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ELECTROSTATIC DEVELOPER MIX

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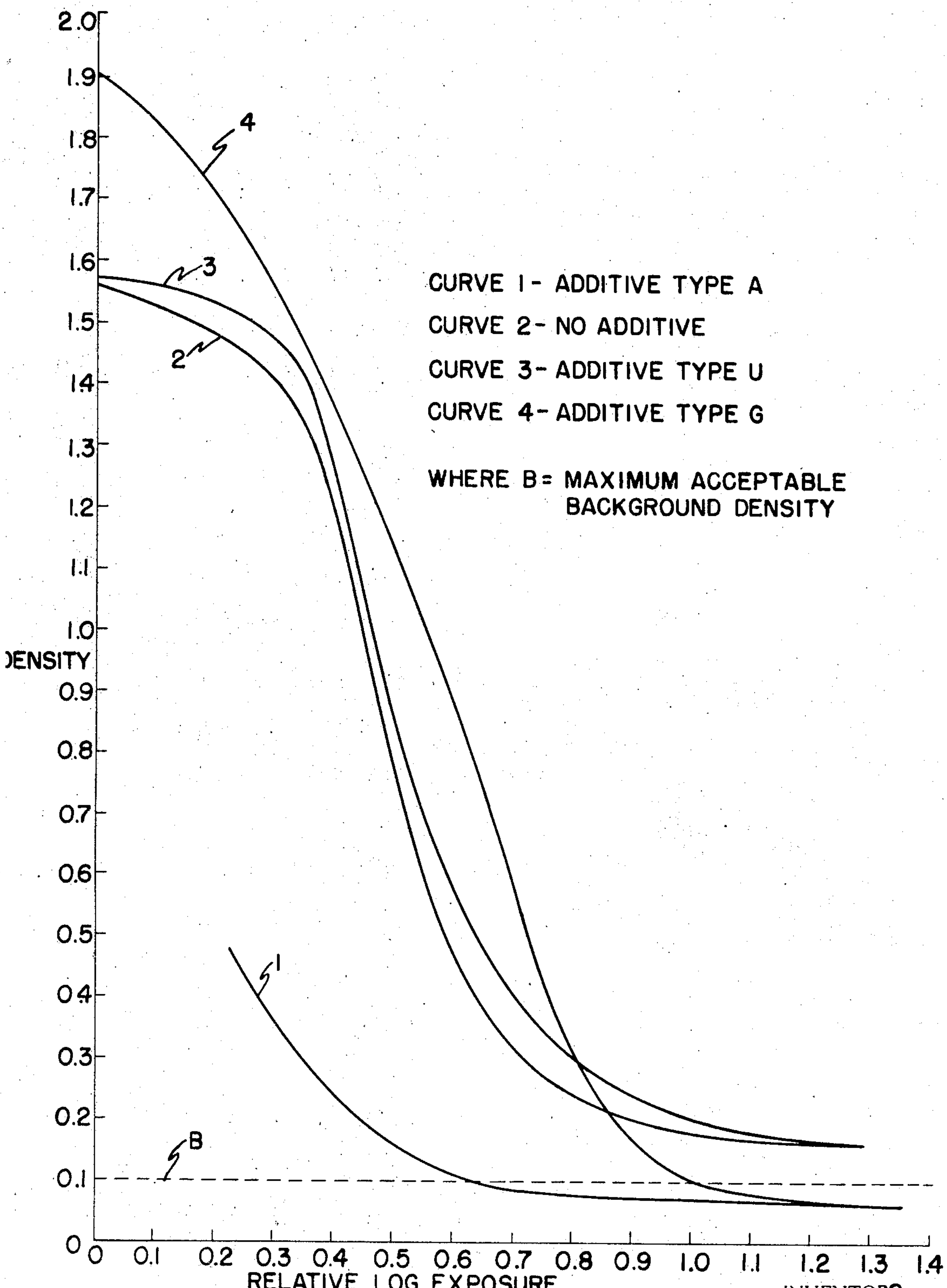

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ELECTROSTATIC DEVELOPER MIX

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This invention relates to improved developer mixtures for developing electrostatic prints and more particularly to the incorporation of additives capable of controlling the spurious deposition of electroscopic powder particles in the background areas and for improving the image density of said prints.

