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3,681,106
**ELECTROSTATIC DEVELOPER CONTAINING
POLYESTER RESIN AND A PROCESS OF
USING SAME**

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ABSTRACT OF THE DISCLOSURE

Electrostatic compositions are disclosed which com-
prise a toner containing a coloring agent and a polyester
resin, and can include carrier particles. The polyester resin
is prepared from a dicarboxylic acid and a polyhydroxy
composition which contains an alkylene oxide derivative
of a bisphenol and an alkylene oxide derivative of a sec-
ond polyhydroxy compound.

This invention relates in general to electrostatic photog-
raphy and in particular to an electrostatic composition
which gives improved performance in the art of direct and
indirect electrostatic photography. More particularly this
invention relates to electrostatic compositions which may
be toner compositions or developer compositions.

In xerography, an indirect electrostatic photographic
process, it is usual to reproduce a master by electrical
photography methods such as, most typically, placing an
electrostatic charge on a photoconductive surface, selec-
tively dissipating such charge by exposure to an optical
image corresponding to the master to be reproduced and
developing the resulting electrostatic image by exposure
to an electroscopic material.

According to one practice in xerography as disclosed in
U.S. 2,618,552 to E. N. Wise, the development of the elec-
trostatic image is accomplished by rolling or cascading
across the image-bearing surface a developer composition
of relatively large carrier particles having on their sur-
faces, for example electrostatically coated thereon, fine
powder particles known as toner particles. As the com-
position cascades or rolls across the image-bearing sur-
face, these toner particles are electrostatically deposited
on and secured to the charged portions of the image and
are not secured on the uncharged or background portions
of the image. Toner particles deposited on these back-
ground portions are physically removed therefrom by the
electrostatic action of the carrier particles passing there-
across. The toner particles are electrostatically secured to
the rolling carrier particles. The result is an excellent copy
of the electrostatic image in the form of an image made
up of the toner particles electrostatically clinging to the
image-bearing surface and removable therefrom by any of
various means such as adhesive transfer, electrostatic
transfer, or the like. Thus the image may be transferred
to a sheet in contact with the image-bearing surface by
applying an electrostatic charge to the sheet while in such
contact. When the sheet is subsequently stripped from the
image-bearing surface it carries with it a substantial pro-
portion of the image to yield a xerographic print which
thereafter may be made permanent by any desired method
such as heating, solvent fixing or the like.

After the image is transferred from the image-bearing
surface to the sheet the photoconductive surface may be
cleaned and then is ready for use in a subsequent xero-
graphic cycle. The photoconductive surface, after being
properly cleaned following a previous xerographic cycle,
is in its original condition and is substantially unimpaired
for future use. Cleaning the photoconductive surface fre-

quently presents difficulties. A problem of not consistent-
ly producing good prints, due apparently to the strong at-
traction of residual toner particles to the photoconductive
surface, has been observed. This problem is evidenced by
stubborn adherence of toner particles as such to the sur-
face with the result that after mechanical cleaning opera-
tions substantial amounts of toner may still remain on the
surface, which builds up on the surface during repeated
cycles and eventually requires additional cleaning opera-
tions, such as, for example, solvent cleaning or the like.

The cleaning problem is further complicated by the fact
that the usual and preferred method of transferring the
toner image from the image-bearing surface to the sheet,
such as sheet paper, is carried out by affixing the image to
the sheet by the application of heat thereby melting the
toner and fusing it onto the sheet. Thus temperatures of
melting for the particular toner compositions and in par-
ticular the resin portion of same must be such that they
do not damage the sheet. When paper is the sheet material
such low temperatures are required for melting that a
tackiness or stickiness of the toner resin at operating tem-
peratures due to the low melting point of the resin is ob-
tained which further complicates producing good prints.
Furthermore, many low melting point resins are very brit-
tle and, in xerographic process manipulations tend to de-
grade to small particle sizes making handling extremely
difficult and causing a fine film of toner powder to con-
tinually build up on the photoconductive surface. The pow-
der so formed further impairs the clarity of the resultant
prints.

A relatively low melting point, a high degree of abra-
sion resistance, and the ability to remain untacky at han-
dling temperatures are physical properties which should
be present in a toner resin, but proper electrostatic prop-
erties are also necessary to achieve a good xerographic
toner composition.

Other xerographic processes using the electrostatic com-
positions of this invention will be set forth below after a
discussion of the preparation of the toner compositions of
this invention.

It is an object of this invention to provide electrostatic
compositions having low melting points, high tack points,
and a high degree of abrasion resistance.

It is another object of this invention to provide an
electrostatic composition which gives clear, sharp xero-
graphic images.

It is another object of this invention to provide devel-
oper compositions for use in a cascade xerographic pro-
cess.

It is another object of this invention to provide toner
compositions.

These and other objects of this invention will become
evident to those skilled in the art from the following de-
tailed description of the invention.

