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XEROGRAPHY DEVELOPER COMPOSITION

Richard B. Landrigan, Columbus, Ohio, assignor, by mesne assignments, to The Haloid Company, Rochester, N. Y., a corporation of New York

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This invention relates in general to xerography and, in particular, to a developer composition of improved performance in the art of xerography.

In xerography it is usual to reproduce a master by electrical photography methods such as, most typically, placing an electrostatic charge on a photoconductive surface, selectively dissipating such charge by exposure to an optical image corresponding to the master to be reproduced and developing the resulting electrostatic latent image by exposure to an electroscopic material. According to one practice in xerography as disclosed in copending application, Serial No. 762,005, now U. S. Patent 2,618,552, the development of the electrostatic latent image is accomplished by rolling or cascading across the image bearing surface a developer composition of relatively large carrier particles having on their surfaces and electrostatically coated thereon fine powder particles known as toner particles. As the composition cascades or rolls across the image bearing surface, these toner particles are electrostatically deposited on and secured to the charged portions of the image and are not deposited on the uncharged or background portions of the image. More than that, toner particles accidentally deposited on these background portions are physically removed therefrom by electrostatic action of the carrier particles passing thereacross, whereby these toner particles are electrostatically secured to the rolling carrier particles and are picked up from the surface in this manner. The result is an excellent copy of the electrostatic latent image in the form of an image of the toner particles electrostatically clinging to the image surface and removable therefrom by any of various means such as adhesive transfer, electrostatic transfer, or the like. Thus the image body may be transferred to a sheet or web such as, generally, a sheet of paper by placing the surface of such sheet in contact with the image body and applying an electrostatic charge to the paper while in such contact. When the paper is subsequently stripped from the image bearing surface it carries with it a substantial proportion of the image body 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 surface to the transfer member, or paper, the image surface may be cleaned and then is ready for use in a subsequent xerographic cycle. The xerographic plate, after being properly cleaned following a previous xerographic cycle, is in its original condition and is substantially unimpaired for future use. However, a problem in prior experience has been caused by the fact that cleaning of the xerographic plate between the cycles is unexpectedly difficult, due apparently to the strong attraction of the residual toner particles to the plate. This is evidenced in two manners: first, by the stubborn adherence of toner particles as such to the plate with the result that after mechanical cleaning operations substantial amounts of such powder may still remain on the image surface, and, second, by the fact that a film or layer builds up on the plate surface during

repeated cycles and eventually requires additional cleaning operations, such as, for example, solvent cleaning or the like.

Either type of residual toner, that is, either toner in its powder form, or toner as a film on the image surface, impairs the subsequent operation of the xerographic plate. Thus, for example, if toner particles remain on the plate, they interfere with the subsequent steps of xerography causing either deletions or background deposition during subsequent steps. Perhaps the more serious trouble, however, since it is more difficult to overcome, is the building up of the film which appears to consist of a gradual accumulation of the toner material on the plate surface, apparently in the form of a smear as the toner particles are mechanically removed therefrom. The presence of this film interferes in many ways. In the first place, this film has different electrical properties from those of the photoconductive layer on the xerographic plate and thus it tends to interfere with the charging or sensitizing step. It also has mechanical or physical properties differing from those of the photoconductive layer, particularly in that it is substantially more sticky or tacky than the clean plate surface. Beyond this, the toner film appears to be somewhat hydroscopic to the extent that in humid weather it detrimentally affects conductivity under exposure to light and insulation properties in the absence of light, particularly where the relative humidity is greater than about 80%.

It is presently believed that a great deal of the difficulty caused by the building up of this film, and, in fact, by incomplete removal of toner particles from the residual image is a function of a physical or mechanical properties of the toner particle in that they tend to be somewhat soft or tacky and apparently adhere to the image surface by mechanical means as well as by electrostatic forces. The problem, moreover, is complicated by the fact that the usual and presently preferred method of transferring the image body from the image surface to the transfer member, such as the paper sheet, preferably is carried out by electrostatic forces, with the result that the mechanical adhesion between toner and image surface cannot be overcome simply by increasing the mechanical transfer force. Beyond this, the difficulties are compounded by the fact that the presently preferred fixing method for permanentizing the xerographic print employs heat fusion to melt the toner particles onto and into the surface of the transfer sheet. Thus, the toner particles must be capable of electrostatic transfer and subsequently must be usable within temperature limits readily tolerated by convenient and economical transfer members such as paper or the like, and the usual methods of lowering melting points generally tend to increase softness. A further and occasionally nagging difficulty is the fact that the toner particles must be charged to correct polarity upon mixing with and coating on the surface of the carrier particles so that the toner will be deposited on the image areas by electrostatic attraction and removed from the non-image areas also by electrostatic attraction. At the present time, xerographic photosensitive members are generally charged to positive polarity for sensitization and thus the toner particles must be such that they are charged to negative polarity by mixing with the carrier particles. These and other problems must be solved while achieving the necessary end results of suitability for xerography, including the ability to form an ink-receptive image useful in lithography.

