United States Patent [19]

Hagenbach et al.

[11] **3,713,819**

[45] **Jan. 30, 1973**

[54] **XEROGRAPHIC IMAGING AND DEVELOPMENT USING METAL OXIDE CARRIER PARTICLES**

[75] Inventors: **Robert J. Hagenbach; Myron J. Lenhard,** both of Rochester, N.Y.

[73] Assignee: **Xerox Corporation,** Rochester, N.Y.

[22] Filed: **Nov. 30, 1970**

[21] Appl. No.: **93,847**

Related U.S. Application Data

[62] Division of Ser. No. 631,192, April 17, 1967, Pat. No. 3,591,503.

[52] **U.S. Cl.** .....**96/1 SD,** 106/53, 117/17.5, 252/62.1

[51] **Int. Cl.** **G03g 9/00,** G03g 13/08

[58] **Field of Search** 96/1; 252/62.1; 117/17.5; 106/52, 53

[56] **References Cited**

UNITED STATES PATENTS

3,326,848	6/1967	Clemens	252/41
2,618,551	11/1952	Walkup	252/62.1

FOREIGN PATENTS OR APPLICATIONS

557,577	5/1958	Canada	252/62.1

Primary Examiner—Charles E. Van Horn
Assistant Examiner—M. B. Wittenberg
Attorney—Frank A. Steinhilper et al.

[57] **ABSTRACT**

A xerographic carrier bead material for use in developing electrostatic latent images comprising a glass composition of from about 10 to about 40 parts oxides of silicon, from about 5 to about 50 parts oxides of barium, and oxides of metals selected from the group consisting of titanium, lead and mixtures thereof.

4 Claims, No Drawings

XEROGRAPHIC IMAGING AND DEVELOPMENT USING METAL OXIDE CARRIER PARTICLES

This is a division of application Ser. No. 631,192, filed in the United States on April 17, 1967, now U.S. Pat. No. 3591503.

BACKGROUND OF THE INVENTION

This invention relates in general to an imaging system and, more particularly, to an electrostatographic material.

Electrostatography is best exemplified by the process of xerography as first described in U. S. Pat. No. 2,297,691 to C. F. Carlson. In this process a photoconductor is first provided with a uniform electrostatic charge over its surface and is then exposed to an image of activating electromagnetic radiation which selectively dissipates the charge in illuminated areas of the photoconductor while the charge in the non-illuminated areas is retained thereby forming a latent electrostatic image. This latent electrostatic latent image is then developed or made visible by the deposition of finely-divided electroscopic marking particles referred to in the art as "toner". The toner will normally be attracted to those areas of the layer which retain a charge, thereby forming a toner image corresponding to the latent electroscopic image. This powdered image may then be transferred to a support surface such as paper. The transferred image may subsequently be permanently affixed to the support surface as by fusing. Instead of forming latent images by uniformly charging a photoconductive layer and then exposing the layer to a light and shadow image, an image may be formed by directly charging the layer or an insulating member in image configuration. The powder image may be fixed to the imaging layer if elimination of the powder image transfer step is desired. Other suitable means such as solvent or overcoating treatment may be substituted for the foregoing heat fixing steps.

Several methods are known for applying the electroscopic particles to the latent electrostatic image to be developed. One well-known commercial method for developing electrostatic images 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 this method a developer material comprising relatively large carrier beads having fine toner particles electrostatically coated thereon is conveyed to or rolled or cascaded across the electrostatic image bearing surface. The composition of the carrier particles is so chosen as to triboelectrically charge the toner particles to the desired polarity. As the image cascades or rolls across the image bearing surface, the toner particles are electrostatically deposited and secured to the charged portion of a latent image and are not deposited on the uncharged or background portion of the image. Most of the toner particles accidentally deposited in the background areas are removed by the rolling carrier, due apparently to the greater electrostatic attraction between the toner and carrier than between the toner and the discharge background. The carrier and excess toner are then recycled.

