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3,512,965

ELECTROPRINTING METHOD

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No Drawing. Filed July 9, 1964, Ser. No. 381,541
Claims priority, application Australia, July 12, 1963, 32,965/63

Int. Cl. G03g 13/10

U.S. Cl. 96—1

6 Claims

ABSTRACT OF THE DISCLOSURE

Improved electrostatic images are achieved by treating the photoconductor or insulating layer with a barrier substance prior to the development of any visible image using a liquid developer. The barrier substance prevents the liquid developer from depositing on or contaminating the background or non-image areas when the developer is applied to the electrically defined (invisible) image; or in other words, the barrier substance restricts the toner liquid to the image and repels it from the background area.

This invention relates to electrostatic printing including electrophotography and more particularly it relates to a method of and means for treating surfaces on which latent electrostatic images and conductivity patterns, herein termed "electrically defined images," are formed and subsequently rendered visible by developing with toner material.

In electrostatic printing an insulating surface is provided with an electrostatic charge pattern in selected areas conforming to an image and such charge pattern is subsequently rendered visible by the application of developer material which may be attracted and held electrostatically to the charged areas of the insulating surface.

In electrophotography a relatively conductive backing member such as metal or paper sheet having deposited thereon a photoconductive layer such as for instance zinc oxide in a resin binder commonly known as an electrophotographic or Electrofax layer is first subjected to a corona discharge whereby a uniform electrostatic charge is deposited onto the photoconductive layer. Such charged photoconductive layer is then exposed to a light or X-ray pattern whereby the irradiated areas become discharged whereas the shielded areas remain charged and thus form a latent electrostatic image. Such latent electrostatic image is then rendered visible by applying a dry developer powder or a developer material suspended in an insulating liquid dispersant in order that such developer may be attracted and held electrostatically to the charged areas. The developed image may be fixed to the surface of the photoconductor or it may be transferred to another surface and fixed thereon, if desired.

In another type of electrophotography the uncharged photoconductive surface is subjected to a radiation pattern whereby the resistivity of such photoconductive surface is changed in proportion to the intensity of the incident radiation and whereby a latent conductivity pattern in the photoconductive layer is formed. Such latent conductivity pattern in the photoconductive layer can be then rendered visible by the liquid developer methods as disclosed in our co-pending patent applications Nos. 27,714 (Australia) and 33,899 (Australia), wherein an electrostatic field is utilized to enhance toner or developer material deposition to render such conductivity pattern visible. We have also found that it is possible to render such conductivity patterns visible especially in electrophotographic layers without an assisting electrostatic

field provided the liquid developers used possess certain characteristics and in particular if such developers are highly sensitive to minor variations in the constitution of the photoconductor surface effected by exposure to radiation.

As referred to in the foregoing, in the liquid developing process it is customary to prepare a liquid developer for electrostatic images by dispersing certain particulate matter such as pigment with an oil or resin or an oleo-resinous varnish in an insulating liquid, the polarity of such particulate matter in respect to the latent electrostatic image to be developed being determined by the nature of the materials selected for the developer or by so called polarity control or stabilizing agents, as for instance described in the U.S. Pat. Nos. 2,907,674 of K. A. Metcalfe et al., and 3,076,722 of H. G. Greig and our patent application No. 237,294 (U.S.), now Pat. No. 3,259,581, granted July 5, 1966.

Certain disadvantages are characteristic of the electrostatic printing processes. One disadvantage is the slow speed of printing relative to mechanical printing. Another disadvantage is the difficulty of keeping the background or non-image areas of the sheet free from toner material. For instance, in facsimile reproduction where the toner material is attracted to all charged areas, in order to fill in large solid areas the toner material must have a relatively high degree of sensitivity which always gives rise to the formation of undesirable background contamination due to residual minute charges attracting the sensitive toner material or due to staining when highly concentrated liquid developers are used for fast image formation. The above faults occur also in reversal reproduction that is where for instance a positive copy is produced from a negative original which in electrophotography is achieved by the so called repulsion development where the developer material is repelled by the latent electrostatic image charges and is caused to deposit onto the exposed areas relatively free of charge. Strong staining of background areas with consequent decrease in contrast occurs particularly when sensitive and highly concentrated liquid developers are used to render visible conductivity patterns as hereinbefore referred to.