Now in accordance with the present invention there is provided a new and improved xerographic toner composition comprising finely divided pigmented resin particles having a particle size less than about 20 microns and preferably between about two and ten microns in average particle size and consisting of a finely divided

uniform mixture of pigment in a tough low melting resin containing substantial proportions of polyvinyl-butyral in a mixture with or blended with a thermoplastic formaldehyde type resin such as, for example, a rosin-modified phenol-formaldehyde resin. The pigment is present in the toner in sufficient quantity to cause it to be highly colored, whereby it will form a clearly visible image on a transfer member. Thus, for example, in the usual case where a xerographic copy of a document or the like is desired, the pigment will be a black pigment such as carbon black or other minutely divided carbonaceous pigment. Desirably the pigment is employed in an amount of at least about 5% based on the total weight of the toner body and generally between about 5% and about 10%.

In the preparation of the toner composition according to the present invention, the ingredients are thoroughly mixed to form a uniform dispersion of the pigment in the resin body and thereafter the body is finely divided to form the desired toner or powder composition. The mixing may be done by various means, including combinations of the steps of blending, mixing, and milling and the presently preferred method includes a step or blending in a rubber mill to assure uniform and fine dispersion of the pigment in the resin.

The general nature and scope of the invention having been set forth, the following specific embodiments are presented in illustration but not in limitation thereof, and it is to be understood that the invention is to be limited only by the appended claims.

Example 1.—A mixture consisting of 25% polyvinyl butyral, 5% carbon black, and 70% of a rosin-modified phenolformaldehyde resin available under the name Amberol F–71 was heated and mixed together. This resin is one of a series of available rosin-modified phenol-formaldehyde resins prepared from between about 1 and 8 parts rosin to each part of phenol-formaldehyde base, and is characterized by softening at about 118 to 125° C., melting at about 142 to 149° C. (ring and ball method) and having an acid number between about 11 and 20. After preliminary mixing the composition was fed to a rubber mill and thoroughly milled to yield a uniformly dispersed composition of carbon black in the resin body. The resulting mixed composition was thoroughly cooled and then finely subdivided in a ball mill to yield a powder composition having an average particle size of about 2 to 5 microns. The resulting powder or toner composition was particularly adapted for use in xerography in combination with vitreous selenium xerographic plates charged to positive polarity for sensitization and exposed to an optical image to yield a positive polarity electrostatic latent image on the selenium surfaced xerographic plate. When deposited on such electrostatic latent image, the powder is susceptible of substantial transfer by electrostatic means to a transfer web such as paper whereon it can be fused by placing in a heated oven at a temperature of 250° C. for a period of 5 seconds. Under these same heating conditions the paper web is not visibly affected by heat. The residual toner image remaining on the xerographic plate after electrostatic transfer is readily removed by desired methods such as cascading thereacross a cleaning composition as disclosed in Copley Patent 2,484,782, or by brushing the surface with a rapidly rotating fur brush. When employed in the xerographic cycle with either of these cleaning operations, the plate was readily cleaned free from detectible residual toner particles and could be recycled for at least 1,000 xerographic cycles without building up significant quantities of film on the surface of the xerographic plate.

When mixed with a carrier composition surfaced with a methacrylic ester base polymer, of a nature as disclosed in application Serial No. 55,645 now United States Patent 2,618,551, the toner prepared according to this example gave clear, sharp and extremely black images of satisfactory contrast, resolution and appearance. The toner particles when mixed with this carrier composition

acquired a negative polarity electrostatic charge whereby they were deposited on a positive polarity electrostatic latent image and removed by the carrier from uncharged surface areas.

Example 2.—The procedure of Example 1 was repeated employing 10% carbon black, 25% polyvinylbutyral and 65% rosin-modified phenol-formaldehyde resin. The mixture was heated until molten and was thoroughly mixed by stirring, after which it was cooled until solidified and ball milled to yield a fine powder. The powder was again heated until molten, thoroughly mixed, cooled and again ball milled to yield a toner composition consisting of pigmented resin particles having an average particle size of about 5 microns. The resulting composition was comparable with that prepared according to Example 1, except that it produced a somewhat denser or blacker xerographic image. This composition also can be used through at least one thousand xerographic cycles without building up a significant coating of film on the xerographic plate.

Example 3.—The procedure of Example 1 was repeated, employing the following mixture compositions: (*a*) 65% rosin-modified phenol-formaldehyde resin, 30% polyvinyl-butyral, 5% carbon black; (*b*) 85% rosin-modified phenol-formaldehyde resin, 5% polyvinyl-butyral, 10% carbon black; (*c*) 45% rosin-modified phenol-formaldehyde resin, 45% polyvinyl-butyral, 10% carbon black. The compositions as thus prepared were generally satisfactory as xerographic toners. The general trends in composition properties were noted as follows: Where 5% polyvinyl-butyral was employed the fusing temperature of the composition was about 310° F. increasing to 325° for the composition according to Example 1 and being somewhat higher for the composition containing 45% polyvinyl-butyral. Correlating to the difference in fusion temperature, the compositions containing the largest proportion of polyvinyl-butyral were more readily cleaned from xerographic plates and permitted the use of the toner composition through a greater number of xerographic cycles.

