

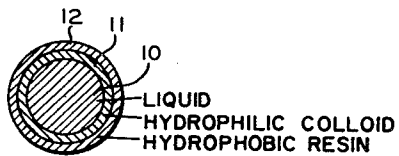
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METHOD OF XEROGRAPHIC DEVELOPMENT

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METHOD OF XEROGRAPHIC DEVELOPMENT
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This invention relates in general to electrostatic recording and in particular to materials and methods for xerography.

In the art of xerography, it is usual to form an electrostatic image on a suitable insulating or photoconductive insulating surface and to develop this image, or in other words make it visible, by presenting to the surface an electroscopic marking material. In the usual embodiments of xerography the electrostatic image is formed on a photoconductive insulating surface by charging the surface and exposing it to an image of light and shadow to be recorded whereupon the electric charge is dissipated in the light areas. Conventionally the image is then developed by dusting the image bearing surface with highly colored pigment materials such as, for example, pigmented thermoplastic resins. Because of requirements of transfer of the powder and re-use of the photoconducting surface and for other reasons, xerographic development has been usually limited to dry materials. In these prior procedures, therefore, it has generally been necessary to employ subsequent fixing steps or operations in order to cause the image material to adhere permanently either to the original image bearing surface or to such other surface as shall be desired for a final image support member. Existing fixing operations have generally been limited to fusing the image material by means of heat or solvent vapor, although other methods such as lacquer spraying, overlaying and the like have occasionally been employed.

An object of the present invention is to provide new image materials and methods for electrostatic recording wherein an electrostatic image may be developed and fixed.

Another object of the invention is to provide a new electroscopic image developing material for xerographic recording which image material is capable of being deposited in response to an electrostatic charge pattern and subsequently made visible on the image support surface by means of pressure.

An additional object of the invention is to provide a new xerographic developing material comprising an encapsulated marking material including a liquid droplet of a color forming composition within a shell having surface triboelectric properties suitable for electrostatic deposition.

A further object is to provide new materials and methods for xerography wherein an encapsulated developing material is combined with an active photoconductor to produce a permanent, visible image.

Additional objects of the invention will in part be obvious and will in part become apparent from the following specification and drawing in which:

The FIGURE is a diagrammatic view of a developer powder particle according to one form of the invention.

It has recently been found that suitable liquid materials can be formed into an extremely finely divided dry composition by separate encapsulation of appropriate

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liquid droplets within a hydrophilic shell. For example, in U.S. Patent 2,800,458, there is disclosed a manufactured preparation of oil-containing capsules of hardened gelatin. Such compositions have numerous uses in pressure recording arts. Unfortunately, it has been found that these compositions are essentially unsatisfactory for electrostatic recording because of their extreme variability in triboelectric properties depending on humidity in the atmosphere. It has now been found that image forming powders of proper triboelectric properties can be produced by encapsulating a liquid droplet of a suitable color forming material within a hydrophilic coating such as gelatin or the like, and in turn encapsulating the hydrophilic material within a tough hydrophobic resin coating. In particular, outer coatings of the polystyrene family including polymerized styrene, polystyrene homologues and mixtures and copolymers thereof, and resins of the acrylic esters acrylic amide and methacrylic esters and amides and mixtures of copolymers thereof, as well as mixtures of styrene and acrylic resins may be produced on hydrophilic capsules by immersion in polymer solutions followed by drying or evaporation of the solvent to produce developer materials for xerography.

The new developer powder composition includes essentially three separate phases or components, such as, for example a liquid droplet 10 encased in a hydrophilic coating 11, in turn within a hydrophobic resin coating 12. The liquid composition comprises essentially an oil base dye intermediate capable of forming, by chemical or physical reactions, a highly colored material, or other composition in liquid form capable of reacting to produce a permanent color visible on a support sheet such as, for example, a sheet of paper or the like having a photoconductive coating thereon. Suitable oil bases include oils and other non-polar fluids generally not miscible with water but such as for example waxes, mineral oils, animal oils and the like, as well as vegetable oils such as olive oil, castor oil, and the like. Desirably, an oil composition may include a solution of a resin material in a suitable solvent such as for example a hydrocarbon solvent together with the color forming material.

