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[54] **CHARGELESS DEVELOPER**

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[63] Continuation of Ser. No. 754,251, Aug. 21, 1968, abandoned, which is a continuation-in-part of Ser. No. 381,347, July 9, 1964, abandoned.

[30] **Foreign Application Priority Data**

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[51] **Int. Cl.** **G03g 9/04**

[58] **Field of Search** 252/62.1

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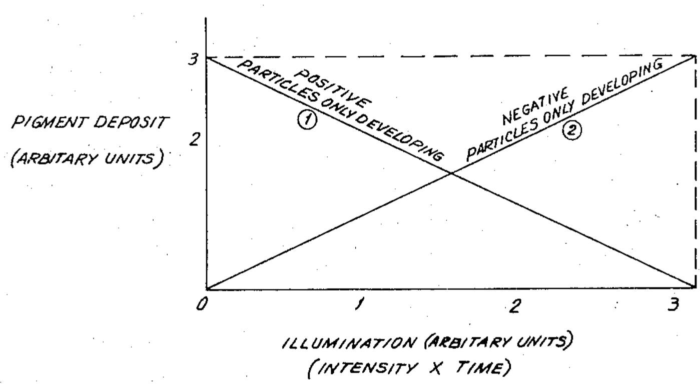
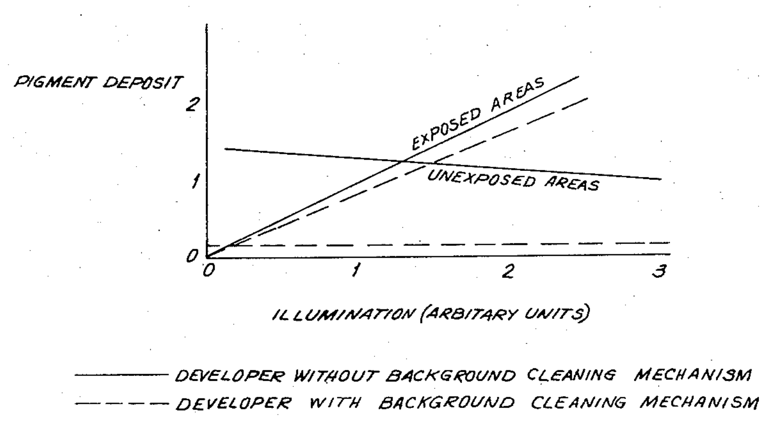
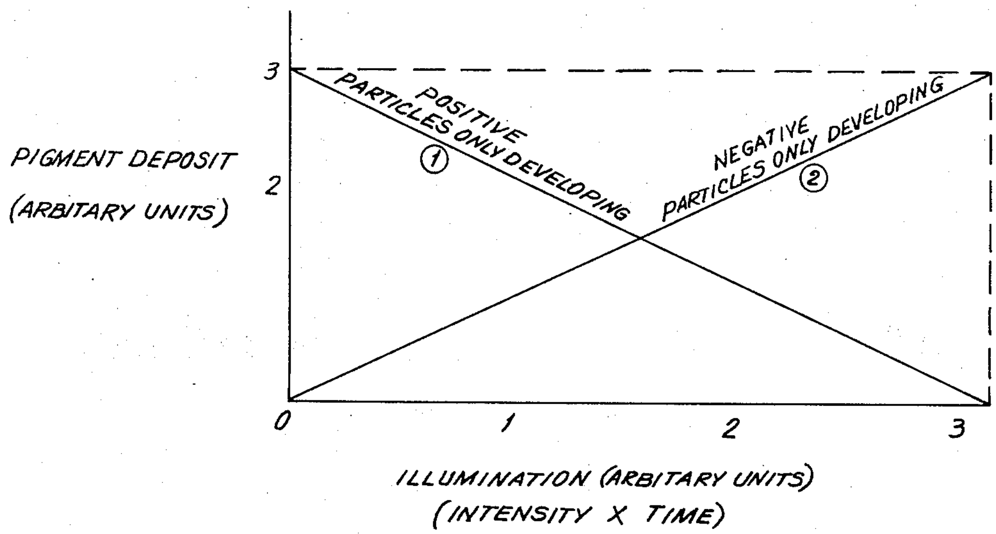
[57] **ABSTRACT**