Accordingly, it is a general object of this invention to provide a novel method of and means for preventing background or non-image contamination in electrostatic printing and in electrophotography employing liquid developers.

A further object of this invention is to provide a method of and means for treating surfaces for use in electrostatic printing and in electrophotography employing liquid developers for the purpose of preventing background or non-image contamination.

A still further object of this invention is to provide a method of and means for treating surfaces for use in electrostatic printing and in electrophotography employing liquid developers for the purpose of increasing image contrast.

Another object of this invention is to provide a method of and means for treating surfaces for use in electrostatic printing and in electrophotography for the purpose of preventing background or non-image contamination and increasing image contrast when sensitive liquid developers capable of forming images at high speeds are employed.

Yet another object of this invention is to provide a method of and means for treating surfaces for use in electrostatic printing and in electrophotography for the purpose of preventing background or non-image contamination and increasing image contrast when high concentrated liquid developers are employed which contain a minimum quantity of the dispersing liquid and thus reduce fire hazard and image drying problems.

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The foregoing objects and other advantages are accomplished in accordance with this invention it having been found that it is possible to treat photoconductive or insulating surfaces containing imagewise electrical patterns, which are to be rendered visible by liquid development, by forming on such surfaces prior to applying the liquid developer a barrier layer comprising a substance or a mixture of substances which, whilst not affecting due to their electrical resistivity or dielectric characteristics the said imagewise electrical patterns, have a greater wetting power in relation to the said surface than the developer liquid in order that such substances may not be desorbed or removed to a substantial extent during the developing step by the developing liquid, for the purpose of protecting the said surface wetted by the said substances forming the barrier layer thereon from being further wetted by the developing liquid during the developing step and for the purpose of preventing developer material from depositing onto non-image areas whilst permitting developer material to deposit onto the surface only under the pronounced influence of the electrical patterns contained imagewise on the said surface. The presence of such barrier layer on a photoconductive or insulating surface enables one to apply highly concentrated and sensitive liquid developer material to such surface because the barrier layer permits the developer material to deposit onto such surface only in areas characterized by the presence of imagewise electrical patterns whilst preventing staining caused by deposition of developer material in non-image areas.

In accordance with the principles of this invention the surface is treated just prior to the developing step wherein a liquid developer is employed said treatment consisting of applying to the surface a barrier layer in the form of a wet surface layer by contacting the surface with a liquid comprising the barrier substance or containing the barrier substance dissolved or dispersed therein. The surface containing the wet barrier layer is subsequently contacted with the liquid developing material.

The barrier layer may be present on the surface in the form of an adsorbed or absorbed or chemisorbed layer or film which may also fill the interstices contained in the surface. Such interstices contained in the surface may also be filled by the barrier substance being incorporated into the material forming such surface. Although it is not intended to be bound to this model, at this state of knowledge it appears that the process depends on the action of the barrier layer contained on the surface in protecting such surface when contacted with liquid developer material from capillary absorption or from adsorption or chemisorption of the developer material in the non-image areas by reason of such barrier layer being capable of preferentially wetting said surface and thus forming a layer therein preventing further wetting of the surface and permitting the developer material to be attracted to the surface only where aided by the pronounced surface changes, particularly in the way of the modification of the interfacial tension between the surface containing the barrier layer or the barrier substance incorporated therein and the developer liquid, induced by an imagewise electrical pattern or by an electric field associated with such pattern. Such electric field may be an electrostatic field associated with a latent image formed by electrostatic charges, an electrostatic field formed by the presence of a conductivity pattern contained in a photoconductive layer or it can be an external electric field. It is also possible that the process depends partly on electrical repulsion between the barrier layer or the barrier substance contained in the surface and the developer material in case both the barrier layer or barrier substance and the developer material carry charges of the same polarity, such repulsion being overcome and developer material being deposited only in areas influenced by an electric field as hereinbefore described. Furthermore it is also possible that the process as applied in

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the second embodiment of this invention depends partly also on the barrier substance contained in dissolved or dispersed form in the liquid or comprising the liquid which is applied to the surface prior to the developing step being of opposite polarity to the developer material to follow and thus depositing under the influence of the aforesaid electric field onto the non-image areas of the final print whereby the field influence or the charges which may have been contained in such non-image areas become neutralized and are thus no more capable of attracting sensitive developer material during the subsequent contact with the liquid developer.

