

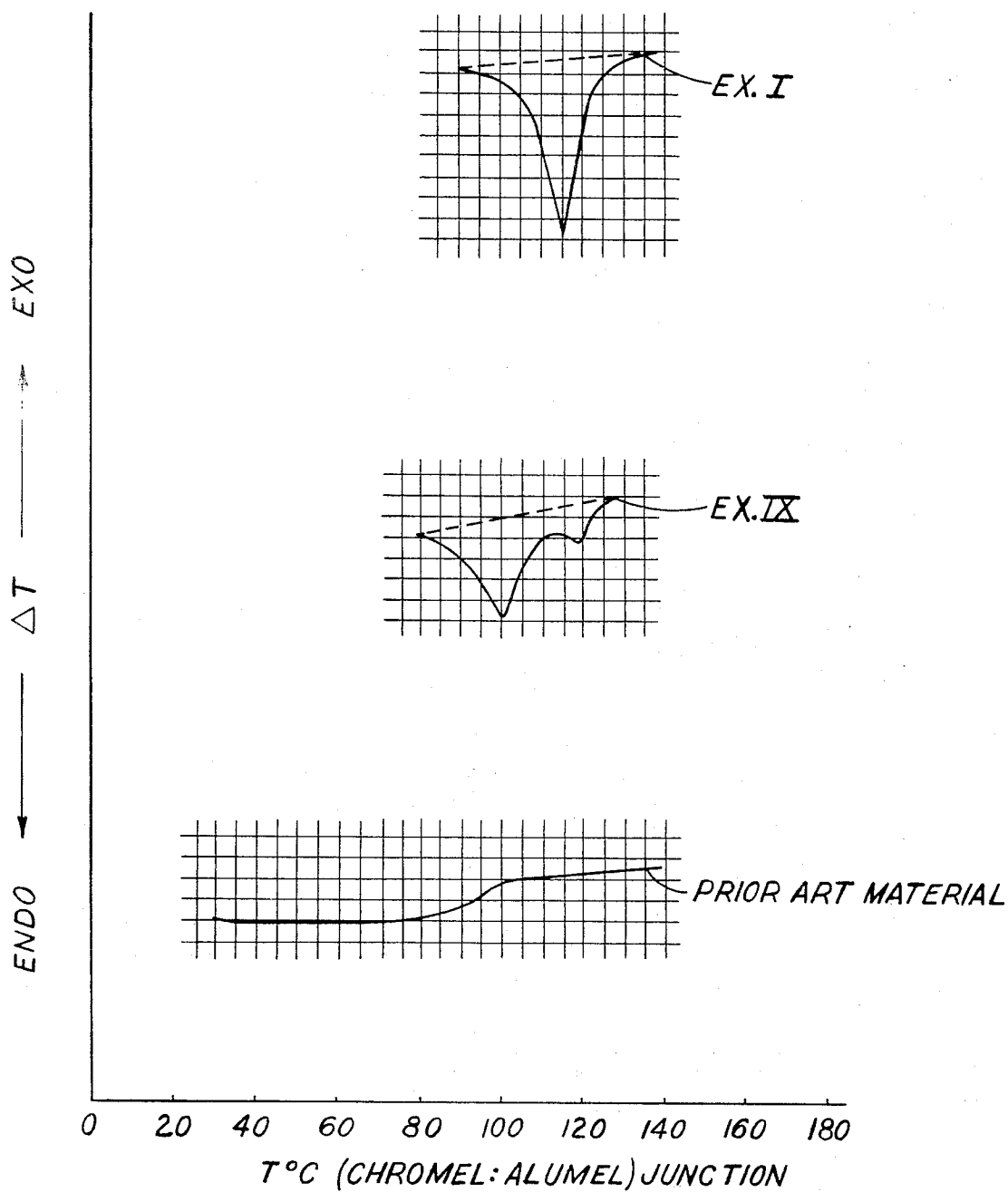
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PHOTOELECTROSTATIC DEVELOPING MATERIALS

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3,829,314 PHOTOELECTROSTATIC DEVELOPING MATERIALS

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ABSTRACT OF THE DISCLOSURE

The developing materials of this invention are used with electrostatic developing processes and the images are fixed by passing the copy sheet through a pair of steel rollers under pressure. The developing materials are composed of aliphatic components having from 6 to 25 carbon atoms. The aliphatic components may also be combined with thermoplastic synthetic resins to control the pressure response level. The pressure response, that is, the fixability of the image onto the copy by pressure, of these materials is correlated to the heat of fusion of the composition as measured by differential thermal analysis.

This application is a continuation-in-part of application Ser. No. 57,013 filed June 9, 1970, which is a divisional of U.S. application Ser. No. 596,476 filed Nov. 23, 1966 both now abandoned.

BACKGROUND OF THE INVENTION

(1) Field of the Invention

This invention relates to electrostatically attractable materials useful in photoelectrostatic imaging processes and, more particularly, relates to the composition of such materials which renders them pressure responsive so that as an imaging material they may be fixed to the image-bearing surface by the application of pressure.

