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CONTROLLED POLARITY LIQUID DEVELOPER

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SOLVENTS		RESINS
PENTANE HEXANE HEPTANE OCTANE CYCLOHEXANE	1.8 1.9 2.0	TEFLON
p-DIOXANE CARBON TETRACHLORIDE BENZENE PERCHLORETHYLENE TOLUENE STYRENE OLEIC ACID NAPHTHALENE	2.1 2.2 2.3 2.4 2.5 2.6	POLYETHYLENE POLYISOBUTYLENE RUBBER CHLORINATED RUBBER ETHYL CELLULOSE POLYSTYRENE
CARBON DISULPHIDE <i>d</i> - α -PINENE	2.7	ISOMERIZED RUBBER
TETRAHYDRONAPHTHALENE	2.75 2.8 2.9 3.0	SILICONES ALKYD RESINS INDENE-COUMARONE RESINS
TRICHTHLORETHYLENE	3.5	BUTADIENE RUBBERS POLYVINYLCHLORIDE VINYLCHLORIDE-VINYL ACETATE COPOLYMERS PHENOL-FORMALDEHYDE RESINS EPOXY RESINS POLYMETHYLMETHACRYLATE POLYVINYLIDENE CHLORIDE POLYAMIDES
AMYL ACETATE CHLOROFORM BUTYL ACETATE CHLOROBENZENE ETHYL ACETATE ACETIC ACID DIBUTYL PHTHALATE CHLOROTHENE	4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0	CELLULOSE NITRATE POLYVINYLACETATE UREA AND MELAMINE FORMALDEHYDE RESINS
ALKYL ARYL SULPHONATES	10.0	
PYRIDINE PENTANOL	11.0 12.0	
CYCLOHEXANOL	13.0	
1-BUTANOL	14.0	

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CONTROLLED POLARITY LIQUID DEVELOPER

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Continuation-in-part of application Ser. No. 440,127, Mar. 16, 1965. This application Mar. 24, 1969, Ser. No. 809,678

Claims priority, application Australia, Mar. 23, 1964, 42,371

Int. Cl. G03g 9/04, 13/10

U.S. Cl. 117—37

9 Claims

ABSTRACT OF THE DISCLOSURE

Controlled polarity liquid developers for electrostatic printing are prepared by suspending a pigment in a carrier liquid to form a developer, adding to the developer a control liquid with a dielectric constant different from that of the carrier liquid and miscible in the carrier liquid, subjecting the developer to a gaseous phase to cause ions to be released to the carrier liquid and applying the developer to a base to develop a latent electrostatic image on said base.

This invention is concerned with the development of electrostatic images and in particular with the development of electrophotographic images both on amorphous photo-insulators such as selenium and particulate photo-insulators such as zinc oxide as well as insulating non-photographic films such as polyester resin films, polybutylmethacrylate films, alkyd resin films and the like.

This application is a continuation-in-part of application Ser. No. 440,127, filed Mar. 16, 1965, now abandoned.

It is well known to develop electrophotographic images with dry powders using methods commonly known as the cascade, magnetic brush, powder cloud and droplet cloud methods and also to develop such images with liquid developers comprising particles suspended in insulating liquids. In each of these methods it is well known to develop an image in a positive or attraction manner in which the developer particles have opposite polarity to that of the charge on the image.

It is also known that developers using pigment particles suspended in insulating hydrocarbon carrier liquids are influenced by coating the pigment particles to influence the particle charge and thus change it relative to the latent electrostatic image. These developers are generally called positive developers because they go down on to the negatively charged areas.

It would be highly advantageous to be able to use such developers as negative developers, that is developers in which the pigment particles go down on the relatively oppositely charged areas, because, as will be appreciated, any surface having a basic image of one polarity will hold such polarity relative to other factors such as particle charge of pigment in the carrier liquid and the characteristics of the carrier liquid itself, and it is this relativity which is made use of in the present invention, and which must be considered as existing between the characteristic of the pigment particles, the surface charge of the base, and the carrier liquid itself.

In an earlier patent on control agents for pigment particles, applicants operated on the charge characteristic on the particle itself in relation to the suspending liquid, and the surface on which the image was to be developed, but in the present invention, since particle control is still required, we modify the carrier liquid, and this means that one now can use the developer according to ap-

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licants' earlier patents and the known art generally, i.e. a developer in which particles are suspended in an insulating liquid, and change the sign characteristic of the developer, still retaining the advantages of the earlier control characteristics.

