximately 21.1% B_2O_3, 34.2% BaO, 38.9% TiO_2 and 3.9% ZrO_2, in bead form of 20–40 mesh, is heated in a kiln at 850°C for about 2.5 hours to produce a ceramic body having a crystalline phase uniformly dispersed in the glassy matrix. The crystalline phase includes $BaTiO_3$.

A developer is prepared using the uncoated glass-ceramic as the carrier and a toner comprising a styrene-n-butyl methacrylate copolymer, polyvinyl butyral and carbon black which is produced as disclosed in Example I of U.S. Pat. No. 3,079,324 to Insalaco, the developer composition having 0.6 percent, by weight, of the toner.

The developer is used to develop a latent electrostatic image formed on a flat selenium plate charged to 700 volts. The image is transferred using 700 volts, and after fusing, the prints are examined.

The prints are of good quality, and the carrier does not stick to either the plate or print.

EXAMPLE VII

Glass which is produced by rapid cooling of a melt having a composition of approximately 10.5% CdO, 30.0% ZrO_2, 10.3% BaO, 23.8% PbO, 5.2% Al_2O_3 and 20.2% SrO_2, in bead form of 20–40 mesh, is heated in a kiln at 925°C for about 2 hours to produce a glass-ceramic body having a crystalline phase uniformly dispersed in the glassy matrix. The crystalline phase includes one or more of the following: $BaZrO_3$, $PbZrO_3$, $CdZrO_3$.

A developer is prepared using the uncoated glass-ceramic as the carrier and a toner comprising a styrene-n-butyl methacrylate copolymer, polyvinyl butyral and carbon black which is produced as disclosed in Example I of U.S. Pat. No. 3,079,324 to Insalaco, the developer composition having 0.6 percent, by weight, of the toner.

The developer is used to develop a latent electrostatic image formed on a flat selenium plate charged to 700 volts. The image is transferred using 700 volts, and after fusing, the prints are examined.

The prints are of good quality, and the carrier does not stick to either the plate or print.

EXAMPLE VIII

Examples I through VII are repeated with a toner comprised of a propoxylated bisphenol A fumarate polyester (ATLAC 382, sold by Atlas Chemical Industries, Inc.) and carbon black with similar results.

The improved electrostatographic developers of the present invention may be employed for developing a latent electrostatographic image in any one of a wide variety of processes which employ two-component developers. Thus, although the invention has been particularly described with reference to a cascade type of development, the developers of the present invention may also be used for fluidized development, as described for example in U.S. Pat. No. 3,380,437 to Swyler or U.S. Pat. No. 3,393,663 to Donalies.

Similarly, although the invention has been particularly described with reference to developing latent images formed by an electrophotographic technique, the developer may also be employed for developing latent images formed by other techniques, e.g., pulsing electrodes, as used for example in electrostatic printing processes.

The electrostatographic developer compositions of the present invention are an improvement over those heretofore employed in the art in that the carriers thereof, although uncoated, have the density, humidity insensitivity and triboelectric qualities required for an effective carrier. As a result, these carriers are not prone to impactation and degradation, thereby increasing the effective life of the carrier. In addition, developer compositions employing the carrier materials of the invention are capable of developing an image at a more rapid rate than developers heretofore employed in the art and are therefore of interest as developers for high rate machines in which the contact time between the developer and the latent image-bearing surface may be limited. Furthermore, the ability to vary the properties of the carrier, without changing the composition thereof; i.e., by changing the amount of crystalline phase present in the carrier, permits the production of a single carrier material which is capable of being employed for different operations.

Numerous modifications and variations of the present invention are possible in light of the above teachings and therefore the invention may be practiced otherwise than as particularly described.

What is claimed is:

1. In an electrostatographic developer comprising toner in association with a solid carrier, the improvement comprising: said carrier being an uncoated glass-ceramic body comprised of a crystalline phase dispersed in a glass matrix, said crystalline phase being comprised of at least one member selected from the group consisting of (a) oxides of Group IV metals and (b) double oxides of a member selected from the group consisting of titanium, hafnium, zirconium, tin and germanium and at least one member selected from the group consisting of alkaline earths, cadmium and lead, said crystalline phase comprising from about 20 percent to about 60 percent by volume of the body.

2. The electrostatographic developer as defined in claim 1 wherein the crystalline phase comprises from about 20 percent to about 40 percent, by volume, of the body.

3. The electrostatographic developer as defined in claim 1 wherein the crystalline phase includes barium titanate.

4. The electrostatographic developer as defined in claim 1 wherein the crystalline phase includes barium zirconate.

5. The electrostatographic developer as defined in claim 1 wherein the crystalline phase includes lead titanate.

6. The electrostatographic developer as defined in claim 1 wherein the crystalline phase includes lead zirconate.

7. In an electrostatographic developer comprised of a toner in association with a solid carrier, the improvement comprising: said carrier being an uncoated glass-ceramic body comprised of a crystalline phase dispersed in a glass matrix, said crystalline phase being comprised of at least one member selected from the group consisting of titanates and zirconates of at least one element selected from the group consisting of cadmium, lead, barium, strontium, and calcium, said crystalline phase being present in an amount from about 20 percent to about 60 percent, by volume, of said body.

8. The electrostatographic developer as defined in claim 7 wherein the constituent oxides of said glass ceramic comprise about 42% PbO, about 18.3% TiO_2, about 2.3% ZrO_2 and about 5.6% BaO and the remainder being primarily SiO_2, all by weight, with said crystalline phase including lead titanate and barium titanate.

9. The electrostatographic developer as defined in claim 7 wherein the glass-ceramic comprises, on an oxide basis, from about 20 percent to about 70 percent of the constituent oxides of said member and from about 30 percent to about 95 percent of a glass forming oxide.

10. The electrostatographic developer as defined in claim 9 wherein the crystalline phase includes barium titanate.

11. The electrostatographic developer as defined in claim 9 wherein the crystalline phase includes barium zirconate.

12. The electrostatographic developer as defined in claim 9 wherein the crystalline phase includes lead titanate.

13. The electrostatographic developer as define in claim 9 wherein the crystalline phase includes lead zirconate.

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