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ELECTROPHOTOGRAPHIC DRY TONER

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ABSTRACT OF THE DISCLOSURE

An electrophotographic dry toner which contains as a resin component a mixture comprising a solid epoxy resin as a main component and 2.5 to 25% by weight, based on the weight of said epoxy resin, of a polyvinyl acetal resin compatible with said epoxy resin. The toner is particularly applicable in transfer type printing.

This invention relates to an electrophotographic dry toner.

More particularly, the invention is concerned with a dry toner which displays excellent properties when used in transfer type printing.

In general, a toner of this kind is prepared by fusing a thermoplastic resin together with small amounts of a coloring pigment and a charge controlling dye, cooling the mixture and then forming the cooled mixture into particles of about 5 to 20 microns, and is used in admixture with an iron or glass powder as a carrier.

In the electrophotographic printing of the transfer type, a single photosensitive sheet is repeatedly subjected to the steps including electrostatic charging, imagewise exposure, toner development, image transfer and toner removal. Accordingly, a toner used in the transfer type printing is required to have, in addition to the properties of a toner used in direct type printing, such properties as excellent transferability, eliminability and durability. That is, the toner should have such properties that when adhered to and developed on a static latent image, it can be effectively transferred onto another paper sheet due to corona charge from the back side of said sheet, and residual toner after the transfer can be wiped off easily and completely by means of a cleaning brush made of an animal fur or the like.

If a toner, which is inferior in such properties as transferability and eliminability, has been used, the resulting copy forms uneven transfer portions, fog and a ghost image (an image in which a fresh image has been superposed on a residual image of the preceding printing cycle) to give a markedly blurred image and, at the same time, the photosensitive sheet, cleaning brush and collection bag, which are repeatedly used, are greatly shortened in service life. Further, when used as a developing agent in admixture with an iron powder or the like carrier, the toner tends to be microfinely divided due to the revolution of developing brush or the like or to the external force applied for the stirring of freshly supplied toner, or a thin toner film is formed on the carrier surface, to deteriorate the durability of the developing agent. It is therefore desired to use a toner which has no such drawbacks as mentioned above.

The transfer efficiency of the toner is affected not only by the amount of charged electricity but also by the granularity thereof, and it is not desirable to use a toner containing fine particles of less than about 5 microns in diameter which are frequently formed when the developing agent is used continuously.

As the thermoplastic resin, which is the main constituent of a dry toner, there has extensively been used hitherto a polymer or copolymer such as polystyrene, polymethacrylate, polyvinyl acetate, polyvinyl chloride or cumarone-indene, a condensation product such as xylene resin, phenol resin or polyamide, or a natural resin such as rosin, ester gum or shellac. However, toners prepared from the above-mentioned known resin components cannot satisfy such requirements as fixability and pulverizability, simultaneously with a series of properties of toners to be used in the aforesaid transfer type printing.

In view of the state of the art as mentioned above, we made extensive studies to find that a toner, which contains as a resin component a mixture composed of a major proportion of a solid epoxy resin and a minor proportion of a polyvinyl acetal resin compatible with said epoxy resin, can overcome the above-mentioned drawbacks and is sufficiently satisfactory. The resin mixture used in the present invention contains 2.5 to 25% by weight of the polyvinyl acetal resin based on the weight of the epoxy resin. In case the amount of the polyvinyl acetal resin is less than 2.5% by weight, no desired effect can be attained, while in case the amount thereof is more than 25% by weight, the toner is excessively solidified to become easily pulverizable, and the fixing temperature thereof becomes undesirably high. When the polyvinyl acetal resin is used in an amount within the above-mentioned range, the resulting toner is excellent in fusibility, durability and fixability.

The epoxy resin used in the present invention is a normally solid compound containing at least two epoxy groups in one molecule which is prepared by reacting epichlorohydrin with bisphenol and phthalic anhydride in the presence of a catalyst and has a molecular weight of 700 to 5,000 and a melting point of about 55° to 155° C. Examples of commercial epoxy resins of this kind include Epikote produced by Shell Co. and Araldite produced by Ciba Ltd.

On the other hand, the polyvinyl acetal resin compatible with said epoxy resin is prepared by acetalizing polyvinyl alcohol with a saturated aldehyde having 1 to 3 carbon atoms in the presence of acid or alkali. The acetalization degree of the polyvinyl acetal resin varies depending on the kind and amount of the aldehyde or the amount of the catalyst used, but is preferably about 75% by weight or more in order to increase the compatibility thereof with the epoxy resin. Examples of commercial polyvinyl acetal resins of this kind include Denkabutyral #2000 D_1 and Denkaformal #50 produced by Denkikagaku Kogyo Co.

