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CONTROLLED AND FIXING LIQUID DEVELOPER FOR ELECTRO-PHOTOGRAPHY AND ELECTRO- RADIOGRAPHY

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This invention relates to the development of electrostatic images produced by electrostatic, electro-photographic or electro-radiographic means.

According to United States Letters Patent No. 2,907,674 liquid developers are described which utilize control and fixing agents to control the charge on pigment particles and to fix the particles to the area where they are deposited.

The present invention is directed to the use of particular groups of substances which are capable of acting both as control and fixing agents in liquid development processes, the object of the invention being to provide a group of substances which will give a selection of characteristics to meet different developing conditions.

In electro-photography it is customary to use a plate or paper having on it a layer of photoconductive material, such as amorphous selenium which in the dark will accept and hold an electrostatic charge, this plate being then exposed in any manner to vary the charge thereon according to the pattern of exposure to light or other influence and the plate is subsequently developed by applying thereto a powder having a charge, so that when the powder is applied to the plate it will be accepted by the plate in conformity with the charge on the various sections of the plate, this then producing an image in the powder.

One of the difficulties with this type of development has been to be able to distribute the powder finely and in uniform consistency because obviously if the powder is unevenly applied, the image will similarly be unevenly built up and will not be a time picture of the original exposure. Another difficulty is to fix the powder on the plate in a permanent manner because obviously in the industrial application of electro-photography it is essential that a permanent image will result, this permanence being at the present time usually obtained by including a resin which, after the dust has been deposited on the plate, can be fixed by subjecting the resin to heat. Another difficulty is to ensure that the powder has the correct polarity in relation to the charge on the plate and where the powder comprises more than one material which it is desired to co-deposit for example so as to form a mixed colour, to ensure that the plurality of materials all have the same polarity in relation to the charge on the plate.

The objects of the present invention are to improve the image and to produce it in a better manner this being achieved by wet development of the image, the invention being directed to the production of an electrostatic image on a suitable surface which is then developed on that surface or transferred to another surface, and developed by wetting the surface with a carrier liquid having an electrical resistivity sufficiently high to prevent destruction of the electrostatic image. This liquid carries dispersed in it a pigment which has a charge of the correct polarity or has added to it a control agent to modify the charge, to act in conjunction with the electrostatic image on the surface to develop the image, and a fixing agent to render

the pigment fast when the carrier liquid is evaporated or removed.

A most important aspect will at once be apparent that where the pigment comprises a plurality of materials, the control agent will act to confer a similar polarity and magnitude of charge on each of the said materials which makes possible the mixing of materials with different bulk chemical properties and different bulk physical properties for example the co-deposition of two or more colours to produce a mixed colour of desired tone shade or tint.

Where the pigment material is carried in a neutral high resistance liquid which will not destroy the charge on the plate, at least during the development period, the whole of the image will be uniformly subjected to the liquid in which the colour material is evenly and generally thinly dispersed and this will result in rapid deposition of the colour material in a density varying in proportion to the charge held by the various parts of the image, and as the suspending liquid is preferably a highly volatile one, evaporation of this liquid from the developed image will rapidly leave the image in a dry condition so that if a fixing agent has been added to the carrier liquid or if the developer has that characteristic, the pigment is left adhering rigidly to the surface which has been developed. The high resistivity insulating liquid also allows the particles carried by it to have and retain the necessary electrical characteristic, which characteristic can be varied by charging the liquid or by adding a control agent operative either on the liquid or the suspended matter.

When liquid development was first envisaged, it was suggested that the pigment particles should be suspended in a carrier liquid having an electrical resistivity sufficiently high to prevent destruction of the electrostatic image being developed such as the image on a photoconductor surface.

This was the state of the art at the time of filing the aforesaid United States Patent application. That specification however takes the liquid development process to a greatly improved form in that it teaches the art of controlling the charge on the pigment particles during development and also the art of simultaneously automatically arranging the conditions whereby the pigment particles are fixed to the surface being developed.

The advantages of using a control substance is that the particles of the pigment material, as well as the impurities present, are given a specific charge value and can thus be closely controlled by their movements.