The substances which can be employed to form a barrier substance in accordance with this invention may contain nonvolatile matter or may be of a completely volatile nature if desired. In each case however the barrier substance must be capable of wetting the surface to such degree that upon later contact with the liquid developer the barrier substance does not desorb from the surface or does not become replaced on the surface by the developing liquid. For this purpose the barrier substance must have a greater wetting power in relation to the surface than the developer liquid and in the case where the barrier substance comprises non-volatile matter it must not be readily soluble in the developer liquid that is to say it must not be fully dissolved by the developer liquid and thus removed from the surface during the developing step which applies particularly in case the barrier layer contains or comprises a substance which due to its electrical properties or polarity characteristics or chemical constitution whilst not affecting the imagewise electrical pattern contained on the surface yet may contaminate the liquid developer due to its incompatibility with the particular composition of such developer. It is also essential that the barrier substance or the liquid containing the barrier substance dissolved or dispersed therein does not affect the surface such as for instance a photoconductive surface for instance by solvating or softening the binder material for the particulate photoconductor or by chemically affecting the photoconductor itself. Furthermore it is preferable that the barrier substance should be substantially colourless or transparent in order that, unless otherwise desired, it may not affect the basic colour of the surface to which it is applied and this is particularly the case when such barrier substance comprises non-volatile matter forming a residual film in the non-image areas of the surface after developing and drying such surface.

The barrier substances can be applied to the surface in the form of a 0.5% to 10% solution or suspension of the barrier substance in a liquid or the barrier substance itself can be a liquid. Barrier substances which can be applied from solution or suspension in a liquid, being representative only of many, are vegetable oils such as safflower oil, linseed oil, dehydrated castor oil, sandalwood oil, clove oil and the like, mineral or synthetic oils such as paraffin oil, engine lubricating oils, chlorinated diphenyls, silicone oil and the like, metallic soaps such as oleates of sodium, of zinc and of copper, stearates of aluminium and zinc, alcohols such as nonyl alcohol up to 10% dissolved or dispersed in a hydrocarbon solvent and iso-propyl alcohol up to 1.5% dissolved or dispersed in a hydrocarbon solvent, waxes such as paraffin wax, stearin wax, beeswax and the like, resins such as long oil alkyds, hydrogenated rosin, ester gum and the like, and other compounds with good wetting properties such as oleic acid, naphthenic acid, cumene, tetralin, dekalin, dipentene, dibutyl phthalate, triethyl phosphate and the like.

The liquid containing the barrier substance in dissolved or dispersed form can be a non-polar aliphatic or aromatic hydrocarbon solvent or it can be a halogenated hydrocarbon solvent. The aliphatic and the aromatic hydrocarbon solvents can be for instance n-hexane, n-heptane, cyclohexane, benzene, toluene, xylene and the like and such solvents can be also selected from the wide range of com-

mercially available petroleum distillates known as petroleum ethers and petroleum spirits possessing various properties with regard to boiling point, flash point, rate of evaporation, viscosity and solvent power in terms of the KB number. The halogenated hydrocarbon solvents can be for instance carbon tetrachloride, perchloroethylene, trichlorotrifluoroethane and the like. Many of these solvents can be employed as the developer liquid carrying the developer material suspended therein. It is thus also possible to apply the barrier substance from solution or suspension in a solvent which is the same liquid as the developer liquid to be employed in the subsequent developing step as in such case the substance applied to the surface forms the actual barrier whereas the solvent as such after application of the barrier layer is not functional in the way of acting as or in the way of forming the barrier.