The toner of the present invention is prepared by mixing according to an ordinary physical dispersion procedure the aforesaid specific resin components with a coloring pigment and a charge-controlling dye which have heretofore been used in electrophotographic toners, and then pulverizing the resulting mixture into fine particles of about 5 to 20 microns in diameter according to the mechanical pulverization or spray-drying process.

When compared with toners individually containing a polystyrene resin and an epoxy resin as resin components,

the thus obtained toner of the present invention has the effects as set forth in the following table:

	Amount of charged electricity (v.)	Transfer ratio (wt. percent)	Elimina-bility	Dura-bility	Fixa-bility	Pulveriza-bility	After 10,000 times' use: Transfer ratio (percent)	After 10,000 times' use: Elimina-bility	After 10,000 times' use: Stains on carrier surface
Polystrene resin	100–120	70	Somewhat favorable.	Poor	Favor-able.	Favor-able.	48	Poor	Observed.
Epoxy resin	50–70	80	do	do	do	do	50	do	Do.
Toner of the present invention	50–70	90	Excellent	Favor-able.	do	do	89	Favor-able.	None.

In the above table:

(1) The amount of charged electricity was measured using a means having a Faraday tube in combination with an electrometer.
(2) The transfer ratio was represented by wt. percent.
(3) The eliminability was evaluated by repeatedly using a photosensitive zinc oxide sheet 1,000 times and examining toner stains on the surface thereof.
(4) The durability was evaluated by examining the degree of pulverization of the toner in a bath of a developing agent comprising the toner and an iron powder as a carrier.

From the above table, it is understood that when compared with the conventional toners, the toner of the present invention is low in electrification (i.e. suitable as a toner for use in transfer type printing), high in transfer ratio and excellent in elimination effect, so that even when used repeatedly, it forms no stains on the surface of the photosensitive sheet, is not repulverized nor leaves toner stains on the carrier surface, and is excellent in abrasion resistance (durability). That is, we conducted a long run test to prepare 20,000 copies according to the magnet brush method using a 3% developing agent of each of the present toner and a conventional toner in admixture with an iron powder carrier. As the result, the amount of formed fine particles of less than 5 microns in diameter was up to 0.1% by weight in the case of the present toner, but was about 1.1% by weight in the case of the conventional toner, and the amount of stains left on the carrier surface was 0.15% (wt.)/total iron powder in the case of the present toner but was about 0.6% (wt.)/total iron powder in the case of the conventional toner. Thus, the toner of the present invention has excellent properties.

In addition, the present toner has such properties that despite of its having practically sufficient abrasion resistance as mentioned above, the toner can be easily pulverized into particles of about 5 to 20 microns in diameter by means of a conventional pulverizer, and the sharpness of the toner image is such that thermal fixing can be advantageously effected due to favorable adhesiveness of the toner to paper sheets at its softening temperature at the time of fusion.

In the above explanation, there has chiefly been mentioned the case where zinc oxide is used as the photoconductive layer and an iron powder is used as the carrier. However, properties required for dry toners are substantially common in the case of other types of electrophotographic printing, so that the above explanation is not limitative.

The present invention is illustrated below with reference to examples.

EXAMPLE 1

90 grams of Araldite #6084 (epoxy resin produced by Ciba Ltd., M.P. 95–105° C.) and 10 g. of Denkabutyral 2000D (polyvinyl butyral produced by Denkikagaku Kogyo Co., butyralation degree 80 wt. percent) were kneaded on two hot rolls, and the resulting mixture was sufficiently kneaded with 10 g. of Mogal A and 2.5 g. of Nigrosine SSB. After cooling, the mixture was pulverized by means of a jet mill to particles of 5 to 20 microns in diameter to obtain a positively charged toner having a charged electricity of +60 v./g. as measured according to the aforesaid method.

30 grams of the thus obtained toner was mixed with 1 kg. of an iron powder of 200 to 300 mesh to prepare a developing agent. Using this developing agent, a negative latent image on a zinc oxide photosensitive paper was developed to obtain a clear positive mirror image. The developed image was electrostatically transferred onto a high quality paper for printing and then fixed. On the other hand, the photosensitive paper was repeatedly used after elimination of residual toner with an animal fur brush. As the result, the transfer ratio was 91% by weight, and the elimination of residual toner was such that no toner stain was left on the photosensitive paper even after 1,000 times' repeated use.

The above-mentioned developing agent was subjected to a printing test for preparation of 10,000 copies, while adequately suplementing the toner. As the result, the developing agent maintained an excellent copying ability substantially identical with the ability at the initial stage.

