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LIQUID DEVELOPER FOR ELECTROSTATIC IMAGES

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This invention relates to method and means for producing black developers, or toners as they are often called, suitable for dispersion in a liquid of relatively high electrical resistivity such as used in the known art of electrophotography as the liquid developer vehicle. In particular this invention relates to the method and means of making the suspended toner particles capable of assuming a positive electrostatic charge in the presence of a latent image formed by a negative electrostatic charge. This particular embodiment of the present invention ensures that such suspended toner particles can become attracted only by negatively charged image areas and that consequently no deposition can take place on non-image areas or on areas free of negative charge.

A further feature of this invention is that developers prepared in a manner as herein described will remain stable in suspension in respect of polarity characteristics for a period of time which is adequate for all practical purposes.

It is known that electrophotographic images can be produced on surfaces containing photoconductive matter, and liquid developer formulations capable of producing images in various colours are also known. If the photoconductor used in the process is zinc oxide, which substance is not capable of supporting a positive electrostatic charge, it is then necessary for the developer particles suspended in a liquid carrier medium to assume positive polarity in respect to the latent electrostatic image formed on the zinc oxide surface, because such latent image on a zinc oxide surface can be formed essentially by a negative electrostatic charge only. With certain exceptions, most pigments when associated with a resin or oil and suspended in an insulating liquid such as the hydrocarbon solvent known under the trade name "Shell X55," of the Shell Company, will assume positive polarity in respect to a latent image formed by a negative electrostatic charge, so that such latent image can be rendered visible because the pigment particles in suspension will deposit by electrostatic attraction onto the image areas.

It has been proposed heretofore to use certain resins or oils termed as "control agents" to impart the desired positive polarity to certain pigments which normally would assume fully or partially negative polarity in respect to a negative electrostatic latent image when suspended in an insulating carrier liquid and would therefore deposit onto the non-image areas to a greater or lesser degree, or would deposit both onto the image and non image areas.

It has been also proposed to introduce such control agents in the form of a thin coating around the particulate pigment matter in suspension and it is said that this can be attained if the pigment is milled or ground with such resin or oil to form a paste which is then dispersed in the carrier liquid. It has been said that such control agents act by imparting their own characteristics of polarity to the enveloped pigment particle.

It is known to those skilled in the art of paint and printer's ink making that carbon black pigments are difficult to wet by oils or oleoresinous varnishes, and that the wetting properties of carbon black are largely dependent on the type and quantity of the gaseous or other matter which is known to be present in the form of an adsorbed

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layer around carbon black particles. Such variation in the adsorbed matter is thought to be also responsible for carbon black particles suspended in an insulating liquid such as Shell X55 in absence of any oil or resin to assume dual polarity in presence of a negative electrostatic field or of a negative electrostatic latent image, with the effect that such carbon black particles will deposit both onto image and non-image areas.

Polarity control agents can be effective only if they remain in the form of a thin adsorbed layer around each pigment particle in suspension. If the control agent is of oleoresinous nature, then this requirement can be achieved only if such oleoresinous matter is insoluble or only partly soluble in the particular carrier fluid for which it is intended to be used and if each pigment particle is uniformly wetted by the control agent. If the wetting of the pigment is done by appropriate mechanical means, such as milling or grinding, the uniformity of wetting will depend on the adsorption characteristics of each pigment particle, which, in case of carbon black pigments, is known to vary due to the presence of gaseous or other matter adsorbed onto the particles.

When suspended in a carrier liquid, the non-uniform wetting of carbon black particles by an oleoresinous control agent causes such oleoresinous matter to dissociate from certain particles more readily than from other particles so that effective polarity control by this method becomes impractical.

As an alternative to oleoresinous control agents, it has been also proposed heretofore to use carbon black pigments in co-suspension with certain other pigments onto which the carbon black particles precipitate in the course of deposition caused by electrostatic attraction and since such other pigments assume a positive polarity in presence of a negative electrostatic field, the carbon black particles are thus also caused to deposit onto the image areas only. The disadvantage of developers prepared in this matter is that their stability in suspension and shelf-life is limited.

In accordance with the present invention an improved liquid developer for electrostatic images comprises an electrically insulating carrier liquid, carbon black particles suspended in the said carrier liquid as a toner, said carbon black particles having previously been wetted by coating with an oil or oleoresinous varnish as a dispensing medium, and a metallic soap in a hydrocarbon solvent in contact with the said coated particles as a polarity stabiliser.

The metallic soaps can be such compounds as oleates, linoleates, octoates, tallates, resinates, palmitates, stearates and naphthenates of such metals as lead, manganese, cobalt, calcium, aluminum, zinc and the like, and the solutions of such metallic soaps in a hydrocarbon solvent can be introduced either by milling together with the carbon black pigment and oil or oleoresinous varnish or they can be introduced directly into the carrier liquid prior, after or during the dispersion of the carbon black pigment which has been milled or ground with an oil or an oleoresinous varnish.

