United States Patent

Hagenbach

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[54] **DEVELOPER SYSTEM**

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[56] **References Cited**

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[57] **ABSTRACT**

Method is provided for forming carrier particles of substantially uniform size by cutting rods of a malleable metal or plastic into lengths substantially equal to the diameter of said rods and causing continuous impingement of said rods with a rigid surface whereby essentially spheroidal carrier particles are obtained within close tolerances. These spheroidal carriers can be admixed with toner to form improved developer compositions.

9 Claims, No Drawings

DEVELOPER SYSTEM

This invention relates in general to imaging systems and, more particularly, to improved developing materials, their manufacture and use.

The formation and development of latent electrostatic images on an electrostatographic imaging surface is well known. The basic electrostatographic process, as taught by C.F. Carlson in U.S. Pat. No. 2,297,691, 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 will normally be attracted to those areas of the layer which retain a charge, thereby forming a toner image corresponding to the latent electrostatic image. This powder 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 heat. Instead of latent image formation by uniformly charging the photoconductive layer and then exposing the layer to a light and shadow image, one may form the latent image by directly charging the layer in image configuration. The powder image may be fixed to the photoconductive layer if elimination of the powder image transfer step is desired. Other suitable fixing means such as solvent or overcoating treatment may be substituted for the foregoing heat fixing step.

Many methods are known for applying the electroscopic particles to the latent electrostatic image to be developed. One development method, as disclosed by E. N. Wise in U.S. Pat. No. 2,618,552 is known as “-cascade” development. In this method, a developer material comprising relatively large carrier particles having finely-divided toner particles electrostatically clinging to the surface of the carrier particles is conveyed to and rolled or cascaded across the latent electrostatic image-bearing surface. The composition of the toner particles is so chosen as to have a triboelectric polarity opposite that of carrier particles. As the mixture cascades or rolls across the image-bearing surface, the toner particles are electrostatically deposited and secured to the charged portion of the latent image and are not deposited on the uncharged or background portions of the image. Most of the toner particles accidentally deposited in the background are removed by the rolling carrier, due apparently, to the greater electrostatic attraction between the toner and the carrier than between the toner and the discharged background. The carrier particles and unused toner particles are then recycled. This technique is extremely useful for the development of line copy images. The cascade development process is the most widely used commercial electrostatographic development technique. A general purpose office copying machine incorporating this technique is described in U.S. Pat. No. 3,099,943.

Another technique for developing electrostatic images is the “magnetic brush” process as disclosed, for example, in U.S. Pat. No. 2,874,063. In this method, a developer material containing toner and magnetic carrier particles is carried by a magnet. The magnetic field of the magnet causes alignment of the magnetic carriers in a brush-like configuration. This “-magnetic brush” is engaged with an electrostatic-image bearing surface and the toner particles are drawn from the brush to the electrostatic image by electrostatic attraction.

CARRIER MATERIAL CRITERIA

The criteria for selection of suitable carrier materials are extremely rigid in that these materials must exhibit a unique balance of electrostatic properties. The carrier must be capable of inducing a triboelectric charge on the toner particles opposite in polarity to that of the image being developed in order to effect deposition of the toner particles on the latent image. However, the carrier must also exhibit sufficient electrostatic attraction for the toner particles to enable the carrier to be an effective scavenger for toner particles deposited on the discharged background of the photoconductive insulating layer.

A property common to all carrier developers is a threshold force which the image developing forces must exceed in order to effect deposition. The retention force of the carrier is probably a combination of coulomb attraction between the toner and carrier, along with short-range “contact” forces. These retention forces account for the high contrast characteristic of all carrier developers as is desirable for line copy reproduction. It contributes to relatively clean, dust-free background or non-image areas, yet permits dense image development.

Residual charge is almost invariably present in the nominally discharged or background areas of the latent image. Relatively low as this charge density is, it may nevertheless be non-uniform, and such irregularities will be a source of small fields capable of trapping toner particles. This electrostatic “noise” in the background areas of the latent image is one of the primary sources of unwanted background toner.

As toner is removed from the carrier by the development fields, the carrier becomes more capable of accepting loosely held toner, especially that not held by fields associated with the latent image. Removal of toner from the carrier leaves upon it an opposite, unbalanced charge that is not immediately neutralized. Thus, developer is intrinsically its own scavenging agent.

