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2,891,011

DEVELOPER FOR ELECTROSTATIC IMAGES

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No Drawing. Application December 26, 1956
Serial No. 630,445

11 Claims. (Cl. 252—62.1)

This invention relates to xerography and more particularly to a composition for developing electrostatic images on xeroradiographic plates.

In the process of xeroradiography, an electrostatic latent image is obtained upon an insulating layer, such as a layer of photoconductive insulating material supported on a conductive backing. For example, a photoconductive insulating layer may be given a uniform electrostatic charge of determined polarity over its surface and then be exposed to X-ray or gamma ray radiation directed through an interposed object so that the rays penetrating to the layer discharge those portions penetrated while leaving electrostatic charges remaining in the object-shaded areas of the layer. In other words, such exposure leaves a latent electrostatic image in the insulating layer. This latent image may then be developed by depositing a finely-divided material on the charged areas of the insulating layer to produce a visible image. Thus, a fine powder may be sprinkled, blown or cascaded across the insulating layer surface after exposure, the powder being preferably charged to a polarity opposite to that to which the insulating layer was initially charged so that electrostatic attraction between the residual image charges in the layer and the powder particles will cause deposition and adherence of the latter on the surface of the layer to produce a visible image of the radiographed object.

The xerographic plate or element commonly used in xeroradiography has a photoconductive layer of insulating material such as amorphous selenium applied to a conductive backing. The photoconductive layer is nearly black in color.

Very often in xeroradiography it is necessary only to inspect the powder image on the plate without making a permanent record thereof. On the other hand, it is often desired to preserve a permanent record of a particular image and whether the record is to be preserved or not is often not known until after a preliminary viewing of the image. Accordingly, it is desirable that the image be visible both against the relatively black background of the xerographic plate and against the white background of paper, the most commonly used material for keeping permanent records. In addition, a powder, to be useful in developing xeroradiographic images, must have good storage life even under highly adverse conditions and must not film on the xeroradiographic plate so that the plates may be cleansed thoroughly and quickly from all powder for each new use.

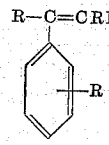
Finally, the general process of developing, that is, making visible electrostatic latent images in xeroradiography, is described in U.S. 2,759,450 to R. G. Vyverberg. The process involves the formation of a powder cloud of discrete powder particles without opportunity for the use of separate charging means as an induction ring, corona charging or capillary charging. Accordingly, the sole method of charging the powder particles in this process is through triboelectric contact with each other in the process of forming the powder cloud. This

process places a severe restriction on the triboelectric properties of the powder particles so that it is extremely difficult to obtain materials having the desired charging characteristics.

Recently there have been described in U.S. 2,753,308 to Richard B. Landrigan and in U.S. patent application Serial Number 373,431, filed on July 29, 1953, by Rheinfrank and Jones, now U.S. 2,788,288, developer compositions combining to an exceptional degree the properties of desirable melting point, toughness and resistance to filming.

The developer composition of Landrigan, as described, comprises a rosin-modified phenol-formaldehyde resin containing about 5% to about 10% pigment and about 5% to 45% polyvinyl butyral, the rosin-modified phenol-formaldehyde being prepared using from about 1 to 8 parts rosin for each part of phenol-formaldehyde base and having a ring and ball melting point of about 142° to 149° C.

The developer composition of Rheinfrank and Jones, as described, comprises a resin blend of about 5 to 25% polymerized butyl methacrylate blended with a polymerized blend of monomers of styrene and styrene homologs of the formula:



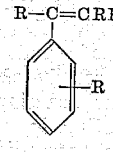
where R is selected from the group consisting of hydrogen and lower alkyl, the polymerized blend of styrene homologs having a ring and ball melting point of about 125° C.

To date, however, it has not been possible to use these superior developer compositions in developing xeroradiographic images because of the difficulty of imparting the correct triboelectric relationship to the resin particles without adversely affecting the other desirable properties of the resin combination and in addition preventing solarization and other difficulties resulting from improper developer properties.