In most commercial processes the cascade technique is carried out in automatic machines. In these machines small buckets on an endless conveyor scoop the developer mixture comprising relatively large carrier beads and smaller toner particles and convey it to a

point above an electrostatic image bearing surface where the developer mixture is allowed to fall and roll by gravity across the image bearing surface. The carrier beads along with any unused toner particles are then returned to the sump for recycling through the developing system. Small quantities of toner material are periodically added to the developer mixture to compensate for the toner depleted during the development process. This process is repeated for each copy produced in the machine and is ordinarily repeated many thousands of times during the usable life of the developer mixture. It is apparent that in this process, as well as in other development techniques, the developer mixture is subjected to a great deal of mechanical attrition which tends to degrade both the toner and carrier particles. This degradation, of course, occurs primarily as a result of shear and impact forces due to the tumbling of the developer mixture on the image bearing plate and the movement of the bucket conveyor through the developer material in the sump.

In prior art processes both coated and uncoated carrier beads were employed with varying degrees of success. Coated carrier beads are subject to deterioration or degradation characterized by the separation of portions of or the entire carrier coating from the carrier core. The separation may be in the form of chips, flakes, or entire layers and is primarily caused by poorly adhering coating materials which fail upon impact and abrasive contact with machine parts and other carrier particles. Carriers having coatings tend to chip and otherwise separate from the carrier core and must be frequently replaced, thereby increasing expense and consuming time. Print deletion and poor print quality occur when carrier particles having damaged coatings are not replaced. Fines and grit formed by the carrier coating disintegration tend to drift and form unwanted deposits on critical machine parts. In addition, the triboelectric properties of the carrier material varies with deterioration of the coating resulting in poor print quality.

Uncoated carrier beads on the other hand have three main deficiencies. First, often they lack the weight required to insure against adherence of the granular carrier material to the charged plate. Desirably, the specific gravity of the carrier material should be between about 3 and about 8. Heavier carrier bead materials cause impact damage to the surface of the image bearing layer. Secondly, the prior art uncoated carrier materials lacked the triboelectric qualities required of an electrostatographic material. Problems encountered when carrier materials lack these properties are set out in the following discussion. In the reproduction of high contrast copies such as letters, tracings and the like, it is desirable to select the electroscopic powder and carrier materials so that their mutual electrification is relatively large; the degree of such electrification being determined in most cases by the distance between their relative positions in the triboelectric series. However, when otherwise compatible electroscopic powder and carrier materials are removed from each other in the triboelectric series by too great a distance, the resulting images are very faint because the attractive forces between the carrier and toner particles compete with the attractive forces between the latent electrostatic image and the toner

particles. Although the image density described in the immediately preceding sentence may be improved by increasing the toner concentration in the developer mixture, undesirably high background toner deposition as well as increased toner impaction and agglomeration is encountered when the developer mixture is overtoned. The initial electrostatographic plate charge may be increased to improve the density of the deposited powdered image but the plate charge would ordinarily have to be excessively high in order to attract the electroscopic powder away from the carrier particle. Excessively high electrostatographic plate charges are not only undesirable because of the high power consumption necessary to maintain the electrostatographic plate at high potentials but also because a high potential causes the carrier particles to adhere to the electrostatographic plate surface rather than merely roll across and off the electrostatographic plate surface. Print deletion and massive carryover of carrier particles often occur when carrier particles adhere to reusable electrostatographic imaging surfaces. Massive carrier carryover problems are particularly acute when the developer is employed in solid area coverage machines where excessive quantities of toner particles are removed from carrier particles thereby leaving many carrier particles substantially bare of toner particles. Further, adherence of carrier particles to reusable electrostatographic imaging surfaces promotes the formation of undesirable scratches on the surfaces during image transfer and surface cleaning operations. It is, therefore, apparent that many materials which otherwise have suitable properties for employment as carrier particles are unsuitable because they possess too high a triboelectric value. Desirably, the triboelectric value for conventional electrostatography measured in micro-coulombs per gram of toner should be between 8 and 30.