In electrostatic printing faithful reproductions of graphic originals are prepared by exposing an electrostatically charged photoconductive insulating surface to a light image. This produces a charged surface in which the electrostatic charge is dissipated in the light struck areas, leaving the unexposed areas of the surface in a charged condition. The electrostatic image thus produced may be rendered visible by applying a mixture of finely divided pigmented electroscopic powder over the photoconductive layer, the finely divided developer powder being electrostatically attracted to the latent electrostatic image. The application of the finely divided powder to the electrostatic image may be accomplished by the well known and widely used magnetic brush technique, by the cascade technique, or by other methods whereby the finely divided pigmented powder is physically mixed with and carried on the surface of larger carrier particles and the developer mixture applied across the image surfaces of the electrophotographic member.

The carrier material and developer powder are separated, one from the other, in the triboelectric series. The developer powder is attracted to the less conducting areas on the photoconductive member when the electroscopic powder bears an opposite triboelectric charge with respect to the charge in the less conducting areas. When the photoconductive material being employed is zinc oxide the less conducting areas bear a negative charge and the electroscopic powder bears a positive triboelectric charge. When the electroscopic powder is triboelectrically charged with the same polarity as is present in the less conductive areas, it will be attracted to the light exposed areas typical of reversal printing. The adhered electroscopic powder is thereafter permanently fixed in place by fusion to the copy sheet surface.

The dry development techniques just described have certain known disadvantages. The prints produced are not uniform in image density, that is, the developing powder is not evenly applied to the image areas. Another significant disadvantage is the spurious adherence of the electroscopic powder in the exposed or more conductive areas during positive or direct printing. It is highly desirable that the positively charged powder adhere only in the unexposed areas of the image surface in order to provide a reproduction having a uniform dense image with no powder adhering to the "background." In the case where selenium is the photoconductor it is usual that the image portions bear a positive charge attracting the electroscopic powder with a triboelectric negative charge developed thereon.

Heretofore, attempts to correct the print developing problems have involved the application of additional charges to the electrostatic printing element or to the powder itself in order to better control the spurious deposition of powder and/or the image density. Powder additives to the developer mix have not been successful because of undesirable side effects such as mix clumping, agglomeration, poor fusing, and excessive deposition in the background areas.

It is therefore the primary object of this invention to provide improved compositions of electrostatic developer mixes.

It is another object of this invention to provide an improved electrostatic developer mix that effectively gives uniform print density and at the same time substantially prevents the spurious deposition of powder in background areas.

It is a further object of this invention to provide a developer mix which is functional for dry developing systems employing carrier particles mixed with an electroscopic powder into which is incorporated liquid additives which modify the density-charge response between the powder and the image areas.

These and other objects are apparent from and are achieved in accordance with the following disclosure in conjunction with the drawing illustrating the relationship between image density and exposure for electrostatic developer mixes, with and without additives which aid in controlling the deposition of electroscopic powder particles on an electrostatically charged surface.

In achieving the foregoing objects and advantages, the conventional developer mixtures are modified by adding a liquid having certain characteristics of a type best described as a tackifying agent acting between the finely ground electroscopic powder and the larger carrier particles without affecting the flow characteristics of the granular mass. The performance of developer mixes is greatly enhanced upon the addition of materials such as oils which are chemically inert and have a resistivity of about 10^4 ohm-centimeters as they impart an adhesive force between the carrier particle and the electroscopic powder. Organopolysiloxane oils, hydrocarbon oils, mineral oils, non-rancidifying animal and vegetable oils, and fatty acid esters of glycol ethers have been discovered as the most successful tackifying agents to promote the necessary adhesion between the carrier particles and the developer powder.

A preferred electroscopic powder that may be used in conjunction with a tackifying agent of this invention is commercially known as a polystyrene toner. The particle size range of the electroscopic powder is from about 1.0 micron to 50 microns. A toner of electroscopic powder of this type consists of pigmented synthetic plastic resin particles made up of pigmenting materials such as carbon black and a dye such as nigrosine dispersed in a mixture of styrene polymers, substituted styrene polymers and styrene homolog polymers. The granular electroscopic powder when in contact with the granular carrier material acquires an electrostatic charge having a polarity opposite to that of the charged photoconductive insulating layer of the photoconductive member.

Magnetically attractable material, such as finely ground iron, magnetite, cobalt, nickel and ferrites, is preferably employed for magnetic brush development. The magnetically attractable materials are in the form of particles, ranging from 25 microns to 150 microns.

