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LIQUID DEVELOPER

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U.S. Cl. 252—62.1 **7 Claims**

ABSTRACT OF THE DISCLOSURE

Liquid developer for developing an electrostatic latent image present on an electrostatographic imaging surface comprising an insulating liquid having dispersed therein positively charged marking particles and also containing at least one charge control agent selected from the group consisting of vinyltriethoxysilane, γ-glycidoxypropyltrimethoxysilane, and β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane.

BACKGROUND OF THE INVENTION

This invention relates to liquid developers for use in electrostatographic imaging systems, and more particularly, to improved liquid developers with novel charge control agents.

The formation and development of images on the surface of photoconductor material by electrostatic means is well known. The basic electrostatographic process as taught by C. F. Carlson in U.S. Pat. 2,297,691 involves placing a uniform electrostatic charge on a photoconductive insulating layer, exposing the layer to a light and shadow image to dissipate the charge on the areas of the layer exposed to the light and developing the resulting electrostatic latent image by depositing on the image a finely divided electroscopic marking material referred to in the art as "toner." The toner will normally be attracted to those areas of the layer which retain a charge thereby forming a toner image corresponding to the electrostatic latent image. The powder image may then be transferred to a support surface such as paper and permanently affixed to the support by any suitable means such as heat fixing or solvent fixing. Alternatively, the powder image may be fixed to the photoconductive layer if elimination of the powder transfer step is desired. In addition, instead of latent image formation by uniform charging followed by imagewise exposure, the latent image may be formed by directly charging the layer in image configuration. Other methods are known for applying electroscopic particles to the imaging surface. Included within this group are the "cascade" development technique disclosed by E. N. Wise in U.S. Pat. 2,618,552; the powder cloud development technique disclosed by C. F. Carlson in U.S. Pat. 2,221,776; and the magnetic brush process disclosed, for example, in U.S. Pat. 2,874,063.

Development of an electrostatic latent image may also be achieved with liquid rather than dry developer materials. In conventional liquid development, more commonly referred to as electrophoretic development, an insulating liquid vehicle having finely divided solid material dispersed therein contacts the imaging surface in both charged and uncharged areas. Under the influence of the electric field associated with a charged image pattern, the suspended particles migrate toward the charged portions of the imaging surface separating out of the insulating liquid. This electrophoretic migration of charged particles results in the deposition of the charged particles on the imaging surface in image configuration. Electrophoretic development of an electrostatic latent image may, for example, be obtained by pouring the developer over the image bearing surface, by immersing the imaging surface in a pool of the developer or by presenting the liquid developer on a smooth surface roller and moving the roller against the imaging surface. The liquid development technique has been shown to provide developed images of excellent quality and to provide particular advantages over other development methods in offering ease in handling.

Typically, the electrostatographic liquid developers are generally dispersions comprising a highly insulating liquid referred to as the carrier liquid and dispersed therein submicron size marking particles which may comprise a pigment. In addition, fixing agents such as resinous materials to assist in fixing the toner particles to the support member and suspending or stabilizing agents may be added to insure uniform suspension of the marking particles throughout the insulating liquid.

To formulate the developer, the marking particles are first dispersed within the continuous phase of any resinous material. Conventional ballmill, three roll mill or sand mill may be employed to provide a homogeneous mixture of resinous material and pigment which is sometimes referred to as a paste or concentrate which may be subsequently diluted with carrier liquid or dispersed in a large volume of a carrier liquid to form the liquid developer. In addition, if desired to improve the dispersion stability of the developer, other additives such as surface active agents may be added.

Furthermore, if desired, one may use concentrated dispersions commercially available such as printing ink, tars or pitches in which the pigment particles are already dispersed in a resinous vehicle. Stable dilute dispersions of these can be prepared merely by dissolving the paste in carrier liquids by means of, for example, ultrasonic devices.

While a satisfactory degree of dispersion and dispersion stability may be readily achieved in general most liquid developers other necessary characteristics of the liquid developer are frequently difficult to achieve and to maintain for an adequate period of time. Since development is achieved by the migration of charged particles through the insulating liquid in response to the charge pattern on the imaging surface charge of proper polarity and magnitude should be maintained on the charged particles. In practice, however, considerable difficulty has been experienced in maintaining this polarity and magnitude of charge on the individual marking particles. The reasons for the alteration in polarity and magnitude of charge on the charged particles are many and include internal and external influences on the liquid developer. In order to control the polarity and the magnitude of charge on the individual marking particles, the practice of adding charge control agents to the liquid developer has been employed. Very often these control agents may also fuction for stabilizing or fixing properties. The choice of materials, particularly resinous materials, suitable for charge control agents is rather limited. Conventionally, alkyd resins and linseed oil have served the dual purpose in liquid developers of functioning not only as the vehicle for the pigments, but also as the desired charge control agent to impart a positive charge to the dispersed particles. However, the suitability of these liquid developers is limited by the specific materials and compositions which are capable of producing the necessary charge control and the flexibility in developer formulation is thereby limited. These limitations are even more strict for printing inks, tars or pitches.