(2) Description of the Prior Art

Photoelectrostatic printing processes involve the production of electrostatic images on an insulating surface. One technique of creating such electrostatic images calls for charging a photoconductive surface and selectively dissipating such charge by exposure to an optical image. The electrostatic image is rendered visible by applying across the image-bearing surface finely divided developer particles or electroscopic particles.

The developer particles are triboelectrically charged in the opposite polarity to the electrostatic charges on the photoconductive layer and, hence, they will deposit in the image areas to produce a visible image. Since the deposition of the particles is governed by electrostatic charges, they are often referred to as electroscopic powders or toners.

The final step in photoelectrostatic printing requires fixing the visible image to the photoconductive surface or in the circumstance where the loose powder image is transferred to another surface it must be fixed onto the receiving surface. The object is to fix the image so that it does not easily rub off or is more or less permanently bonded to the image-bearing surface.

The term "fixing" as used hereinafter in the description of the instant invention defines bonding or affixing to the substrate the loose toner particles with the same degree of permanency as encountered in ordinary printing with ink.

The known toner formulations that are used in electrostatic printing are generally permanently affixed to the substrate by heat. Since most of the electroscopic powders are made up primarily of thermoplastic resins, they

are affixed by raising the temperature of the powder to its melting point causing the particles to coalesce and flow together and at the same time adhere to the substrate.

The technique of heat fusing the powdered images has been widely used and quite successfully with the photoelectrostatic copying equipment in general use today. The technique, however, is not without disadvantages which have limited the full impact of this new copying medium on such applications as print-out systems for rapid computer devices, duplicating machines, high-speed reproduction equipment which employ cathode ray tubes as the imaging source, and imaging inputs from magnetic tape systems.

One disadvantage is the time it takes to bring a thermoplastic particle up to its melting point. The time required to effect fusion is usually the slowest step in the photoelectrostatic copying process and, hence, is the time limiting factor. More heat would speed up the process, however, the environment is governed by the flammability of the substrate. Since paper is very widely used as a support for the electrostatic images the temperature of the fusing system must be below the char point of the paper.

In order to speed up the fixing step, use has been made of lower melting point thermoplastic resins. This produced other problems such as poor character definition in the final image and the loss of sharpness in the image formations.

Another disadvantage is the everpresence of heat energy emanating from the fusing devices and represents a source of heat to the general working environment. This contributes to the general discomfort of the persons in the immediate working area of the equipment.

Another deficiency of the copying equipment which depends on heat to fix the thermoplastic materials employed is that after a period of shutdown, startup is not instantaneously achieved. Startup of the equipment is attended with some delay until the oven portion reaches the proper operating temperature. In order to have the equipment ready to meet a copy demand anytime after startup, it must be kept in a standby condition in which the oven is kept at near operating temperature ready to fuse the image. This, then, results in wasting heat energy during periods when no copy demands are made on the machine.

With the advent of high-speed copying and duplicating equipment, which makes increased use of photoelectrostatic imaging techniques, attempts to cope with the above-recited disadvantages have resulted in complex, expensive, and cumbersome equipment. In summation, it can be said that the processing equipment for making photoelectrostatic reproductions can be simplified, rendered more efficient and made to operate at a higher rate of copy output.

It is a general object of this invention to provide an improved toner composition useful in creating images by the photoelectrostatic process that can be fixed without heat.

It is an object of this invention to provide an improved toner composition that is useful in the development of photoelectrostatic images onto a copy which can be completely fixed by the application of pressure.

It is a further object of this invention to provide an improved method of photoelectrostatic reproduction that is rapid and employs greatly simplified equipment to fix the developed powder image.

It is another object of this invention to provide an improved toner composition for magnetic brush-type development of photoelectrostatic images which can be permanently fixed onto a support base by the application of a nominal amount of pressure.

SUMMARY OF THE INVENTION

In carrying out the objects of this invention, the toners are formulated of materials which are pressure responsive. By pressure responsive, it is meant that the particles will

undergo several distinct physical changes when placed under pressure.

First, under the influence of pressure, they will tend to adhere to one another so that they are no longer in distinct particulate form. Second, the particle will be somewhat deformed when exposed to compressive forces and, therefore, will be forced to conform to the support surface, adhering thereto. In a case where the support surface is paper, the particle will be forced into the interstices of the paper fibers to be bonded to the paper surface. These physical changes under pressure represent the visco-elastic properties of a material.

The mechanism by which the materials of this invention respond to pressure and become fixed to a substrate, such as paper, is not fully understood. In terms of results obtained, it can be stated that the materials that comprise pressure responsive toners adhere to the paper because they are forced into the interstices of the paper. The visco-elastic properties permit the material to flow or deform. The amount of flow in the absence of heat that takes place preferably should be insufficient to spread the image to where the characters become filled-in or result in a broadened image but sufficient so that the material adheres to the support surface.

It is suggested as a possible explanation that these pressure responsive materials must possess some degree of organization, that is, an ordered structure typical of crystalline materials. When exposed to a compressive force, the crystalline material will remain physically unchanged until a point is reached at which the ordered structure yields. At this point the material experiences a change of state. In this change of state it more readily conforms to the surface to which it has been attracted and, therefore, adheres to the support surface or substrate.