In general the electrostatic compositions of this inven-
tion comprise a toner containing a coloring agent and a
polyester resin. The polyester resin is comprised of a di-
carboxylic acid and a polyhydroxy composition which con-
tains an etherified diphenol hereinafter described. Said
polyester resins have a liquid point of less than 110° C.
and a tack point of greater than about 60° C. The color-
ing agent is either a pigment or a dye or a combination
of both. The pigment is usually present at a level of from
about 1 part to 20 parts and levels as high as 50 parts by
weight per 100 parts by weight of the toner have been used.
Preferably from about 5 to about 10 parts by weight of
pigment are used.

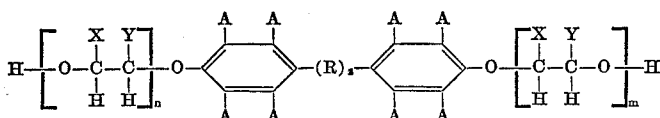
In one method of preparation of the toner composition
of the present invention, the ingredients are thoroughly
mixed to form a uniform dispersion of pigment or dye
in the resin and the mixed ingredients are finely divided

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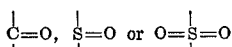
to a desired toner composition particle size. The mixing may be done by various means including combination of the steps of blending, mixing, milling, and presently a preferred method includes the step of blending in a rubber mill to assure uniform dispersion of the pigment in the resin. In an alternative procedure the polyester resin and the pigment or dye may be mixed together with the polyester resin in a relatively viscous state. The mixture is then cooled and the resulting solid suspension of pigment in polyester resin is ground to the desired particle size. The polyester resin is usually present at a level of from 50 to 99 parts by weight of said toner and preferably from 90 to 95 parts by weight. Usually the toner consists of particles having an average size of about 40 microns.

As stated above in addition or instead of the pigment the toner composition may have a dye present. A dye is normally used where a color reproduction is desired. The dyes are usually present at levels of about 2 to 20 parts by weight per hundred parts of toner. Exemplary of the dyes are naphthol B, erichrome B, lithol rubine, phthalocyanine blue, and sulphone thalocyanine blue. Other ingredients of the toner include plasticizers and resin fillers which may improve the handling properties of the toner or adapt the toner for a particular electrostatic printing process. These additional ingredients may be present at levels up to about 30 parts per 100 parts of toner by weight.

The etherified diphenols which may be used in polyhydroxy compositions from which the above polyester resin may be prepared may be characterized by the following formula



wherein z is 0 or 1, R is an alkylene radical containing from 1 to 5 carbon atoms, a sulfur atom, an oxygen atom,



X and Y are individually selected from the group consisting of alkyl radicals containing from 1 to 3 carbon atoms, hydrogen, and a phenyl radical with the limitation that at least X or Y is hydrogen in any X and Y pair on adjacent carbon atoms, n and m are integers with the proviso that the average sum of n and m is from about 2 to about 7; and each A is either a halogen atom or a hydrogen atom. An average sum of n and m means that in any polyol blend some of the etherified diphenols within the above formula may have more than 7 repeating ether units but that the average value for the sum of n and m in any polyhydroxy composition is from 2 to about 7. Examples of compounds within the above general formula are

polyoxystyrene(6)-2,2-bis(4-hydroxyphenyl) propane;
polyhydroxybutylene(2)-2,2-bis(4-hydroxyphenyl) propane;
polyoxyethylene(3)-2,2-bis(4-hydroxyphenyl) propane;
polyoxypropylene(3)-bis(4-hydroxyphenyl) thioether;
polyoxyethylene(2)-2,6-dichloro-4-hydroxyphenyl, 2',3',6'-trichloro-4'-hydroxyphenyl methane;
polyoxypropylene(3)-2-bromo-4-hydroxyphenyl, 4'-hydroxyphenyl ether;
polyoxyethylene(2.5)-p,p-bisphenol;
polyoxybutylene(4)-bis(4-hydroxyphenyl) ketone;
polyoxystyrene(7)-bis(4-hydroxyphenyl) ether;
polyoxypentylene(3)-bis(2,6-diiodo-4-hydroxyphenyl) propane; and
polyoxypropylene(2.2)-2,2-bis(4-hydroxyphenyl) propane.

A preferred group of said etherified diphenols are those where the average sum of n and m is from about 2 to

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about 3. Thus although the sum of n and m in a given molecule may be as high as about 20, the average sum in the polyol composition will be about 2 to about 3. Examples of these preferred etherified diphenols include

polyoxyethylene(2.7)-4-hydroxyphenyl-2-chloro-4-hydroxyphenyl ethane;
polyoxyethylene(2.5)-bis(2,6-dibromo-4-hydroxyphenyl) sulfone;
polyoxypropylene(3)-2,2-bis(2,6-difluoro-4-hydroxyphenyl) propane; and
polyoxyethylene(1.5)-polyoxypropylene(1.0)-bis(4-hydroxyphenyl) sulfone.