In applicants' earlier patents the control substances were generally solid substances, particularly natural and synthetic resins of all kinds, which were able to form the coating on the pigment particles, and in those cases where the control agents were oils, these again attached to the particles to form the control film and were similar in action to the resins so far as their control characteristics are concerned.

The present invention however utilizes solvent liquids, that is liquids compatible with the carrier liquid to be dissolved therein, which when selected according to their dielectric constant can be used either to increase the positive characteristic of the developer particles or the negative characteristic of the particles, depending on whether a high or a low dielectric constant liquid is selected.

It is essential that the solvent liquids, or control liquids as they will be called, be intimately admixed, preferably by strong agitation, just prior to being put into use, because it has been found that this causes the liquid to give maximum control action by ensuring effective distribution.

The accompanying drawing shows the basis of the present invention, the solvents or control liquids being shown on the left of the center line showing the dielectric constant scale while the resins which were previously used as control means are shown on the right-hand side of the center line. It will be realized that only a few of the materials are shown to give some indication of the type of substances which are involved.

The present invention is not concerned with resins and solid substances which are attached to the pigment particles by grinding or the like according to prior art, although the solid pigment particles are preferably still so treated to ensure uniformity of charge sign, but the substances concerned are solvent liquids which, it will be noted, vary from the highly insulating type below a dielectric constant of approximately 2 but increase in conductivity as the dielectric constant increases. In the prior art the carrier liquids themselves had a dielectric constant less than about 3 to avoid undue destruction of the latent electrostatic image, and we have now found that by adding control liquids having a lower dielectric constant than that of the carrier liquid, and subjecting the liquid to a gas, a positive characteristic of the pigment results whereas when adding a control liquid having a higher dielectric number a negative characteristic is given to the pigment particles. The added liquid must be capable of releasing ions in the presence of a gas.

Thus by a simple selection of the added control liquid, which must be dissolved in the carrier liquid to avoid its action as a developer itself, and the quantity thereof, pigment particles can be influenced to act either as a negative or a positive developer, the extent of which depends also on the original surface activity of the particle or the surface activity of the control agent on the particles themselves which exist at the interface with the now controlled liquid carrier.

The importance of this ready control need not be stressed because it does not involve grinding with the resin or oil to form a permanent film on the developer particles, but in its simplest form involves adding a selected control liquid which is soluble in the carrier liquid, and agitating to ensure uniformity of distribution of one liquid in the other and maximum distribution of the solid developer medium therein, and then develop-

ing, the agitation also aiding ion release by subjecting the liquid to a gaseous phase such as air or ozone or the like.

The methods of achieving the change in dielectric constant can vary as will be appreciated when considering this specification.

The amount of change to the carrier liquid must of course be considered, because by decreasing the resistivity of the carrier liquid due to ion release or presence there will be a greater destruction of the latent electrostatic image, but we have found that provided development is fast enough no problem results, and even with highly polar substances, as the proportions required are very low, destruction of the image is not great compared to the highly effective development which results.

The method of reversing the polarity of liquid developers for electrostatic printing according to this invention therefore consists in adding to the carrier liquid in which the pigment particles are suspended, a control liquid which is compatible with the carrier liquid to be fully dissolved therein and which changes the dielectric constant of the carrier liquid and thus changes the polarity of the toner particles at the interface with the modified carrier liquid.

The method involves either adding to the carrier liquid itself a liquid which varies the dielectric constant, or by treating the carrier liquid with a material which by reaction with the carrier liquid changes the dielectric constant, or by attaching to the pigment particles a material which, when the particles are suspended in a carrier liquid, enter the carrier liquid in solution, or react with the carrier liquid, to change the dielectric constant of the carrier liquid relative to the pigment particles and also in relation to the base on which development is to take place, the change in the carrier liquid of course affecting the movement of the pigment particles by changing their relative attraction or repulsion to charged areas whereby particles which without the control material in the carrier liquid would go down on an area of one polarity are forced down on an area of relatively opposite polarity to give a reversed image. The changed movement is thus relative also to the base, which carries the latent electrostatic image.