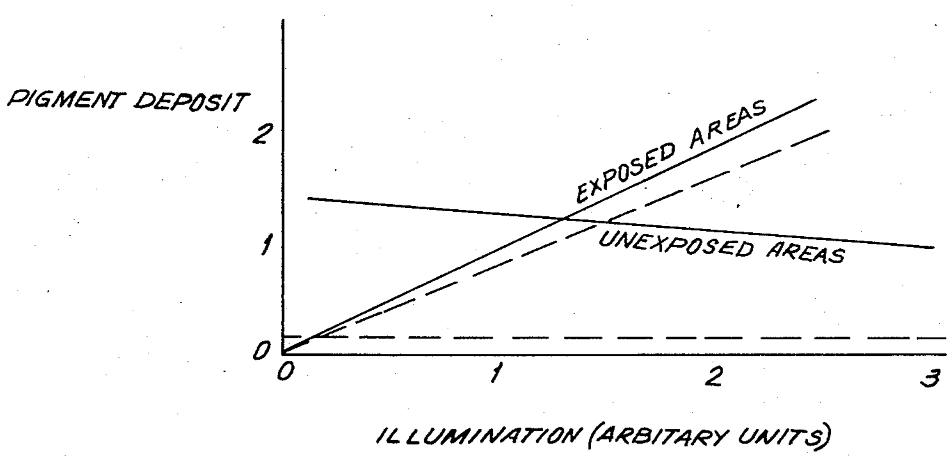
An improved developer for xerographic surfaces in which an image is produced without an applied charge, in which a controlled developer pigment of one polarity is suspended in an insulating carrier liquid, and a second developer medium also capable of acting as a developer, but of opposite polarity and incapable of wetting the first pigment, is used to enhance deposition of the first pigment in image areas and to shield the non-image areas against deposition of the first developer.

1 Claim, 1 Drawing Figure









——— DEVELOPER WITHOUT BACKGROUND CLEANING MECHANISM

– – – – DEVELOPER WITH BACKGROUND CLEANING MECHANISM

CHARGELESS DEVELOPER

This application is a continuation of Ser. No. 754,251, filed Aug. 21, 1968 and now abandoned which in turn is a continuation in part of Ser. No. 381,347 filed July 9, 1964 and now abandoned.

In normal electrophotography, using a layer of photoconductor distributed in an insulating body, a surface charge is placed on the aforementioned layer by a corona discharge. The electrostatic image is formed by exposing areas of the layer to light. Development is achieved by attracting charged particles to the unexposed areas which still retain a surface charge.

In the chargeless system, no surface charging is required. The surface of the layer, if kept in the dark for some days, will attract positively charged particles. This attraction can be stopped if the layer is exposed to light, so certain areas can be illuminated and an image produced that is a direct reproduction of the light image.

There is little evidence to indicate whether the visible image is formed by adsorption of developer material, or deposited by fields from the layer, or by fields from the developing particles, but it is certain that for these areas to develop, the liquid developer suspension must contain positively charged particles and it is these particles which form the image.

Where the layer is activated by light or X-rays and absorption of light or X-rays and activation by them is greater near the surface of the layer, the creation of charge carriers near the surface results in a field outside the layer, the direction of which is consistent with a layer of positively charged particles at the irradiated surface. An opposite field is also detectable at the opposite surface of the layer, that is where radiation leaves the layer.

The reason for suggesting the limitation that the absorption of radiation must be greatest near the surface is that if the radiation is sufficiently intense and prolonged, charge carriers will be formed to a saturation density throughout the layer and the positive field cannot be detected or developed.

The electrons and holes created near the irradiated surface, will diffuse away from these maximum absorption layers to regions of lower carrier concentration.

With zinc oxide, or any other photoconductor having unequal mobilities for the hole and electron, or with unequal trapping possibilities, one carrier may diffuse more than the other. If this occurs then the fixed carrier will have a greater concentration near the irradiated surface. In the case of zinc oxide, the holes have very low mobility and only the electrons diffuse away from the surface. This results in a potential gradient or hill similar to the junction potential of n and p type doped semiconductors, that is, the same resultant field as produced by a layer of positive ions on the surface of the layer.

For the direct image described, this diffusion field opposes the deposition of positively charged particles and gives the image a clean background.

Using negatively charged particles it is possible to develop the irradiated areas. If the dark-rested areas are designated negative because they attract positively charged particles and the irradiated areas are designated positive because they attract negative particles and we consider that the development of negative areas may be due to adsorption we find an explanation for the background density which occurs when an attempt is made to develop the positive areas. This background may be due to surface adsorption in the absence of a repulsion or shielding mechanism.