A preferred polyhydroxy composition used in said polyester resins are those polyhydroxy compositions containing up to 2 mol percent of an etherified polyhydroxy compound, which polyhydroxy compound contains from 3 to 12 carbon atoms and from 3 to 8 hydroxyl groups. Exemplary of these polyhydroxy compounds are sugar alcohols, sugar alcohol anhydrides, and mono and disaccharides. A preferred group of said polyhydroxy compounds are sorbitol, 1,2,3,6-hexanetetrol; 1,4-sorbitan; pentaerythritol, xylitol, sucrose, 1,2,4-butanetriol, 1,2,5-pentanetriol; xylitol; sucrose, 1,2,4-butanetriol; and erythro and threo 1,2,3-butanetriol. Said etherified polyhydroxy compounds are propylene oxide or ethylene oxide derivatives of said polyhydroxy compounds containing up to about 10 molecules of oxide per hydroxyl group of said polyhydroxy compound and preferably at least one molecule of oxide per hydroxyl group. More preferably the molecules of oxide per hydroxyl group is from 1 to 1.5. Oxide mixtures can readily be used. Examples of these

derivatives include polyoxyethylene(20) pentaerythritol, polyoxypropylene(6) sorbitol, polyoxyethylene(65) sucrose, and polyoxypropylene(25) 1,4-sorbitan. The polyester resins prepared from this preferred polyhydroxy composition are more abrasion resistant and usually have a lower liquid point than other crosslinked polyesters herein disclosed.

The means of oxide addition in preparing both the etherified diphenols and the alkylene oxide derivatives of the polyhydroxy compounds may be the standard oxide addition techniques well known in the art. Also as is known in the art, a phenolic hydroxyl group is much more reactive than an aliphatic hydroxyl group formed upon the alkylene oxide addition of an alkylene oxide to a phenol. Thus the etherified diphenols illustrated by the above formula will usually have at least one alkylene oxide group attached to each phenolic hydroxyl group residue due to the greater reactivity of the phenolic hydroxyl hydrogen.

The dicarboxylic acids which may be used in preparing the polyester compositions used in accordance with this invention may be either saturated or unsaturated acids. Thus exemplary of these acids are maleic acid, cyclohexane dicarboxylic acid, fumaric acid, glutaric acid, phthalic acid, isophthalic acid, terephthalic acid, succinic acid, malonic acid, and the anhydrides of these acids.

In general the polyester resins of this invention may be prepared by reacting a particular dicarboxylic acid with a polyhydroxy composition disclosed above at a temperature of about 200° C. and under inert atmosphere. Catalyst or promoters used in preparing polyesters can be added to enhance the activity of the particular reactants. The ratio of the number of hydroxyl groups of said polyol composition to the number of carboxyl groups of said dicarboxylic acid may be from 1.2 to 0.8; it is preferably about 1.

The polyester resins used in the electrostatic compositions of this invention must have a tack point of greater

than 60° C. and a liquid point of less than 110° C. and be physically tough. Preferably the liquid point of the resin is between 85 and 100° C. A better resin is achieved if the liquid point is within the 85 to 100° C. temperature range, and the tack point is at most 20° C. less than the liquid point.

The liquid and tack points of the resins of this invention are calculated by using a Kofler Heizbank, Type 7841, hot bench, manufactured by C. Reichert Optische Werke Ag. of Vienna, Austria. This hot bench is an electrically heated variable heat source. First the bench is heated to obtain a 95° C. temperature in the middle of the bench and corresponding lower and higher temperatures at either end of the bench. Then about 5 grams of finely divided resin are sprinkled evenly across the bench surface. The bench temperature at which the resin cannot be brushed from the hot bench using a small artist brush is considered to be the tack point, whereas the bench temperature at which the resin forms liquid globules is considered the liquid point.