It is also possible to form a barrier layer in accordance with this invention consisting of only a liquid or of a mixture of liquids. Such liquid barrier substance can be again an aliphatic or aromatic hydrocarbon solvent or a halogenated hydrocarbon solvent as hereinbefore described but such solvent can not be the same liquid as the developer liquid to be employed in the subsequent developing step because such liquid barrier substance must have a greater wetting power in relation to the surface than the developer liquid. Since higher viscosity and boiling point and lower rate of evaporation generally indicate higher wetting power, the inspection of the physical properties of the solvents will readily enable one skilled in the art to select solvents for application as liquid barrier substances to suit any desired developer liquid. We have also found that in addition to the aforesaid properties, aliphatic or aromatic hydrocarbon solvents, or halogenated hydrocarbon solvents or mixtures of such having a solvent power higher than that of the developer liquid by a number of at least 8 expressed in terms of the KB value can be employed as liquid barrier substances for the lower solvent power developer liquids because such lower solvent power developer liquids are not capable of further wetting the surface or removing from such surface the stronger solvent present in the form of the barrier layer.

We have found that all of the barrier substances mentioned in the foregoing can be employed irrespective as to whether the liquid developer to follow is a positive one or a negative repulsion developer notwithstanding that some of these barrier substances were found to be more effective in positive liquid development whereas others were found to be more effective in negative repulsion development. Therefore in the examples following this disclosure the barrier substances will be defined also with regard to their suitability for a particular type of development.

The application of the barrier substance to the surface can be carried out by any known method such as for instance by dipping the surface in a body of liquid comprising the barrier substance or containing the barrier substance in dissolved or dispersed form or by spraying the surface or by employing an applicator device for instance of the roller type or by other known means. As the barrier layer is applied to the surface just prior to the developing step a special applicator for the barrier layer could be incorporated in any known type of liquid developing device for the purpose of treating the surface prior to the developing step.

It will be thus seen that this invention can be also applied to a machine designed to incorporate a series of rollers to carry out the application of the barrier layer followed by rollers which apply the liquid developer in highly concentrated form that is to say in the form of a printing ink containing no solvent or containing only a minimum quantity of a solvent forming the developing liquid to enhance developer particle mobility, in each case the bulk of solvent used as the developer liquid being limited to a minimum thus reducing fire hazard, image

drying and solvent disposal problems. Such machine can be so designed that the said rollers contact only one surface of the printing material with the barrier substance or developer. Such machine may also include means to replenish the material as it is used, together with provision to apply an external electrical field such as a biasing field or a polarity reversing field or transfer means and furthermore such machine may be applied to the development of electrophotographic surfaces containing latent electrostatic charge patterns or conductivity patterns and also to the development of charge patterns contained on non-photographic insulating surfaces as well as to improve electrostatic transfer.

The following examples will further illustrate the manner in which barrier layers can be formed on surfaces and since one skilled in the art utilizing the teachings of this invention can readily select from the wide range of materials disclosed in the foregoing suitable substances for forming barrier layers on photoconductive or insulating surfaces without departing from the scope of this invention it is intended that all matter contained in the following examples shall be interposed as illustrative and not in a limiting sense.

In the following examples reference is made to an electrophotographic sheet, to latent electrostatic images, to conductivity patterns and to liquid developers. This terminology can be explained as follows:

The electrophotographic sheet which can be used in the following examples 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 developer liquid. 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.

The latent electrostatic image contained on a photoconductive surface can be formed as follows: The electrophotographic sheet prepared in the above manner can be sensitised by subjecting it to a corona discharge from a series of wires or points held at a relatively high direct current potential such as 500-10,000 volts 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 or X-ray 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.

The conductivity pattern contained on a photoconductive surface can be formed as follows: The electrophotographic sheet prepared in the above manner is subjected without the preceding charging step to a light or X-ray pattern whereby the electrical resistivity of the photoconductive surface becomes affected in that such resistivity is lowered in the exposed areas in proportion with the intensity of illumination or radiation received. A typical exposure through a line transparency in contact with the surface would be of 5 seconds employing a 50 foot candle incandescent light source located 2 feet above the surface. It should be noted that in the thus obtained conductivity pattern the areas characterised by higher conductivity

correspond to higher intensity illumination obtained through the original and therefore when a sensitive liquid developer is employed which is capable of developing the higher conductivity areas this process lends itself to the reversal reproduction of originals that is for instance to produce a positive copy from a negative original.