The heretofore critical requirement of the carrier material (e.g., iron) for magnetic brush development to be free of alcohol-soluble impurities (commonly identified in the prior art as "alcoholized iron") need not obtain. It is sufficient that the carrier material merely be free of impurities which would interfere with the electrostatic properties of the system. The granular carrier material is selected so that the particles acquire a charge having the same polarity as that of the charged photoconductive insulating layer bearing the latent electrostatic image. The attraction between the electroscopic powder and the carrier particles understandably must be substantially less than the attractive force exerted thereon by the charged areas of the electrostatic latent image, and greater than the attractive force between the electroscopic powder and the non-image areas on the photoconductive insulating surface.

It has been discovered that the addition of from 0.01% to 1.0% of additive (by weight of carrier particles which comprise the developer mix) significantly increases the uniformity of print density of the developed image and at the same time significantly decreases the amount of electroscopic powder deposition in the non-image or background areas. The results are true not only for magnetic brush type development but also for cascade type development. Other advantages and improvements are realized by the use of the tackifying agents of this invention, such as an increase in the length of time that the developer mix will continue to function in the apparatus, identified as "mix life." It has been found that the use of the oil additives increases the latitude of the ratio of the electroscopic powder to carrier particles that will give optimum performance.

The following liquid additives, when included in the developer mix in the concentrations described herein, have proven to be successful tackifying agents and are possessed of the necessary characteristics to be hereinafter described:

(1) Synthetic organopolysiloxane oils, such as polydialkylsiloxanes, polydiarylsiloxanes, and polyalkyarylsiloxanes, including polydimethylsiloxane, polydiethylsiloxane, polymethylphenylsiloxane and similar substances wherein the alkyl and aryl radicals contain 1 to 8 carbon atoms;

(2) Hydrocarbon oils, such as lubricating oils and mineral oil;

(3) Vegetable oils, such as peanut oil, sesame oil, rape seed oil;

(4) Fish and animal oils, such as cod liver oil, halibut oil, menhaden oil, shark liver oils, and tuna oil;

(5) Glycerol;

(6) Fatty acid esters of glycol ethers, such as:

diethylene glycol monolaurate,
diethylene glycol monooleate,
diethylene glycol monoricinoleate,
diethylene glycol monostearate,
polyethylene glycol 200 monooleate,
polyethylene glycol 200 monoricinoleate,
polyethylene glycol 400 monooleate,
polyethylene glycol 600 monooleate,
ethylene glycol monobutyl ether laurate,
ethylene glycol monobutyl ether oleate,
ethylene glycol monoethyl ether laurate,
ethylene glycol monoethyl ether ricinoleate,
ethylene glycol monomethyl ether ricinoleate, and
ethylene glycol monomethyl ether stearate;

(7) Fatty acid amine surfactants of the general formula $C_nH_{2n}NH_2$, wherein n is a value from 12 to 18.

The above listed materials must possess certain basic properties in addition to their ability to function as a tackifying agent, if they are to be compatible in developer mixes. It is desirable that the liquid be electrically conductive with respect to the developer powder itself, but have a maximum conductivity limit. It has been found that a conductivity below 10^{-4} mho/centimeter is required whereas the conductivity of the electroscopic powder is in the range of 10^{-13} to 10^{-19} mho/centimeter.

The liquid additive must be chemically inert with respect to the thermoplastic resins and the carrier particles. It is obvious that the thermoplastic resins should be insoluble in the additive and that the carrier particles be free from chemical attack by said material. It is important, particularly with regard to vegetable and animal oil, that the additives be stable and not subject to rancidification or decomposition in the environment used.

In formulating the developer mixtures the viscosities of the oils must permit them to uniformly flow over and

coat the granular mass, said viscosities being in the range of from about 20 centipoise to 1000 centipoise.

The triboelectric relationship of the additive in the system should approach that of the carrier particle to electroscopic powder, namely that it have the same polarity as the carrier. It is believed, however, that the additives assume a neutral character in the system.