An essential active agent included in the liquid droplet within the encapsulated particle is the color forming compound, optionally in itself substantially colorless, capable of producing a highly colored material upon release by pressure rupture of the capsule in contact with a suitable chemical or physical reagent. According to a presently preferred embodiment of the invention the reagent for reaction with such colorless color forming compound is an acidic adsorbent photoconductive material capable of inclusion in an insulating resin binder to produce a photoconductive insulating layer. Thus, for example, photoconductive insulators such as zinc oxide, mercuric iodide, zinc sulfide, cadmium sulfide, cadmium dioxide, and the like, may be included in insulating resin binders such as silicone resins, acrylic resins, polystyrene and the like, as is known in the art, to produce image forming xerographic layers. Such layers generally act as acidic type adsorbents and accordingly are reactive with many color forming materials to produce highly colored image materials.

In combination with acidic type adsorbents such as zinc oxide and others, the following substantially colorless color forming compounds may be included in the encapsulated liquid droplet: Crystal violet lactone (3,3-bis-

(4 - dimethylaminophenyl) - 6-dimethylamino-phthalide), malachite green lactone (3,3 - bis - (4 - dimethylaminophenyl)-phthalide), dimethyl malachite green lactone (3, 3 - bis - (4 - dimethylamino-3-methylphenyl)-phthalide), Michler's hydrol (bis-(4-dimethylaminophenyl)-carbinol), Michler's hydrol methyl ether (bis-(4-dimethylaminophenyl)-methyl methyl ether), diethyl crystal violet lactone (3,3 - bis-(4-dimethylamino-3-ethylphenyl)-6-dimethylamino-phthalide), and mono-methylamino crystal violet lactone (3,3-bis(4-methylaminophenyl)-6-methylamino-phthalide).

The oil composition is contained within a hydrophilic colloid material such as, for example, gelatin casing or the like and may be formed into an encapsulated powder with materials and methods disclosed in Green et al. U.S. Patent 2,800,457. Suitable encapsulating material includes gelatin, hydrophilic cellulose materials such as hydrophilic cellulose esters and ethers, gums and the like.

Suitable capsules such as, for example, capsules as disclosed in the Green et al. patent may be coated with a resin to form a xerographic developer composition. As a preferred procedure, the gelatin capsule material is dipped or immersed into a solution of a mixture of polystyrene and polystyrene homologues dissolved in toluene, xylene, or a similar non-aqueous organic solvent. The mixture is suitably agitated and dried by spray drying or the like to produce capsules substantially uniformly coated with the polystyrene type resin. According to a presently preferred procedure a polystyrene type material believed to consist of a polymerized mixture of styrene and styrene homologues and available under the name "Piccolastic D-125" is employed. This resin is dissolved in xylene, and the capsules are immersed in the solution. Excess liquid is filtered off and the coated capsules air dried with occasional mixing. Alternatively the capsules may be dried according to conventional spray drying procedures.

In one procedure for producing a xerographic developer the polystyrene coated capsule powder is mixed with a granular bead-like carrier material such as disclosed in Walkup Patent U.S. 2,816,551, generally in the amount of 1% of the powder composition and 99% of the carrier composition. The mixed developer material is useful in xerographic image development as, for example, by cascading the mixture across the surface of the electrostatic image bearing xerographic plate or across the surface of an electrostatic image bearing insulating surface.

Alternatively, the powder material may be employed for image development by blowing it into an air cloud and directing the air cloud to the image surface, by mixing the powder material with a ferromagnetic material and magnetically conveying the mixture into brushing contact with the image surface, or by dusting the powder material into a brush such as, for example, a fur brush and brushing the image surface. Other image development methods may include dispersing the powder in an inert liquid and applying a liquid suspension by dipping or immersing or by pouring the liquid suspension across the image surface or the like.