Thus, it is of critical importance in obtaining a suitable carrier material that it can be capable of imparting charge to the toner particles through triboelectrification and yet exhibit sufficient electrostatic charge relative to the discharged portions of the photoconductor to attract stray toner particles thereby maintaining a clean background without interfering with the attraction of the toner particles by the latent image. Thus, the triboelectric relationship of the toner and carrier must be such that an acceptable development of the latent electrostatic image is produced, i.e., a dense image with low background. An excessively high triboelectric relationship produces low density image with clean background because of the inability of the electrostatic image to attract sufficient toner particles from the carrier. A low triboelectric relationship produces a so-called “dusty” developer which will develop very low contrast electrostatic patterns but will also produce high background densities. In order to obtain a practical developer, these extremes must be avoided. In use, the average triboelectric relationship for the developer decreases with time because of cumulative physical damage to the carrier. Therefore, the ideal carrier is a material exhibiting a proper triboelectric relationship with the toner, uniformity of size within close tolerances and resistance to physical damage and impaction which can impair this critical relationship.

While ordinarily capable of producing good quality images, conventional developing materials suffer serious deficiencies in certain areas. The developing materials must flow freely to facilitate accurate metering and even distribution during the development and developer recycling phases of the electrostatographic process. Some developer materials, though possessing desirable properties such as proper triboelectric characteristics, are unsuitable because they tend to cake, bridge and agglomerate during handling and storage. Adherence of carrier particles to reusable electrostatographic imaging surfaces causes the formation of undesirable scratches on the surfaces during image transfer and surface cleaning steps. The tendency of carrier particles to adhere to imaging surfaces is aggravated when the carrier surfaces are rough and irregular. The coatings of most carrier particles deteriorate rapidly when employed in continuous processes which require the recycling of carrier particles by bucket conveyors partially submerged in the developer supply such as disclosed in U.S. Pat. No. 3,099,943. Deterioration occurs when portions of or the entire coating separate from the carrier core. The separation may be in the form of chips, flakes or entire layers and is primarily caused by fragile, poorly adhering coating materials which fail upon impact and abrasive contact with machine parts and other carrier particles. Carriers having coatings which tend to chip and otherwise separate from the carrier core must be frequently replaced thereby increasing expense and consuming time. Print deletion and poor print quality occur when carriers having damaged coatings are not replaced. Fines and grit formed from carrier disintegration tend to drift and form unwanted deposits on critical machine parts and this coating has a charge which adds to the background on the electrostatographic imaging surface. Many carrier coatings having high compressive and tensile strength either do not adhere well to the carrier core or do not possess the desired triboelectric characteristics. The triboelectric and flow characteristics of many carriers are adversely affected when relative humidity is high. For example, the triboelectric values of some carrier coatings fluctuate with changes in relative humidity and are not desirable for employment in electrostatographic copying systems, particularly in automatic machines which require carriers having stable and predictable triboelectric values. Another factor affecting the stability of carrier triboelectric properties is the susceptibility of carrier coatings to "toner impaction". When carrier particles are employed in automatic machines and recycled through many cycles, the many collisions which occur between the carrier particles and other surfaces in the machine cause the toner particles carried on the surface of the carrier particles to be welded or otherwise forced into the carrier coatings. The gradual accumulation of permanently attached toner material on the surface of the carrier particles causes a change in the triboelectric value of the carrier particles and directly contributes to the degradation of copy quality by eventual destruction of the toner carrying capacity of the carrier. Thus, there is a continuing need for a better system for developing latent electrostatic images.

In view of the above, it is apparent that requirements for suitable carrier materials are quite stringent and cannot withstand substantial deviation from close tolerances. It has heretofore been found that spherical carriers are preferred so as to facilitate their movement in gravitating over the electrostatographic imaging surface. Moreover, greater equipment life can be achieved as a result of reduced friction where spherical carriers are employed.

Obtaining spheroids of substantially uniform size and within close dimensional tolerances has heretofore proved difficult and expensive. For example, steel shot has heretofore been employed as a carrier; however, the process generally employed to make such shot involves dropping molten steel into an atomized spray of cold liquid, generally water, wherein it is cooled and the internal surface tension of the molten droplet acts to spheroidize the droplet. This process, however, results in particles of considerably different particle size. Normally, the size distribution of particles obtained by such process ranges, for example, from about 200 microns to about 2,000 microns. Conventional separation procedures are insufficient to obtain particles of sufficiently close tolerances. Special procedures can be employed, if necessary; however, these procedures are tedious and expensive. Close tolerances are required for carrier particles in order to insure uniform development of the images. It would therefore be desirable to provide a method for forming essentially spheroidal carrier particles within close tolerances.