As an explanation of the basis of this invention it is noted that electrostatic separation of a solid particle from its environment, such as a pigment particle from a carrier liquid, gas or liquid, is effected by the forces which occur in the electric field associated with the images. The forces on a particle in an electric field may be due either to an initial electric charge on the particle or merely to a difference between the dielectric constants of the particle and the surrounding medium, in this case the carrier liquid and the base. These forces are always directed in such a manner that the resulting motion will cause a maximum decrease in the total energy of the system. Dipoles or particles already charged, and conductors, will be acted on similarly to particles of high dielectric constant.

The behavior of conductors is due to the fact that the electric field is shorted through their conductive surfaces, the conductors having mobile charges. In addition, the fluid medium does not remain unaffected by the electric field and in fluids such as oil or air convective cellular vortices are produced which contribute to the movement of particles suspended therein. In addition to the forces exerted on a charged particle by an externally applied field, a force may be exerted due to the field of the particle itself. When a charged particle approaches an initially uncharged surface and the dielectric constant of the surface is higher than the dielectric constant of the medium surrounding the two, an attraction results, for example all solid surfaces in air. When the dielectric constant of the medium is higher than that of the surface, a repulsion results. Similar behavior is obtained if dipoles are substituted for singly charged particles.

It has been discovered in liquid development that in most cases the dielectric constant of the surface is higher than the carrier medium surrounding the particles and the electrophotographic surface and also that as a general rule the particles are positively charged if present as a single species; they are attracted to negatively charged areas and are repelled by positively charged areas giving positive and negative development respectively.

However, it has been found possible to reverse the migration of the particles by changing the dielectric constant of the carrier medium, by releasing ions, relative to the developer particles and base, and if therefore a developer is prepared in the normal manner in which the particles of pigment go down on to an image area of one polarity this migration can be changed to cause migration to the opposite polarity by varying the dielectric constant of the carrier liquid. This is the basis of the present invention.

The invention may thus be said to consist in a method for relating the polarity of liquid developers for electrostatic printing to the carrier and base by means of additives which change the relative dielectric constant of the carrier liquid due to ion release.

Thus if a pigment substance such as carbon black is wetted with a vegetable oil, such as sunflower oil in which oil there are contained polar complex organic acids containing ion-forming compounds which, on being dispersed or dissolved in the liquid medium result in an increase in the dielectric constant of the liquid, thereby raising its value relative to the developable surface so that the pigment substance now develops negatively on a negatively-charged surface.

The sources of ions in the hydrocarbon insulating media which effect resistivity and dielectric constant include:

(a) Small amounts of oxygen dissolved in the media which can oxidize the liquid dielectric or suspended material or the developable surface (agitation aiding ion release due to air or water vapor in the air).

(b) Presence of the catalytically active metals such as copper or iron. In addition to being catalytically active, these metals participate in reactions that form metal-containing organic compounds that are ion-producing in nature

(c) Nitrogenous compounds (amino and imino derivatives) which tend to donate electrons or, alternatively, accept protons to form cations

(d) Photochemical excitation of small gas pockets in the media.

To remove the ions once formed, should it be necessary to reduce the ion concentration, treatment methods found to be effective include subjecting the liquid to clay and filtering, the ionic species being adsorbed by the clay, or to resin ion exchangers, or to the passage of suitable gases such as hydrogen, where for instance a removal of negative ions in favor of positive ions is required. Some complex amines can be used to inhibit the occurrence of anions. Aromatic hydrocarbons can be ionized by dissolving therein for example, 20 moles per liter of myristic acid and subjecting the liquid to the action of ozone for about one hour. Following this treatment the conductivity of the liquid increases. Additions of naphthalene or tetralin (1,2,3,4-tetrahydronaphthalene) to the aromatic hydrocarbon liquid followed by treatment with ozone also causes an increase in conductivity. Inhibitors for ionization and consequently producers of higher resistivity include small quantities of olefins, for example, cyclohexene or octene. Substances which can be added in large amounts to hydrocarbon liquids to cause minor ionization include lanoline, naphthenic acid and oleic acid. Substances which can be added to hydrocarbon liquids to cause ionization but only in small amounts include ethyl alcohol and dibutylphosphate. In all cases the ion release is aided by agitation.