As heretofore mentioned, the polyester resins which are used in the electrostatic compositions of this invention have to be abrasion resistant, that is they must be a tough resin. A procedure for determining the toughness of a resin is to subject particles of a resin to a grinding means and determine how badly the resin has been degraded by the grinding means. A suitable test procedure used to determine the toughness of the resins, used in the toner compositions of this invention, is the following: 115 grams of the polyester resin which has been previously ground to a relatively uniform particle size, that is all the polyester resin particles will pass through a 60 mesh screen but will be retained on a 80 mesh screen, are placed in a size 00 Roalax jar mill by U.S. Stoneware Company with 1,000 grams of Burundum grinding cylinders which are $\frac{13}{16}$ inch long x $\frac{13}{16}$ inch in diameter. To prevent caking 0.5 gram of a silicone anti-caking agent is added. After the mill has been run for approximately 60 minutes, 100 grams of the resin are separated from the grinding cylinders and placed on a series of pre-weighed screens having mesh sizes of 60, 80, 100, 120, 140, and 200 U.S. mesh. A collection pan is placed under the bottom most screen. The screens are placed in descending size order on a Roto-tap shaker and the resin placed on the 60 mesh screen. After 10 minutes of shaking the resin on each screen and the resin collected on the bottom pan is determined. The polyester resin of this invention are sufficiently tough that no more than 30 percent of the polyester resin charged to the Roto-tap shaker is collected on the pan and preferably no more than 20 percent is degraded sufficiently to pass the 200 mesh screen. Whenever a resin is said to be abrasion resistant in this application, it will refer to the resin having been tested by the above procedure and having no more than 30 weight percent degraded sufficiently to pass a 200 U.S. mesh screen. Furthermore, if a resin is said to have an abrasion resistance of 20 it will mean that only 20 weight percent of a resin sample tested passed through a 200 U.S. mesh screen.

In order for those skilled in the art to more fully understand the preparation of the resins used in the toner compositions of the instant invention and the preparation of the toner compositions of this invention, the following non-limiting examples are presented:

EXAMPLE 1

1,865 grams of polyoxypropylene(2.2) - 2,2 - bis(4-hydroxyphenyl) propane and 2.9 grams of polyoxypropylene(6) sorbitol are charged to a 3 liter, 4 necked, round-bottom reaction flask which is fitted with a thermometer, a stainless steel stirrer, a glass inlet tube, and a meter, a stainless steel stirrer, a glass inlet tube, and a downward condenser. The flask is supported in a Glas-Col electric heating mantle. Through the glass inlet tube nitrogen gas is allowed to flow thereby sparging

the polyol blend and resulting in an inert atmosphere in the reaction vessel. The agitator and heating mantle are then activated and the polyol blend is heated to 50° C. at which time 628 grams of fumaric acid and 1.25 grams of hydroquinone are added to the reaction vessel. The nitrogen gas flow is then regulated at a setting of 2.5 on a Sho-Rate meter of the Brooks Rotometer Company. The reaction mass is heated to a temperature of 210° C. over a period of 5 hours. Water of the esterification reaction is removed as it is formed and the mass is maintained at 210° C. for an additional 6½ hours. The course of the reaction is followed by acid value determinations at hourly intervals. At the end of the reaction, when an acid value of about 20 is achieved, the resin is cooled to room temperature. The resin has an acid value of 18.6, a ball and ring softening point of 104° C., a tack point of 75° C., and a liquid point of 100° C. The ratio of hydroxyl groups to carboxyl groups in the preparation of this resin is 1 to 1. The abrasion resistance of this resin is 19.

EXAMPLE 2

According to the procedure of Example 1, 1810.0 grams of polyoxypropylene(2.2) - 2,2 - bis(4 - hydroxyphenyl) propane and 29.7 grams of polyoxypropylene(6) sorbitol are charged to a reaction vessel. To this polyol mixture is then added 664.0 grams of fumaric acid which results in an equivalence ratio of 1 hydroxy group for every 1.06 carboxyl groups. Also added is 1.25 grams of hydroquinone. As in Example 1, the acid and the hydroquinone are added after the reaction mixture of polyols reaches 50° C. The reaction mixture is then heated to 210° C. and held there until the acid number is less than about 30 at which point the resinous mixture is cooled to room temperature. The resulting polyester has an acid value at room temperature of 23.8 and a ball and ring softening point of 121° C. It has a tack point of 78° C. and a liquid point of 109° C. The abrasion resistance of this resin is 16.0.

EXAMPLE 3

According to the procedure of Example 1, 1,882 grams of polyoxypropylene(2.2) - 2,2 - bis(4 - hydroxyphenyl) propane and 1.49 grams of polyoxypropylene(6) sorbitol are added to a reaction vessel. The reaction vessel is heated and sparged with nitrogen. When the reaction mixture reaches 50° C., 616 grams of fumaric acid and 1.25 grams of hydroquinone are added. The reaction mixture is allowed to heat to 210° C. at which time the reaction mixture is maintained at 210° C. and the water of reaction is removed. The resin upon completion of the reaction, is cooled to room temperature. This resin has an acid value of 18.1 a ball and ring softening point of 99° C., a tack point of 70° C., and a liquid point of 92° C. The abrasion resistance of this resin is 30.

