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PRESSURE FIXABLE ELECTROSCOPIC PRINTING POWDER

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ABSTRACT OF THE DISCLOSURE

A pressure fixable toner for electrostatic image development, that can be fixed on a receiving member by pressure, formulated with a polyamide resin in the range of 25% to 35%, a frangible resin 40% to 50%, and a polyolefene such as polymethylene or polyethylene in the range of 2.0% to 15% and the remainder consisting of color agents, and such optional ingredients as a metal soap or a polyhydric alcohol, the critical components being the polyamide resin and the polyolefin resin.

BACKGROUND OF THE INVENTION

This invention relates to electroscopic printing powders which are useful for developing latent electrostatic images produced by photoelectrostatic copying techniques into a visible material image. More particularly, it relates to electroscopic powders which have been formulated with polyolefinic resins which serve to improve the fixability of the powder onto the copy sheet through the use of pressure.

Photoelectrostatic copying processes in which a photoconductive medium is imaged to produce a differential electrostatic charge which is then developed with an electroscopic powder are well known. A wide variety of photoconductive media may be employed such as inorganic photoconductive insulating metal ion crystalline containing materials, organic photoconductors and elemental photoconductors.

A wide variety of techniques are known for developing the differentially charged photoconductive medium such as magnetic brush, powder cloud, liquid development and cascade developing techniques.

The formulation of electroscopic powders to be compatible in a particular photoelectrostatic copying environment has been widely explored in this art and is well developed. For the most part, the powders are applied by the various techniques mentioned hereinabove and ultimately the powder image requires fixing so that it will adhere to the copy material. The copy material may be the photoconductive paper itself, such as in the case of zinc oxide which is the metal ion crystalline containing materials. In other processing systems, the powder image is first produced on a photoconductive drum and then transferred to a sheet of plain paper where the powder image must be, fixed. In either case, the electroscopic powder requires that it be permanently fixed to the material which is to become the permanent copy.

In the copying systems disclosed heretofore, the techniques of fixing the image onto the copy depended on the use of heat in order to fuse the thermoplastic resin powder onto the copy material. The use of heat energy is generally acceptable, but it is not without serious deficiencies. For example, the equipment requires that it be warmed up to an operating temperature level where the heating system will properly fuse the powder. The presence of heat has always presented the hazard of igniting the papers in the circumstance that there is a paper jam in the paper delivery systems, and at the very least was known to char the papers.

In terms of the design of the equipment, the use of heat required provision for large power inputs to the

equipment which made it costly to manufacture and maintain.

Another undesirable aspect of using heat to fuse the powder images is the introduction of heat into the working environment causing some discomfort.

One important consideration is the time which is required to impart sufficient heat to the thermoplastic powder so that it will properly soften and coalesce. In most copying systems, the rate of output of reproductions is only as fast as the slowest processing step, which heretofore was the heat fusing operation.

SUMMARY OF THE INVENTION

Electroscopic powders have been suggested which are formulated especially for pressure fusing. It has been found that because of their broad range of melting points, they tend to produce reproductions whose images are feathered and generally of poor resolution when heat fused because of the presence of very low melting point constituents, which when combined together with higher melting point materials cause the images to spread out.

It has been found that by compounding the prior art toners which were primarily heat fusible with a polyolefinic resin in the range of 2% to 15% based on the weight of resin, that these formulations then became uniquely and surprisingly responsive to pressure in the range of 300 pounds per lineal contact inch so that they may be permanently bonded to the image receiving surface.

It is a general object of the instant invention to provide an improved electroscopic powder having utility in high speed photoelectrostatic copying machines which can be used to equal advantage in systems which require the image powders to be fused by heat or by pressure.

It is another object of the instant invention to provide an improved electroscopic powder for use in high output photoelectrostatic copying machines capable of producing high quality images when fixed by pressure.