The liquid developers which can be employed in these examples can be of the type as commonly known in the prior art. In addition the following developers can be used:

Positive developer.—This developer is one containing developer material which is attractable by negative electrostatic charges forming a latent electrostatic image and thus this developer can be used to produce a facsimile or positive reproduction of an original on a charged and exposed electrophotographic sheet containing zinc oxide as the photoconductor. The developer comprises a concentrate which is dispersed in the developer liquid to produce the liquid developer. The concentrate is prepared by grinding or milling

	Grams
Isol Ruby BKS red pigment	20
Bodied linseed oil	20
Lithographic varnish	20

The concentrate thus prepared can be dispersed in any developer liquid possessing the required electrical properties that is a volume resistivity of at least 10^9 ohm cm. and a dielectric constant of preferably less than 3. The following liquids are suitable: n-hexane, n-heptane, Shell X55, Shell X4, Shellsol T, Mineral Turpentine, cyclohexane, Colvesso 100, Freon 113, perchloroethylene and the like.

Negative developer.— This developer contains developing material which is repelled by negative electrostatic charges forming a latent electrostatic image and which deposits onto areas free from such charges or containing the minimum of such charges and thus this developer can be used to produce a negative or reversal reproduction of an original on a charged and exposed electrophotographic sheet containing zinc oxide as the photoconductor. This developer is also sufficiently sensitive to develop conductivity patterns on the photoconductive surface as hereinbefore referred to. The developer comprises a concentrate which is dispersed in the developer liquid to form the liquid developer. The concentrate is prepared by grinding or milling

	Grams
Carbon black pigment	10
Automotive oil SAE 40	100

This concentrate can be dispersed in the developer liquids as described in connection with the positive developer.

Both of the above developers can be used in the concentration of approximately 5 grams of the concentrate to 1,000 ml. of the developer liquid in which case line images can be developed with weak fill-in of large areas and relatively clean background but developing time is relatively long, such as for instance 30 to 60 seconds, employing for instance the technique of developing the surface by immersion in a body of the liquid developer. At high concentrations such as for instance 5 grams of the concentrate to 100 ml. of the developer liquid, the developing time becomes very short such as for instance 1 to 3 seconds, large areas can be filled in but objectionable background staining occurs. By employing the principles of this invention as disclosed in the following examples this background staining was eliminated whilst retaining the rapid developing action and fill-in characteristics.

EXAMPLES 1-53

In accordance with the invention the electrophotographic sheet was treated by applying to the photoconductive surface of the sheet just prior to the developing

step the following barrier substances dissolved or dispersed in solvents:

- (1) 5% of linseed oil in n-heptane.
- (2) 5% of safflower oil in n-heptane.
- (3) 5% of safflower oil in Shellsol T.
- (4) 5% of safflower oil in cyclohexane.
- (5) 6% of dehydrated castor oil in n-heptane.
- (6) 6% of tung oil in n-heptane.
- (7) 5% of sunflower oil in n-heptane.
- (8) 7% of sandalwood oil in n-heptane.
- (9) 7% of cedarwood oil in n-heptane.
- (10) 7% of clove oil in n-heptane.
- (11) 7% of clove oil in cyclohexane.
- (12) 7% of clove oil in Shellsol T.
- (13) 8% of paraffin oil in n-heptane.
- (14) 5% of automotive oil in n-heptane.
- (15) 5% of automotive oil in cyclohexane.
- (16) 5% of automotive oil in Shell X55.
- (17) 5% of automotive oil in Shellsol T.
- (18) 5% of automotive oil in Freon 113.
- (19) 5% of chlorinated diphenyl in n-heptane.
- (20) 8% of silicone oil in n-heptane.
- (21) 2% of silicone oil in cyclohexane.
- (22) 5% of silicone oil in Shell X55.
- (23) 0.5% of sodium oleate in n-heptane.
- (24) 0.5% of zinc oleate in cyclohexane.
- (25) 0.5% of copper oleate in Shell X55.
- (26) 1.5% of aluminium stearate in Shell X55.
- (27) 1.5% of zinc stearate in cyclohexane.
- (28) 10% of nonyl alcohol in Shellsol T.
- (29) 8% of cetyl alcohol in n-heptane.
- (30) 1.5% of iso-propyl alcohol in Shell X55.
- (31) 3% of paraffin wax in Shell X55.
- (32) 2% of lauric acid in n-heptane.
- (33) 5% of stearic acid in cyclohexane.
- (34) 3% of myristic acid in Shell X55.
- (35) 5% of Paralac 10 in Shell X55.
- (36) 5% of Desmalkyd RS165 in n-heptane.
- (37) 10% of Desmalkyd RS165 in Shell X55.
- (38) 7% of Desmalkyd RS165 in cyclohexane.
- (39) 5% of Desmalkyd in Freon 113.
- (40) 4% of Desmalkyd RS165 in Shellsol T.
- (41) 5% of hydrogenated rosin in n-heptane.
- (42) 5% of ester gum in Shell X55.
- (43) 3% of Pentacite P-423 in cyclohexane.
- (44) 8% of oleic acid in n-heptane.
- (45) 3% of naphthenic acid in Shell X55.
- (46) 5% of dibutyl phthalate in n-heptane.
- (47) 5% of triethyl phosphate in n-heptane.
- (48) 8% of cumene in n-heptane.
- (49) 5% of cumene in cyclohexane.
- (50) 3% of cumene in Freon 113.
- (51) 5% of cumene in Shellsol T.
- (52) 5% of tetralin in n-heptane.
- (53) 8% of dipentene in n-heptane.