In addition, other additives frequently are employed to improve the electrophoretic performance of liquid developer. Typically, these additives are soluble in the carrier liquid and exhibit a marked charged controlling capability without reducing the volume resistivity of the liquid developer to a value lower than the critical threshold. However, only a limited number of compounds such as cobalt naphthenate, and copper oleate are capable of meeting these requirements. Thus, there is a continuing need for additional and more effective charge controlling agents for electrostatographic liquid developers.

SUMMARY OF THE INVENTION

It is therefore an object of this invention to provide liquid developers which overcome the above noted deficiencies.

It is another object of this invention to provide novel charge control agents for liquid developers.

It is another object of this invention to provide liquid developers of high electrical resistivity including positively charged toner particles.

It is another object of this invention to provide a liquid developer capable of maintaining the desired polarity and magnitude of charge on the individual marking particles.

It is another object of this invention to provide liquid developers of increased flexibility in compositions which are easy to formulate.

It is another object of this invention to provide an imaging method capable of producing clear high density prints.

It is another object of this invention to provide a liquid development method capable of consistent print quality.

The above objects and others are accomplished, generally speaking, by employing as a charge controlling agent in electrostatographic liquid developers selected organosilicon compounds. More specifically, liquid developers of the present invention are characterized in that they contain at least one compound selected from the group consisting of vinyltriethoxysilane, γ-glycidoxypropyltrimethoxysilane, and β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane in amounts of from about 0.5% to about 2.0% by volume of the developer. Since generally speaking, organosilicon compounds are sufficiently polar to dissolve in alcohol, acetone or water thereby markedly decreasing the volume resistivity of the developer it is quite surprising that the three recited organosilicon materials are capable of functioning as superior charge controlling agents for electrostatographic liquid developers. This capability is believed to be due to the fact that the materials according to this invention are readily soluble in many nonpolar solvents such as cyclohexane, kerosene, toluol, xylol and isoparaffinic hydrocarbons.

A particularly important feature of the present invention lies in the fact that it provides liquid developer capable of excellent performance without requiring specialized complicated manufacturing processes since the charge control function of the charge control agents of this invention may be achieved merely by adding the recited compounds to the dispersion of marking particles in the insulating liquid. Furthermore, since the developer of the present invention includes only positively charged toner, an image of improved optical density may be obtained. In addition, since the charge control agents of the present invention are so effective in controlling the electrophoretic performance of the liquid developer a wider selection of other additives and particularly resinous materials is possible. The resinous materials which in the past were unacceptable since they would not function alone adequately in their charge controlling properties can now be used in conjunction with the charge control agents of this invention to provide superior liquid developers. Furthermore, the charge control agents of the present invention may be used to improve the electrophoretic performances of developers made from commercially available printing inks, tars, or pitches. Since the charge control agents of the present invention may be readily mixed with the liquid developer the range of raw materials capable of use in liquid developers may in some instances be greatly enlarged.

The organosilicon compounds may be present in the liquid developer in any suitable amount. If too small an amount is incorporated in the liquid developer, the charge controlling effect is inadequate. On the other hand, if too large an amount of charge control agent is added to the liquid developer, the volume resistivity of the developer may be lowered to a degree such that on contact with the developer, an electrostatic charge pattern may be discharged. In addition, in some cases, coagulation of marking particles may occur. Typically, the charge control agent is present in an amount of from about 0.5% to about 2.0% by volume of the developer.

The charge control agents of the present invention may be added to any suitable electrostatographic liquid developers. Typically, the liquids employed have relatively high insulating values generally having a volume resistivity greater than about 10^{10} ohm-cm. so as not to effect the electrostatic charge pattern on the insulating layer and low dielectric constant of less than about 3.5. Typical specific vehicles include hydrocarbons such as benzene, xylene, hexane, naphtha, kerosene, cyclohexane, Decalin, isoparaffinic hydrocarbons and halogenated hydrocarbons such as carbon tetrachloride, trichloroethylene, and chloroform. Typical electroscopic marking particles include among others, charcoal, carbon black, magnesium oxide, lithopone, cadmium yellow, chrome yellow, cobalt blue, cadmium red, burnt siena, Hansa yellow, rose bengal and phthalocyanine which are present in an amount of from about 2 to about 20 grams per liter. The electroscopic marking particles are conventionally dispersed and suspended in the liquid by stirring or agitation and where a highly uniform and stable suspension is desired, this suspension may be passed through a colloid mill. As discussed above, if desired, suspending or dispersing agents may be added for their well known functions.

The liquid developer according to the present invention may be employed to develop an electrostatic charge pattern present on any suitable imaging surface. Basically, any material capable of holding the charge pattern may be employed. Typical materials include dielectric layers and photoconductors. A particularly preferred material for use in automatic copiers is a photosensitive paper comprising photoconductive pigment particles in an insulating binder layer. Typically, this paper comprises zinc oxide photoconductive particles present in an insulating binder layer which is overcoated on the paper substrate. The particular imaging member and particular development technique may be readily determined by one skilled in the art. The photosensitive paper described above, for example, may be substituted with photoconductive materials made from cadmium sulfide, zinc sulfide, zinc selenide, cadmium selenide, titanium dioxide, phthalocyanine and polyvinylcarbazole.