It is a still further specific object of the instant invention to provide an electroscopic powder which is specifically adapted for high volume photoelectrostatic copying machines employing a magnetic brush developer system.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In carrying out the above objects, electroscopic powders of the instant invention comprise a thermoplastic resin component which is a polyamide resin in the range of 15 to 35 percent, preferably 25% to 35% by weight, a frangible or brittle resin component in the range of 30 to 50 percent, preferably 40% to 50% by weight, such as a rosin modified maleic anhydride-polyhydric alcohol resin, an unsaturated co-ester resin such as a diphenol resin esterified with a fatty acid or a pure non-heat reactive phenolic resin and a third component which is a polyolefinic resin selected from polymethylene and polyethylene resins in the range of 2.0% to 15% by weight plus various coloring agents 1% to 10% and certain optional ingredients as hereinafter described.

The resin blend may optionally include additives such as polyol resins, toluene sulfonamides or butylated-hydroxy-toluene which are utilized as agents tending to decrease the melt viscosity of the thermoplastic resin mixture.

In describing the combination of thermoplastic resins, it will be understood that the various resins must be compatible with one another in their molten state. Compatibility as used in this application refers to the resins being dispersable or otherwise soluble in one another so that a uniform mixture may be obtained.

The preferred polyamide resins are produced by the reaction of high molecular weight polyene fatty acids and their esters and an amine. By reacting ammonia, a primary or secondary amine, a hydroxy amine, or an alkanolamine, with a high molecular weight carboxylic acid or an ester thereof, either saturated or unsaturated said acid or ester being obtainable by polymerizing at elevated temperatures, said polyene fatty acid or esters thereof, and in the case of the esters, converting the polymers to the corresponding acid if desired, there are produced the preferred polyamides. Examples of polyene fatty acids in esterified form are 9, 11- and/or 9, 12-octadecadienoic acid (obtained from soybean oil) and dehydrated castor oil, linoleic acid, alpha and beta-eleostearic acid (obtainable from tung oil). The preferred esters are those derived from methanol, ethanol and propanol. Primary and secondary amines may be used, such as for example, methyl amine, ethyl amine, propyl amine, ethylenediamine, tetramethylenediamine, pentamethylenediamine, piperizine and diethylenetriamine. The polyamide materials are sold by General Mills Company under the trademarks "Versamid." Other suitable polyamide resins are also available from the Krumbhaar Resin Division of Lawter Chemicals Incorporated under the trademark "Polymid."

The second thermoplastic constituent in the electroscopic powder contributes a degree of frangibility to the mixture. A suitable, frangible, thermoplastic resin is a rosin-modified phenolic resin, such as those prepared by a rosin-modified phenol formaldehyde resin, or the reaction product of maleic anhydride and rosin with a polyhydric alcohol such as glycerol or pentaerythrythol. Such rosin-modified phenolic resins are sold under the trademark "Amberol" manufactured by Rohm and Haas Company, and a similar resin is manufactured by the Krumbhaar Division of Lawter Chemical sold under the trade designation K1813B. The condensation resins formed by reacting cyclohexanone and formaldehyde are acceptable materials manufactured by Badische Aniline GmbH of Germany under the trade name Ketone A. A resin which is the condensation of cyclohexanone sold by the same company under the trade name Ketone N can be used successfully. Another frangible resin component is a diphenolic resin esterified with Soya Oil and phenol formaldehyde available from Nelio Chemical Corporation sold under the trade designation VBR–800.

The important component, in terms of rendering the toner formulation pressure fixable, is a polyolefin such as polymethylene or polyethylene. Suitable polyolefinic materials are as follows: "Polywax," the Bareco Division—Petrolite Corporation, Tulsa, Okla.; "Resin 7004 and 7006," Sinclair Kopers Company, Port Arthur, Tex.; EAM–6006 and EMB–6050, Philips Petroleum Company, Bartlesville, Okla.; Polyethylene AC–629A, 680, 6A and 8A, Allied Chemical, Morristown, N.J.; DOWC–0355, DYLT, DYDT and CPR–1, Union Carbide Corporation, New York, N.Y. Paraflint RG is a polymethylene available from More and Munger Corporation.