The advantages of the automatic fixing of the particles are obvious, doing away with subsequent treatment and similar problems.

The present invention extends further the range of substances which can be used for specific types of development and relates to those substances which act as both control and fixing agents. In general the invention comprises mixtures of colouring material with combined control and fixing agents and carrier liquids for developing electrographic images and to methods of applying the mixtures.

In preparing the mixture of pigment together with the control agent in the carrier liquid, no special precautions need be observed. It has been found that the ratio of the pigment material to the carrier liquid is not critical although it is preferred that there be sufficient pigment material in the mixture to print more than one average print. It has been shown that the density of the image deposit may be varied by varying the ratio of the pigment material to the carrier liquid mixtures where the ratio of pigment material to the carrier liquid mixtures was equal to or greater than 1 to 100 parts by weight. Micronized powders have proved to be highly satisfactory, the particles having a mean diameter between 1 tenth micron

and 10 microns. Larger particles can be used where the resolution desired in the image is not critical.

An essential feature of the pigment-resin-carrier combination is that the combination should be a good insulator. Combinations of lesser insulation tend to discharge the electro-photograph without properly developing it. The pigment itself however need not be an insulator as long as the remaining components are; for example, use of metallic particles is permissible.

The invention is considered to function in the following manner: each small volume of carrier liquid has dispersed in it a number of the controlled particles which automatically have a charge of magnitude and polarity governed by the control agent. As the liquid contacts the plate the particles are given up to the charged areas on the plate, the attraction between the particles and the charged areas being stronger than that between the carrier liquid and the particles. The liquid picks up and carries away any particles which may tend to settle on uncharged areas, or if the plate is developed face down these particles gravitate away. If the liquid is selected to have a high specific gravity the pigment material may be more readily dispersed and utilised for development because of greater buoyancy.

It is necessary for the fixed image to be permanent and stable under the conditions normally encountered by printed materials, that it should not decompose or bleach by light or be readily attacked by micro-organisms. The completed image should also be relatively hard but sufficiently tough to be resistant to chipping under conditions of handling and use. The pigment material and fixing agent must be free of any reactive material such as acids which deleteriously react with the paper or other bases to cause deterioration in storage (unless there is an end use requiring reactivity to acid).

It is of course necessary that the toner have a prescribed colour either by virtue of the pigment or the bonding material. For general use in copying and printing a dense black is required but sometimes coloured images are wanted. The pigment material must be capable of dispersion to fine particle size such as 0.1 to 10 microns. In lithographic applications the pigment material must be transferable to or developable on a paper or metal master and when in position be ink accepting.

The compositions of the present invention meet the varied and exacting requirements mentioned above and comprise developers capable of producing permanent images on cloth, paper, plastic and metal surfaces and are also capable of forming printing images which are wettable by lithographic inks and are capable of bonding to both metal and paper offset plates to form durable printing plates for printing thousands of copies.

The characteristics of the substances forming the basis of this invention are as follows:

The substance must be capable of being softened or dissolved so that it can be applied as the outer phase to pigment particles (i.e., it coats said particles).

The substance must be such that it can remain as the outer phase throughout the development time to ensure that the substance is the electrically dominating factor but at the same time the substance must be capable of being held in a softened or partly dissolved state so that there is the required tackiness to allow the substance to be attached to the surface being developed and which on evaporation of the carrier liquid will then harden or otherwise change to fix the image.

Amongst the control agents, which also act as fixing agents, falling within the above category we have the rubber solutions which are a blend of natural and synthetic rubber such as the Dunlop Rubber solution, the safflower oil modified alkyds, the linseed oil modified penta-erythritol alkyds, and polystyrene.

The following examples are given to show how these various substances can be used as combined control and fixing agents.

EXAMPLE 1

Rubber

Synthetic and natural rubbers have been found to be useful in the compounding of liquid developer bases. These materials have been tested in conjunction in the form of a proprietary adhesive of the following composition:

	Grms.
10 Natural rubber -----	10
Hycar -----	10
Benzene -----	90

This material contains sufficient solvent to wet the pigment and form a developer paste of suitable consistency for hand grinding.

The mixed synthetic and natural rubbers would be expected to be usable as combined control and fixing agents due to the different solubilities of the two components. Thus it could be expected that Hycar would under certain conditions be usable as a control agent while the natural rubber could be expected to have fixing properties.

As it is desired to use the mixed rubbers as combined control and fixing agents, solvent or carrier choice becomes somewhat critical. It was found for instance that while satisfactory dispersions of rubber based developers could be made in Shellite, the control properties of such developers were somewhat erratic due to the degree of solution of Hycar in Shellite. This resulted in a developer which deposited on both image and non-image areas, with a consequent serious loss of definition. The desired solvent selectivity was found to be available in trichlorotrifluoroethane (Freon 113) which was consequently used as the base liquid for subsequent tests.

Varying quantities of the rubber mixture described were blended with carbon black using hand grinding techniques. These results are tabulated below.

Rubber sol., grms.	Carbon Black, grms.	Freon 113, ml.	Development results on zinc oxide paper (neg. charge)
5	2	100	Positive unfixed image.
10	2	100	Do.
20	2	100	Positive partially fixed image.
20	1	160	Positive fixed image.

It was found that, while a relatively small quantity of Hycar was sufficient to attain control of particle charge, the amount of natural rubber necessary in solution to attain adequate fixing was almost one order more.

The finally preferred rubber developer therefore contains 20 grms. rubber solution to 1 gm. carbon black, dispersed in trichlorotrifluoroethane (Freon 113) in the proportions of 1-5 grms. developer base/100 ml. trichlorotrifluoroethane.

Such a developer has a high degree of elasticity due to the characteristic of the rubber.

EXAMPLE 2

Safflower modified alkyd resins

The safflower oil modified alkyd resins are suitable for use in developer and coating formulations.

One resin of this group which is particularly effective is "Rhodene L45/60" by the Polymer Corporation

This is safflower oil modified alkyd resin of oil length 50%, acid value 6-10 and specific gravity 0.940-0.950.

Although the resin contains only 60% solids it was found to be necessary to add extra solvent in order to hand grind the desired resin/pigment ratio.

The formulations used was as follows:

	Grms.
Rhodene L45/60 -----	10
Mineral turpentine -----	10
Carbon black -----	20

The mix was hand ground using a pestle and mortar and the resultant base dispersed in Shellite. Varying proportions from 0.5-5.0 grms. base/100 ml. Shellite were found to be usable.

"Shellite" is the trade name for an aliphatic hydrocarbon solvent.

The developed image showed the resin to act as a positive control agent with a definite but slow fixing action.

EXAMPLE 3

Pentaerythritol alkyd resins

The pentaerythritol resins have been found useful as fixing agents due to their relative solvency in the various carrier liquids. Pentaerythritol alkyd resins act as control agents with enough solubility to act also as fixing agents.

A suitable resin is that sold by the Polymer Corporation under the trade name "Rhodene PC2/70."

This is a linseed oil modified pentaerythritol alkyd resin, of oil length 70%, acid value 6-10 and specific gravity 20° C. 0.955-0.965.

This resin, supplied as a 70% solution in mineral turpentine, is of vary long oil length, and provides a suitable combination of hardness and flexibility.

In compounding the base, Rhodene PC2/70 was used in two different forms. The first was the as-received material containing 30% mineral turps, which was hand ground with pigment to form a developer base. Proportions used were as follows:

	Grms.
Rhodene PC2/70 (as received) -----	10
Carbon black -----	14

The second form was the base resin which had dried on standing to be virtually pure resin at least partly polymerised. This material was heat-blended in mineral turps to form a solution before hand-grinding with pigment. Proportions used were as follows:

Rhodene PC2/70 (dried) -----	10 grms.	} Heat blended
Mineral turpentine -----	10 grms.	
Carbon black -----	20 grms.	

Materials from each of the preceding formulations were used separately as liquid developer bases. These were dispersed in various carrier liquids and used as liquid developers. They were found to disperse readily in Shellite, so this was the preferred carrier liquid. Dispersions of various concentrations were tested, generally 0.5 to 5.0 grms. developer base/100/ml. Shellite was found to be the most satisfactory range of concentration suitable for development of images on zinc oxide paper.

Rhodene PC2/70 base developers were found to be satisfactory for development of zinc oxide image surface, that is the resin acts as a positive control agent. It also exhibited strong fixing properties. Thus Rhodene PC2/70 can be classed as a resin useful as a combined control and fixing agent when used in conjunction with the carrier liquid Shellite.

EXAMPLE 4

Polystyrene solutions

The standard technique of grinding the dissolved resin or the like with the pigment was used and therefore the first requirement was the solution of the polystyrene in a suitable liquid. The most promising liquids were the aromatic and aromatic-containing hydrocarbons and hydrocarbon mixtures toluene, benzene and mineral turpentine. Solutions of the polystyrene in each of these liquids were therefore prepared and each was then separately ground with carbon black to form a developer base.

A polystyrene/mineral turpentine/pigment developer base was formed as follows:

The polystyrene was dispersed in mineral turpentine and also in benzene, and used as a developer. A positive fixed image was obtained.

When polystyrene is dissolved in toluene as the control agent (the pigment being hand ground with the polystyrene sol to form a developer base, and then dispersed separately into the carrier liquids) it was found that dispersed in mineral turpentine it formed a stable suspension which gave a positive partially fixed image, but when dispersed in a small quantity of mineral turps, and benzene was then added, a developer giving a high quality fixed image results.

If Shellite is added, the developer is also satisfactory but must be used immediately. A further series of tests was carried out using benzene as the solvent.

Polystyrene in benzene was tested in various carrier liquids and it was found that in mineral turpentine it dispersed to give a stable suspension which gives a high density positive permanent fixed image, and in perchloroethylene it gives a stable dispersion which gives a positive partially fixed image.

A method of preparing the developer base is as follows:

Polystyrene is first dissolved in benzene. 10 grms. polystyrene were digested in 70 grms. benzene and concentrated to a solution of total weight 47 grms., that is the final solution contains 10 grms. polystyrene and 37 grms. benzene or 21.3% polystyrene. Various weights of carbon black were ground with fixed portions of the solution to form developer bases of various pigment concentrations. The optimum was found to be a blend of polystyrene and benzene, and carbon black in a ratio of about 7:5 grams as follows:

	Grms.
21% polystyrene in benzol sol -----	7
Carbon black -----	5

Dispersed 1 gram. paste/100 grms. mineral turpentine.

Polystyrene base developer prepared as above gave a positive control with a heavy well fixed image deposit.

What is claimed is:

1. A controlled and fixing liquid developer for electric-photography and electro-radiography comprising a particulate pigment substance, a control agent coating the said particulate substance and constituting a control coating thereon, said control agent influencing the electrostatic behavior of said substance said control agent including in combination natural and synthetic rubbers, said agent forming a base with the pigment substance, and an electrically insulating carrier liquid for the coated pigment substance, said control agent being sufficiently soluble in said liquid to maintain the outer surface of the control coating in a partly dissolved state to constitute a fixing agent, said agent being sufficiently insoluble in said liquid to insure retention of at least part of the control coating on said substance throughout a developing operation, said coated pigment substance being suspended in the carrier liquid.

2. A developer as claimed in claim 1 wherein said liquid is trichlorotrifluoroethane.

3. A developer as claimed in claim 1 wherein said control agent is a blend including said rubbers and carbon black in a proportion of 20 grams of rubber to 2 grams of carbon black to 100 millilitres of said liquid, said liquid being trichlorotrifluoroethane.

4. A controlled and fixing liquid developer for electric-photography and electro-radiography comprising a particulate pigment substance, a safflower oil modified alkyd resin constituting a control agent coating the said particulate substance and further constituting a control coating thereon, said control agent influencing the electrostatic behavior of said substance, said agent forming a base with the pigment substance, and a carrier liquid for the coated pigment substance, said coated pigment substance being suspended in the carrier liquid, said control

7

agent being sufficiently soluble in said liquid to maintain the outer surface of the control coating in a partly dissolved state to constitute a fixing agent, said agent being sufficiently insoluble in said liquid to insure retention of at least part of the control coating on said substance throughout a developing operation.

5. A controlled and fixing liquid developer for electric-photography and electro-radiography comprising a particulate pigment substance, a control agent coating the said particulate substance and constituting a control coating thereon, said control agent influencing the electrostatic behavior of said substance, said agent forming a base with the pigment substance, and a carrier liquid for the coated pigment substance, said control agent being sufficiently soluble in said liquid to maintain the outer surface of the control coating in a partly dissolved state to constitute a fixing agent, said agent being sufficiently insoluble in said liquid to insure retention of at least part of the control coating on said substance throughout a developing operation, said coated pigment substance being suspended in the carrier liquid; said control agent being a blend including a safflower oil modified alkyd resin and mineral turpentine, said liquid being an aliphatic hydrocarbon solvent.

6. A controlled and fixing liquid developer for electric-photography and electro-radiography comprising a particulate pigment substance, a control agent coating the said particulate substance and constituting a control coating thereon, said control agent influencing the electrostatic behavior of said substance, said agent forming a base with the pigment substance, and a carrier liquid for the coated pigment substance, said control agent being sufficiently soluble in said liquid to maintain the outer surface of the control in a partly dissolved state, said agent being sufficiently insoluble in said liquid to insure retention of at least part of the control coating on said substance throughout a developing operation, said coated pigment substance being suspended in the carrier liquid, said control agent being a blend including a safflower oil modified resin, carbon black and mineral turpentine in a ratio of 10:20:10 grams, said liquid being an aliphatic hydrocarbon solvent in an amount of 100 millilitres for about 40 grams of said blend.

7. A controlled and fixing liquid developer for electric-photography and electro-radiography comprising a particulate pigment substance, a control agent coating the said particulate substance and constituting a control coating thereon, said control agent influencing the electrostatic behavior of said substance, said agent forming a base with the pigment substance, and a carrier liquid for the coated pigment substance, said control agent being sufficiently soluble in said liquid to maintain the outer surface of the control coating in a partly dissolved state, said agent being sufficiently insoluble in said liquid to insure retention of at least part of the control coating on said substance throughout a developing operation, said coated pigment substance being suspended in the carrier liquid, said control agent including a pentaerythritol alkyd resin.

8

8. A developer as claimed in claim 7 wherein said resin is a linseed oil modified pentaerythritol alkyd resin, said liquid being an aliphatic hydrocarbon solvent.

9. A developer as claimed in claim 7 wherein said control agent is a blend including a linseed oil modified pentaerythritol alkyd resin, mineral turpentine and carbon black in a ratio of about 10:10:20 grams, said liquid being an aliphatic hydrocarbon solvent.

10. A controlled and fixing liquid developer for electric-photography and electro-radiography comprising a particulate pigment substance, a polystyrene agent coating the said particulate substance and constituting a control coating thereon, said control agent influencing the electrostatic behavior of said substance, said agent forming a base with the pigment substance, and a carrier liquid for the coated pigment substance, said control agent being sufficiently soluble in said liquid to maintain the outer surface of the control coating in a partly dissolved state, said agent being sufficiently insoluble in said liquid to insure retention of at least part of the control coating on said substance throughout a developing operation, said coated pigment substance being suspended in the carrier liquid.

11. A developer as claimed in claim 10 wherein said control agent is a blend including polystyrene and hydrocarbon solvent.

12. A developer as claimed in claim 10 wherein said control agent is a blend including polystyrene and benzene, and carbon black in a ratio of about 7:5 grams, said liquid being mineral turpentine.

13. A method of fixing a developer substance, which is suspended in an electrically insulating liquid carrier, on a surface having an electrostatic image; said method comprising coating said substance with a material influencing the electrostatic behavior thereof and which substance is partly soluble in said carrier dispersing the thusly coated substance in said carrier whereby said material is rendered tacky, applying said carrier with the coated developer substance to said surface to deposit said coated developer substance on said image, and physically bonding said developer substance to said surface by means of said material.

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