After applying the barrier layer the wet surface was contacted with the liquid developer for the developing step. Each developer concentrate was dispersed separately in each of the developer liquids n-heptane, Shellsol T, Shell X55 and cyclohexane. These various dispersions were each used in conjunction with each of the Examples 1 through 53. In each instant where the developer liquid was different from the solvent for the barrier substance it was found that such difference was insignificant as the effectiveness of the barrier layer depended solely on the choice of the barrier substance. Whilst the barrier substances of Examples 1, 5, 19 through 35, 44, 45 and 48 through 53 were found to be equally effective with the positive developer as well as with the negative developer applied both as repulsion developer and to develop conductivity patterns, the barrier substances of Examples 2 through 4, 6 and 7 were found to be most effective with the positive developer, the substances of Examples 7 through 17, 36 through 43, 46 and 47 were

found to be most effective with the negative developer, the barrier substances of Examples 10 through 12, 14 through 18 and 36 through 42 having been particularly suitable when conductivity patterns were developed. The developing time for the conductivity patterns was ten seconds compared with 60 seconds when the diluted developer was employed as hereinbefore described.

EXAMPLES 54-71

In accordance with the invention the electrophotographic sheet was treated by applying to the photoconductive surface of the sheet just prior to the developing step a barrier substance consisting of a liquid having a solvent power higher than that of the developing liquid by a number of at least 8 expressed in terms of the KB value. After applying the barrier layer the wet surface was contacted with the liquid developer for the developing step.

(54) Each of the developer concentrates was dispersed separately in the developer liquid Shellsol T having a KB value of 26. Prior to development the photoconductive surface was wetted with the solvent n-heptane having a KB value of 35.

(55) The n-heptane of Example 54 was replaced with the solvent Shell X55 having a KB value of 40.

(56) The n-heptane of Example 54 was replaced with the solvent cyclohexane, KB value 58.

(57) The Shellsol T of Example 54 was replaced with the solvent Freon 113, KB value 31. Prior to development the photoconductive surface was wetted with the solvent Shell X55, KB value 40.

(58) The Shell X55 of Example 57 was replaced with the solvent cyclohexane, KB value 58.

(59) The Shell X55 of Example 57 was replaced with the solvent Freon 11, KB value 60.

(60) The Shellsol T of Example 54 was replaced with the solvent n-heptane, KB value 35. Prior to development the photoconductive surface was wetted with the solvent Mineral Turpentine, KB value 55.

(61) The Mineral Turpentine of Example 60 was replaced with the solvent cyclohexane, KB value 58.

(62) The Mineral Turpentine of Example 60 was replaced with the solvent Freon 11, KB value 60.

(63, 64 and 65) The n-heptane of Examples 60, 61 and 62 was replaced with the solvent Shell X55, KB value 40.

(66) The Shellsol T of Example 54 was replaced with the solvent cyclohexane, KB value 58. Prior to development the photoconductive surface was wetted with the solvent perchloroethylene, KB value 90.

(67) The perchloroethylene of Example 66 was replaced with the solvent Solvesso 100, KB value 93.