The preferred polyolefin is one which has high degree of crystallinity such as in the range of 30% to 97%, preferred range means 50% to 98%. Another physical property of the polyolefinic materials that is a measure of their suitability for use in pressure responsive toners of this invention is density. The operable density range is from 0.88 gram per cubic centimeter to 0.98 gram per cubic centimeter, the preferred range being from 0.93 gram per cubic centimeter to 0.98 gram per cubic centimeter. Polyethylene CPR–1 and DOWC–0355, Union Carbide, and Polywax 2000, Petrolite Corporation, have the proper degrees of crystallinity and density. A suitable polymethylene is "Paraflint R.G." manufactured by Moore and Munger of Stanford, Conn.

The resin mixture that forms the electroscopic powder, preferably should not soften or become tacky at temperatures below 130° .

As an optional ingredient, there may be added to the composition fluxing agents which tend to improve the mixability of the various ingredients and improves flow when they are in their molten state. However, it should be understood that the use of these fluxing agents is optional and the formulations of the instant invention perform successfully without the aid of the fluxing agents. Successful fluxing agents are provided by the group of polyhydric alcohols sold by the Shell Chemical Company under the trademark "Polyol X–450." Purified wood rosins, such as those sold by the Hercules Powder Company under the trade name "M–Wood Rosins" and toluene sulfonamides available under the trademark "Santicizer 8" and "Santicizer 9" sold by Monsanto Chemical Company, are also suitable agents.

An optional ingredient in the pressure fixing toner is the metal soap such as, for example, sinc, barium or lithium soaps of stearatic, lauric and palmitic acid which are found necessary where the developer mix is exposed to the excessive stresses present in high speed machines. It has been found that the presence of these metal soaps prolongs the life of the developer mix where it is tumbled and compacted rapidly in the developer such as when producing 50 to 60 copies per minute. The metal soaps have been found to prolong the life of the mix where the equipment is used for long periods of time at high speeds. However, it is not necessary to include the metal soaps where the speed of the machine is operated at slower copymaking speed or at high speeds intermittently. Completely acceptable toners which were pressure fixable as well as heat fusible can be produced without the metal soaps.

In preparing the electroscopic powders of this invention, the resinous materials are first reduced to their molten state and mixed together in suitable blending equipment. When the resinous materials, such as for example, polyamide and the rosin-modified phenolic resins are thoroughly mixed, there is then added the various coloring agents such as pigments and dyes and the fluxing agents to assure proper mixing and/or dispersion of the ingredients. The next ingredient to be added is the polyolefin material in the amounts called for together with the metal soaps.

To correctly orient the black toner powder, the polyolefin resin must contain a pigment or dye, such as Nubian black resin. It is important here to recognize that the addition of the metal soaps called for by the instant formulas is for the purpose of providing a longer life of the electroscopic powder during printing in the environment of a high speed machine. Metal soaps which have been utilized to advantage are zinc, lithium, cadmium, and barium soaps of lauric, stearic acid and palmitic acid in the range of from 0.01 percent to 3.0 percent.

The following examples are given to illustrate the preferred embodiments comprising electroscopic powders of this invention. It will be understood that these examples are merely for the purpose of illustration and it is not intended that this invention be limited to the specific examples.

In all the examples, the amounts shown represent percent by weight of the total electroscopic powder formulation.

EXAMPLE I

Ingredients:	Percent
Polyamide resin "Polymid 1060"—Lawter Chemical Company	27.6
Maleic anhydride-modified rosin Amberol 800 —Rohm and Haas Company	48.8
Polyethylene DOWC 0355—Union Carbide Corporation	3.0
Nubian Resin Black—Keystone Aniline and Chemical Co.	6.5
Carbon Black — 4PCO5 manufactured by Capital Color Company	2.4
Lithium stearate	2.0
Polyhydric alcohol (optional)—Polyol X–450	9.7