It has also been found that only one of the areas can be fully developed in a liquid developer. If an image is formed so that negative and positive areas exist on a layer, whether induced or otherwise, and the whole layer is immersed in a developer to fully develop one of the areas, then after development it is not possible to place the layer in a developer of the opposite polarity in order that the second area may be fully developed. Both areas develop in a developer, the area rendered visible denotes the polarity of visible particles in the developer which have the greatest sensitivity and concentration. If two or more particles are in suspension and a layer having positive and negative areas is immersed in the liquid, the type of image obtained is decided by the following considerations.

1. The speed of development and final density increases with concentration of a particular particle type in the suspension.

2. The final image-forming pigment is the particle with the greatest sensitivity, provided that it is present in sufficient concentration relative to other particle concentrations. A concentrated particle suspension may develop but later be displaced by a second particle of the same or opposite polarity which was not concentrated enough to gain first place on the layer, but by virtue of its sensitivity and relative concentration, replaced the deposited pigment either in the same area or in undeveloped areas by depositing in these areas as the previously developed image moves from the surface and into suspension.

This allows clean background and maximum image density to be achieved in the following manner.

A developer of the required polarity is used in a concentrated form in order to achieve greater image density. In direct (developing the negative areas) or reverse (developing the positive areas) chargeless development, this high concentration gives background, particularly in the reverse system where the negative areas may be developing partly by adsorption.

A second developer medium of opposite polarity is now incorporated in the suspension and if it is sensitive but of low concentration it will act as a low intensity developer for the areas which form the background of the visual image by virtue of its sensitivity. The low concentration will stop it from developing to such an extent as to decrease the visual (developed) image area density.

Although this effect can be demonstrated, it is by no means the only possibility because many pigments can be made to co-deposit on the same areas, but the above system illustrates why a means must be incorporated in a chargeless developer to obtain low background density and why both areas cannot be developed fully by using two developer types sequentially.

If only one pigment particle is present in the developer, the background charge is still satisfied because to achieve pigment sensitivity it is coated with a partly or fully soluble polymer and this polymer can satisfy the background adsorption or charge requirements to the exclusion of the visible or opaque pigment.

Although the dark adapted areas and illuminated areas have been designated negative and positive for ease of description, the development occurs as a difference between the fields from these areas and some reference level so that if a layer is exposed to radiation in discreet steps, development of the negative areas decreases with these steps. However, development of the positive areas, which increases with radiation up to saturation, does not require a certain constant value of illumination to erase the negative areas.

The development of positive areas is proportional to radiation for the first part of the curve at zero radiation. This means that some areas can be developed either direct or reverse.

The graph designated FIG. 1 shows the relationship between illumination and deposit.

It has been found that attempts to increase the deposit on positive areas, that is, reverse development were accompanied by an objectionable increase in background, but that this could be improved by satisfying these unwanted areas with a pigment or a polymer.

According to this invention the improvement consists in an improved developer which develops areas of a zinc oxide layer or other photoconductive layer to a denser image by virtue of a control layer placed on the pigment particle, which develops an even denser image by placing a soluble dispersing agent in the carrier liquid which has the property of keeping the suspended coated particles apart without interfering with their behaviour except to make them more sensitive because they are more finely divided; and which gives increased density and a clean background by having in the carrier liquid a second developer of opposite polarity to the major developing particle and of less concentration or a soluble control agent which is opposite in electrical effect on particles to the first control layer and which satisfies the background areas which are required to be kept undeveloped by pigment.

The improved developer can be said to consist of five parts:

A. The carrier liquid, usually an insulating vehicle such as an hydrocarbon which is commonly used in liquid electrophotographic developers.

B. A pigment, preferably of the same polarity as the desired final developing particle, that is, opposite in charge sign to the area to be developed.

C. A control coating which will make the pigment particle oppositely charged with respect to the surface to be developed, or increase its charge if it is already charged in the desired polarity.

D. A dispersing agent which will aid the dispersion of the mixture of B and C in the carrier A and create a finer suspension. (note: D can be a control agent for B in which case C is not used)

E. Separate from the aforesaid pigment, a dispersion of opposite charge polarity to the resultant particle charge after B and C are combined; or a control agent of opposite (polarity) effect to the one (c) which has been placed on the pigment, and which will exist dissolved in the carrier liquid if the particle is already coated, and act as a developer of opposite sign. Thus where C is stated as Cp for positive or C*n* for negative E, is hereafter sometimes referred to as Cn or Cp respectively.