In the research work carried out to determine the basis for the unique properties imparted by the tackifying agents. it was learned that their performance may be measured in terms of a tackifying factor which is related to the force necessary to separate a particle of electroscopic powder from the carrier, according to the following mathematical expression:

$$F=(s)(n)[1+\text{cosine } A_1)+(1+\text{cosine } A_2)]$$

wherein F is the tackifying factor or value, s is the surface tension of the additive with respect to air at room temperature (72° F.), n is the viscosity of the additive, A_1 is the particular wetting angle formed between the liquid additive and the resin and A_2 is the wetting angle formed between the liquid and the carrier particle, determined in accordance with ASTM Method No. T–458–M–59. The minimum value for F as an acceptable tackification value is about 1×10^2 units and the upper limit is 1.5×10^5 units.

The applicability of the above equation in terms of force required to separate the particle from the carrier represents the physical holding force or adhesive force in addition to the electrostatic attractive force which holds electroscopic powder to the carrier. In the use of such materials as "alcoholized iron" only the electrostatic force due to the triboelectric relationship is responsible for retaining the electroscopic powder on the carrier. As presently understood, the tackifying agent holds the electroscopic powder particle in contact with the carrier, the electroscopic powder being pulled away only by the greater attractive force of the charged portions of the photoconductor sheet. The rotating action of the magnetic brush or the cascading of the developer mix across the surface of the photoconductor sheet does not disturb the particles deposited thereon since the tackifying agent is also acting between the particles of the electrostatic developer mix. The background area or the non-image area tends to remain free of spurious developer powder since the attractive force due to the residual charge in those areas is not sufficiently large to overcome the adhesive force of the tackifying agents. Additionally, it was found that in the cascading technique and magnetic brush development techniques the amount of "throw out," that is, the amount of powders which are rendered air-borne due to the developing procedure, is greatly minimized, tending to make for a much cleaner operation.

This theory is sustained by the fact that a study of the surface charge required to produce a certain level of print density established that a somewhat higher charge is required in the circumstance where an electroscopic powder containing tackifying agent is employed as opposed to the prior art developer mixes. In the instance of the photoconductor sheet requiring the slightly higher charge in order to achieve the same print density the amount of deposition of electroscopic powder in the background was substantially eliminated. Thus, it may be summarized that the introduction of the tackifying agent requires a greater attractive force to be exerted by the photoconductive member in order for printing to occur. The greater force is necessary to overcome the physical force of said tackifying agent which tends to hold the electroscopic powder in contact with the carrier.

In some instances, however, there is no observable difference in print density at the same charging potential level while a marked improvement in the amount of background produced on the print is in evidence. It is believed, in this instance, that the tackifying agent contributes significantly to the flowability of the thermoplastic resin when it is reduced to the molten state during the fusing step such that it forms a continuous film on the image surface producing a more uniform density print. It is believed that a more complete wetting of the molten electroscopic powder occurs to give complete surface coverage in the print area and therefore increases print density.

The following table sets forth the performance of a number of liquid materials which are representative of the various classes of materials listed hereinabove and which were studied in applying the mathematical expression for the tackifying value as related to over-all print quality.

Material	Surface tension (dynes/cm.)	Viscosity (cps.)	Angle of wetting, degrees		Tackifying factor	Performance
			Iron	Toner		
Glycerol	63.4	1,500	95	90	1.8×10^5	A
Polydimethylsiloxane (Dow Corning 200)	21.1	1,000	40	10	7.9×10^4	A
Triethanolamine	47.9	500	50	60	7.5×10^4	A
SAE 30 lubricating oil	33.4	300	40	40	3.5×10^4	G
Diethylene glycol monoricinoleate	20.0	540	30	30	3.3×10^4	G
SAE 20 lubricating oil	32.1	200	30	30	2.4×10^4	G
Mineral oil (U.S.P.)	32.3	104	15	30	1.3×10^4	G
SAE 10 lubricating oil	32.7	100	15	15	1.3×10^4	G
Peanut oil	31.8	70	25	30	8.3×10^3	G
Polydimethylsiloxane (Dow Corning 200)	20.9	100	15	5	8.3×10^3	G
SAE 5 lubricating oil	30.2	50	5	5	6.0×10^3	G
Diethylene glycol monolaurate	75.0	20	30	30	5.6×10^3	G
Cod liver oil	31.8	40	25	30	4.9×10^3	G
$C_nH_{2n}NH_2$ (n=16 to 18)	31.5	40	25	25	4.9×10^3	G
Polydimethylsiloxane (Dow Corning 200)	20.5	20	3	3	1.6×10^3	G
Isopropanol	21.7	4	1	1	3.5×10^2	U
Water	73.4	1	80	80	2.5×10^2	U