Upon image development in any of these methods it has been found that a powder image is formed on the image bearing surface. The image may be made permanently visible and affixed to the original image surface by means of pressure rollers or the like, or may be transferred to an adjacent surface and subsequently affixed to such an adjacent surface. Thus, for example, a xerographic image may be formed on a selenium coated metal plate or drum by applying an electrostatic charge to the selenium surface. The image may be developed by the methods of the invention and transferred to a piece of coated paper placed in contact with the image bearing selenium plate or drum by means of corona discharge or the like and the image permanently affixed to the paper by means of pressure rollers. According to a presently preferred embodiment of the invention the electric image is directly formed on a paper backed photoconductor such

as zinc oxide in an insulating silicone, polystyrene, acrylic resin or the like and is developed and fixed *in situ*.

As an illustrative example of the present invention an encapsulated material may be prepared of one of the color formers, such as crystal violet lactone. This color former is encased in a hardened gelatin encapsulating wall coated with a polystyrene layer as described hereinbefore. In a preferred embodiment of the invention the toner composition produced by the methods described is mixed with iron filings in a ratio of about 20 parts iron filings to 1 part toner by weight and the mixture employed as a developer according to the method of Young U.S. 2,786,441. A suitable zinc oxide containing xerographic paper compatible with the toner composition is available under the name LectroX Paper, from the Haloid Company, Rochester, New York, and includes a photoconductive layer having as an active agent zinc oxide capable of imparting photoconductivity to the layer and capable of reacting with the active agent within the encapsulated droplet. An electrostatic image is formed on the coated paper by electrically charging the paper and exposing the charged paper to an image of light and shadow to be recorded. The mixture of iron filings and toner material is then brushed across the surface of the xerographic paper bearing an electrostatic image, and the toner deposits in image configuration. The resulting powder deposit can be made highly colored and permanently visible on the zinc oxide layer by rupturing the encapsulating walls, for example, by passing the image bearing paper through hard pressure rollers.

The present invention permits the use for xerography of a wide variety of color forming materials without regard to the triboelectric properties of such color formers. There may be employed, moreover, carbon black and other carbonaceous materials and other color intensifying materials in the liquid droplet or in the particle shell itself in addition to the color formers dispersed or dissolved in oil base. The xerographic developer compositions prepared with such marking materials are independent of the triboelectric characteristics of the composition of the droplet itself or of the encapsulating materials in which the color forming materials are mutually encased. It has been found that desired triboelectricity and humidity resistance can be imparted to the composition by polymerized styrene and polymerized acrylic resins and that such resins may be employed without regard to the nature of the color former or the oil base.

What is claimed is:

1. The method of xerography comprising forming an electrostatic image comprising information to be recorded on a composite photoconductive layer wherein zinc oxide is the photoconductive constituent by the combined action of light and electric field acting on said layer, developing the image bearing layer by electrostatically depositing thereon a xerographic toner composition consisting of particles triboelectrically adapted independently of ambient humidity and in a size range for use in conjunction with a xerographic carrier to form a toner carrier system for developing xerographic images, said particles consisting of an inner core of a substantially colorless color forming liquid capable of reacting with an acidic adsorbent to form a highly colored material and encapsulated in a rupturable hardened hydrophilic colloid shell, and an outer rupturable shell of hydrophobic resin coated on said colloid shell, said hydrophobic resin being triboelectrically adapted for use with a xerographic carrier and selected from the group consisting of polystyrene resins and polyacrylic resins, and rupturing said particles on the photoconductor layer to cause a color forming reaction between the liquid in said particles and the zinc oxide photoconductor.

2. The method of claim 1 in which said color forming liquid includes as an active ingredient thereof a material selected from the group consisting of crystal violet lactone (3,3 - bis-(4-dimethylaminophenyl)-6-dimethyl-

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amino-phthalide), malachite green lactone (3,3-bis-(4-dimethylamino-3-methylphenyl)-phthalide), Michler's hydrol (bis-(4-dimethylaminophenyl)-carbinol), Michler's hydrol methyl ether (bis-(4-dimethylaminophenyl)-methyl methyl ether), dimethyl crystal violet lactone (3,3 - bis - (4-dimethylamino-3-ethylphenyl)-6-dimethylamino-phthalide), and mono-methylamino crystal violet lactone (3,3-bis-(4-methylaminophenyl)-6-methylamino-phthalide).

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