As an example of the choice of B, C, D and E the following facts are noted.

Examples of B

Pigment	Chargeless response when A and B are mixed.
Carbon Blacks	negative
Peerless Blacks	positive
Monolite Blacks (ICI)	positive
Irgalite Fast Blue (Geigy)	positive
Vivid Magenta (Reichold)	negative
Brilliant Green (Coates)	negative

Examples of C

1. The vegetable and animal oils listed turn the following pigments negative or more negative.

Oils	Pigments to form a negative particle with these oils.
Linseed oil	
Sunflower seed oil	
Safflower oil	Carbon Black (Coates)
Tung oil	Vivid Magenta
Tall oil	Brilliant Green (Coates)
Peanut oil	Rose Red
Maize oil	Carbon Black (Kohinoor)
Soya oil	Carbon Black, Excelsior
Poppyseed oil	
Oiticics Oil	
Lanoline	
Castor Oil	
Boiled Linseed Oil	

2. The following mineral type oils and resins form positive particles when coated on the listed pigments.

B.P. Viscostatic Motor Oil	Irgalite fast brilliant blue GNS
Polybutyl methacrylate	Coates Brilliant Green
Various mineral lubricating oils	Monolite Black XS
Bitumen (Petroleum type)	Rubine toner R013/2B
	Rose Red

Examples of D

The following long oil alkyd resins can be used to disperse the product of B and C without decreasing their effectiveness as developers.

Super Beckosol	+ 1352– (Reichold Corp.)
Rhodene resin	+ PC2/70 (Polymer Corp.)
Paralac 10	(Imperial Chemical Industries)

Examples of E

1. The following can be added to reduce the background when incorporated in the developing product of B and C when B plus C is *negatively charged.*

a. The positive forming agents of C(2) above

b. Alcohols soluble or miscible

c. Pigments which are strongly positive, but low in concentration

d. Bitumen (Petroleum type)

2. The following can be incorporated in the developer to clean the image background when the developing product of B and C is *positively charged.*

a. All the negative forming oils

b. Low concentrations of negative pigments dispersed with any long oil alkyd of the series D.

It will be noted that the polymer system is composed of four parts and for a reverse developer to develop positive areas the role of each is as follows:

A — The carrier liquid-insulating medium

C — The charge forming control agent (e.g. a Vegetable oil)

D — The dispersing agent (e.g. a long oil alkyd resin)

E — The background cleaning agent, usually a control agent opposite to C (e.g. Bitumen)

The following examples illustrate the action of the components in the system as described earlier. The tables show the behaviours of various systems when in order in which the components are added is changed and the developer is tested after each change.

TABLE I

Effect of sequence of wetting on polarity.

Developer 1

1 gram Pigment (B):	Coates Fast Brilliant Green
3 grams Negative control agent (Cn):	Sunflower seed oil
2 grams Dispersant (D)	Long oil alkyd resin such as Super Beckosol 1352, Reichold Corp.
5 grams Background cleaner (Cp) being a Positive control agent:	B.P. Viscostatic Motor oil, British Petroleum Co. This cleans background but if used alone tends to turn a pigment positive.

Developer 2.

1 Gram Pigment (B):	Brilliant Green, for example Coates & Co.
5 grams Positive Control agent (Cp):	B.P. Viscostatic Motor oil
2 grams Dispersing agent (D):	Long oil alkyd resin, e.g. Super Beckosol + 1352
3 Grams Background cleaner (Cn) being a negative Polymer:	Sunflower Seed oil

Developer No. 1 is a reverse developer consisting of negative developing particles and deposits on radiated or illuminated areas.

Developer No. 2 is a direct developer consisting of positive developing particles and deposits on the darkrested areas, shielded from radiation or illumination.

TABLE II

Pigment (B)

1 gram "Brillfast" Vivid Magenta 3964 (Reichold Chemical Ind.)

3 grams negative control agent (cn): Sunflowe seed oil

2 grams Dispersant (D): A long oil alkyd resins such as Super Beckosol 1352.

5 grams Background cleaner (Cp) B.P. Viscostatic Motor

being a positive control agent: Oil, British Petroleum Co.