As the tackifying value exceeds 1.5×10^5 units the charge potential on the electrophotographic member becomes insufficient to overcome the attractive force of the additives and consequently poor print density occurs. Where excellent performance was observed when compared to prior developer mixtures, the performance of that material is identified with the letter G. Those tackifying agents which resulted in producing prints which were acceptable as having substantially decreased deposition of spurious particles in the background but which required a greater charging potential as exhibited by slight decrease in print density are marked A. Certain of the additives gave no improved performance when added to standard developer mixes and they are identified as U.

Referring to the chart, those materials giving excellent performance have a tackifying value which falls in the range of from about 0.2×10^4 to 4×10^4 and are identified with the letter G. Triethanolamine and glycerine give acceptable performance as indicated by the letter A since they require slightly higher charge in order to obtain an equivalent print density. These materials have a tackifying value ranging from 7×10^4 to 1.5×10^5. Water and isopropanol are marked U, affording no observable improvement, having a tackifying value range below 4×10^2.

Print quality studies were carried out using the tackifying agents at the lower limit of concentration of about 0.025% by weight of carrier present. As greater concentrations of tackifying agent are employed a corresponding effect on the print quality is observed. It is desirable to use a small quantity of tackifying agent within the limits of approximately 0.025% to 1.0% by weight of the carrier present since the use of larger percentages can result in some loss in print density and affect the flowability of the granular mass. The developer mix that may be employed in conjunction with the tackifying agents of this invention consists essentially of from 10 to 20 parts by weight of magnetic particles having a particle size range of from 25 to 500 microns, per part of electroscopic powder which have an average particle size of from 1 to 50 microns, preferably in the range of from 5 to 25 microns. The electroscopic particles are constituted of a resin having a resistivity greater than 1×10^{13} ohm-centimeters pigmented with a suitable pigment or a dye. The pigmented resin is mixed with magnetic particles

in the proportion given above to which has been added a tackifying agent as hereinabove described, in the range of from 0.025% to 1.0% by weight of the carrier particle present.

Referring to the drawing, there is plotted the density values in the image and non-image areas as a function of exposure. Since the originals which are to be copied present graphic subject matter which varies in density there will be reflected therefrom a certain amount of light unless it is a solid black area in which case it will reflect little energy. The range of image densities encountered is exemplified in a typical photographic step wedge.

In developing, electrostatic prints are made from an original having a range of densities thereon similar to that found in a step wedge with the prior art developer mixes. The density of the image areas obtained follows the density curve represented by curve **2** of the drawing. The image area does not develop up to the maximum density of the original and the areas corresponding to the non-image areas pick up the electroscopic powder to produce undesirable background.

The inclusion of certain additives which gave the performance values identified as G is shown in the curve **4** where greater print densities of the same original are obtained using the same exposures. Further examining curve **4** it will be seen that it continues to drop off to a level where the background areas corresponding to the non-image areas on the original, which reflect the most amount of light energy, do not pick up a significant amount of electroscopic powder.

Curve **1** is illustrative of the additives rated as A which permit the development of prints substantially free of background but in which prints of a very low image density are produced when exposing the original to the same amount of light as provided in curve **4**. In effect any gray areas on the original would not be reproduced when using A type developer additives.

The final curve **3** on the plot shows the effect of using an additive that is of U type of performance. It gives slightly greater density at lower exposures but no improvement in decreasing the amount of background produced.

The resin constituent of the electroscopic powder can be any resin having a resistivity greater than 1×10^{11} ohm-centimeters, which can be fused at a temperature below the char point of paper. Suitable resins are polystyrene resins and blends thereof, acrylic resins, rosin, asphalt, gilsonites, polyvinyl resins, and other thermoplastic resins having the softening point within the range of 50° C. to 140° C., preferably 100° C. to 140° C., and having the indicated resistivity characteristicss. The values presented are merely exemplary, the requirement being that the conductivity of the oil should be at least that of the resin employed. The resins are pigmented or colored with carbon black or other suitably colored dyes or pigments. In the case of polystyrene, an amount of pigment as much as 6% of the amount of resin can be used.