EXAMPLE 4

1,865 grams of polyoxypropylene(2.2) - 2,2 - bis(4-hydroxyphenyl) propane is charged to a 3 liter, 4 necked, round-bottom flask fitted with a thermometer, a stirrer, a glass inlet tube, and a condenser for removal of water of esterification. The flask is placed in an electric heating mantle and the heating mantle and the agitator are started. When the temperature in the reaction medium reaches 50° C., 628 grams of fumaric acid and 1.25 grams of hydroquinone are added to the reaction mixture. Nitrogen gas flow is started at a setting of 2.5 on a Sho-Rate meter produced by the Brooks Rotometer Company. The heating is continued with stirring until 210° C. is reached after about five hours. The water of reaction is removed as it is formed through the condenser and the temperature is then maintained at 210° C. The course of the reaction is followed by determining the acid value at hourly intervals. When the acid value reaches a value of about 50, 2.9 grams of polyoxypropylene(6) sorbitol is added to the reaction mixture and the reaction

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is continued until an acid value of less than about 25 is determined. At this point, the resin is cooled to room temperature and is found to be a solid, friable material. The abrasion resistance of this resin is 19.

EXAMPLE 5

In accordance with the procedure of Example 1, 985 grams of polyoxyethylene(3) bis(4-hydroxyphenyl) ketone and 44.3 grams of polyoxyethylene(30) pentaerythritol are placed in a 3 liter, round-bottom flask. This mixture is heated and when the reaction temperature reaches 50° C., 348 grams of succinic acid is added. The reaction mixture is then heated to a temperature of 215° C. and the water of reaction is continually removed. The course of the reaction is followed by taking hourly samples in determining the acid value. After an acid value of 30 is reached the heat is removed and the reaction mixture is slowly cooled to room temperature. The resulting polyester is a hard, tough solid.

EXAMPLE 6

According to the procedure of Example 4, 1520 grams of polyoxyethylene(2) bis(4-hydroxyphenyl) thioether is charged to a 4 liter, round-bottom flask. The thioether is then heated and sparged with nitrogen to maintain an inert atmosphere. When the temperature in the reaction vessel reaches 50° C., 665 grams of phthalic anhydride is added to the reaction vessel. The water of esterification is removed during the heat up period and the continuing reaction period. When 205° C. is reached, 21 grams of

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EXAMPLE 9

100 grams of the resin prepared in Example 1 and 10 grams of carbon black pigment obtained from Columbian Carbon Company under the name, Neo Spectra Mark II powder, are blended together in a rubber ball mill to a uniform particle size of about 30 microns. The resulting composition is a xerographic toner useful for black and white prints.

When 1% of this toner is combined with a carrier such as glass beads, in a 2 component developer, similar to those described in U.S. Pat. No. 2,618,551, and cascaded across an electrostatic image-bearing surface, the image which is developed by the deposition of the toner on the electrostatic image plate is found to be a clean electrostatic image.

EXAMPLE 10

75 grams of the polyester resin of Example 2 and 5 grams of carbon black are heated to a temperature of 120° C. The resin carbon black mixture is slowly stirred with a magnetic stirrer until the carbon is uniformly dispersed in the liquid resin. The resin carbon mixture are then cooled down to room temperature and ground to a 10 micron size.

In accordance with the procedures of either Example 9 or 10 additional toner compositions are prepared using various pigments at various pigment levels in accordance with the teachings of this invention. The compositions of these toners are presented in Table I. The average particle size of the toners of Examples 11 to 14 is 20 microns.

TABLE I.—TONER COMPOSITIONS

Example	Polyester resin of Example—	Parts resin	Pigment	Parts pigment	Procedure of Example—
11-----	5	75	Iron oxide-----	25	9
12-----	6	98	Carbon black-----	2	9
13-----	7	94	do-----	3	9
14-----	8	90	do-----	8	10

polyoxyethylene(15) sucrose is added. The reaction is continued at 205° C. with hourly samples taken and the acid value determined. When the acid value reaches less than 25, the reaction mixture is cooled down. The resulting resin is a hard, friable, tough material.

EXAMPLE 7

According to the procedure of Example 1, 2190 grams of polyoxyethylene(2.5) - 2,2 - bis(4 - hydroxy - 2,6-chlorophenyl) propane and 21 grams of polyoxyethylene(12) xylitol are placed in a 4 liter flask. This mixture is heated and when a temperature of 50° C. is obtained, 465 grams of maleic acid and 1.5 grams of hydroquinone are added. The heating is continued until a temperature of 210° C. is achieved at which point the temperature is maintained at 210° C. the water of esterification is removed as it is formed through a condensed. The acid value of the reaction mixture is tested at hourly intervals and when the acid number is less than 30, the reaction mixture is cooled to room temperature. The resultant polyester is a tough solid resin.

EXAMPLE 8

614 grams of polyoxystyrene(3) 2,2-bis(4-hydroxyphenyl) sulfoxide, 20 grams of polyoxypropylene(6) erythritol, and 140 grams of succinic acid are charged to a 4 liter reaction vessel. The reaction vessel is then heated to a temperature of 200° C. to 210° C. and maintained within this temperature range for the remainder of the reaction. During the course of the reaction, hourly samples of the reaction mixture are taken and an acid value is determined. When the acid value is less than about 20, the reaction is considered over. The reaction product is removed from the heat source and cooled. The resulting product is a tough, solid polyester resin.