DESCRIPTION OF PREFERRED EMBODIMENTS

The following preferred examples further define and describe the preferred materials and methods of the present invention. Examples II, III and V are presented for comparative purposes. Unless otherwise indicated, all parts and percentages are by weight.

EXAMPLE I

An electrostatic latent image present on an electrophotographic member which has been uniformly charged and exposed to a light and shadow pattern in conventional manner is developed by contacting the surface with a liquid developer formed in the following manner: To 1000 ml. of kerosene, 5 grams of black offset printing ink "Jet King G process H Black" (commercially available from Toyo Ink Manufacturing Company) is added and dispersed therein by means of an ultrasonic dispersing device. To this dispersion 1.0% by volume of developer of vinyltriethoxysilane (available from Shin-etsu Chemical Industry under the trade name "KBE 1003+") is added to provide a liquid developer wherein the carbon black is positively charged. When applied to the surface of the electrophotographic plate, a black tar image having high optical density is obtained. Upon repeated development, no change in print quality is observed.

EXAMPLE II

The procedure of Example I is repeated except that the vinyltriethoxysilane is omitted from the liquid developer. While the toner particles remain positively charged in this liquid developer, the electrophoretic performance of the developer fluctuates from portion to portion of the original printing ink.

EXAMPLE III

An electrostatic latent image of negative polarity is formed on an electrophotographic plate by charging the plate negatively and exposing it to a light and shadow pattern in conventional manner. The electrostatic latent image is developed with a liquid developer made in the following manner: Two grams of channel black and 50 grams of an alkyd resin purchased from Japan Reichold Chemical Industry under the trade name "Beckosol El 8002" are blended in a 500 ml. ball mill jar for about two days to prepare a concentrated paste which is subsequently dispersed in about 2000 ml. of an isoparaffinic solvent (Isopar H, available from Humble Oil and Refining Company). The majority of the toner particles in this liquid developer acquire a positive charge. However, particles bearing a negative charge are also present and when the developer is applied to the electrophotographic plate a low density toner image with hallow and streaks around high contrast image areas is obtained.

EXAMPLE IV

The procedure of Example III is repeated except that about 1.0% by volume of the developer of beta-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (available as "KBM 303" from Shin-etsu Chemical Industry is added to the liquid developer described in Example III. Development of the electrostatic latent image on the electrophotographic plate provides print of reduced hallow and streaks as well as increased image density.

EXAMPLE V

An electrostatic latent image present on an electrophotographic plate which has been conventionally uniformly negatively charged and exposed to a light and shadow pattern is developed with a liquid developer prepared in the following manner: A homogeneous paste is prepared by blending about 200 grams of R–4 varnish available from Toyo Ink Manufacturing Company and about 10 grams of channel black in a three roll mill. Fifty grams of this paste are dispersed in 2000 mil of kerosene in an ultrasonic dispersing device. When used to develop the electrostatic latent image present on the electrophotographic member, the electrophoretic performance of this liquid developer is observed to change depending on the manufacturing conditions of the developer. In general, a very unclear low density image is produced.

EXAMPLE VI

The procedure of Example I is repeated except that 1.5% by volume of the developer of γ-glycidoxypropyltrimethoxysilane ("KBM 403" available from Shin-etsu Chemical Industry is added to the liquid developer. When employed as a liquid developer in the development of electrostatic latent images present on electrophoto-

graphic layers, a stable positively charged electrophoretic developer is observed to provide consistent print quality with a marked reduction in performance fluctuation.

Although specific materials and operational techniques are set forth in the above exemplary embodiments using the charge control agents and techniques of this invention, they are merely intended as illustrations of the present invention. There are other materials and techniques than those listed above which may be substituted for those in the examples with similar results. Other modifications of the present invention will occur to those skilled in the art upon a reading of the present disclosure which modifications are intended to be included within the scope of this invention.

What is claimed is:

1. An electrostatographic liquid developer comprising an insulating carrier liquid and substantially uniformly dispersed thereon finely divided positively charged electroscopic marking particles, said liquid developer further comprising from about 0.5 to about 2.0% by volume of the developer, a charge control agent selected from the group consisting of the vinyltriethoxysilane, γ-glycidoxypropyltrimethoxysilane, and β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane and mixtures thereof sufficient to provide a stable positive charge on the electroscopic marking particles.

2. An electrostatographic liquid developer according to claim **1** further comprising a resinous fixing agent.

3. An electrostatographic liquid developer according to claim **1** wherein said charge control agent is vinyltriethoxysilane.

4. An electrostatographic liquid developer according to claim **1** wherein said charge control agent is γ-glycidoxypropyltrimethoxysilane.

5. An electrostatographic liquid developer according to claim **1** wherein said charge control agent is β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane.

6. An electrostatographic liquid developer according to claim **1** wherein said charge control agent is soluble in said carrier liquid.

7. An electrostatographic liquid developer according to claim **1** wherein said electroscopic marking particles are present in the liquid developer in an amount of from about 2 to about 20 grams per liter.

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