Whichever method is used, the metallic soaps adsorb in suspension preferentially onto the carbon black particles and surprisingly render such particles capable of assuming a positive electrostatic charge in presence of a negative field or of a negative electrostatic latent image.

It will be readily realised that there is great advantage in using polarity stabilising substances which adsorb from solution or suspension and which exhibit particular preference for adsorbing onto carbon black because subsequent dissociation of such adsorbed substance is very unlikely and therefore stability of polar behaviour is ensured.

It was found that depending on the oleoresinous var-

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nish, the grade of carbon black pigment and the carrier fluid, a combination of two or more metallic soaps may be more effective than one type of metallic soap only and in the following formulations it will also be found that the manner in which the soaps can be incorporated varies accordingly.

The resins and oleoresinous varnishes used in accordance with this invention are present essentially as wetting agents for breaking up particle agglomerates during milling and for the purpose of aiding dispersion.

The following is a detailed description of the method by which a black electrophotographic image can be produced using the embodiment of this invention:

The photoconductive material can be a relatively conducting backing or support such as paper or metal sheet or film upon which is deposited a coating comprising a particulate photoconductor capable of supporting a negative electrostatic charge such as zinc oxide or the like in a resin binder and such resin binder being capable of attaining a degree of hardness sufficient to prevent the resin from being attacked or softened during contact with the carrier fluid. The following photoconductive coating can be used in the liquid developer process:

	Grams
Zinc oxide Durham special Z	900
Rhodene M8/50	600
Toluol	250
4% manganese naphthenate	2.5
3% cobalt naphthenate	2.5

The ingredients can be milled together, diluted if required, and then deposited on a relatively conducting support by any known coating method. An alternative to this formulation is the following:

	Grams
Zinc oxide Durham special Z	750
Dyal XOR 36	416
Toluol	200
15% lead naphthenate	8.5
4% manganese naphthenate	3.5
3% cobalt naphthenate	4.5

Here again, the ingredients can be milled together, diluted if required, and deposited onto a support by any known coating method. The photoconductive material thus prepared and sufficiently hardened can be now sensitized by subjecting it to a corona discharge from a series of wires or points held at a relatively high direct current potential above the base plate upon which the material is placed, the polarity being such as to impart a negative electrostatic blanket charge to the photoconductive layer. The material is then subjected to a light pattern whereby non-image areas are rendered conductive and permit the charge to dissipate into the relatively conducting support or backing whereas under the shielded image areas a latent image consisting of the remaining negative charge is formed.

This latent image can now be rendered visible by developing it in any one of the liquid developers hereafter described. The developing step can be performed by immersing the photoconductive material in a vessel containing the liquid developer, or by mechanical means such as wet roller and squeegee, or cascading and the like. The liquid developer can be made up by dispersing any of the toners described in the following examples in the specified liquids in proportions ranging from 1 part toner to 100 or 200 parts of liquid by weight, or less or more, depending on the developing process preferred.

The following examples of toner formulations illustrate the use of metallic soaps in accordance with this invention and it will be realised that this invention is not restricted by the cited combinations of metallic soaps and varnishes and that one skilled in the art of making electrophotographic developers can adjust and select metallic soaps to suit particular varnishes, particular grades of carbon black and particular carrier liquids.

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EXAMPLE 1

A toner is prepared in two stages as follows.

Compound A:	Grams
Carbon black SRF (pigment)	100
Bodied linseed oil (wetting agent)	125
Reflex blue in varnish No. 69884 (added toner)	10
3% calcium naphthenate (drier)	3.5
Cold blend ingredients and mill.	

Compound B:	Grams
Compound A	100
Pentacite P-423 (50% solution in toluol) (control)	40
Carnauba wax (30% solution in turpentine) (anti-scuffing agent)	8
Aluminum stearate (2% solution in Solvesso 100), (polarity stabiliser)	25

These components are hot blended, the heating being continued for such time as is necessary to reduce the volume of the compound by one quarter, due to solvent evaporation, after which the toner is remilled.

This toner is stable in respect of polarity in carrier liquids such as Shell X55, Freon 113, n-hexane, n-heptane and cyclohexane.

EXAMPLE 2

In perchloroethylene and Solvesso 100 the stability of the toner from Example 1 may be found to be inadequate. For increasing the stability in respect to polarity in perchloroethylene and Solvesso 100, mix—

	Grams
Toner from Example 1	10
6% cobalt octoate (in a hydrocarbon solvent) polarity stabiliser	1

EXAMPLE 3

	Grams
Carbon black ISAF (pigment)	40
Reflex blue in varnish No. 69884 (added toner)	4
Superbeckacite 2100 resin varnish in bodied linseed oil (20% resin) (wetting and dispersing agent)	100
15% lead naphthenate (in hydrocarbon solvent) polarity stabiliser	50
50% calcium resinate (solution in Solvesso 100) polarity stabiliser	200
Cold blend ingredients and mill.	