It has been found that for pressure responsive materials there is a correlation between their visco-elastic properties and their heat of fusion. Temperature differential studies on the various materials believed to have an ordered structure compared to non-crystalline materials, or a reference material that is not pressure responsive, reveals that the heat of fusion helps to identify the toner compositions that comprise this invention. It has been found that in order to be pressure responsive the toner must have a heat of fusion greater than 10 millicalories/mg. The measurement and relationship of heat of fusion will be discussed in greater detail hereinafter.

Another requirement for the materials comprising the toner of this invention is that the granular mass of toner develop a triboelectric charge when combined with particles of a dissimilar material. This effect of producing opposite charges on dissimilar materials when they are rubbed together is the well-known triboelectric effect and the selection of the materials according to their disposition in a triboelectric range is well-known in this art. The triboelectric forces tend to produce both positively and negatively charged particles dependent on the materials employed.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In a preferred embodiment of the present invention, there is provided a new and improved toner composition comprised of from 80-99 parts by weight of an aliphatic component, containing from 6 to 25 carbon atoms, selected from the group consisting of petroleum waxes, ester type waxes, animal waxes, fatty acids, metal salts of fatty acids, primary amides, secondary amides, tertiary amides, and hydroxylated fatty acids and mixtures thereof, and from 1 to 20 parts by weight of a pigment or dye in order to render the aliphatic component particles highly colored. The preferred materials are the primary and secondary amides.

These materials must be capable of being rendered pulverulent in the particle size range of from about 5 microns to 15 microns and develop a suitable triboelectric charge,

either positive or negative, when combined with a suitable carrier material such as iron particles.

The electroscopic powders of this invention may be applied to the latent image-bearing surface by any one of the conventional techniques such as powder cloud, magnetic brush or cascade development.

Another preferred embodiment of this invention comprises toners which are pressure fusible and are particularly suited for use with duplicating equipment employing photoelectrostatic copying processes whereby a powder image is first created on a photoconductive surface and the developed material image is then transferred under pressure to another surface such as a receiving sheet and fixed thereon. The composition must selectively resist being fused at the transfer step and respond when the image is to be fixed on the receiving sheet. This embodiment contemplates a blend of known thermoplastic components along with the aliphatic constituent. The thermoplastic components that are suitable for formulation with the aliphatic components include styrene butadiene copolymers, polystyrene, polyethylene, polyvinylchloride, acrylics, and terpene resins, aryl-sulfonamideformaldehyde resins and mixtures thereof. The preferred thermoplastic resins are polyamides and modified resins. It will be appreciated that the polyamides in this embodiment are high molecular weight polymers and are distinct from the amides disclosed earlier in connection with the first embodiment. The thermoplastic component and aliphatic component are combined in a ratio of about 50 to 90 parts by weight of the aliphatic component with 10 to 50 parts by weight of the thermoplastic resin, and from 1 to 5 parts by weight of a dye or pigment to render the toner highly colored.

The aliphatic components which can function as pressure toners are quite numerous. The following is a list of exemplary aliphatic components useful for the manufacture of pressure responsive toners according to one embodiment of this invention.

(I) Waxes:	Melt point (° C.)
(a) Carnauba wax ¹ -----	28-30
(b) Montan wax ¹ -----	28-29
(c) Microcrystalline wax ¹ -----	15-34
(d) Beeswax ¹ -----	16-18
(e) Microwax 15 ¹ -----	21-30
(f) Moltwax ML-445 ¹ -----	37-40

¹ All of the above materials are manufactured by the International Wax Refining Company.

(g) Chlorinated paraffins ² -----	95-110
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² Chlorowax 70—sold by the Diamond Alkali Company.

(h) Synthetic wax-octadecanamide, Acra-wax C ³ -----	140-143
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³ Glycol Products Company, Brooklyn, N.Y.

(II) Fatty acids:	Melt point (° C.)
(a) Octadecanoic acid (stearic acid) -----	67-70
(b) Hexadecanoic acid (palmitic acid) -----	59-62
(c) Tetradecanoic acid (myristic acid) -----	53-55
(d) Dodecanoic acid (lauric acid) -----	41-44
(e) Decanoic acid (capric acid) -----	31-33

All of the above are available from the Witco Chemical Company, New York, N.Y.

(III) Amides:	Melt point (° C.)
Primary:	
(a) 9-12 octadecanamide ¹ -----	72
(b) 9 octadecanamide ¹ -----	75
(c) Octadecanamide ¹ -----	98
(d) Hexadecanamide ¹ -----	95
(e) Tetradecanamide ¹ -----	97
(f) Dodecanamide ¹ -----	97-99
(g) Decanamide ¹ -----	79-81
(h) Octanamide ¹ -----	93-96
(i) Hexanamide ¹ -----	93-96

¹ All of the above compounds are available from the Armour Chemical Company, Chicago, Ill., sold under the trade name "Armold."