Now, in accordance with the instant invention, there is provided a composition and a method of manufacture thereof which completely satisfies these diverse and difficult specifications. In general, the invention comprises a developer composition formed by mixing either:

(1) A rosin-modified phenol-formaldehyde resin containing about 5% to 45% polyvinyl butyral, the rosin-modified phenol-formaldehyde being prepared using from about 1 to 8 parts rosin for each part of phenol-formaldehyde base and having a ring and ball melting point of about 140 to 180° C.; or

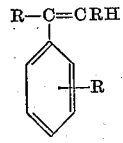
(2) A resin blend of up to 25% polymerized butyl methacrylate blended with a polymerized blend of monomers of styrene and styrene homologs of the formula:



where R is selected from the group consisting of hydrogen and lower alkyl, the polymerized blend of styrene monomers having a ring and ball melting point of about 125° C.; or

(3) A copolymer resin prepared from a monomer blend of about 5 to about 50% of at least one methacrylate ester selected from the group consisting of ethyl,

propyl and butyl methacrylate and with the balance at least one styrene of the formula:



where R is selected from the group consisting of hydrogen, methyl, ethyl and propyl.

In each case the resin or resin mixture is blended with a zinc salt of 8-hydroxyquinoline and with either Prussian Blue or Malachite Green dye. The combination gives a toner of excellent triboelectric properties, great toughness, desirable melting point, no filming characteristics ideally adapted for use under the most adverse conditions in the xerographic process and readily visible against either a black background or a white background. It is believed that the zinc salt of 8-hydroxyquinoline imparts the necessary triboelectric properties to the individual particles.

The following examples are presented in illustration but not in limitation of the invention and it is to be understood that the invention is to be limited only by the appended claims:

Example I

The invention is carried out in a preferred embodiment by employing as the electroscopic developing powder an electroscopic powder having a fine particle size, for example of approximately 3 to 7 microns, and being a mixture approximately in parts by weight of:

Amberol M–93 (a trade name of Rohm & Haas Company for a rosin-modified phenol-formaldehyde having a ball and ring melting point of 172°–180° C.)	70
Vinylite XYHL (a trade name of Union Carbide & Carbon Corp. for a polyvinyl butyral resin)	25
Prussian Blue	10
Fluorescent 2500 (a trade name of the New Jersey Zinc Company for a zinc salt of 8-hydroxyquinolone)	14⅓

The Amberol M–93 is added to a batch mixer and heated to the point of plasticization; then the Vinylite XYHL is added and the mixing continued for about two minutes. Finally, the Prussian Blue is added and the mixing continued until thorough dispersion of the components is obtained—generally in about 5 minutes. Overheating must be avoided, particularly after the Prussian Blue is added. The material is then removed from the mixer and further blended on a two roll mill. The Fluorescent 2500 is added on the mill where the material is blended for about one-half hour. The mixture is then removed from the mill, cooled, crushed and pulverized to obtain the desired particle size.

The material so obtained has excellent triboelectric properties for use even under the difficult conditions of xeroradiography as described in the aforesaid Vyverberg patent. A quantity of the resin was stored for two weeks in an oven at 140° F. without deterioration or fusing. Plates developed with this developer composition were easily and readily cleaned without building up annoying and trouble-causing films. The composition was also outstanding in uniformity and ease of usability both on the xeroradiographic plate and on paper.

Example II

A mixture was prepared comprising 10 parts of Malachite Green Oxalate, 12 parts of Fluorescent 2500 (a trade name of the New Jersey Zinc Company, for a zinc salt of 8-hydroxyquinoline) and 400 parts of a pulverized blend of polymerized styrenes. The blend of polymerized styrenes is available under the trade name Piccolastic Resin D125 and is believed to be a mixture of medium high molecular weight styrenes having a ring and ball melting point of 257° F.

The mixture was ball milled and 78.5 parts of isopropyl alcohol added and ball milling continued for four hours. The material was dried and screened to yield a powder composition having an average particle size of about 5 microns.

The material so obtained has excellent triboelectric properties for use even under the difficult conditions of xerography as described in the aforesaid Vyverberg patent. Plates developed with this composition were easily and readily cleaned without building up annoying and trouble-causing films. Images developed with the composition were characterized by excellent physical properties including absence of solarization and other image difficulties.

Example III

A developer composition was prepared as in Example II except that the amount of Fluorescent 2500 was increased from 12 parts to 25 parts. The developer composition so prepared was also characterized by excellent triboelectric properties in the xeroradiographic process, high image quality, absence of solarization, no filming and excellent cleanability from the xerographic plate.

Example IV

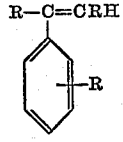
A developer composition was prepared as in Example II except that the amount of Malachite Green Oxalate was increased to 25 parts. The developer composition so prepared was characterized by excellent triboelectric properties in the xeroradiographic process, high quality of the developed image, absence of solarization and exceptional ease of cleanability and absence of annoying filming properties.