Components and Sequence	Polarity	Density	Background Sensitivity (Arbitrary units)
A. B.	negative	0.4	very weak 1.0
A+B+Cn	negative	0.5	weak 2.0
A+B+Cn+D	negative	2.6	weak 3.0
A+B+Cn+D+Cp	negative	0.3	strong 6.0
A+B+Cp	zero	0.0	no image
A+B+Cp+D	negative	0.5	very weak 1.0
A+B+Cp+D+Cn	negative	0.4	weak 2.0

This pigment can be turned positive if the sequence and relative quantities of Cp and Cn are varied as the above results are not the only ones possible. It will be noted that the positive and negative control agents have opposite charge forming characteristics. The pigment used in this example can be formed negative or positive depending on whether the negative or the positive control agent was first placed on the pigment. Many pigments respond in this way but this is one which can be changed either way and which will remain in the desired state. In many cases the pigment itself is strongly charged, opposed the tendency to move its charge in the opposite direction, and slowly reverted to its natural polarity but with marked decrease in chargeless response. If the pigment has a natural polarity and the control agent is of the type to move the charge to greater magnitude in that direction, then the best results are obtained. TABLE II illustrates a negative pigment and shows that maximum chargeless response and low background density obtained only when the correct and complete sequence is used.

Providing that the pigment and the first control agent have sufficient affinity for each other it is often possible to produce developers by grinding B, C, D and E together using only a fraction of the desired quantity of E.

The following formula gives a reverse developer for illuminated areas and all components can be milled together because of affinity between B and Cn. However the effect of leaving out one of the components is illustrated by TABLE III.

Developer No. 3.		
1 gram Pigment (B):	"Kohinoor" Carbon Black	100 grams
3 grams Control (Cn):	Sunflower Seed Oil	300 grams
2 grams Dispersant (D)	Long oil alkyd resin such as Super Beckosoi 1352 Reichold Corp.	200 grams
5 grams Background Cleaner and control (Cp): B.P.	Viscostatic Motor Oil	500 grams

Bar mill all the ingredients, and disperse 10 grams of concentrate in 100 grams of carrier liquid (A) which is "Shellite". The background cleaner (Cp) required can be made by dispersing 10 grams of B.P. Viscostatic Motor oil in Shellite and this is used as a predip, either before or after exposure and with or without drying by evaporation. The reflection density readings for this developer when combined part by part is as follows:

Components present	Polarity	Image Density	Background Density
			(No prewash of Cp)
A+B	Negative	0.0	0.0
A+B+Cn	Negative	0.06	0.04
A+B+Cn+D	Negative	0.57	0.44
A+B+Cn+D+Cp	Negative	0.54	0.04
A+B+Cp+D+Cn	Negative	0.53	0.09

As shown earlier in this specification, if one surface polarity is developed heavily, the other will only develop lightly due to the fields set up, and this factor is used in this invention to obtain a maximum contrast by a heavy image deposit and a light background controlling deposit.

While it is difficult to assess the exact conditions which apply when unequal dual development is effected as described, as pointed out earlier in this specification, it may help to consider that with the methods known heretofore the latent image produced by a modification of a darkrested photoconductor layer by light or the like will produce a charge pattern or gradation which will cause the non-image or lesser image areas to have a relatively different potential due to field lines induced by the charge so that it can be assumed that during development the non-image areas will be of relatively opposite charge and will tend to repel the developer particles, but as the developer builds up on the image areas the presence of the developer on the image, because it is of the opposite polarity to the initial image, modifies the fields in such a way that the repulsion of the developer particles from the non-image areas is reduced with consequent deposition of some developer particles in the non-image areas.

To overcome this, the present invention includes with the developer particles, a substance of opposite polarity, but of lesser effect due to quantity or other factors, which has the effect of driving down more developer particles on to the appropriate image area and also of shielding the background areas against contact with pigment particles.

For separate deposition of the two opposite developer components it is essential that both the pigment particles and the shielding medium be kept mobile, and this is achieved by the dispersing agent which lessens attraction between these substances in spite of their opposite charge and therefore even if the oppositely charged components coelesce, it will be obvious that the pigment particles, as they move into the field of the oppositely charged areas will separate from the shielding medium which will move into the background areas at least partly by reason of the induced field.