Finally, the triboelectric value of a carrier material should not be significantly affected by ambient humidity conditions since such affect would destroy print quality at higher humidities and complicate machine design and operation, prior art uncoated glass materials were never commercially successful because of their great humidity sensitivity.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide a system for developing electrostatic latent images which overcome the above noted deficiencies.

It is another object of this invention to provide a system for developing electrostatic latent images which is relatively insensitive to humidity conditions.

It is another object of this invention to provide a carrier material, which is relatively resistant to abrasion.

It is another object of this invention to provide a homogeneous carrier material which has relatively improved triboelectric properties.

It is another object of this invention to provide a homogeneous carrier material which has a relatively high density.

The foregoing objects and others are accomplished in accordance with this invention by an electrostatic latent image developing system wherein an electrostatic latent image is formed on an imaging surface and the electrostatic image is then contacted with a developer mixture comprising finely-divided particles of toner electrostatically adhering to the surface of uncoated glass carrier beads. The carrier beads, in general, are a homogeneous mixture of a glass composition comprising from about 10 to about 40 parts oxides of silicon, from about five to about 50 parts oxides of barium, and oxides of metals selected from the group consisting of titanium, lead and mixtures thereof. A portion of the toner particles are attracted to and held on the surface of the image bearing member in accordance with the electrostatic latent image forming a visible image.

For electrostatographic purposes the preferred composition comprises about 16 to 20 parts oxides of titanium, four to six parts oxides of barium, 30 to 32 parts oxides of silicon, 40 to 44 parts oxides of lead, and about two to four parts oxides of zirconium. For economic reasons, however, the preferred composition comprises about 34 to 37 parts oxides of titanium, 43 to 48 parts oxides of barium, 11 to 13 parts oxides of silicon, and 3.5 to 4.5 parts oxides of calcium.

The uncoated carrier beads of this invention have a specific gravity of from about 3.0 to about 6.0 and produce high quality images over a wide range of ambient humidity conditions.

Although other components may be present to aid in manufacture of the glass beads or as natural impurities resulting from the manufacture of the beads, it has been found that the presence of over about 5 percent by weight, either singularly or in combination, of the oxides of sodium, potassium and lithium cause the carrier bead material to be sensitive to high ambient humidity. That is, the presence of these materials impart to the carrier beads humidity sensitivity which prevents the use of such beads in electrostatographic processes which are exposed to high ambient humidity.

A carrier bead diameter of from about 30 microns to about 1,000 microns is preferred for electrostatographic use because the bead then possess sufficient inertia to avoid adherence to the latent electrostatic images.

Any suitable pigmented or dyed electroscopic toner material may be employed with the uncoated carriers of this invention. Typical toner materials include: gum copal; gum sandarac; rosin; cumaromeindene resin; asphaltum; uintaite; phenol formaldehyde resins; rosin modified phenol formaldehyde resins; methacrylic resins; polystyrene resins; polypropylene resins; epoxy resins; polyethylene resins and mixtures thereof. The particular toner material to be employed depends upon the separation of the toner particles from the treated carrier beads in the triboelectric series and whether a negatively or positively charged image is to be developed. Among the patents describing electroscopic toner compositions are U. S. Pat. No 2,659,670 to Copley; U. S. Pat. No. 2,753,308 to Landrigan; U. S. Pat. No. 3,079,342 to Insalaco; U. S. Pat. No. Re. 25,136 to Carlson, and U. S. Pat. No. 2,788,288 to Rheinfrank et al. These toners generally have an average particle diameter between about 1 and 30 microns. A toner comprising a styrene-N-butyl methacrylate copolymer, polyvinylbutyral and carbon black produced by the method disclosed by M. A. Insalaco in Example 1 of U. S. Pat. No. 3,079,342 is preferred because of its excellent triboelectric qualities and its deep black color.