As stated above the novel toner compositions of this invention have exceptional utility in developing electrostatic images. In the normal xerographic process such images are created and developed on the surface of a photoconductive surface which is generally amorphous selenium. However, other photoconductive surfaces, such as those made from a photoconductive pigment such as zinc oxide, zinc cadmium sulfide, tetragonal lead monoxide, or titanium dioxide incorporated in an insulating resin binder may be used.

In addition, rather than developing the electrostatic image on the photoconductive surface, if desired the electrostatic image may be transferred to an electrically insulating film such as a film of polyethylene terephthalate. This process is described more fully in U.S. Pat. No. 2,825,814 to L. E. Walkup. The toner composition of the instant invention may then be used to develop the electrostatic image on this insulating film to form a toner image corresponding to the electrostatic image thereon. The resulting toner image may then be either permanently affixed to the insulating film or transferred to a support member as paper, metal, plastic, etc., and the insulating film cleaned and reused in the process.

In any event, as used in developing an electrostatic image the toner composition of the instant invention is electrostatically coated on a suitable carrier surface which is then in turn contacted with the surface bearing the electrostatic image whereby the toner particles are transferred to the surface bearing the electrostatic image to form thereon a powder image corresponding to the electrostatic image. The most widely used method of carrier development is known as cascade carrier development has been referred to supra and is more fully described in U.S. Pat. No. 2,618,551, to L. E. Walkup; U.S. Pat. No. 2,618,552, to E. N. Wise; and U.S. Pat. No. 2,638,416 to

L. E. Walkup and Wise. In this process the toner is desirably mixed with a granular carrier either electrically conducting or insulating, magnetic or non-magnetic, provided that the particles of granular material when brought in close contact with the powder particles acquire a charge having an opposite polarity to that of the powder particles adhering to and surrounding the granular carrier particles.

The selection of a carrier is an art. If a positive reproduction of the electrostatic image is desired, the carrier is selected so that the toner particles acquire a charge having the opposite polarity to that of the electrostatic image. Alternatively, if a reversal reproduction of the electrostatic image is desired, the carrier is selected so that the toner particles acquire a charge having the same polarity as that of the electrostatic image. Thus, the materials for the granular material are selected in accordance with their triboelectric properties in respect to the toner so that when mixed or brought into contact one material is charged positively if the other is below it in a triboelectric series, and negatively if the other material is above it in a triboelectric series. By selecting materials in accordance with their triboelectric effects, the polarities of their charge when mixed are such that the toner particles adhere to and are coated on the granular carrier particles and also adhere to the electrostatic charges on the photoconductive surface which thus retain the toner in the charge areas that have a greater attraction for the toner than the granular carrier particles have. Typical carrier particles are composed of glass, steel, iron, NH_4Cl , NaCl , and phenol-formaldehyde resins.

The carrier particles are at least ten times the size of the toner particles. The carrier particles are shaped to roll across the image-bearing surface. Generally speaking, the carrier particles should be of sufficient size so that their gravitational or momentum force when rolling across the image-bearing surface is greater than the force of attraction of the toner particles for the carrier in the charge areas in order that the granular carrier particles will not be retained by the toner particles. At the same time, the momentum of the carrier must not be so great that it interferes with the toner particles being held or repelled, as the case may be, by the charged or uncharged areas of the plate. It has been found best to use granular carrier particles of a size larger than about 200 mesh, usually between about 20 and about 100 mesh, and toner particles of a size from about 1 to 30 microns. The granular carrier particles may, if desired, be somewhat larger or smaller as long as the proper size relationship to the toner is maintained and as long as the granular carrier particles will flow easily over the image surface by gravity when the plate is inclined without requiring additional means or measurement to remove them.

The degree of contrast or other photographic qualities in the finished image may be varied by changing the ratio of granular carrier to toner material. Successful results have been had with from about 10 to about 200 parts by weight of granular carrier particles capable of being passed through a 20 mesh screen and being collected on a 60 mesh screen to 1 part of the toner having a particle size of 1 to 30 microns. Generally a carrier-to-toner weight ratio in the order of about 100 to 1 is satisfactory and preferred compositions run from about 70 to 1 to about 150 to 1. In such preferred compositions the carrier acts effectively to remove any toner particles which might tend to adhere to a non-image area and the toner itself forms a dense readily transferable and fusible image.

Developer compositions may therefore be prepared in accordance with this invention by combining a carrier and a toner within the specific particle size relationship and composition relationship enumerated above. The developers are prepared by simple mixing of the ingredients or by blending in a jar mill, rubber mill, ribbon blender or other mixing device used for solid materials.