Secondary:	
(j) N-methyl-9-12-octadecanamide	72
(k) N-butyl-octadecanamide	75
Tertiary:	
(l) Di-methyl-octadecanamide	70
(m) Di-butyl-9 octadecanamide	71
(IV) Metal salts of fatty acids: Softening point (° C.)	
(a) Aluminum stearate	143-148
(b) Lead stearate	102-104
(c) Barium stearate	155-160
(d) Magnesium stearate	135-140
(e) Zinc stearate	123-125
(f) Zinc palmitate	115-125
(g) Lithium stearate	195-200
The above compounds sold by Witco Chemical Company.	
(V) Fatty acid derivatives: Melt point (° C.)	
(a) Methylhydroxy stearate (trade name—Paracin 1)	52
(b) Glycerol monohydroxy stearate	53
(c) Glycerol tri-12-hydroxy stearate (castor wax)	87
(d) Partially hydrogenated castor oil	80-90
(e) Cocoa butter	105-109

All of the above materials are available from the Baker Castor Oil Company.

The preferred coloring agent is a soluble organic dye such as Nubian resin black, although other pigments and dyes can be used, such as Neo-spectra black pigment, Nigrosine dye, and other organic dyes which are soluble in the resins and/or waxes and produce colors which are stable when exposed to ordinary daylight. Generally, the amount of dye or pigment added is that amount sufficient to produce suitably colored particles.

In the preparation of the toner, the aliphatic constituents of the toner are rendered molten, and the pigment and/or dye are added in an amount ranging from about 1% to about 20% of the weight of the aliphatic component employed, and preferably in the range of 2% to 10%. The pigment and/or dye are distributed throughout the molten resin so that a homogeneously colored solution or dispersion is produced. The material is poured into shallow pans and permitted to cool, thereafter being ground or milled to an average particle size in the range of from 1 to 50 microns, preferably in the range of from 5 to 15 microns.

The resin powder when in contact with a suitable carrier material such as glass beads or iron particles, acquires an electrostatic charge having a polarity opposite to that of the charged photoconductive insulating layer of the photoconductive member.

The invention is disclosed in further detail by means of the following examples which are provided for the purpose of illustration only. It will be readily appreciated by those skilled in the art that various modifications in toner formulations, carrier particles, relative proportions of materials and variations of particle sizes can be made without departing from the invention as herein described. In this application, various quantities of materials are given in parts by weight.

EXAMPLE I

85 parts of octadecanamide, Armid 18, sold by Armour Chemical Company, is melted in a suitable container such as a steam jacketed kettle to which is gradually added 15 parts of a black dye, such as Nubian resin black, while agitating the mass until the coloring agent is uniformly distributed.

The molten mass is poured off into shallow pans, cooled until solidified and placed in a pulverizing mill and reduced to a particle size in the range of 1 micron to 50 microns, preferably in the range of 5-15 microns. The heat of fusion of the toner material measured 29 millicalories per milligram.

The granular mass is then sifted to remove particles that would not pass through a 200 mesh screen.

The sifted particles are then mixed with iron powder in a weight ratio ranging from 8 to 50 parts by weight of iron to one part by weight of toner, preferably in the range of from 10-20 parts iron per part by weight of toner. The iron particles have a particle size ranging from 20 to 75 microns, preferably in the range of 25 to 40 microns.

The mixture of iron particles and toner is charged into a developer assembly of the magnetic brush type such as disclosed in U.S. Pat. 3,145,122 granted Aug. 18, 1964 to P. B. Streich. A photoelectrostatic member of the zinc oxide-resin binder type is applied a blanket negative electrostatic charge and exposed to a pattern of light and shadow and then passed through the developer assembly.

The toner particles adhere to the negatively charged image areas. The loose powder image is then passed between a pair of highly polished metal rollers in contact with one another under pressure.

It will be obvious to those skilled in the art that the pressure employed may be controlled by varying the diameter of the rolls as well as applying a force through the bearing mount. For the purpose of this invention, reference will be had to a roll pressure per lineal contact inch which defines the pressure exerted by a set of 2½" diameter highly polished solid metal rollers 10" in length to which is applied various loadings at each bearing mount. A roll pressure of 20 pounds per lineal contact inch, for example, under these conditions may be achieved by applying 100 pounds load at the bearings (including the weight of the roller) of a 2½" diameter roll, solid steel 10" long. The operable range of pressure is from 20 to 30 pounds per lineal contact inch. The roller diameters for applying pressure may range from .75" to 2½". It is to be understood that the pressure per lineal contact inch for a given bearing load increases or decreases proportionately to the diameter of the roll depending on the visco-elastic properties of the material.

While the operable pressure range 20-30 pounds per lineal inch has been described as successfully fixing the toner powder image to the receiving sheet, under certain conditions of use, particularly repeated abrasion or rubbing the image tends to be partially removed. It has been found that the degree of image fixing or adherence may be improved by applying greater amounts of pressure. As a result of performance studies made relating to the function of pressure versus improved adherence, it has been found that for most applications pressures in the range of about 150 pounds per lineal inch give good applying pressure in the range of up to 300 pounds per lineal inch.