In conventional xerography a uniform positive charge is placed on the surface of a photoconductive member. Subsequent exposure to a light image discharges the exposed areas of the plate. A powder material is then chosen which is triboelectrically negative in respect to the carrier bead material of this invention. However, the advantages of this invention apply equally to the development of latent electrostatic images which are negative. In the case where the latent image is comprised of negative electrostatic charges, an electroscopic powder and carrier combination should be selected in which the powder is triboelectrically positive to the carrier material. The selection of suitable toner materials can be made by anyone skilled in the art from the many materials that have been tested and occupy recognized positions in the triboelectric series. The dimension of the charge acquired by any particular toner through triboelectric contact with any designated carrier material is easily and readily determined by the test method described more fully herein.

DESCRIPTION OF PREFERRED EMBODIMENTS

The following examples further specifically illustrate the present invention. The examples below are intended to illustrate the various preferred embodiments of the improved carrier materials. The parts and percentages are by weight unless otherwise indicated.

In the following examples the triboelectric values are determined as follows: The relative triboelectric values generated by contact of carrier beads with toner particles are measured by means of a Faraday Cage. The device comprises a brass cylinder having a diameter of 1 inch and a length of 1 inch. A 100 mesh screen is positioned at each end of the cylinder. The cylinder is weighted, charged with 2 grams of a mixture of carrier and toner particles and connected to ground through a capacitor and an electrometer connected in parallel. Dry compressed air is then blown through the brass cylinder to drive all the toner from the carrier. The charge on the capacitor is then read on the electrometer. Next, the chamber is reweighed to determine the weight loss. The resulting data is used to calculate the toner concentration and the charge in micro-coulombs per gram of toner. Since triboelectric measurements are relative, the measurements should for comparative purposes be conducted under substantially identical conditions. Thus, a toner comprising a styrene-n-butyl methacrylate copolymer, polyvinylbutyral and carbon black produced by the method disclosed by M. A. Insalaco in Example I of U. S. Pat. No. 3,079,342 is used as a contact triboelectrification standard and as toner in all of the examples. Obviously, other suitable toners such as those listed above may be substituted for the toner used in the examples.

EXAMPLE I

A developer mixture is produced by mixing one part colored styrene copolymer toner particles having an average particle size of about 10 to about 20 microns with about 100 parts glass carrier bead particles having an average particle size of about 600 microns. The glass bead composition comprises about 71% SiO_2, about 2% Al_2O_3, about 13% CaO and about 14% Na_2O and has a specific gravity of about 2.4.

The following tests are run at an ambient temperature of about 70°F. and an ambient relative humidity of about 40 percent.

The relative triboelectric value of the carrier measured by means of a Faraday Cage is about 9 micro-coulombs per gram of toner. The developer mixture is cascaded across an imaging surface bearing a positively charged electrostatic image. The resulting developed image is transferred by electrostatic means to a sheet of paper whereon it is fused by heat. The resulting image is dense and substantially free of background toner deposits.

EXAMPLE II

The experiment of Example I is repeated except that the tests are performed in the presence of an ambient temperature of about 70°F. and an ambient relative humidity of about 80 percent. The relative triboelectric value of the carrier measured by means of a Faraday Cage is about 3 micro-coulombs per gram of toner. The resulting fused image prepared as in Example I is characterized by a faded, washed out appearance and has high background toner deposits.

EXAMPLE III

A developer mixture is produced by mixing one part colored styrene copolymer toner particles described in Example I with about 100 parts glass carrier bead particles having an average particle size of about 600 microns.

The glass bead composition comprises about 71% SiO_2, about 10% Na_2O, about 7% K_2O, and about 12% PbO and has a specific gravity of about 2.8.

The following tests are run at an ambient temperature of about 70°F. and an ambient relative humidity of about 40 percent.