This toner is stable in respect to polarity in liquid carriers such as Shell X55, Freon 11, Freon 113, n-hexane, n-heptane and cyclohexane.

EXAMPLE 4

	Grams
Carbon black SRF	40
Superbeckacite 2100 resin varnish in bodied linseed oil (20% resin)	100
8.5% cobalt linoleate (in hydrocarbon solvent) polarity stabiliser	60
16% lead tallate (in hydrocarbon solvent) polarity stabiliser	10
Cold blend ingredients and mill.	

This toner is stable in respect to polarity in carrier liquids such as Shell X55, n-hexane, n-heptane, Freon 11, Freon 113, cyclohexane, Solvesso 100 and perchloroethylene.

EXAMPLE 5

	Grams
Carbon black Sterling MT	30
Reflex blue in varnish No. 69884	3
Calcium resinate varnish in bodied linseed oil (25% resin) partial polarity stabiliser	75
3% calcium naphthenate (in hydrocarbon solvent) polarity stabiliser	30
Cold blend ingredients and mill.	

The polarity of this toner is stable in Freon 113.

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EXAMPLE 6

	Grams
Toner from Example 5	30
15% lead naphthenate (in hydrocarbon solvent) additional polarity stabiliser	10
Blend ingredients and mill.	

The polarity of this toner is stable in Shell X4 and n-hexane.

EXAMPLE 7

Carbon black Vanblack HAF	30
Reflex blue in varnish No. 69884	3
Caladene 25 resin varnish in bodied linseed oil (20% resin)	75
15% lead naphthenate (in hydrocarbon solvent) polarity stabiliser	50
Cold blend ingredients and mill.	

Dilute then with 5 parts of Solvesso 100 to one part of paste by weight.

The polarity of this toner is stable in Shell X55, Shell X4, n-hexane, n-heptane, Freon 11, Freon 113, and cyclohexane.

The following are descriptions of materials which have been referred to under their trademarks or registered trademarks.

Carbon black ISAF, particle size 23 millimicrons, manufactured by Australian Carbon Black Pty. Ltd.

Carbon black SRF, particle size 80 millimicrons, manufactured by Australian Carbon Black Pty. Ltd.

Carbon black Sterling MT, manufactured by Cabot Co., U.S.

Carbon black Vanblack HAF, manufactured by R. T. Vanderbilt Co., U.S.

Reflex blue in varnish No. 69884, tinting ink for black, manufactured by Reichhold Chemical.

Rhodene M8/50, short linseed oil alkyd, manufactured by Polymer Corp., Australia.

Dyal XOR 36, modified ether resin, manufactured by Sherwin-Williams Co.

Pentacite P-423, pentaerythritol resin, manufactured by Reichhold Chemical.

Superbeckacite 2100, oil reactive phenolic resin, manufactured by Reichhold Chemical.

Caladene 25, cresylic resin, manufactured by Polymer Corp., Australia.

Solvesso 100, hydrocarbon solvent, boiling range 160-174° C., KB value 93, Standard Oil Co.

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Shell X4—petroleum fraction, boiling range 58-70° C., KB value 30.

Shell X55—petroleum fraction, boiling range 58-140° C., KB value 40.

Freon 11—dichloromonofluoromethane, manufactured by Du Pont.

Freon 113—trichlorotrifluoroethane, manufactured by Du Pont.

What I claim is:

1. A liquid developer for electrostatic images consisting essentially of an electrically insulating carrier liquid of volume resistivity in excess of 10^{10} ohm centimeter and a dielectric constant less than 3, particles of carbon black suspended in said carrier liquid as a toner, said carbon black particles having been previously wetted by grinding in an oil-containing dispersing medium, and a metallic soap in contact with said suspended particles of carbon black as a polarity stabilizer imparting positive polarity to such particles at least in the presence of a negative electrostatic field, said metallic soap being present in such quantity that the metal content of the soap is at least one percent by weight of the carbon black particles in suspension, and said metallic soap being selected from the group consisting of the linoleates of the metals cobalt, manganese, lead and zinc, naphthenates and resinates of the metals calcium, cobalt, manganese, lead and zinc, octoates and oleates of the metals calcium and cobalt, palmitate of the metal zinc and stearates of the metals aluminum, calcium, lead and zinc.

2. A liquid developer for electrostatic images in accordance with claim 1 wherein the linoleates, naphthenates, palmitate, stearates and resinates are present in such quantity that the metal content is not less than 1% and not greater than 25% by weight of the carbon black particles in suspension.

3. A liquid developer for electrostatic images in accordance with claim 1 wherein the octoates and oleates are present in such quantity that the metal content is not less than 1% and not greater than 2% by weight of the carbon black particles in suspension.

References Cited by the Examiner

UNITED STATES PATENTS

2,907,674	10/1959	Metcalfe et al.	117-37
3,038,799	6/1962	Metcalfe et al.	96-1
3,079,253	2/1963	Greig	117-17.5

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