The limiting factor in respect of the amount of pressure that can be applied is the distortion or damage which is imparted to the sheet to which the image is affixed. At pressures in excess of 300 pounds per lineal inch certain physical properties of the sheet are changed, so that it tends to distort the sheet. For example, the caliper of the sheet changes with increase of pressure. Any change in caliper which compresses the sheet more than 25% from its original thickness is undesirable.

At high pressures the smoothness of the sheet is changed because of the calendering effect of the rollers. Changes in smoothness which increase the reflectivity of the imaging surface are undesirable. The detrimental effect of increased smoothness produces a polishing of the image surface. It is particularly undesirable where the receiving sheet is of the zinc oxide type, in which the photoconductive pigment is dispersed in a resin binder and applied to a base support. In this case a highly reflective surface makes it extremely difficult to read the subject matter which has been printed on the sheet.

Another adverse effect of high pressure is the change in sheet stiffness. Any decrease, to the extent that it amounts to a drop of 25% from the original stiffness value of the sheet, should be avoided.

Finally, the amount of pressure necessary to fix should not emboss the side of the sheet opposite to the powder

bearing surface, in order to pressure fix the powder onto the sheet.

The distortions or damage to the sheet which have been described are undesirable for the reason that they detract from the acceptability of the sheet, in terms of its handling characteristics, changes in the readability of the image thereon, or the increase in bulk of a stack of sheets in the circumstance that one surface becomes embossed, due to the high pressure.

In the instant example the copy sheet with the loose adhering powder image is passed between rollers at a lineal speed of about 30 feet per minute. The rate at which this sheet passes between the rollers may be a factor in the completeness of the fixing of the powder to the base support. The sheet emerges from the rollers with a fixed image which is permanently adhered to the substrate. The image can be handled and worked with in the same manner and to the same extent as a heat fused image or the ordinary ink-printed copy.

The copy sheet with the loose adhering powder image is passed between the rollers at a lineal speed of about 30 feet per minute. The rate at which the sheet passes between the rollers may be a factor in the completeness of the fixing of the powder to the base support. The sheet emerges from between the rollers with a fixed image which is permanently adhered to the substrate. The image can be handled and worked with in the same manner and to the same extent as a heat fused image or the ordinary ink printed copy.

The toner powders of the following examples are prepared in the same general manner as described in connection with Example I.

EXAMPLE II

Carnauba wax	85
Nubian resin black	15
Heat of fusion: 33 mcal./mg.	

EXAMPLE III

Acrawax C (a synthetic wax-octadecanamide)	90
Nubian resin black	5
Carbon black pigment (Neo-spectra-Mark II)	5
Heat of fusion: 31 mcal./mg.	

EXAMPLE IV

Acrawax C	24
Carnauba wax	20
9-octadecanamide	41
Nubian resin black	10
Carbon black pigment (Neo-spectra-Mark II)	5
Heat of fusion: 42 mcal./mg.	

EXAMPLE V

9-12 octadecanamide	50
Tetradecanoic acid	20
Acrawax	15
Nubian resin black	15
Heat of fusion: 41 mcal./mg.	

EXAMPLE VI

Sodium stearate	50
Acrawax C	20
Tetradecanoic acid	20
Nubian resin black	10
Heat of fusion: 20 mcal./mg.	

EXAMPLE VII

Hexanamide	46
Paraffin wax	30
Hydroxylated fatty acid	10
Nubian resin black	12
Carbon black pigment (Neo-spectra-Mark II)	2
Heat of fusion: 29 mcal./mg.	

EXAMPLE VIII

Lithium stearate	18
Methylhydroxy stearate (Paracin 1)	22
Halogenated wax, Halowax 1001	40
Octadecanamide (Armid)	14
Nubian resin black	6
Heat of fusion: 16 mcal./mg.	

In practicing the second preferred embodiment of this invention the toner powders comprise a blend ranging from 1 part to 9 parts by weight of the aliphatic component with 1 part by weight of thermoplastic resin. The blend is rendered highly colored by the addition of the dyes and pigments described above in connection with the first embodiment of this invention.

Thermoplastic materials that may be incorporated with the aliphatic component, comprising the pressure responsive portion of the toner blend, tend to produce a somewhat more brittle or friable powder. Among the thermoplastic resins which are operative are polystyrene, vinyl and acrylic resins, polyethylene and blends thereof. Other thermoplastic materials which are suitable include rosin, asphalt, and gilsonites. The preferred thermoplastic materials are polyamides such as low molecular weight nylon, which are distinct from the amides cited in the first embodiment, rosin-modified phenolic resin such as those prepared by modifying a phenol-formaldehyde resin with the reaction product of maleic anhydride and rosin or a polyhydric alcohol such as glycerol or pentaerythritol. The polyamide resins are sold under the trade name Versamid 930, 940 and 950, manufactured by the General Mills Company, and the rosin-modified phenolic resins are sold under the trade name Amberol, manufactured by Rohm & Haas Company. Other phenolic materials esterified with soya fatty acids available from the Johnson Wax Company, Racine, Wis., and from Khrumbar Resin Division of Lawter Chemicals Company, are also satisfactory. The toner should have a softening point measured by the ball and ring method in the range of from 106° to 115° C.