EXAMPLE 2

A toner comprising a resin mixture of 85 g. of Epikote #1002 (epoxy resin produced by Shell Co., M.P. 75–85° C.) and 15 g. of Denkaformal #50 (polyvinyl formal produced by Denkikagahu Kogyo Co., formalation degree more than 81% by weight) was prepared and used for transfer type printing in the same manner as in Example 1. As the result, the charged electricity of the toner was +65 v./g., the transfer ratio was 89%, and the elimination of residual toner was such that no toner stain was left at all on the photosensitive layer even after 1,000 times' repeated use.

Further, the developing agent was subjected to a fatigue promotion test by use of a ball mill in such a manner that 300 g. of the developing agent was charged into a 300 cc. ball mill case and revolved for 48 hours without using balls. Thereafter, the developing agent was subjected to a printing test to obtain clear copies which were entirely identical with those in the case where the fatigue promotion was not effected.

In the test, the number of continuously printed copies was about 500 per hour of the treating time of the fatigue promotion test.

EXAMPLE 3

85 grams of Bakelite #2003 (epoxy resin produced by Bakelite Co., M.P. 92.2–103° C.) and 20 g. of Denkabutyral 2000D were kneaded on two hot rolls, and the resulting mixture was sufficiently kneaded with 5 g. of carbon black and 0.5 g. of Zapon Black. After cooling, the mixture was pulverized by means of a jet mill to particles of 5 to 20 microns in diameter to obtain a negatively charged toner having a charged electricity of −70 v./g.

20 grams of the thus obtained toner was mixed with 1 kg. of carrier particles, which had been formed by repeatedly coating cellulose acetate resin on glass beads of 60 to 80 mesh, to prepare a developing agent. Using this developing agent, a positive latent image on a photosensitive selenium plate was developed to obtain a positive mirror image. The developed toner was electrostatically transferred onto a high quality paper and then fixed by heating. On the other hand, the photosensitive plate was repeatedly used after elimination of residual toner with

an animal fur brush. As the result, the transfer ratio was 90% by weight, and the elimination of residual toner was such that no toner stain was left on the photosensitive plate even after 10,000 times repeated use.

EXAMPLE 4

Using the developing agent of Example 1, a negative latent image on a polyethylene-coated electrostatic recording paper was developed to obtain a clear positive copy. Further, the developing agent was subjected to treatment for 48 hours according to a fatigue promotion test method using a ball mill and then subjected to a printing test to obtain clear copies which were entirely identical with those in the case where the fatigue promotion was not effected.

EXAMPLE 5

75 grams of Epikote #1004 (epoxy resin produced by Shell Chemical Co., M.P. 97–103° C.), 15 g. of Denkaformal and 10 g. of Hilac-110 resin (ketone resin produced by Hitachi Chemical Co., M.P. 110–130° C.) were kneaded on two hot rolls, and the resulting mixture was sufficiently kneaded with 5 g. of carbon black and 2.5 g. of Nigrosine SSB. After cooling, the mixture was pulverized by means of a jet mill to particles of 5 to 20 microns in diameter to obtain a positively charged toner having a charged electricity of +67 v./g. The thus obtained toner was subjected to the same test as in Example 1. As the result, the transfer ratio was 90% by weight, and the elimination of residual toner was such that no toner stain was left on the photosensitive layer even after 1,000 times repeated use.

Further, the developing agent was subjected to treatment for 48 hours according to a fatigue promotion test method using a ball mill and then subjected to a printing test to obtain clear copies which were entirely identical with those in the case where the fatigue promotion was not effected.

What we claim is:

1. An electrophotographic dry toner having a particle diameter of about 5–20 microns which contains as a resin component a mixture comprising a solid epoxy resin containing at least two epoxy groups in one molecule which is prepared by reacting epichlorohydrin with bisphenol and phthalic anhydride as a main component and 2.5 to 25% by weight, based on the weight of said epoxy resin, of a polyvinyl acetal resin compatible with said epoxy resin.

2. An electrophotographic dry toner as claimed in claim **1**, wherein said polyvinyl acetal resin is the acetalization product obtained by the reaction of polyvinyl alcohol with a C_1 to C_3-saturated aliphatic aldehyde.

3. An electrophotographic dry toner as claimed in claim **1**, wherein said polyvinyl acetal resin has the acetalization degree of more than about 75%.

4. An electrophotographic dry toner as claimed in claim **1**, further comprising a coloring pigment, a charge-controlling dye and a carrier.

5. In an electrophotographic dry toner composition comprising (1) a carrier and (2) toner particles having a particle diameter of about 5 to 20 microns of a fused mixture comprising a resin, pigment and a charge controlling dye, the improvement comprising a resin comprising a solid epoxy resin containing at least two epoxy groups in one molecule which is prepared by reacting epichlorohydrin with bisphenol and phthalic anhydride as a main component and 2.5 to 25% by weight, based on the weight of said epoxy resin, of a polyvinyl acetal resin compatible with said epoxy resin.

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