The developer composition may be used to prepare either positive prints or reversal prints as described in the aforesaid Vyverberg patent. In addition, images developed with the composition of the instant invention are singularly free from solarization, agglomeration, graininess and similar defects.

While specific examples may be described, variations within the scope of the claims are possible and are contemplated. There is no intention, therefore, to limit the invention to the exact details shown and described.

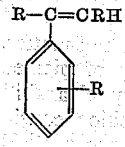
I claim:

1. As a composition of matter, a xerographic developing powder consisting essentially of between about 2% to about 20% of a zinc salt of 8-hydroxyquinoline, between about 2% to about 10% of a dye selected from the group consisting of Prussian Blue and Malachite Green and the balance of said composition being a resin selected from the group consisting of (*a*) a rosin-modified phenol-formaldehyde resin containing about 5% to 45% polyvinyl butyral, the rosin- modified phenol-formaldehyde being prepared using from about 1 to 8 parts rosin for each part of phenol-formaldehyde base and having a ring and ball melting point of about 140 to 180° C.; (*b*) a resin blend of up to 25% polymerized butyl methacrylate blended with a polymerized blend of monomers of styrene and styrene homologs of the formula:



where R is selected from the group consisting of hydrogen and lower alkyl, the polymerized blend of styrene monomers having a ring and ball melting point of about 125° C.; and (*c*) a copolymer resin prepared from a monomer blend of about 5 to about 50% of at least

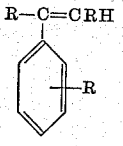
one methacrylate ester selected from the group consisting of ethyl, propyl and butyl methacrylate and with the balance at least one styrene of the formula:



where R is selected from the group consisting of hydrogen, methyl, ethyl and propyl.

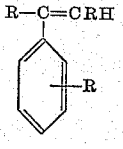
2. As a composition of matter, a xerographic developing powder consisting essentially of between about 2% to about 20% of a zinc salt of 8-hydroxyquinoline, between about 2% to about 10% of a dye selected from the group consisting of Prussian Blue and Malachite Green and the balance of said composition being a rosin-modified phenol-formaldehyde resin containing about 5% to 45% polyvinyl butyral, the rosin-modified phenol-formaldehyde being prepared using from about 1 to 8 parts rosin for each part of phenol-formaldehyde base and having a ring and ball melting point of about 140 to 180° C.

3. As a composition of matter, a xerographic developing powder consisting essentially of between about 2% to about 20% of a zinc salt of 8-hydroxyquinoline, between about 2% to about 10% of a dye selected from the group consisting of Prussian Blue and Malachite Green and the balance of said composition being a resin blend of up to 25% polymerized butyl methacrylate blended with a polymerized blend of monomers of styrene and styrene homologs of the formula:



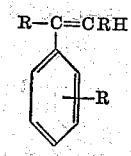
where R is selected from the group consisting of hydrogen and lower alkyl, the polymerized blend of styrene monomers having a ring and ball melting point of about 125° C.

4. As a composition of matter, a xerographic developing powder consisting essentially of between about 2% to about 20% of a zinc salt of 8-hydroxyquinoline, between about 2% to about 10% of a dye selected from the group consisting of Prussian Blue and Malachite Green and the balance of said composition being a copolymer resin prepared from a monomer blend of about 5 to about 50% of at least one methacrylate ester selected from the group consisting of ethyl, propyl and butyl methacrylate and with the balance at least one styrene of the formula:

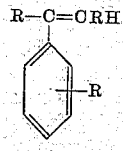


where R is selected from the group consisting of hydrogen, methyl, ethyl and propyl.

5. As a composition of matter, a xerographic developing powder consisting of pigment powder compositions characterized by easy cleanability and melting below 350° F., the composition consisting essentially of particles having an average size between 0.5 and 10 microns and consisting essentially of between about 2% to about 20% of a zinc salt of 8-hydroxyquinoline, between about 2% to about 10% of a dye selected from the group consisting of Prussian Blue and Malachite Green and the balance of said composition being a resin selected from the group consisting of (*a*) a rosin-modified phenol-formaldehyde resin containing about 5% to 45% polyvinyl butyral, the rosin-modified phenol-formaldehyde being prepared using from about 1 to 8 parts rosin for each part of phenol-formaldehyde base and having a ring and ball melting point of about 140 to 180° C.; (*b*) a resin blend of up to 25% polymerized butyl methacrylate blended with a polymerized blend of monomers of styrene and styrene homologs of the formula:



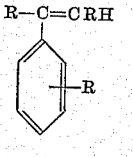
where R is selected from the group consisting of hydrogen and lower alkyl, the polymerized blend of styrene monomers having a ring and ball melting point of about 125° C.; and (*c*) a copolymer resin prepared from a monomer blend of about 5 to about 50% of at least one methacrylate ester selected from the group consisting of ethyl, propyl and butyl methacrylate and with the balance at least one styrene of the formula:



where R is selected from the group consisting of hydrogen, methyl, ethyl and propyl.