Examples of the developers of this invention include the following:

TABLE II.—DEVELOPER COMPOSITIONS¹

Example	Toner composition of example—	Parts toner	Carrier	Parts carrier
15	9	1	Glass beads	100
16	10	2	NH_4Cl	250
17	11	1	Glass beads	150
18	12	1	NaCl	70

¹ Parts are by weight.

The toner particles in Examples 15 to 18 have an average size of 20 microns and the carrier particles are an average of 250 microns and all pass a 50 U.S. mesh screen.

Instead of the use of granular particles to provide the carrier surface, the bristles of a fur brush may be used. Here also, the toner particles acquire an electrostatic charge of polarity determined by the relative position of the toner particles and the fur fibers in the triboelectric series. The toner particles form a coating on the bristles of the fur clinging thereto by reasons of the electrostatic attraction between the toner and the fur just as the toner clings to the surface of the granular carrier particles.

Even more closely related to the cascade carrier development is magnetic brush development. In this process a granular carrier is selected having ferromagnetic properties and selected relative to the toner in a triboelectric series so as to impart the desired electrostatic polarity to the toner and carrier as in cascade carrier development. On inserting a magnet into such a mixture of toner and magnetic granular material the carrier particles align themselves along the lines of force of the magnet to assume a brush-like array. The toner particles are electrostatically coated on the surface of the granular powder carrier particles. Development proceeds as in regular cascade carrier development on moving the magnet over the surface bearing the electrostatic image so that the "bristle" of the magnet brush contact the electrostatic image-bearing surface.

Still another method of carrier development is known as sheet carrier development in which the toner particles are placed on a sheet of paper, plastic, or metal. This process is described in U.S. Pat. No. 2,895,847 to C. R. Mayo. As described therein the electrostatic attraction between the sheet surface and toner particles may be obtained by leading the sheet through a mass of electroscopic toner particles whereby there is obtained a rubbing or sliding contact between the sheet and the toner. Usually it is desirable to spray the surface of the sheet bearing the electroscopic toner particles with ions of the desired polarity as by the use of a corona charging device as described in the patent of Mayo.

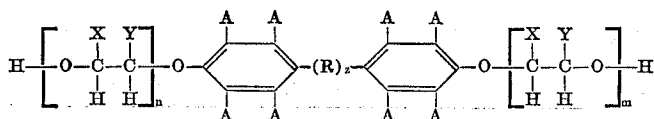
The novel toners of the instant invention may also be formulated to possess both electrostatic and magnetic properties by utilizing a magnetic powdered pigment as the pigment therein. Thus, magnetic iron oxide or similar materials may be used as the pigment in such toners. In this instance substantially larger amounts are used in formulating the toner than when conventional coloring pigments or dyes are used. Thus, a toner having both electroscopic and magnetic properties desirably contains a higher proportion of pigment (note Example 20 above). In such cases up to 50%, by weight of pigment.

Having thus described the invention, the following is claimed:

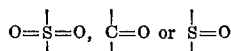
1. An electrostatic composition comprising a toner containing a coloring agent and a polyester resin of a di-

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carboxylic acid and a polyhydroxy composition containing an etherified diphenol represented by the formula:



wherein z is either 0 or 1, R is an alkylene radical containing from 1 to 5 carbon atoms, a sulfur atom, an oxygen atom,



X and Y are alkyl radicals containing from 1 to 3 carbon atoms, hydrogen, or a phenyl radical with the limitation that in any X and Y pair on adjacent carbon atoms at least X or Y is hydrogen; each A is individually selected from halogen atoms and hydrogen; and n and m are integers with the proviso that the average sum of m and n is from about 2 to about 7;

and up to about 2 mol percent of an etherified polyhydroxy compound which polyhydroxy compound contains from 3 to 12 carbon atoms, from 3 to 8 hydroxyl groups, and up to about 10 mols of oxyethylene or oxypropylene per mol of etherified polyhydroxy compound;

wherein said polyester resin has a liquid point of less than 110° C. and a tack point of more than about 60° C.

2. An electrostatic composition according to claim 1 wherein said toner consists of particles having an average size of less than about 40 microns.

3. An electrostatic composition according to claim 1 wherein said etherified diphenol is selected from the group consisting of ethoxylated or propoxylated dihydric bisphenols wherein R is propylene or sulfone.

4. An electrostatic composition according to claim 1 wherein said pigment is carbon black and said polyester resin is the reaction product of fumaric or maleic acid with an etherified diphenol selected from the group consisting of polyoxyethylene and polyoxypropylene derivatives of bis(2,6-dibromo-4-hydroxyphenyl) sulfone; 2,2-bis(2,6-dichloro-4-hydroxyphenyl) propane; and 2,2-bis(4-hydroxyphenyl) propane; wherein the mol ratio of oxyethylene and/or oxypropylene per mol of bisphenol is between from about 2 to about 3.

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10. A process of xerography wherein an electrostatic image is made visible which comprises contacting a photo-

conductive surface bearing an electrostatic image thereon with an electrostatic composition of claim 3.