Thus during development, the pigment substance will deposit on the areas where it is attracted by the field of the image on the photoconductor surface while the shielding medium will deposit on the background areas under influence at least in part of the induced field.

As the developer builds up on the image areas, so the induced field lines are modified with the result that the repelling medium and any pigment deposited on it may be released, to clear the background area.

Thus during the developing action there is deposited in the background areas a shielding substance on to which developer particles may deposit but this shielding substance is released or releases the pigment particles as the induced field is modified and a clean background is then left. Agitation or washing may enhance this cleaning.

It will be realised from the illustration that both surfaces cannot be developed fully in relation to the charges existing and therefore the background developing medium is chosen to develop to a lesser amount while the developer itself is arranged to deposit in a much greater amount. The further apart in intensity of development in which these two developer phases can be kept, the better the contrast due to the clean background and a heavily developed image.

As stated earlier the added opposite developer medium increases developer particle sensitivity to give a heavier deposition, while shielding the background areas from visible contamination.

The foregoing tables and explanations show the considerations which must be understood to carry the invention into effect, and the following examples show how actual developers were prepared, using the invention outlined in this specification.

EXAMPLE 1

A developer paste was prepared by mixing the following materials together in the order given:

Brillant Green pigment (Brilliant Vivid Green 3458, Smith Reichold Colours Ltd., Sydney Australia): 100 grams

Sunflower seed oil (Meggitts Ltd. Australia): 300 grams

The pigment was wetted with the sunflower seed oil and milled to form a paste.

To this paste was added the following alkyd resin:

Super Beckosol 1352 (product of Smith Reichold) Colours, Sydney, Australia): 200 grams

The resultant mixture was then milled with the following cleaning agent:

B.P. Viscostatic motor oil (B.P. Aust. Ltd.): 500 grams

The paste obtained as a result of mixing these materials together in the order given was diluted with Alsol 35/140 in the proportions 1 part by volume of paste to 100 parts of insulating carrier liquid, but is should be stated that any suitable insulating carrier liquid could have been used. Greater dilutions may be used if necessary. Alsol 35/140 is a hydrocarbon liquid containing 11 per cent aromatics supplied by the Esso Standard Oil Co. Ltd., Australia.

EXAMPLE 2

A developer paste was prepared by mixing together the following materials in the order given:

"Kohinoor" Carbon Black (A.C. Hatrick Ltd. Australia): 100 grams

Sunflower seed oil (Meggitts Ltd. Australia): 300 grams

These materials were milled together to form a paste. To this paste was added the following materials:

Super Beckosol 1352 resin (an alkyd resin supplied by Smith Reichold Colours Ltd. Sydney Australia): 200 grams

These materials were then milled together to a paste consistency, following which a background cleaning agent was added and milled into the mixture. A suitable cleaning agent was found to be a dispersion of blow bitumen (petroleum type) comprising 1 part by weight of bitumen in

100 parts of Alsol 35/140: 500 grams

Bitumen of suitable type was obtainable from B.P. Australia Limited as solid bitumen. The paste which was obtained by mixing these materials constitutes a developer concentrate and was then diluted with a suitable hydrocarbon liquid or other insulating liquid such as a silicone oil or fluid to form a developer. A suitable liquid as is for example Shell solvent X4 and the proportions are typically 1 part of paste by weight to 100 parts of X4 but a large range of dilutions is acceptable. X4 is a solvent marketed by Shell Chemicals Ltd., and contains 1 per ent aromatics and has a boiling range of 55° to 72° C.

EXAMPLE 3

A developer paste was made from the following materials mixed together in the given order:

Irgalite Fast Brilliant Blue GLSM (Geigy, Switzerland): 100 grams

Maize oil (Meggitts Ltd., Sydney, Australia): 300 grams

The pigment was wetted with the maize oil and milled to form a paste to which was subsequently added the following resin:

Rhodene resin PC2/70 (Polymer Corporation, Sydney, Australia): 200 grams

(Linseed oil modified pentaerythritol alkyd resin, acid value 6–10, 70 per cent oil length)

A background cleaning agent was then added as follows:

Shell lubricating oil, S.A.E. 20: 300 grams

The resultant developer concentrate was then diluted with a suitable insulating liquid such as Shellsol T, a product of the Shell Chemicals Co. Sydney, Australia, in the proportions of 1 part of concentrate to 100 parts of liquid diluent. Shellsol T is a hydrocarbon solvent having a boiling range of 180° to 206° C. and a flash point of 130° F.