The relative triboelectric value of the carrier measured by means of a Faraday Cage is about 10 micro-coulombs per gram of toner. The developer mixture is cascaded across an imaging surface bearing a positively charged electrostatic image. The resulting developed image is transferred by electrostatic means to a sheet of paper whereon it is fused by heat. The resulting image is dense and is substantially free of background toner deposits.

EXAMPLE IV

The experiment of Example III is repeated except that the tests are performed in the presence of an ambient temperature of about 70°F. and an ambient relative humidity of about 80 percent. The relative triboelectric value of the carrier measured by means of a Faraday Cage is about 4 micro-coulombs per gram of toner. The resulting fused image prepared as in Example II is dense but possesses a relatively high background toner deposition.

EXAMPLE V

A developer mixture is produced by mixing one part colored styrene copolymer toner particles described in Example I with about 75 parts glass carrier bead particles having an average particle size of about 600 microns.

The glass bead composition comprises about 50% SiO_2, about 13% Na_2O, about 30% BaO and about 7% TiO_2 and has a specific gravity of about 3.5.

The following tests are run at an ambient temperature of about 70°F. and an ambient relative humidity of about 40 percent.

The relative triboelectric value of the carrier measured by means of a Faraday Cage is about 4.8 microcoulombs per gram of toner. The developer mixture is cascaded across an imaging surface bearing a positively charged electrostatic image. The resulting developed image is transferred to a sheet of paper whereon it is fused by heat. The resulting fused image is characterized by very high background and poor resolution.

EXAMPLE VI

The experiment of Example V is repeated except that the tests are performed in the presence of an ambient temperature of about 80°F. and an ambient relative humidity of about 85 percent. The resulting fused image prepared as in Example V is characterized by extremely poor resolution and very high background.

EXAMPLE VII

A developer mixture is produced by mixing one part colored styrene copolymer toner particles described in Example I with about 150 parts glass carrier bead particles having an average particle size of about 400 microns.

The glass bead composition comprises about 12% SiO_2, about 1% NaO, about 4% CaO, about 1% B_2O_3, about 45.5% BaO, and about 36.5% TiO_2 and having a specific gravity of about 4.2.

The following tests are run at an ambient temperature of about 70°F. and about 50 percent ambient relative humidity.

The relative triboelectric value of the carrier measured by means of a Faraday Cage is about 19.2 microcoulombs per gram of toner. The developer mixture is cascaded across an imaging surface bearing a positively charged electrostatic image. The resulting developed image is transferred to a sheet of paper whereon it is fused by heat. The resulting fused image has excellent resolution, excellent density and substantially no background.

EXAMPLE VIII

The experiment of Example VII is repeated except that the images are produced in the presence of an ambient temperature of about 80°F. and an ambient relative humidity of about 85 percent. The resulting fused image prepared as in Example VII has excellent resolution, good density and substantially no background.

EXAMPLE IX

A developer mixture is produced by mixing one part colored styrene copolymer toner particles described in Example I with about 120 parts glass carrier bead particles having an average particle size of about 400 microns.

The glass bead composition comprises about 46% BaO, about 20% TiO_2 and about 34% SiO_2 and has a specific gravity of about 4.5.

The following tests are run at an ambient temperature of about 70°F. and an ambient relative humidity of about 50 percent. The relative triboelectric value of the carrier measured by means of a Faraday Cage is about 10.1 micro-coulombs per gram of toner. The developer mixture is cascaded across an imaging surface bearing a positively charged electrostatic image. The resulting developed image is transferred by electrostatic means to a sheet of paper whereon it is fused by heat. The resulting fused image is dense, has good resolution and substantially no background.

Example X

The experiment of Example IX is repeated except that images are produced in the presence of an ambient temperature of about 80°F. and an ambient relative humidity of about 85 percent. The resulting fused image prepared as in Example IX is dense, has good resolution and substantially no background.

EXAMPLE XI

A developer mixture is produced by mixing one part colored styrene copolymer toner particles described in Example I with about 100 parts glass carrier bead particles having an average particle size of about 400 microns.