6. As a composition of matter, a xerographic developing powder consisting of pigment powder compositions characterized by easy cleanability and melting below 350° F., the composition consisting essentially of particles having an average size between 0.5 and 10 microns and consisting essentially of between about 2% to about 20% of a zinc salt of 8-hydroxyquinoline, between about 2% to about 10% of a dye selected from the group consisting of Prussian Blue and Malachite Green and the balance of said composition being a rosin-modified phenol-formaldehyde resin containing about 5% to 45% polyvinyl butyral, the rosin-modified phenol-formaldehyde being prepared using from about 1 to 8 parts rosin for each part of phenol-formaldehyde base and having a ring and ball melting point of about 140 to 180° C.

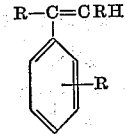
7. As a composition of matter, a xerographic developing powder consisting of pigment powder compositions characterized by easy cleanability and melting below 350° F., the composition consisting essentially of particles having an average size between 0.5 and 10 microns and consisting essentially of between about 2% to about 20% of a zinc salt of 8-hydroxyquinoline, between about 2% to about 10% of a dye selected from the group consisting of Prussian Blue and Malachite Green and the balance of said composition being a resin blend of up to 25% polymerized butyl methacrylate blended with a polymerized blend of monomers of styrene and styrene homologs of the formula:



where R is selected from the group consisting of hydrogen and lower alkyl, the polymerized blend of styrene monomers having a ring and ball melting point of about 125° C.

8. As a composition of matter, a xerographic developing powder consisting of pigment powder compositions characterized by easy cleanability and melting below 350° F., the composition consisting essentially of particles having an average size between 0.5 and 10 microns and consisting essentially of between about 2% to about 20% of a xinc salt of 8-hydroxyquinoline, between about 2% to about 10% of a dye selected from the group consisting of Prussian Blue and Malachite Green and the balance of said composition being a copolymer resin prepared from a monomer blend of about 5 to about 50% of at

least one methacrylate ester selected from the group consisting of ethyl, propyl and butyl methacrylate and with the balance at least one styrene of the formula:

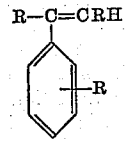


where R is selected from the group consisting of hydrogen, methyl, ethyl and propyl.

9. As a composition of matter, a xerographic developing powder consisting of a pigment powder composition characterized by easy cleanability and melting below 350° F., the composition consisting essentially of particles having an average size between 0.5 and 10 microns and consisting essentially of a rosin-modified phenol-formaldehyde resin, between about 5% and about 10% of a dye selected from the group consisting of Prussian Blue and Malchite Green, about 20 to 35% polyvinyl butyral and between about 10% and 20% of a zinc salt of 8-hydroxyquinoline, said rosin-modified phenol-formaldehyde resin prepared using from about 1 to 8 parts rosin to each part of phenol-formaldehyde base and having a ring and ball melting point of about 140 to 180° C.

10. As a composition of matter, a xerographic developing powder consisting of pigment powder compositions characterized by easy cleanability and melting below 350° F., the composition consisting essentially of particles having an average size between 0.5 and 10 microns and consisting essentially of a resin body prepared by copolymerizing a mixture of about 10 to 35% butyl methacrylate and the remainder styrene, between about 5% and about 10% of a dye selected from the group consisting of Prussian Blue and Malachite Green and between about 10% and 20% of a zinc salt of 8-hydroxyquinoline.

11. As a composition of matter, a xerographic developing powder consisting of pigment powder compositions characterized by easy cleanability and melting below 350° F., the composition consisting essentially of particles having an average particle size between 0.5 and 10 microns and consisting essentially of a polymerized blend of monomers of styrene and styrene homologs of the formula:



where R is selected from the group consisting of hydrogen and lower alkyl, the polymerized blend of styrene monomers having a ring and ball melting point of about 125° C., between about 5% and about 10% of a dye selected from the group consisting of Prussian Blue and Malachite Green and between about 10% and about 20% of a zinc salt of 8-hydroxyquinoline.

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