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EXAMPLE 1

The pigment Vulcafors Fast Yellow EGS, produced by I.C.I. A.N.Z., consisting of benzidine yellow, when dispersed in Shellsol T, a hydrocarbon solvent containing 100% aliphatic hydrocarbons, carries a positive charge and develops direct reproductions on negatively charged surfaces. The addition of butyl alcohol to the dispersion results in the pigment becoming relatively negatively charged and developing reverse reproductions on negatively charged surfaces or direct reproductions on positively charged surfaces. A typical developer has the following composition:

	Grams
Vulcafors Fast Yellow EGS	1
Shellsol T	10

These materials are ground together to form a paste and then dispersed by stirring into 490 grams of Shellsol T. This developer is characterised by positively charged particles. A typical reversed developer has the following composition:

	Grams
Vulcafors Fast Yellow EGS	1
Butyl alcohol (which dissolves water vapor to produce ions on shaking)	1
Shellsol T	10

These materials are ground together to form a paste and then dispersed by stirring into 490 grams of Shellsol T. This developer is characterised by negatively charged particles. (Air of course contains nitrogen and oxygen and water vapor which provides hydrogen ions.)

EXAMPLE 2

In this example the Shellsol T of Example 1 is replaced by Shellite, X4, X55, chlorinated fluorinated hydrocarbons, mineral turpentine and the like in substantially similar proportions with similar results.

EXAMPLE 3

In this example the pigment of Example 1 is replaced by similar proportions of carbon black, and the same polarity change occurred.

EXAMPLE 4

In this example the butyl alcohol of Example 1 is replaced by alcohols such as isopropyl alcohol, nonyl-alcohol, hexanol and the like, again with similar results but to a lesser extent as they dissolve less water.

EXAMPLE 5

In this example the developer is based on perchlorethylene, mineral turpentine and the like and the additive is Shellsol T X4 a low aliphatic hydrocarbon solvent, hexane, chlorinated fluorinated hydrocarbons and the like and these reduce the dielectric constant of the mixture, causing the developer to become more positive. Through this mixture is then passed an organic amine gas such as methylamine.

EXAMPLE 6

In this example the developer is based on X55 or the like and silicon oil is added to render the developer more positive.

EXAMPLE 7

Resins such as polystyrene, silicones, hydrocarbon resins, polyesters and polybutylmethacrylate, are dissolved in hydrocarbon solvents in which they are respectively soluble, such as toluene, to modify the dielectric constant of the liquid. For example polystyrene is dissolved in toluene or perchlorethylene to reduce the net dielectric constant and to increase the positive characteristic. Agitation of this in air, or by bubbling air—particularly moist

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air—therethrough will increase ion release, or bromine vapor can be passed through the developer with enhanced effect.

EXAMPLE 8

A developer concentrate is prepared by mixing together the following materials:

	Grams
Isol Ruby Red BKS, 7520, (a red pigment by Koge, Copenhagen)	50
Brillfast Rose Red, 444 (a red pigment by Smith Reichold, U.S.A.)	30
Pale lowering lithographic varnish	80
Rhodene alkyd resin L42/70 (a long oil alkyd resin by Polymer Corporation, Australia)	200

These materials are ground by bar milling to produce a paste which can be sealed in air tight cans for storage. To prepare a developer the concentrate is dispersed by grinding into the carrier liquid for example mineral spirits, Shellsol T, Shellite, cyclohexane and the like. The polarity of this developer is positive and serves to develop attraction images on negatively charged surfaces and repulsion or reversal images on positively charged electrophotographic surfaces.

For modification of the dispersion to produce a negatively charged developer the following solution is added in the proportion of 0.01 to 0.1 percent of solution by volume in the carrier liquid:

	Grams
Sodium dioctyl sulphosuccinate	1
Carbon tetrachloride	10

These two components are heated together to dissolve the sodium dioctyl sulphosuccinate in the solvent. This solution is added to the carrier liquid in the above proportions to produce the reversal.

It will be appreciated that the sodium dioctyl sulphosuccinate can be ground or evaporated or filmed on to the pigment particles to be released when these are dispersed in the carrier liquid in which the substance must be soluble. An organic amine bubbled through this increases ion release.