The glass bead composition comprises about 46% BaO, about 14% SiO_2, about 33% TiO_2 and about 7% ZrO_2 and has a specific gravity of about 3.7.

The following images are produced in the presence of an ambient temperature of about 70°F. and an ambient relative humidity of about 50 percent.

The developer mixture is cascaded across an imaging surface bearing a positively charged electrostatic image. The resulting developed image is transferred by electrostatic means to a sheet of paper whereon it is fused by heat. The resulting fused image is dense, has good resolution and substantially no background.

EXAMPLE XII

The experiment of Example XI is repeated except that images are produced in the presence of an ambient temperature of about 70°F. and an ambient relative humidity of about 85 percent. The resulting fused image prepared as in Example XI is dense, has good resolution and substantially no background.

EXAMPLE XIII

A developer mixture is produced by mixing one part colored styrene copolymer toner particles described in Example I with about 60 parts glass carrier bead particles having an average particle size of about 600 microns.

The glass bead composition comprises about 50% BaO, about 25% SiO_2 and about 25% TiO_2 and has a specific gravity of about 4.3.

The following images are produced in the presence of an ambient temperature of about 70°F. and an ambient relative humidity of about 50 percent.

The developer mixture is cascaded across an imaging surface bearing a positively charged electrostatic image. The resulting developed image is transferred by electrostatic means to a sheet of paper whereon it is fused by heat. The resulting fused image is dense, has good resolution and substantially no background.

EXAMPLE XIV

The experiment of Example XIII is repeated except that the images are produced in the presence of an ambient temperature of about 70°F. and an ambient relative humidity of about 85 percent. The resulting fused image prepared as in Example XIII is dense, has good resolution and substantially no background.

EXAMPLE XV

A developer mixture is produced by mixing one part colored styrene copolymer toner particles described in Example I with about 150 parts glass carrier bead particles having an average particle size of about 250 microns.

The glass bead composition comprises about 32% SiO_2, about 42% PbO, about 6% BaO, about 18% TiO_2, and about 2% ZrO_2 and has a specific gravity of about 5.2.

The following tests are run at an ambient temperature of about 70°F. and an ambient relative humidity of about 50 percent.

The relative triboelectric value of the carrier measured by means of a Faraday Cage is about 23.5 microcoulombs per gram of toner. The developer mixture is cascaded across an imaging surface bearing a positively charged electrostatic image. The resulting developed image is transferred by electrostatic means to a sheet of paper whereon it is fused by heat. The resulting fused image is dense, has excellent resolution and substantially no background.

EXAMPLE XVI

The experiment of Example XV is repeated except that images are produced in the presence of an ambient temperature of about 70°F. and an ambient relative humidity of about 85 percent. The resulting fused image prepared as in Example XV is dense, has excellent resolution and substantially no background.

EXAMPLE XVII

A developer mixture is produced by mixing one part colored styrene copolymer toner particles described in Example I with about 100 parts glass carrier bead particles having an average particle size of about 400 microns. The glass bead composition comprises about 12% SiO_2, about 45% PbO, about 25% BaO, and about 18% TiO_2 and has a specific gravity of about 5.0.

The following images are produced in the presence of an ambient temperature of about 70°F. and an ambient relative humidity of about 50 percent.

The developer mixture is cascaded across an imaging surface bearing a positively charged electrostatic image. The resulting developed image is transferred by electrostatic means to a sheet of paper whereon it is fused by heat. The resulting fused image is dense, has good resolution and substantially no background.

EXAMPLE XVIII

The experiment of Example XVII is repeated except that images are produced in the presence of an ambient temperature of about 70°F. and an ambient relative humidity of about 85 percent. The resulting fused image prepared as in Example XVII is dense, has good resolution and substantially no background.

EXAMPLE XIX

A developer mixture is produced by mixing one part colored styrene copolymer toner particles described in Example I with about 100 parts glass carrier bead particles having an average particle size of about 400 microns.