11. An electrostatic composition according to claim 2 which contains from 70 to 150 parts of a carrier particle to one part of toner particle and said carrier particles are at least 10 times as large as said toner particles.

12. An electrostatic composition according to claim 11 wherein said carrier particles are selected from the group consisting of glass, iron, steel, NH₄Cl, NaCl, and phenol-formaldehyde resins.

13. An electrostatic composition of claim 1 wherein the average sum of m and n is from about 2 to about 3.

14. An electrostatic composition of claim 3 wherein the ethoxylated or propoxylated bisphenols contain from about 2 to about 3 mols of oxyethylene or oxypropylene per mol of bisphenol.

15. An electrostatic composition of claim 14 wherein

15. An electrostatic composition of claim 14 wherein the polyester resin has a liquid point between 85° C. to liquid point.

16. An electrostatic composition of claim 13 wherein the polyester resin has a liquid point between 85° C. to 100° C. and a tack point of at most 20° C. less than said liquid point.

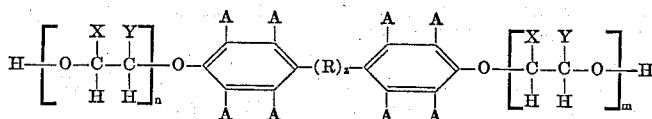
17. An electrostatic composition of claim 1 wherein the ratio of the number of hydroxyl groups of said polyhydroxy composition to the number of carboxyl groups of said dicarboxylic acid is from 1.2 to 0.8.

18. A process of xerography wherein an electrostatic image is made visible which comprises contacting a photoconductive surface bearing an electrostatic image thereon with an electrostatic composition of claim 13.

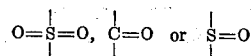
19. A process of xerography wherein an electrostatic image is made visible which comprises contacting a photoconductive surface bearing an electrostatic image thereon with an electrostatic composition of claim 14.

20. An electrostatic composition comprising a toner containing a coloring agent and a polyester resin of a dicarboxylic acid and a polyhydroxy composition containing

an etherified diphenol represented by the formula:



wherein z is either 0 or 1, R is an alkylene radical containing from 1 to 5 carbon atoms, a sulfur atom, an oxygen atom,



X and Y are alkyl radicals containing from 1 to 3 carbon atoms, hydrogen, or a phenyl radical with the limitation that in any X and Y pair on adjacent carbon atoms at least X or Y is hydrogen; each A is individually selected from halogen atoms and hydrogen; and n and m are integers with the proviso that the average sum of m and n is from about 2 to about 7;

5. An electrostatic composition according to claim 2 wherein said pigment is present in a proportion of from 1 to 20 weight percent of the toner composition.

6. An electrostatic composition according to claim 1 wherein said coloring agent is a pigment and is present in a weight percent of from 5 to 10.

7. An electrostatic composition according to claim 2 wherein the particle size of said toner particles is from 1 to 30 microns.

8. A process of xerography wherein an electrostatic image is made visible comprising contacting a photoconductive surface bearing an electrostatic image thereon with an electrostatic composition of claim 2.

9. A process of xerography wherein an electrostatic image is made visible comprising contacting a photoconductive surface bearing an electrostatic image thereon with an electrostatic composition of claim 3.

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and up to about 2 mol percent of an etherified polyhydroxy compound which polyhydroxy compound contains from 3 to 12 carbon atoms, from 3 to 8 hydroxyl groups, and up to about 10 mols of oxyethylene or oxypropylene per mol of etherified polyhydroxy compound.

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J. P. BRAMMER, Assistant Examiner

U.S. Cl. X.R.

96—1R, 1.4; 252—62.1; 260—40 R, 47 R

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,681,106 Dated August 1, 1972

Inventor(s) Joseph P. Burns and Joseph Feltzin

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

Column 3, line 6, "alternative" should read -- alternate --.

Column 3, line 69, "polyoxypentylene(3)-bis(2,6-diiodo-4-hydroxyphenyl)" should read -- polyoxypentylene(3)-2,2-bis(2,6-diiodo-4-hydroxyphenyl) --.

Column 4, line 22, "soribitol" should read -- sorbitol --.

Column 5, line 72, delete the line "meter, a stainless steel stirrer, a glass inlet tube, and a".

Column 6, Example 2, line 27, "hydroxy" should read -- hydroxyl --.

Column 7, line 57, "condensed" should read -- condenser --.

Column 9, line 32, "time" should read -- times --.

Column 9, line 38, "charge" should read -- charged --.

Column 12, Claim 15, line 26, delete the line "15. An electrostatic composition of claim 14 wherein".

Column 12, Claim 15, line 28, after the words "85°C. to" and before "liquid", insert the line -- 100°C. and a tack point of at most 20°C. less than said --.

Signed and sealed this 26th day of December 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents