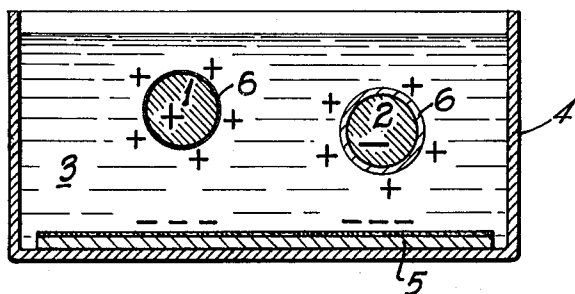


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CONTROLLED DEVELOPER FOR USE IN ELECTRO-PHOTOGRAPHY
AND ELECTRO-RADIOGRAPHY
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**CONTROLLED DEVELOPER FOR USE IN
ELECTRO-PHOTOGRAPHY AND ELEC-
TRO-RADIOGRAPHY**

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This invention relates to an improved controlled developer for use in electro-photography and electro-radiography.

According to United States Letters Patent No. 2,907,674 development processes for use in electro-photography and electro-radiography can be improved by providing a liquid developer which comprises developer pigment material suspended in an electrically insulating liquid and applying the developer to an electrostatic pattern.

To improve the control of the pigment movement, the aforesaid patent teaches the art of using a control agent for the pigment particles, which control agent has the effect of influencing the movement of the particles in the electrocally insulating liquid.

In said patent, the principal control agents are alkyl resins for a positively charged developer, and boiled linseed oil for a negatively charged developer, the control agent being applied to the particles by intimate mixing, such as milling, prior to suspending the particles in the carrier liquid.

The present invention relates to further substances which can serve as control agents under special operating conditions, and allow still further control of the development by giving a greater selection of the control agents.

Before referring to the control agents which form the subject of the present invention, it is desirable to discuss briefly the action of control agents on the developer particles as used in a liquid developer.

Any particle suspended in an insulating liquid has a surface charge dependent on the characteristic of the particle and the nature of the insulating liquid.

Where the suspending liquid has a sufficiently high electrical resistivity to prevent rapid bleeding away of this charge, the particle can readily be moved in such liquid under influence of an electrical field, such as the field caused by an electrostatic image.

The pigment particle may, however, not have the particular charge desired for developmental purposes, and the reason for using a control agent is to give the particle the necessary and required charge.

It will also be obvious that in a developer, foreign particles having a different charge sign or a different charge value might be present which would then be differently deposited, and if that is so, it will be found that the image developed will not have its true characteristic but surfaces which, for instance, should not have any developer deposited thereon might have the impurities deposited to cause a dirty image.

It therefore becomes highly important if effective development is to result, free from unwanted depositions, that the particle of the pigment shall be of the correct electrical characteristic, and it has been found that this can be effectively achieved by contacting the particles with a control agent and ensuring that the control agent is such that it will be the predominant characteristic effecting movement of the particles in the field.

The proportion of a control agent should be such that the particles can be adequately combined with the con-

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trol agent to ensure firstly that every pigment particle or impurity is given either a coating or is combined with the control agent to ensure that the control agent is the dominating factor, and secondly it is desirable to use up all of the control agent during such coatings so that there is not a surplus of free control agent in the liquid itself during development.

It is therefore an object of the present invention to provide a control agent suitable under the various conditions, and this has been achieved by selecting a control agent which is insoluble in a carrier liquid. For example, a suitable control agent can be selected from the group of substances comprising epoxy resins, the cresylic resins, the phenolic resins, the styrene modified epoxy resins, the synthetic rubber substances, and polystyrene.

In this specification control agents are considered as surface coating materials, the purpose of which is the modification of the electrokinetic properties of the coated material. Further, a control agent is one which coats the particle but is not soluble in the suspending medium.

The sole FIGURE of the drawing is a sectional and diagrammatical view of an apparatus for practicing the method of the invention.

In the drawing, particle 1 and particle 2 are shown as having opposite charges in the insulating liquid 3.

When suspended as shown in a vessel 4, the particles normally tend to agglomerate as they are attracted towards each other.

Assuming that 5 is a photo-conductor surface bearing an image charge thereon of a negative potential, the particle 1 would then be attracted to it whereas the particle 2 would be repelled.

However, if both the particle 1 and the particle 2 have a control agent 6 coated thereon which results in both particles having a positive effective charge, then the two particles will not agglomerate because they tend to move apart yet both particles will tend to be attracted to the photo-conductor surface to be deposited at the negatively charged localities.

The control agents must be such that they remain on the particles as otherwise the initial characteristic of the particles may become predominant and they will then not be moved in accordance with the characteristics required.

It is desirable in some cases to have a control agent which will not simultaneously act as a fixing agent, such as when it is desired to develop an electrostatic image and evaporate the carrier liquid and then to transfer the image to another surface, such as an adhesive surface.

The following examples illustrate the invention:

EXAMPLE 1

Cresylic Resins

A modified cresylic resin, being one of the methyl-phenol-formaldehyde condensates soluble in drying oils when modified with rosin and subsequently esterified with glycerol i.e. glycerolester of rosin modified methyl-phenol-formaldehyde is suitable as a control agent according to the invention.

One such resin is known under the trade name of "Caladene 5H" which is an alcohol-soluble modified cresylic.

This is a hard resin designed for use in low price general purpose varnish media and spirit varnishes, and has the following specification:

Acid value	90-110.
Color	15 max.
Melting range	105-115° C.
Sp. gr.	1.06.

Manufacturer: Polymer Corporation Interstate Pty. Ltd.

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As a hard resin this material needs to be dissolved in some solvent before being combined with other resins and pigments for use as a developer. This solvent must be compatible with the chosen developer carrier liquid and must be of suitable electrical properties. Lighting kerosene fulfils these requirements.

The pigment chosen was carbon black, a material normally difficult to use as a developer pigment in the as-received state, and consequently one which shows admirably the effect of any control agent under test.

The resin is digested in kerosene, and then mixed with carbon black pigment in the proportion of 1 part resin, 4 parts kerosene and 1 part carbon black, and the resultant paste is suspended in "Shellite" in the proportion 1 gm. paste to 100 grms. "Shellite." "Shellite" is an aliphatic hydrocarbon marketed by the Shell Company.

This is used as a developer to develop a line copy contact print on negatively charged zinc oxide paper, and gives a positive unfixed image.

"Caladene 5H" thus acts as a control agent which has no particular fixing properties.

This formulation may be used particularly where a hard, thermoplastic resin is required which can be heat-transferred or fused.

EXAMPLE 2

Pentaerythritol Alkyd Resins

A suitable resin from this sub-group is as follows: "Rhodene L42/70" (Safflower oil modified pentaerythritol alkyd), oil length 64%, acid value 6-10, specific gravity 0.965-0.975, manufacturer—Polymer Corporation.

This resin is supplied as 70% non-volatile in white spirit and consequently does not require heat blending. While white spirit is not an ideal carrier liquid the quantity present is insufficient to cause significant changes in electrical properties. Any further dilution is however preferably carried out with lighting kerosene or to a lesser extent toluene. The resin is sufficiently insoluble in the higher aliphatics for the resin to act as a control agent rather than a fixing agent.

In one case, 15 grms. of this resin were ground with 60 grms. carbon black in a pestle and mortar, with some dilution by lighting kerosene to aid the wetting of the pigment. The resultant paste was dispersed in "Shellite" in the ratio of 5 grms. paste to 100 grms. "Shellite."

When used as a developer, this suspension gives a positively controlled deposit with no particular fixing qualities.

Various proportions of resin/pigment were tested in order to assess the fixing properties of the resin, a condition to be avoided for this purpose. While reduction of the resin content to as low as 10 grms./100 of pigment did not materially affect control, raising the resin content to 100 grms./100 of pigment did not give appreciable fixing properties, and also resulted in loss of image deposit due to lowering of volume resistivity of the carrier. It will therefore be seen that the resin "Rhodene L42/70" is a useful control agent with no particular fixing properties.

EXAMPLE 3

5 grms. of a modified phenolic resin, acid value 90-110, melting range 105-115° C., specific gravity, 1.06, such as that known under the registered trademark "Caladene 6" of the Polymer Corporation is mixed with 10 grms. of lighting kerosene and heat-blended to cause solution of the resin in the kerosene, 15 grms. of carbon black being then ground into the mixture until the carbon black is coated with the resin.

The paste so formed is subsequently suspended in "Shellite" in the proportion of 0.5-5 grms. of the paste to 100 millilitres of "Shellite."

This is again a thermoplastic resin and has similar advantages to Example 1.

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EXAMPLE 4

Epoxy Ester Resins

The resin used in this example is "Epidene E168/50" by the Polymer Corporation.

40% Epon ester on tall oil.

Acid value..... Less than 5.

Fatty acid content..... 50%.

Solvent..... 100% aromatic.

This resin is strictly speaking not compatible with the normal carrier liquids, but when used as a coating on the pigment particles, does allow dispersion. The most suitable liquid appears to be mineral turpentine.

Formulation of Developer Base

The base used was compounded as follows:

	Grms.
Epidene E168/50	10
Carbon black	10

These were ground together using a pestle and mortar. In quantity preparation a ball mill would be suitable. The base was then suspended in various solvents.

Ground in mineral turpentine it gave an unfixed positive image.

It does not disperse in "Shellite," perchlorethylene, "Freon 11," "Freon 113," carbon tetrachloride or toluene.

Preferred Formulation

This resin only gives a stable developer when ground in a small quantity of mineral turps and then diluted with mineral turps to the required concentration as follows:

1 gm. of paste of section 9.1 is dispersed by grinding in 5 grms. mineral turpentine, the concentrated dispersion is then diluted with a further 95 grms. mineral turpentine to give a positive developer with no fixing properties.

A test was made to see whether a fixing agent could be added to this developer in the form of the Polymer Corporation resin "Rhodene L59/60," but this was unsuccessful as the "L59/60" appears to destroy the insulative properties of the carrier liquid. Carrier liquids used were perchlorethylene, "Freon," mineral turpentine and a mixture of perchlorethylene and "Shellite." Although stability of the suspensions was improved developer action was seriously impaired and the end result was not achieved. Thus this developer is useful for transfer operations only, or for use as a removable protective layer, having no significant fixing action.

EXAMPLE 5

10 grms. of styrene modified epoxy ester resin base on a blend of semi-drying dehydrated castor oils, oil length 35%, acid value 3.5-7, specific gravity 0.965, as sold under the registered trademark "Scopon 1130X" as sold by Styrene Copolymers Limited, is mixed with 10 grms. of benzol and 15 grms. of carbon black.

The mixture is ground until the required particle size is achieved and the particles of carbon black have been thoroughly coated with the resin.

Prior to use, 0.5-5 grms. of the paste is mixed with 100 millilitres of the suspending agent as follows: Firstly disperse the paste in 50 millilitres of benzol and then slowly add 50 millilitres of "Shellite" while stirring.

This is an acid and alkali resistant developer useful for say the name plates of washing machines and the like where the print is subject to the action of soaps and other materials.

EXAMPLE 6

5 grms. of methyl methacrylate as known under the trademark of "Kallodent" and marketed by Iclanz, is mixed with 5 grms. of carbon black and grinding is effected until the required particle size is reached and the particles are covered with the methyl methacrylate.

Before development, 0.5 to 5 grms. of this paste is suspended in 100 millilitres of "Shellite."

As "Kallodent" is of liquid consistency, it does not require prolonged grinding and can therefore be used where easy application of the control agent is required.

EXAMPLE 7

Synthetic rubber (butadieneacrylonitrile copolymer) known under the trademark of "Hycar" is mixed with benzene and carbon black in the proportions of 10 grms. of Hycar to 90 grms. of benzene and 5 grms. of carbon black.

After thorough mixing and milling, 1 grm. of this paste is suspended in 100 grm. of trichlorotrifluoroethane, as sold under the registered trademark "Freon 113" and the mixture used as a developer.

A synthetic rubber control agent is particularly useful where the trichlorotrifluoroethane is the carrier liquid, the rubber retaining its control characteristic in this agent.

All of the above stated control agents act by being intimately mixed and ground with the pigment substance so that each pigment particle has a coating or an adhesion of the control agent, the forming of a paste, in these cases where the substances which are ground together themselves would not form a paste being assured by including a solvent for the control agent during grinding to dissolve the control agent and ensure that it is applied to the surface of the particle in a liquid or semi-liquid phase where it will then form the outer phase of the particle and consequently be the controlling factor as far as the electrical charge of the coated particle is concerned.

As it is essential that such a control agent shall remain on the pigment particles irrespective of the suspending liquid which carries the particles during development, the liquid in which the suspension takes place is of such a nature that solution of the control agent does not take place, or if it does take place, the action is so slow and slight that even for the longest period of development, the particles will still remain coated to a sufficient depth to ensure that the control agent predominates electrically for determination of the surface charge and does not act as a fixer.

It will be realized that where the control agent is not soluble in the suspending liquid, and the initial solvent for the control agent during the production of the paste has been used in coating the particles, no adhering of the particles will take place and consequently after development the particles can be transferred to another surface or removed from their original site.

We claim:

1. An improved controlled but unfixed liquid developer for a xerographic image consisting essentially of, pigment particles in finely divided particulate form, an organic dielectric material capable of forming a resinous coating on the pigment particles, coating said pigment particles and adapted for insuring that the particles have a charge of substantially uniform polarity and magnitude, and a carrier liquid for said pigment particles in which said material is insoluble whereby said particles are moved and deposited under influence of the charge of the material when suspended in said insulating liquid but are not fixed to the image after evaporation of the carrier liquid.