The following is a listing of other suitable thermoplastic resins that could be used in the toner powders of this invention:

- (1) Polyvinyl chloride copolymers, such as:
 - (a) Vinylite VAGH—91% vinyl chloride, 3% vinyl acetate, 6% vinyl alcohol;
 - (b) VYCM—91% vinyl chloride, and 9% vinyl acetate;
 - (c) VMCH—86% vinyl chloride, 13% vinyl acetate, 1% dibasic acid.
- (2) Styrene-butadiene copolymers, such as:
 - (a) Pliolite S-5 (The Goodyear Tire & Rubber Company, Akron, Ohio), and
 - (b) Piccotax 120 (Pennsylvania Industrial Chemical Company, Clairton, Pa.).
- (3) Acrylates and acrylic copolymers, such as: Acryloid A-101 Rohm & Haas Company, Philadelphia, Pa.
- (4) Thermoplastic hydrocarbon terpene resins, such as: Piccolyte S-135 (Pennsylvania Industrial Chemical Company, Clairton, Pa.).
- (5) Polystyrene, such as: Piccolastic resin C-125 (Pennsylvania Industrial Chemical Company, Clairton, Pa.).
- (6) Polyethylene, such as: Mirrothene 620 (U.S. Industrial Chemicals Company, New York, N.Y.).
- (7) Aryl sulfonamide-formaldehyde condensation resin, such as: Santolite MHR (Monsanto Chemical Company, St. Louis, Mo.).
- (8) Polyvinyl chloride, such as: Bakelite VYMH (Union Carbide Corporation, New York, N.Y.).

The electroscopic powders comprising this preferred embodiment, produced by blending the thermoplastic resin with the aliphatic component, require slightly greater pressures in order to fix the powder image onto a substrate. The pressures required to fix the electroscopic powders of the first embodiment described above were in the range of 20 to 30 pounds per lineal contact inch applied through a set of steel rollers having equal diameters of 2½". With the addition of the thermoplastic resin to the aliphatic component, the toner requires increased pressure for fixing in the range of 25 to 75 pounds per lineal contact inch and preferably in the range of 35 to 50 pounds per lineal contact inch. As in the previous embodiment the roller diameters may vary in the range of .75" up to 2½" requiring adjustment in the load applied at the bearing.

Electroscopic powders of this preferred embodiment will respond to various pressures in the same manner and to the same extent as discussed hereinabove in Example I. As in the case of the toner formulations of Examples I thru VIII, the toner formulations of the following Examples will also respond to pressures in the range of 25 to 300 pounds. In applying pressures between 150 and 300 pounds, a high degree of permanence with excellent resistance to rubbing is achieved.

As described earlier in the discussion of this invention, the application of pressures in excess of 300 pounds per lineal inch tends to distort the sheet, affecting its handling characteristics due to changes in caliper and stiffness. Readability is affected by increasing the smoothness and, hence, the reflectivity of the surface of the sheet. Embossing the surface of the sheet opposite to the surface carrying the image tends to increase the bulk of the sheet element which becomes readily apparent in a large stack of such reproductions.

The general method of preparation of the toner calls for reducing the thermoplastic resin constituents to the molten state. The pigment and/or dye is added in an amount ranging from about 1 to 17 parts by weight of the total amount of resin employed, preferably in the range of from 7 to 15 parts. To the colored molten resin is then added the aliphatic component in an amount ranging from about 35 to 70 parts by weight of the final toner composition, preferably in the range of from 45 to 60 parts by weight. The pigment and/or dye is distributed throughout the resin so that a homogeneously colored solution is achieved. The material is then processed in a manner as described hereinbefore being ground to an average particle size in the range of from 1 to 50 microns, preferably in the range of from 5 to 15 microns.

Examples of the second embodiment are as follows:

EXAMPLE IX

Polyamide resin (Versamid 930) -----	25.3
Modified wood rosin (Amberol 800) -----	20.6
9-12 octadecanamide (Armid 18) -----	24.0
Synthetic wax-octadecanamide (Acrawax C) -----	16.0
Nubian resin black -----	14.1
Heat of fusion: 11 mcal./mg.	

EXAMPLE X

Polystyrene (Piccolastic C-125) -----	12.5
Polystyrene (Piccolastic D-100) -----	12.5
Modified wood rosin (Amberol 800) -----	20.6
Armid 18 -----	24.0
Acrawax C -----	16.0
Nubian resin black -----	14.9
Heat of fusion: 19 mcal./mg.	

EXAMPLE XI

Polyvinyl chloride (Bakelite VYLF) -----	20.3
Modified wood rosin (Amberol 801) -----	25.6
Octadecanamide (Armid 18) -----	24.0
Acrawax C -----	16.0
Nubian resin black -----	14.1
Heat of fusion: 23 mcal./mg.	