In the various specific examples described herein numerous types of carbon black pigments have been employed. These include lamp blacks, channel blacks, furnace blacks and the like with the general result that carbon blacks of the various types have been found satisfactory. Variations to be expected with different types of pigment compositions in this order are greater or lesser ease of blending with the resin composition and greater or lesser density of the resulting image. In the same manner varying percentage compositions of pigment in the toner material likewise produce variations in the density of the xerographic print formed by the toner, these variations being capable of partial compensation or offset by selection of darker or less dark carbon black materials. Furthermore, it will be understood that instead of carbon black as the pigment, other black or colored pigments may be employed, and, if desired, red, green, blue or like colored xerographic toners may be prepared by appropriate choice of pigments or pigment mixtures.

By utilization in xerography the composition described in the examples is particularly adapted to be mixed with a carrier composition such as is disclosed in co-pending applications Serial No. 762,005 and 55,645. The carrier compositions generally should be made up of individual relatively large particles, usually spherical or approximately spherical in shape, whereby they are adapted to roll easily across the surface. These large or carrier particles have at least their surfaces coordinated with the composition of the toner particles so that by surface action between the carrier and toner the toner particles are coated on the surface of the carrier particles and generally receive a negative electrostatic charge. The proportion of toner in the mixed developer composition can be changed over a relatively wide range and the optimum ratio, varying with the particle compositions employed, can best be determined experimentally. In general, how-

ever, it will be found that a carrier to toner ratio in the order of about 100 to 1 will be satisfactory although this ratio may vary at least as widely as between 250 to 1 and 25 to 1 depending on the particular components selected. When the toner is combined with a carrier component consisting of spherical particles in the order of 20 to 30 mesh having a surface coating thereon of a polymerized acrylic or methacrylic ester, a desirable operating range will be between about 80 to 1 for a fresh developer mixture to about 150 to 1 for a developer mixture which has been repeatedly used and which is therefore largely depleted in toner component.

It will be recognized that numerous variations may be made in the carrier component or in the surface material of the carrier component. Thus, the carrier component may desirably be prepared from acrylic or methacrylic esters, amides, esters, or the like, vinyl resins, such as vinyl chloride, vinyl acetate, and mixtures, and copolymers thereof, melamine-formaldehyde resins, butadiene polymers and copolymers prepared with butadiene and including chlorinated and other substituted derivatives thereof. It will be understood that wide variations in the electrical and mechanical properties can be achieved through the use of selected carrier components and through similar variations.

The new toner compositions prepared according to this invention have significant advantages as compared with toner compositions of the prior art. These compositions generally are fusible at temperatures sufficiently below the char point of paper, namely temperatures below about 350° F. and preferably not higher than about 325° F., to be adapted to use in combination with paper members for the formation of xerographic prints. Because of their ability to be cleaned readily from xerographic image surfaces, these compositions are particularly suited to use in continuous or automatic xerographic machines, devices, and processes by virtue of the fact that they are fully compatible with rapid and lengthy re-cycling of the xerographic process. The compositions are highly compatible with selenium in its vitreous form and thereby are non-deleterious to the selenium photoconductive surface generally employed in xerography. The compositions form clear, sharp images which retain their sharpness

during electrostatic transfer and which yield xerographic prints of fine quality and prints which are pleasing to the eye. The toner compositions, furthermore, achieve the combination of toughness, whereby they can be cleaned from a surface without smearing, while remaining of sufficiently low fusion temperature as to be compatible with the use of paper transfer members for xerographic print formations.

What is claimed is:

1. As a composition of matter, a xerographic developing powder consisting of a pigmented resin powder composition characterized by easy cleanability and melting below about 350° F., the composition consisting of particles less than 20 microns in size and consisting of a rosin modified phenol-formaldehyde resin, between about 5% and about 10% pigments and between about 5% and about 45% polyvinylbutyral, said rosin-modified phenol-formaldehyde resin prepared from between 1 and 8 parts rosin to each part of phenol-formaldehyde base and having a ring and ball melting point of about 142° to 149° C.

2. As a composition of matter, a xerographic developing powder consisting of a pigmented resin powder composition characterized by easy cleanability and melting below about 350° F., the composition consisting of particles having an average size between two and ten microns and consisting of a rosin-modified phenol-formaldehyde resin, between about 5% and about 10% carbon black pigment and about 25% polyvinyl-butryral, said rosin-modified phenol-formaldehyde resin prepared from between 1 and 8 parts rosin to each part of phenol-formaldehyde base and having a ring and ball melting point of about 142° to 149° C.

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