EXAMPLE 9

A developer concentrate is prepared by milling together the following materials:

	Grams
Brillfast Black (Smith Reichold U.S.A.)	70
Brillfast Rose Red (Smith Reichold U.S.A.)	7
Phthalocyanine Blue (Geigy, Switzerland)	2
Pale lowering lithographic varnish	160
"Rhodene" alkyd resin L42/70 (a long oil safflower modified long oil resin by Polymer Corporation)	250

These materials are ground together by bar milling to produce a paste which may be sealed in air tight cans for storage or transport. Developers can be made from these concentrates by dispersing them in a carrier liquid having high volume resistivity such as Shellsol T, mineral spirits, cyclohexane, Freon 113 and the like. The polarity of these developers is positive and serve to develop attraction images on negatively charged surfaces or reversal images on positively charged surfaces.

In one example of the modification of these developers to produce repulsion or reversal images the above paste can be dispersed in a carrier liquid such as carbon tetrachloride to which is subsequently added a polarity control solution having the following composition:

	Grams
Sodium diamyl sulphosuccinate	1
Oleic acid	10

The control solution is added in the proportions 0.02 to 0.1 percent of solution by volume in the carrier liquid.

EXAMPLE 10

A developer concentrate is prepared by mixing together the following materials:

	Grams
Brilliant Green pigment (Coates Ltd. Aust.)	100
Isophthalic alkyd resin, Super Beckosol 1352 (Reichold Corp. U.S.A.)	250
Mineral turpentine	100

The resin is dissolved in the mineral turpentine and then stirred into the pigment. The mixture is ground in a ball mill for 8 hours. The concentrate (8 parts) is dispersed in Shell solvent X55 (1000 parts) for example and the dispersion completed by ultrasonic mixing. The developer shows positive polarity.

For modification of polarity to produce repulsion development a solution of sodium bis(tridecyl)sulphosuccinate in X55 solvent is added. The solution is a 10% solution which is added to give a final content of 0.1% by volume in the carrier liquid.

What we claim is:

1. A method for controlling the relative polarity of liquid developers for electrostatic printing, said method comprising forming a developer by suspending in a hydrocarbon insulating substance, pigment particles which are capable of developing a charged area on a base containing a latent electrostatic image, adding to the developer a control liquid which is capable of releasing ions when contacted with a gaseous phase selected from the group consisting of ozone, bromine vapor, water vapor and methylamine and having a dielectric constant different from that of the hydrocarbon insulating substance, and being compatible with and dissoluble in said hydrocarbon insulating substance, agitating the developer to which said control liquid has been added to effect mixture thereof and introducing said gaseous phase through the resulting mixture to cause ions to be released from the control liquid to the hydrocarbon insulating substance and thereby change the conductivity of the developer, applying the mixture to a latent electrostatic image, in consequence of which the relative attraction between the pigment particles and the field on an image-bearing base will cause deposition of the particles on areas in conformity with the changed dielectric constant.

2. The method of claim 1 wherein the gaseous phase is ozone.

3. The method of claim 1 wherein the gaseous phase is bromine vapor.

4. The method of claim 1 wherein the gaseous phase is water vapor.

5. The method of claim 1 wherein the gaseous phase is methylamine.

6. A method as claimed in claim 1 wherein the control

liquid is selected from the group consisting of alcohols, aldehydes, esters and ketones.

7. A method as claimed in claim 1 wherein the control liquid is myristic acid.

8. A method as claimed in claim 1 wherein the control liquid is 1,2,3,4-tetrahydronaphthalene.

9. A method for controlling the relative polarity of liquid developers for electrostatic printing, said method comprising forming a developer by suspending in a hydrocarbon insulating substance, pigment particles which are capable of developing a charged area on a base containing a latent electrostatic image, adding to the developer naphthalene, which is a compound having a dielectric constant different from that of the hydrocarbon insulating substance, agitating the developer to which naphthalene has been added to effect mixture thereof, passing ozone through the resulting developer to cause ions to be released from the naphthalene to the hydrocarbon insulating substance and thereby change the conductivity of the developer, applying the mixture to a latent electrostatic image, in consequence of which the relative attraction between the pigment particles and the field on an image-bearing base will cause deposition of the particles on areas in conformity with the changed dielectric constant.

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