EXAMPLE XII

Polystyrene (Piccolastic C-125) -----	36.9
9-octadecanamide (Armid 18) -----	28.2
Synthetic octadecanamide (Acrawax C) -----	28.7
Nigrosine black -----	5.0
Carbon black pigment (Neo-spectra Mark II) -----	1.2
Heat of fusion: 19 mcal./mg.	

Referring to FIG. 1, there are shown temperature differential studies of various toner compositions. The plot of change in temperature of a given quantity of toner having a composition such as described in Examples I and IX when they are heated under controlled conditions is compared with a prior art toner composition that is heat fusible.

The curve shown for Example I is typical of the first preferred embodiment where the toner is fixed directly onto the photoconductive member by passing the member between a metal roller assembly of a construction described hereinabove. The area under the curve represents the heat of fusion calibrated in terms of millicalories per milligram which for this toner is 29.58 mcal./mg.

The curve marked Example IX is typical of the pressure responsive toner in which the image is transferred by pressure from a drum to a receiving sheet, such as plain paper, and then fixed by passing the plain paper sheet through a pressure roller assembly. Its heat of fusion is 11.15 mcal./mg.

The prior art material is predominantly a polyamide resin such as described in the patent application, Ser. No. 357,743, of Loren E. Shelfo, filed Apr. 6, 1964, now abandoned, and assigned to the same assignee as the instant invention. The prior art toner produces a curve which is essentially flat lacking peak changes in temperature.

The plots are obtained in thermal analyzer equipment such as the Model 900 Differential Thermal Analyzer. The analysis is made by comparing the temperature differential between a sample and reference. The sample and reference are placed close together in an environment which is heated or cooled through an appropriate temperature range. Means are included to measure the environmental temperature and to control the rate of heating or cooling.

As the environmental temperature is changed, the temperatures of sample and reference also change. In the absence of physical or chemical changes, the temperature differential, Δt (sample temperature minus reference temperature) remains zero. When the temperature is reached where a physical or chemical change occurs in the sample, which does not occur in the inert reference material, the sample temperature no longer equals the reference temperature, and either a positive or negative Δt results.

This change in temperature measured under calibrated conditions for a given mass represents the heat of fusion expressed in millicalories per milligram. The following chart shows the heat of fusion of each of the examples described herein:

Example:	Heat of fusion
I -----	29
II -----	33
III -----	31
IV -----	42
V -----	41
VI -----	20
VII -----	29
VIII -----	16
IX -----	11
X -----	19
XI -----	23
XII -----	19
Prior Art Toner -----	None

The curve for Example I shows that the temperature begins to drop off from the base at about 86° C. This marks the onset of the differential portion of the curve.

The temperature continues to drop in the endothermic direction reaching a peak and then begins to recover until it levels off at 138° C. where it reaches the base line level. Each one inch along the ordinate represents 1½° C. The area under the curve bounded by onset, peak and recovery portions formed when a line is drawn connecting the onset and recovery points, represents the heat of fusion when the instrument is calibrated in terms of millicalories/° C.-min.

The heat of fusion is obtained by multiplying the area under the curve by the temperature sensitivity of the ordinate and abscissa in ° C./in. and the heat of fusion represents the quotient obtained by dividing the quantity of the area under the curve in square inches multiplied by the temperature sensitivity of the ordinate and abscissa in ° C./inch by the divisor quantity of mass of sample in milligrams times the heating rate. This value is corrected by a calibration coefficient for the particular equipment. The area bounded by the curve for Example I represents a heat of fusion of 29 millicalories/milligram where each one inch along the ordinate represents a Δt of 1½° C. These toners pressure fix in the range of 20-30 pounds per lineal contact inch.

The thermogram for Example IX shows an onset in the endothermic direction at about 78° C. and then goes through a first peak at 100° C., begins to recover and then goes through a second peak at about 117° C. completing the recovery and leveling off at 130° C. The base line is drawn by correcting the point where onset begins and recovery levels off. The double peak is indicative of the presence in the system of the two aliphatic components. The area bounded by the curve represents a heat of fusion of 11 millicalories/milligram where each one inch along the ordinate represents ½° C. Materials typical of Example IX respond to pressure in the range of 25 to 75 pounds per lineal contact inch.

Referring to the thermogram of the prior art toner, it will be seen that it shows no peak temperature change Δt . The distance of one inch along the ordinate represents a Δt of ½° C. The thermogram reveals that over the temperature range of 30° C. to 140° C. there is only a temperature inflection for the material at about 80° C. This is an indication that the material lacks an ordered structure or the necessary crystallinity and, hence is not suitable for pressure fixing in the range of pressures disclosed herein.

The value of the heat of fusion that corresponds to the pressure responsive materials disclosed herein ranges from 10 to 45 millicalories/milligram, and the operable range for direct pressure responsive materials is from 20-45 millicalories/milligram and for transferable-type pressure responsive materials 10-25 millicalories/milligram.

The heat of fusion is indicative of the pressure responsiveness of the toner compositions described herein and serves to define via a physical measurement the group of materials that are pressure responsive.