Accordingly, it is an object of the present invention to provide a process for forming carrier particles which are essentially spherical in shape.

It is another object of this invention to provide a process for preparing spherical carrier particles within close tolerances.

These as well as other objects are accomplished by the present invention which provides a method of forming spheroidal particles of substantially uniform size comprising cutting rods of a malleable metal or plastic into lengths substantially equivalent to the diameter of said rods, continuously causing impingement of the cut rods with a rigid surface whereby essentially spheroidal particles are obtained within close tolerances.

Any malleable material which can be drawn into or formed as wire rods, threads, etc., referred to herein collectively as "rods", can be employed. For example, metals such as steel, copper, nickel, aluminum, brass and the like, as well as plastics such as polystyrene, polycarbonates, polysulfones, poly(methylmethacrylate), poly(phenylene oxide) and the like can be suitably employed.

The desired malleable material can be drawn into or formed as a rod of suitable diameter for use as a carrier particle. Generally, carrier particles range in diameter from about 50 to about 1,000 microns. Carrier particles within such range possess sufficient density and inertia to avoid adherence to the electrostatic image during the cascade development process. The rods can then be cut either individually or in sheaths or strands to a length essentially equal to the diameter of said rods.

The cut particles of malleable material which are generally in the form of right cylinders having a length to diameter ratio (L/D) of about 1 are then subjected to a spheroidizing process wherein they are deformed and cold worked until the particles assume a generally spheroidal shape. This can be conveniently accomplished through continuous impingement of the cut particles with a rigid surface or particle. Various types of apparatus can be suitably employed for this purpose, for example, ball mills, tumbling mills, vibrating mills, blast mills, centrifugal mills and the like.

The spheroidization process of the present invention is rapid and efficient producing a high yield of spheroidal carrier particles within very close tolerances, generally of about ±0.010 inches. Surprisingly, it has been found possible to obtain extremely close tolerances of about ± 0.002 inches through use of the present process.

The spherical carrier particles of the present invention may be employed uncoated or coated with suitable film forming materials by conventional techniques to alter the triboelectric properties thereof. Carrier coating materials are well known and disclosed for example in U.S. Pat. Nos. 2,618,551 and 3,467,634.

The following examples further define, describe and compare methods of preparing the spherical particles of the present invention and of utilizing them to form developers for electrostatic latent images. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

A spool of stainless steel wire, 250 microns in diameter, is fed into a wire pellet cutting machine set to cut pellets of a length equal to the diameter of the wire. The pellets are formed at the rate of about 25 kilograms per hour.

The pellets are fed to a vibrating mill comprising a spring-mounted cylinder with dual eccentric mechanisms running horizontally on each side of the mill. Discrete targets, in the form of ceramic balls of relatively large diameter with respect to the pellets, occupy a major portion, i.e., about 80 percent of the mill volume. In operation, the pellets are charged to the mill and caused to undergo vibration and rotation at high speed subject to the action of the milling media caroming off each other as well as the walls of the chamber, giving rise to repeated impingement of the pellets with the ceramic balls causing deformation and cold working of the pellets. The effluent from the mill is essentially spherical steel particles of uniform diameter (250 microns) with a tolerance of ± 0.002 inches (50 microns).

The carrier particles so produced are suprisingly uniformly spherical. The spherical particles are then admixed with a toner comprising a styrene-n-butyl methacrylate copolymer, polyvinyl butyral and carbon black prepared by the method described in U.S. Pat. No. 3,079,342, in a ratio of 1 part toner to 200 parts carrier particles obtaining a substantially uniform coating thereof on all surfaces. The resulting developer mixture is fed to an automatic electrostatographic copying apparatus and employed therein for a period of 25,000 cycles. All reproductions obtained during this period are uniform with essentially no background deposits or dark spots.

EXAMPLE II

Low carbon steel wire having a diameter of 250 microns is cut into pellets having a length equal to the diameter of the wire as described in Example I.