The polyamide resin called for in this example, together with the maleic anhydride-modified rosin, is heated in a suitable vessel which is equipped with a mixer such as a conventional impeller-type stirrer. The resins are reduced to a molten state so that the stirrer can agitate the mixture. The agitation or stirring continues until the resins are uniformly mixed together into a uniform molten mass which held at temperature in the range of 360° F. to 370° F. To the molten resin system is then added lithium stearate. The mixture is stirred until the metal soap is dispersed or melted with the polyamide resin. The black dye and carbon black are added next followed by the polyhydric alcohol, if this ingredient is selected to be added. Upon thorough dispersion of the coloring agents, the polyethylene is added while the batch is being mixed.

The molten mass is removed from the mixing vessel and immediately poured into shallow pans so as to form large thin wafers. These are rapidly cooled, such as by forced air, in order to prevent the polyethylene from separating out of the mixture or otherwise stratify. The large wafer formations are crushed and pulverized to an average particle size ranging from under one micron to about 50 microns in size.

The powder is classified according to particles which pass through a 100-mesh screen so that the largest particle size is under 149 microns.

The softening point of the toner of Example I is in the range of 106° C. to 111° C. measured in accordance with ASTM method No. E28–58T.

In order to prepare a developer mix, the powder is combined with a suitable carrier wherein the ratio of toner to carrier is in the range of 1:15 to 1:60. In this case, iron particles were used to form a developer mix to be used with a magnetic brush system. The ratio of toner powder to iron was 1 to 40 for such an application.

To equal advantage, the toner may be combined with glass beads of the type used in cascade systems in which case the ratio of parts of toner to parts of glass beads is one to 80.

The amount of developer mix placed into the magnetic brush developer unit of a photoelectrostatic copier was about 2½ pounds. The copier was of the high speed variety which generated copies at the rate of 30 to 50 per minute. This amount of developer mix, together with a replenishment supply of the toner for replacing toner which was used up in the copy making process, produced more than 30,000 copies without showing signs of significant deterioration.

After 30,000 copies were produced, the initial charge of developer mix was removed and replaced with a fresh charge. At a copy-making rate of 50 copies per minute, the developer mix-life was about 10 hours of continuous use.

It will be appreciated that the toner composition of Example I in the environment of a system that produces 20 or less copies a minute would have an appreciable longer performance life. The environment of 20 copies or less assumes that the developer unit turns more slowly so that the stress placed on the developer mix is much less.

The image copies produced were of uniform density indicating complete and thorough mixing between the carrier and the toner powder particles.

The apparatus was equipped with a pressure fixing device so that the powder could be permanently adhered to the photoconductive member by passing between a pair of pressure rollers. The powder readily adhered to the coated paper under a pressure of 300 pounds per lineal inch assuming a line contact between the pressure rollers. The pressure device which was used is described in some detail in U.S. patent application Ser. No. 51,089, filed June 30, 1970, in the name of R. S. Brenneman et al., and assigned to the same assignee as the instant invention.

In order to measure the effectiveness of the pressure fixing step of the powder image, a procedure is used whereby the surface of the image is mechanically rubbed with a piece of white cloth attached to a mechanical wiper under controlled conditions of pressure and rubbing action.

A standard piece of test equipment is utilized to make this measurement and is identified as an AATCC Crock Meter (American Association of Textile Colorists and Chemists). This device is equipped with a mechanically operated finger that applies a constant rubbing action to the surface of a copy sheet bearing a pressure fixed image. The finger applies a force of 319 grams to the surface over which it rubs. The rubbing surface of the finger is 1.5 centimeters in diameter covered with a special white cloth, and the rubbing action is back and forth in a straight line along a 10.2-centimeter distance across the surface of the test specimen.

In order to determine the permanence of the pressure fixed image, the density of the electrostatic copies is adjusted so that the solid areas measure of 1.0 to 1.10 density units, the image density measurement obtained by using a Macbeth RD–100 densitometer. This image density represents a standard value so that the test results are comparable between different toners and/or copy machines or paper and the like. The surface of the rubbing finger, covered with a piece of the special test cloth, is allowed to move across the surface of the sample through five rubbing cycles, each rubbing cycle representing a 20.4-centimeter movement or a total rubbing distance of 102 centimeters.