What is claimed is:

1. The method of producing a copy having a fixed powder image from an electrophotographic member through the formation of a pressure responsive powder image comprising the steps of:

- (a) imparting a blanket electrostatic charge to said member;
- (b) exposing the member to a pattern of light and shadow, to produce an electrostatic latent image thereon;
- (c) applying an electroscopic powder having a heat of fusion in the range of from 10 mc./mg. to 45 mc./mg. which electrostatically adheres to the image portions; and
- (d) fixing the formed powder image to the copy by applying pressure in the range of 20 pounds per lineal inch to 300 pounds per lineal inch against said copy whereby said powder image is bonded to the copy without damaging said member.

2. The method as claimed in Claim 1 wherein said copy is produced by transferring the powder image from the electrophotographic member to a receiving sheet and applying pressure against both surfaces of said copy to bond the transferred powder image to the copy.

3. The method of making a reproduction of a graphic original on a photoconductive medium, comprising the steps of:

- (a) applying a sensitizing charge to the surface of the photoconductive medium;
- (b) exposing the medium to a pattern of light and shadow to produce a latent electrostatic image thereon;
- (c) applying an electroscopic powder comprising a compound selected from a long chain fatty acid, having from 6 to 25 carbon atoms, monoamides, derived from ammonia and amides derived from primary or secondary aliphatic amines, having from 2 to 10 carbon atoms, petroleum waxes, ester type waxes, synthetic waxes, animal waxes or fatty acid derivatives which are solid at room temperature, a coloring agent selected from the group consisting of dyes and pigments, said toner having a heat of fusion in the range of 10 to 45 millicalories per milligram;
- (d) fixing the electroscopic powder to the photoconductive medium by applying pressure in the range of from 20 pounds to 300 pounds per lineal contact inch, against said medium whereby the powder image is fixed thereon without damaging said photoconductive medium.

4. The method as claimed in Claim 3 wherein said compound is present in said toner, in an amount ranging from 50% to 90% by weight of said toner, and said toner further includes a polymeric thermoplastic resin component in an amount ranging from 5% to 50% by weight.

5. The method as claimed in claim 3 wherein said coloring agent is present in an amount ranging from 2% to 10% by weight of said toner.

6. The method as claimed in Claim 4 wherein the thermoplastic resin is a polyamide.

7. The method as claimed in Claim 4 wherein the thermoplastic resin is polystyrene.

8. The method as claimed in Claim 4 wherein the thermoplastic resin is polyethylene.

9. The method of making a reproduction of a graphic original on a copy sheet through the use of a photoconductive medium comprising the steps of:

- (a) applying a blanket sensitizing charge to the surface of the photoconductive medium;
- (b) exposing the medium to a pattern of light and shadow to produce a latent electrostatic image thereon;
- (c) applying an electroscopic powder comprising a compound selected from petroleum waxes, ester type waxes, synthetic waxes, animal waxes, a long chain fatty acid having from 6 to 25 carbon atoms, monoamides derived from ammonia and amides derived from primary or secondary aliphatic amines having from 2 to 10 carbon atoms, or fatty acid derivatives which are solid at room temperature, and a coloring agent selected from the group consisting of dyes and pigments, said toner having a heat of fusion in the range of 10 to 45 millicalories per milligram;
- (d) transferring the electroscopic powder image to said copy sheet;
- (e) fixing the electroscopic powder to the copy sheet by applying pressure in the range from 20 pounds to 300 pounds per lineal contact inch against said copy whereby the powder is bonded thereto without damaging said copy sheet.

10. The method as claimed in Claim 9 wherein the compound is present in said toner in an amount ranging from 50% to 90% by weight and said toner includes a polymeric thermoplastic resin component in an amount ranging from 5% to 50% by weight.

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11. The method as claimed in Claim 10 wherein the thermoplastic resin is a polyamide.

12. The method as claimed in Claim 10 wherein the thermoplastic resin is polystyrene.

13. The method as claimed in Claim 10 wherein the thermoplastic resin is polyethylene.

14. The method of making a reproduction of a graphic original on an image receiving member through the use of electrophotographic reproduction techniques, which include the use of a photoconductive medium comprising the steps of:

(a) applying a blanket sensitizing charge to the surface of the photoconductive medium;

(b) exposing the medium to a pattern of light and shadow to produce a latent electrostatic image thereon;

(c) applying an electroscopic powder to the photoconductive medium having a heat of fusion in the range of from 10 millicalories per milligram to 45 millicalories per milligram, which electrostatically adheres to the image portions on said photoconductive medium; and

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(d) fixing the formed powder image to the image receiving member by applying pressure in the range of from 20 pounds per lineal contact inch to 300 pounds per lineal contact inch against said member whereby said powder image is bonded thereto without damaging said image receiving member.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,829,314 Dated August 13, 1974

Inventor(s) Loren E. Shelffo

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, Line 71, "formuated" should read --formulated--.

Column 6, Line 48, at the end of the line after the word "good", the following should appear:

--adherence. A high degree of image fixing is attained by--.

Signed and sealed this 28th day of January 1975.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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