The cut pellets are then subjected to a spheroidizing process wherein the cut pellets are caused to impinge against discrete, hardened steel targets through use of a centrifugal throwing wheel. The pellets are continuously recirculated via a bucket conveyor and hurled at high velocities by a high speed revolving vaned wheel against the discrete steel targets which are being continuously, freely rotated in a rotating drum. The resulting sphericle particles are discharged from the drum through a screening separator and collected. The sphericle particles exhibit a diameter of 250 microns with a tolerance of ±0.002 inches (50 microns).

The carrier particles obtained in the above manner are coated with a terpolymer reaction product described in Example IV of U.S. Pat. No. 3,467,634. The coated carrier beads are then mixed with a toner composition comprising a styrene-n-butyl methacrylate copolymer, polyvinyl butyral and carbon black prepared by the method described in U.S. Pat. No. 3,079,342, in a ratio of 1 part toner to 175 parts carrier and the resulting developer is placed in an automatic electrostatographic apparatus for 200,000 cycles. All reproductions obtained during this period are uniform with essentially no background deposits or dark spots.

EXAMPLE III

Employing the procedure described in Example II, pellets cut from aluminum wire 600 microns in diameter are subjected to the spheroidizing process. In this Example, a hardened steel plate was employed as the target and was situated with respect to the high speed revolving vaned wheel so that the full velocity of the particles is concentrated on the plate. Spherical particles are obtained exhibiting a diameter of 600 microns with a tolerance of ±0.010 inches (250 microns).

EXAMPLE IV

Employing the procedure described in Example II, pellets cut from brass wire 600 microns in diameter are subjected to the spheroidizing process. In this Example, ellipsoidal pieces of hardened steel having a major axis of about 2–3 inches are employed as the target and undergo continuous rotation in the rotating drum. These discrete targets, in the form of ellipsoidal pieces of steel, freely rotate and tumble about within the rotating zone. Ellipsoidal or spherical targets of this type are preferred because the pellets undergoing spheroidization tend not to break in their presence and tend to undergo spheroidization at a faster rate. Spherical particles are obtained exhibiting a diameter of 600 microns with a tolerance of ±0.002 inches (50 microns).

Although specific materials and conditions are set forth in the above exemplary processes in making and using the spherical carrier materials of this invention, these are merely intended as illustrations of the present invention. Various other toners, carrier cores, substituents and processes such as those listed above may be substituted in the examples with similar results.

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

What is claimed is:

1. Method of forming spheroidal particles of substantially uniform size comprising:
   cutting rods of a malleable material into lengths substantially equivalent to the diameter of said rods;
   charging said cut rods into a cold working zone;
   continuously, freely rotating discrete targets having rigid surfaces within said cold working zone; and
   cold working said cut rods by causing impingement of said cut rods with said rigid surfaces of said discrete targets as said discrete targets are undergoing continuous, free rotation within said cold working zone, whereby essentially spheroidal particles are obtained.

2. Method as defined in claim **1** wherein spheroidizing of the cut pellets is continued until spheroids having a diameter of from about 50 to about 1,000 microns are obtained.

3. Method as defined in claim **2** wherein spheroidizing of the cut pellets is continued until spheroids of substantially uniform diameter are obtained with the deviation from average particle size being within the range of 0.010 inch.

4. Method for forming electrostatographic carrier particles of substantially uniform size comprising:
   cutting rods of a malleable material into lengths substantially equivalent to the diameter of said rods;
   charging said cut rods into a cold working zone;
   continuously, freely rotating discrete targets having rigid surfaces within said cold working zone; and
   cold working said cut rods by causing impingement of said cut rods with said rigid surfaces of said discrete targets as said discrete targets are undergoing continuous, free rotation within said cold working zone, whereby essentially spheroidal particles of substantially uniform diameter are obtained with the deviation from average particle size being within the range of ±0.010 inch.

5. Method as defined in claim **4** wherein the cold working zone is a milling zone, the major portion of which contains targets in the form of rigid balls, wherein said cut rods undergo vibration and rotation at high speed in said zone subject to the repeated impingement of said balls therewith to form essentially spherical carrier particles which are thereafter discharged from said zone.

6. Method as defined in claim **4** wherein the cold working zone is a continuously rotating zone and the cut rods are repeatedly hurled into said continuously rotating zone and against said targets maintained in said rotating zone.

7. Method as defined in claim **6** wherein said targets are ellipsoidal or spherical and said cut rods are hurled thereagainst by a centrifugal throwing wheel.

8. Method as defined in claim **1** wherein the malleable material is a metal.

9. Method as defined in claim **4** wherein the malleable material is a metal.

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