The test cloth is removed from the finger and the optical density of the toner picked up on the surface of the cloth as a result of the rubbing action is read on using the same Macbeth RD–100 densitometer. By a series of statistical studies, it has been found that the removal of toner, as measured by the optical density of the Crock Meter cloth, should be less than 0.65 densitometer units for acceptable image fixing. If the Crock Meter cloth reads an optical density greater than 0.65 densitometer units, then the image is deemed not to be permanently fixed.

Electrostatic copies prepared using the toner powder of Example I to create an image thereon was fixed by a pressure device such as described in United States patent application Ser. No. 51,089, filed June 30, 1970 and now abandoned, at a pressure of about 300 pounds per lineal contact inch. The test cloth which tests the permanence of the image measured 0.55 density units. This reading, being less than 0.65, represented a permanently pressure fixed powder image.

EXAMPLE II

	Percent
Polyamide resin—Polymid 1060—Lawter Chemical Company	24.0
Maleic anhydride-polyhydric alcohol rosin-modified resin—K1813B—Lawter Chemical Company	42.5
Polyolefin resin—Polymethylene Paraflint RG—Moore and Munger Corporation	15.0
Nublian black resin	6.0
Carbon black—ELF-5—Cabot Carbon Company	1.6
Polyhydric alcohol (optional)—Polyol X–450—Shell Corporation	8.4
Zinc laurate	2.5
	100.0

The electroscopic powder of the Example was pressure fixed by passing it through between pressure rollers applying in the range of about 300 pounds per lineal contact inch and resulted in a rub-off density value of about 0.50 units. The softening point of the toner powder was in the range of 120° C. to 125° C.

EXAMPLE III

	Percent
Polyamide resin—Versamid 948—General Mills Corporation	27.3
Cyclohexanone and formaldehyde—Ketone A (BASF)—Badische Aniline Company	23.6
Condensation resin of cyclohexanone—Ketone N (BASF)—Badische Aniline Company	24.8
Metal soap—Zinc laurate	1.9
Channel black—ELF-5 Carbon black	1.1
Nubian resin black	6.4
Polyolefin resin—Polymethylene Paraflint RG	14.9

The powder images prepared using the toner of Example III were fixed by passing through rollers set at a pressure of about 250 to 280 pounds per lineal contact inch. The softening point range of the toner was 97° C. to 99° C. Rub off densitometer readings=.52 unit.

EXAMPLE IV

Ingredients:	Percent
Polyamide resin—"Polymid 1060"—Lawter Chemical Company	27.6
Maleic anhydride-modified rosin—"Amberol 800"—Rohm and Haas Company	36.8
Polyethylene resin—DOWC 0355—Union Carbide Corporation	15.0
Nubian resin black	6.5
Carbon black—4PC05 manufactured by Capital Color Company	2.4
Lithium stearate	2.0
Polyhydric alcohol (optional)—Polyol X-450	9.7

The toner of Example IV was formulated into a developer mix for use in a magnetic brush developing system. Pressure fixing of the image was accomplished by applying a pressure of about 300 pounds per lineal contact inch. Results of the rub-off test were 0.58 density units and the softening point was 95° C. to 105° C.

EXAMPLE V

	Percent
Polyamide resin—Versamide 930	28.5
Roson modified-phenol formaldehyde resin—Amberol B/S-I—Rohm and Haas Company	51.5
Polyethylene resin—Polywax 2000—Bareco Division of Petrolite Corporation	10.0
Nubian resin black	6.0
Carbon black—ELF-5	2.0
Zinc stearate	2.0

The toner was employed to prepare an electrostatic copy which was fixed by pressure in the range of 300 pounds per lineal inch contact inch. The rub-off test showed a pick-up of toner on the cloth in the range of 0.50 densitometer units which was acceptable. The softening point range of the toner powder was 102° C. to 110° C.