The glass bead composition comprises about 11% SiO_2, about 0.5% NaO, about 3.5% CaO, about 48% BaO, about 36% TiO_2, and about 1% B_2O_3 and having a specific gravity of about 4.2.

The following tests are run at an ambient temperature of about 70°F. and about 50 percent ambient relative humidity.

The relative triboelectric value of the carrier measured by means of a Faraday Cage is about 19 microcoulombs per gram of toner. The developer mixture is cascaded across an imaging surface bearing a positively charged electrostatic image. The resulting developed image is transferred to a sheet of paper whereon it is fused by heat. The resulting fused image has good resolution, good density and substantially no background.

EXAMPLE XX

The experiment of Example XIX is repeated except that the images are produced in the presence of an ambient temperature of about 70°F. and an ambient relative humidity of about 85 percent. The resulting fused image prepared as in Example XIX has good resolution, good density and substantially no background.

EXAMPLE XXI

The experiment of Example XIX is repeated except that the images are produced in the presence of an ambient temperature of about 90°F. and an ambient relative humidity of about 85 percent. The resulting fused image prepared as in Example XIX has good resolution, good density and substantially no background.

Although specific components and proportions have been stated in the above description of preferred embodiments of the invention, other typical materials as listed above where suitable may be used with similar results. In addition, other materials may be added to the mixture to synergize, enhance, or otherwise modify the properties of the carrier beads. For example, a material to improve the sphericity of the beads may be incorporated during manufacture.

Other modifications and ramifications of the present invention will occur to those skilled in the art upon a reading of the disclosure. These are intended to be included within the scope of this invention.

What is claimed is:

1. A method of forming a visible image comprising the steps of:

a. forming an electrostatic latent image on a surface;

b. contacting said electrostatic latent image with an electrostatographic developer mixture comprising finely divided electroscopic toner particles having an average particle size less than about 30 microns electrostatically adhering to the surface of substantially homogeneous glass carrier particles having an average particle size between about 30 microns and about 1,000 microns, each of said toner particles comprising a resin and a colorant selected from the group consisting of dyes and pigments and each of said homogeneous glass carrier particles having a specific gravity between about 3 and about 6 and consisting essentially of from about 10 percent to about 40 percent by weight of oxides of silicon, from about 4 percent to about 50 percent by weight of oxides of barium, from about 15 percent to about 40 percent by weight of oxides of titanium, less than about 45 percent by weight

of oxides of lead, less than about 4.5 percent by weight of oxides of calcium and less than about 5 percent by weight of oxides of metals selected from the group consisting of sodium, potassium, lithium and mixtures thereof;

c. until at least a portion of said finely divided toner particles are attracted to and held on said surface in conformance to said electrostatic latent image.

2. A method of forming a visible image according to claim 1 wherein said glass carrier particles comprise from about 11 percent to about 13 percent by weight of oxides of silicon, from about 43 percent to about 48 percent by weight of oxides of barium, from about 34 percent to about 37 percent by weight of oxides of titanium, less than about 45 percent by weight of oxides of lead, less than about 4.5 percent by weight of oxides of calcium, from about 0.5 percent to about 1.5 percent by weight of oxides of boron and less than about 5 percent by weight of oxides of metals selected from the group consisting of sodium, potassium, lithium and mixtures thereof.

3. A method of forming a visible image according to claim 1 wherein said glass carrier particles comprise from about 30 percent to about 32 percent by weight of oxides of silicon, from about 4 percent to about 6 percent by weight of oxides of barium from about 16 to about 20 percent by weight of oxides of titanium, less than about 45 percent by weight of oxides of calcium, from about 2 percent from about 4 percent by weight of oxides of zirconium and less than about 5 percent by weight of oxides of metals selected from the group consisting of sodium, potassium, lithium and mixtures thereof.

4. A method of forming a visible image according to claim 1 wherein said toner particles comprise colored styrene copolymer particles.

* * * * *