In the preparation of the electroscopic powder, the resin constituents of the toner are rendered molten, and the pigment and/or dye are added in an amount ranging from about 1% to about 17% of the weight of the amount of resin employed, preferably in the range of from 3% to 6% pigment and/or dye by weight of resin. The pigment and/or dye are distributed throughout the molten resin so that a homogeneously colored solution or dispersion is achieved. The material is poured into shallow pans and permitted to cool, thereafter being ground or milled to the particle size range of from 1 to 50 microns, preferably in the range of from 5 to 25 microns in size. In the final step the pigmented resin particles are combined in the ratio of 1 part electroscopic powder to from 5 to 50 parts by weight of carrier particles, preferably in the range of from 10 to 20 parts by weight of carrier per part of electroscopic powder, said carrier particles having had dispersed thereon the tackifying agent.

The viscosity range of the materials which are usable as tackifying agents range from 1 to 1000 centipoises and is such that the additive is readily distributed over the carrier particles in a rotating tumbler type device. Any one of the tackifying agents set forth in the table and whose performance has been evaluated by the code letters G and/or A having a tackifying value which is below that of glycerol may be included in the developer mix hereinabove by adding it to the carrier particle prior to combining it with the developer powder comprising from 0.025% to 1.0% by weight of the carrier present.

The discussion of the operation of the invention has been described in terms of magnetically attractable carrier particles suitable for magnetic brush type development. However, it is not intended that it be limited thereto and the mathematical expression for relating the tackifying value to performance applies also to the use of carrier particles suitable for cascade type development techniques. In the circumstance where glass (or any other carrier material having specific triboelectric relationship to the electroscopic powder) is used as a carrier, it becomes necessary to determine the angle of wetting of the liquid with respect to the specific carrier and the specific resin, in substituting these values along with the viscosity and surface tension into the mathematical expression for the tackifying value. The liquid additive will be suitable as a tackifying agent where the tackifying value is equal to or less than that for glycerol.

We claim:

1. A developer mixture for developing a visible image on an electrophotographic member having an electrostatic charge pattern thereon of image and non-image areas, said developer mixture consisting essentially of a granular mass of 1 part of electroscopic powder in physical mixture with 5 to 50 parts of carrier particles for said electroscopic powder, said carrier particles having uniformly dispersed thereon 0.01% to 1% by weight of an inert organic oleaginous liquid which is insoluble in said electroscopic powder and which has a conductivity below 10^{-4} mho/centimeters, a viscosity of 20 to 1500

centipoises and an adhesive force of 1×10^2 to 1.5×10^5, the adhesive force of said inert organic liquid being F in the equation

$$F=(s)(n)[(1+\text{cosine } A_1)+(1+\text{cosine } A_2)]$$

wherein s is the surface tension in dynes per centimeter with respect to air at 72° F., n is the viscosity in centipoises, A_1 is the wetting angle with the electroscopic powder particles and A_2 is the wetting angle with the carrier particles.

2. A developer mixture as defined by claim **1** wherein the carrier particles are magnetically attractable.

3. A developer mixture as defined by claim **2** wherein the quantity of the inert organic oleaginous liquid dispersed on the carrier particles is from 0.1% to 1% of the weight of said carrier particles.

4. A developer mixture as defined by claim **3** wherein the viscosity of the inert organic oleaginous liquid is in the range from 20 to 1000 centipoises.

5. A developer mixture as defined by claim **4** wherein the inert organic oleaginous liquid is an organopolysiloxane oil, a hydrocarbon oil, a stable vegetable, fish or animal oil, glycerol, a fatty acid ester of a glycol ether or an alkylamine wherein the alkyl radical contains 12 to 18 carbon atoms.

6. A developer mixture as defined by claim **5** wherein the inert organic oleaginous liquid is mineral oil having a viscosity of about 100 centipoises.

7. A developer mixture as defined by claim **5** wherein the inert organic oleaginous liquid is polydimethylsiloxane.

8. A developing powder for use in the magnetic brush system of developing electrostatic images comprising a mixture of ferromagnetic carrier particles and toner particles, said carrier particles being coated with from 0.01% to 0.5% by weight of an oleaginous substance based on the weight of said carrier particles.

9. A developing powder for use in developing electrostatic images comprising a mixture of toner particles and carrier particles for said toner particles, said carrier particles being coated with from 0.01% to 1% by weight of an oleaginous substance based on the weight of said carrier particles.

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