EXAMPLE VI

	Percent
Polyamide resin—Polymid 1060	28.5
Maleic anhydride-polyhydric alcohol rosin-modified resin—K1813B	47.5
Polyethylene resin—CPR-1—Union Carbide Corporation	14.8
Carbon black—ELF-5 carbon	1.3
Nubian resin black	6.0
Lithium stearate	2.0

The toner was employed to prepare an electrostatic copy the image on which was fixed by pressure in the range of 250 to 300 pounds per lineal inch. The rub-off test showed a pick-up of toners on the test cloth in the range of 0.50 densitometer units. The softening point range of the toner powder was 108° C. to 115° C.

EXAMPLE VII

	Percent
Polyamide resin—Polymid 1060	27.8
Maleic anhydride-polyhydric alcohol rosin-modified resin—K1717—Lawter Chemical Company	47.6
Polyethylene resin—CPR-1	13.5
Carbon black—4PC05	3.1
Nubian resin black	6.0
Lithium stearate	2.0

Copies developed with the toner formulation of Example VII were pressure fixed at about 250 pounds per lineal contact inch with a rub-off test value of 0.60 units. The softening point of the toner was 100° C. to 110° C.

EXAMPLE VIII

This example follows the formulation and procedure of Example I with the exception that in place of the maleic anhydride polyhydric alcohol rosin-modified resin the frangible component was a diphenolic resin esterified with soya oil and phenol formaldehyde sold by Nilio Chemicals under its trade designation UBR-800.

Images developed with the toner of Example VIII were pressure fixed in the range of about 300 pounds per lineal contact inch. The pressure fixed images measured 0.60 density units on the rub-off test. The softening point range was 97° C. to 101° C.

In each of the foregoing examples, the electroscopic powders were found to have the dual capability of being fixed on the photoconductive member by either heat fusing or pressure fixing.

As pressure fixable toners, they were fixed to the substrate so as to pass the rub-off test as described hereinabove using the AATCC Crock Meter. As heat fusible powders, they exhibited sharp melting characteristics and therefore produced images of excellent resolution.

The unique feature of the instant invention resides in the combination of a polyamide resin, a frangible resin component and a polyolefin selected from the group of polymethylene and polyethylene, which produces a toner formulation which is pressure fixable, but also can be easily adapted to be heat fusible and demonstrates surprising longevity when combined with carrier particles in the environment of high speed electrostatic copier giving acceptable performance in terms of density of image, clean background of copy, and the ability to be pressure fixed to the copy sheet by using pressures in the range of 175 to 350 pounds per linear inch, preferably 275 to 350 pounds per lineal contact inch.

What is claimed is:

1. An electroscopic granular powder for developing electrostatic images having improved fixability when using pressure to fix the developed powder image comprising a resin blend of a polyamide resin in the range of from 15 percent to 35 percent by weight of the granular powder, a thermoplastic, frangible resin in the range of from 30 percent to 50 percent by weight selected from the group consisting of a rosin modified-phenol formaldehyde resin, maleic anhydride-polyhydric alcohol modified resin, esterified diphenolic resins and a condensation resin formed by the reaction of cyclohexanone and formaldehyde and a polyolefin in the range of from 2 percent to 15 percent by weight selected from the group consisting of polyethylene, polymethylene.

2. The electroscopic powder as claimed in claim **1** in which the polyolefin has a crystallinity in the range of from 30% to 97%.

3. The electroscopic powder as claimed in claim **1** in which the granular powder is combined with a carrier in the range of one part toner with 15 to 60 parts by weight carrier to produce a granular developer mix.

4. The electroscopic powder as claimed in claim **3** wherein said carrier consists of magnetically attractable particles.

5. The developer mix as claimed in claim 3 to which there is added a metal soap selected from the group consisting of lithium stearate, zinc stearate and aluminum palmitate, present in an amount in the range of from 0.01% to 3.0% by weight based on the weight of carrier in the developer mix.

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