EXAMPLE 4

A developer paste was made from the following materials mixed together in the following order:

Brillfast Vivid Magenta 3964 (Smith Reichold Colours Ltd., Sydney, Australia): 100 grams

Tung Oil (China-wood oil) (Meggitts Ltd., Sydney, Australia): 300 grams

These materials were milled together to form a paste to which was subsequently added the following:

Paralac 10, oil modified alkyd resin (Imperial Chemical Industries of Australia and New Zealand): 250 grams

A background cleaning agent was then added and milled into the mixture to form a paste, for example:

Solution of Lucite 2046 in toluol comprising 25 per cent of Lucite by weight: 25 grams

The resultant concentrate was then diluted with a suitable insulating liquid such as X4 solvent, a product of the Shell Chemicals Co., Australia, in the proportions of 1 part of concentrate by weight to 200 parts of X4. Lucite is a copolymer of n-butyl and isobutyl methacrylate and is a product of the DuPont Corporation, United States of America.

EXAMPLE 5

A developer concentrate was made from the following materials mixed together in the order given below:

Monolite Black XS (Product of Imperial Chemical Industries of Australia and New Zealand): 100 grams

Poppyseed oil (Meggitts Limited, Australia): 200 grams

These materials are mixed together to form a paste to which was added subsequently an alkyd resin such as:

Super Beckosol 1352 (Smith Reichold Colours Limited, Australia): 200 grams

A background cleaning agent was then added and milled into the concentrate such as:

Liquid paraffin oil WM 6 (B.P. Australia Limited): 300 grams

The resultant paste was a developer concentrate which was then dispersed in a suitable insulating liquid, such for instance as Isopar H, in the proportions of 1 part of concentrate to 200 parts of Isopar H by volume. Isopar H is an isoparaffinic solvent with a high boiling range containing zero aromatics supplied by Esso Standard Oil (Aust.) Limited.

EXAMPLE 6

A developer concentrate was made from the following materials mixed together in the following order:

Brillfast Vivid Green pigment G3248, (Smith Reichold Colours Limited, Australia): 90 grams

B.P. Viscostatic motor oil, product of B.P. Australia Limited, containing polyester resins and zinc dithiophosphate as a surfactant: 450 grams

These materials were milled together to form a paste to which was subsequently added the following material:

Dispersing agent, long oil alkyd resin, Rhodene L42/70 (Product of Polymer Corporation Limited, Australia): 180 grams

The following material was added subsequently to act as a background cleaner in relation to the foregoing materials of this example:

Oiticica oil (Meggitts Limited): 270 grams

The final concentrate was added to an insulating liquid to form a developer; a typical carrier liquid for this purpose being Shellsol T or Isopar H. Other liquids which may be used include perchloroethylene, the fluorinated-chlorinated hydrocarbons such as the Freons and Arctons, cyclohexane, deodorized kerosene and the like.

We claim:

1. An improved developer for use in chargeless developing of a xerographic surface having thereon a latent electrical image of a first polarity and a background outside of said image and of a relatively different polarity, said developer consisting essentially of a hydrocarbon liquid carrier having an electrical resistivity sufficiently high and a dielectric constant sufficiently low to avoid destruction of said latent image, pigment particles suspended in and possessing an electrical charge in the said carrier liquid and mobile therein to form a developer medium for the image, a control agent coating the surface of the pigment particles to form controlled pigment particles and control the polarity thereof and to increase the charge of the controlled particles in a direction opposite to that of the image on the surface to be developed, a dispersing agent for the pigment particles in the carrier liquid to enhance dispersion of the controlled pigment particles in said carrier, and a second developer medium of a polarity opposite to the polarity of the controlled pigment particles dispersed in the said liquid carrier, said second developer medium being such that it does not wet the pigment particles and is therefore mobile independently of the particles and does not alter the charge of the latter, said second developer medium being an organic or a mineral oil or bitumen having a charge of lesser electrical magnitude than the pigment and forming in said liquid carrier a suspension which is of a polarity opposite that of the background and controlled pigment particles and which thereby deposits outside of the image on said background to form a shield during development to lessen contamination of the background of the image by the pigment particles, there being approximately 1 gram of pigment particles to about 3 to 5 grams of control agent for the pigment and about 2 grams of dispersing agent and about 3 to 5 grams of the second developer medium.

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