2. An improved controlled but unfixed liquid developer for a xerographic image consisting essentially of, pigment particles in finely divided particulate form, an organic dielectric material capable of forming a resinous coating on the pigment particles coating said pigment particles and adapted for insuring that the particles have a charge of substantially uniform polarity and magnitude, said material being a cresylic resin, and a carrier liquid for said pigment particles in which said material is insoluble whereby said particles are moved and deposited under influence of the charge of the material when suspended in said insulating liquid but are not fixed to the image after evaporation of the carrier liquid.

3. An improved controlled but unfixed liquid developer according to claim 2 wherein the cresylic resin is an alcohol soluble modified cresylic resin in kerosene and in mixture with the pigment and in suspension in an aliphatic hydrocarbon as the carrier liquid.

4. An improved controlled but unfixed liquid developer for a xerographic image consisting essentially of, pigment particles in finely divided particulate form, an organic dielectric material capable of forming a resinous coating on the pigment particles coating said pigment particles and adapted for insuring that the particles have a charge of substantially uniform polarity and magnitude, said material being a pentaerythritol alkylid resin, and a carrier liquid for said coated pigment particles in which said material is insoluble whereby said particles are moved and deposited under influence of the charge of the material when suspended in said insulating liquid but are not fixed to the image after evaporation of the carrier liquid.

5. An improved controlled but unfixed liquid developer according to claim 4 wherein the pentaerythritol alkylid resin is a safflower oil modified resin in mixture with the pigment and kerosene in dispersion in an aliphatic hydrocarbon as the carrier liquid.

6. An improved controlled but unfixed liquid developer for xerographic images consisting essentially of, pigment particles in finely divided particulate form, an organic dielectric material capable of forming a resinous coating on the pigment particles coating said pigment particles and adapted for insuring that the particles have a charge of substantially uniform polarity and magnitude, said material being a phenolic resin, and a carrier liquid for said pigment particles in which said material is insoluble whereby said particles are moved and deposited under influence of the charge of the material when suspended in said insulating liquid but are not fixed to the image after evaporation of the carrier liquid.

7. An improved controlled but unfixed liquid developer according to claim 6 wherein the phenolic resin in mixture with kerosene and in suspension in an aliphatic hydrocarbon as the carrier liquid.

8. An improved controlled but unfixed liquid developer for xerographic images consisting essentially of, pigment particles in finely divided particulate form, an organic dielectric material capable of forming a resinous coating on the pigment particles coating said pigment particles and adapted for insuring that the particles have a charge of substantially uniform polarity and magnitude, said material being an epoxy ester resin, and a carrier liquid for said pigment particles in which said material is insoluble whereby said particles are moved and deposited under influence of the charge of the material when suspended in said insulating liquid but are not fixed to the image after evaporation of the carrier liquid.

9. An improved controlled but unfixed liquid developer according to claim 8 wherein the epoxy ester resin is in mixture with mineral turpentine and with the pigment to give a paste, the pigment being coated with the resin, the paste being in suspension in mineral turpentine as the carrier liquid.

10. An improved but unfixed liquid developer according to claim 8 wherein the epoxy ester resin is a styrene modified resin base on a blend of semi-drying dehydrated castor oil.

11. An improved controlled but unfixed liquid developer for xerographic images consisting essentially of, pigment particles in finely divided particulate form, an organic dielectric material capable of forming a resinous coating on the pigment particles coating said pigment particles and adapted for insuring that the particles have a charge of substantially uniform polarity and magnitude, said material being methyl methacrylate, and a carrier liquid for said pigment particles in which said material is insoluble whereby said particles are moved and deposited under influence of the charge of the material when

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suspended in said insulating liquid but are not fixed to the image after evaporation of the carrier liquid.

12. An improved controlled but unfixed liquid developer according to claim 9 wherein the methyl methacrylate coats said particles and forms a paste, and the said paste being in suspension in an aliphatic hydrocarbon as the carrier liquid.

13. An improved controlled but unfixed liquid developer for xerographic images consisting essentially of pigment particles in finely divided particulate form, an organic dielectric material capable of forming a resinous coating on the pigment particles coating said pigment particles and adapted for insuring that the particles have a charge of substantially uniform polarity and magnitude, said material being a synthetic rubber, and a carrier liquid for said coated pigment particles in which said material is insoluble whereby said particles are moved and deposited under influence of the charge of the material when suspended in said insulating liquid but are not fixed to the image after evaporation of the carrier liquid.

14. An improved controlled but unfixed liquid developer according to claim 13 wherein the synthetic rub-

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ber is in mixture with benzene and said pigment particles to produce a paste in which a coating of the synthetic rubber is formed over the said pigment, the said paste being suspended in trichlorotrifluoroethane as the carrier liquid.

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