(68) The perchloroethylene of Example 66 was replaced with the solvent toluene, KB value 100.

(69) The Shellsol T of Example 54 was replaced with the solvent perchloroethylene, KB value 90. Prior to development the photoconductive surface was wetted with the solvent toluene, KB value 100.

(70) The toluene of Example 69 was replaced with the solvent dipentene, KB value 105.

(71) The toluene of Example 69 was replaced with the solvent carbon tetrachloride, KB value 114.

The following is a description of materials listed in the foregoing by trade names or registered trademarks:

Zinc Oxide Durham Special Z is an indirect process photoconductive zinc oxide manufactured by Durham Chemicals, Australia.

Isol Ruby BKS is an organic red pigment manufactured by Koge, Denmark.

Rhodene M8/50 is an isophthalic short oil alkyd manufactured by Polymer Corporation, Australia.

Desmalkyd RS165 is a polyurethane modified long oil alkyd manufactured by Bayer, Germany.

Paralac 10 is a long oil alkyd manufactured by I.C.I.

Pentacite P-423 is a pentaerythritol resin manufactured by Reichold Chemical.

Freon 11 is a trichloromono-fluoromethane solvent manufactured by Du Pont.

Freon 113 is a trichlorotrifluoroethane solvent manufactured by Du Pont.

Shell X4 is an iso-hexane solvent manufactured by Shell Chem.

Shell X55 is a substantially aliphatic hydrocarbon solvent, boiling range 58-140 deg. C., manufactured by Shell Chem.

Shellsol T is an aliphatic hydrocarbon solvent, boiling range 180-207 deg. C., manufactured by Shell Chem.

Mineral Turpentine is a hydrocarbon solvent containing approximately 45% aromatics, boiling range 150-198 deg. C., manufactured by Shell Chem.

Solvesso 100 is an aromatic hydrocarbon solvent, boiling range 160-174 deg. C., manufactured by Esso Petroleum.

What I claim is:

1. An improved method of developing electrically defined images on a printing element surface wherein said printing element surface contains a particulate photoconductor in an insulating resin binder, which method consists in treating such printing element surface immediately prior to liquid development of the image with a liquid medium selected to provide a layer on said surface wherein said layer has a greater wetting power for said surface than that of the liquid developer to be subsequently applied, wherein such layer forms a barrier substance which reduces absorption or adsorption by said surface when a liquid developer is subsequently applied, and then while the barrier substance is still wet developing the said image with a liquid developer, whereby said developer is attracted and held to said surface only under the influence of the electrical field defining the image or pattern.

2. A developing method according to claim 1 wherein the barrier substance consists of a wet film formed by applying to the surface an 0.5 to 10 percent solution in an electrically insulating solvent a substance selected from the group consisting of a mineral oil, a vegetable oil, a synthetic oil, a metallic soap, a resin, a wax, a non-polar wetting agent, and an alcohol.

3. A developing method according to claim 1 wherein the barrier substance consists of a wet film formed by applying to the surface an electrically insulating liquid possessing a solvent power higher than that of the developer liquid by a number of at least 8 expressed in terms of the KB (Kauri Butanol) value.

4. An improved method of developing electrically defined images on printing element surfaces having a particulate photoconductor in a resin layer, which consists in first forming the electrically defined image on said photoconductor layer, then applying to said photoconductor layer prior to the development of any visible image a barrier substance, said barrier substance being selected from the group consisting of a solution of a mineral oil, a vegetable oil, a synthetic oil, a metallic soap, a resin, a wax, a non-polar wetting agent, isopropyl alcohol, nonyl alcohol and cetyl alcohol, said solution being selected so as to have an electrical resistivity sufficiently high to avoid destruction of the image on the photoconductor layer, then while the barrier substance is still wet rendering the image visible by applying a liquid developer to said element which liquid developer comprises an electrically insulating carrier liquid having a lesser wetting power for the said surface of the element than the barrier substance and in which is suspended a pigment medium whereby the said developer pigment is attracted and held to the said surface only under influence of the electrical field defining the image or pattern.

5. An improved method of developing electrically defined images on a printing element surface wherein said

printing element surface contains a particulate photoconductor in an insulating resin binder which consists in first forming the electrically defined image on said photoconductor, then applying to the photoconductor prior to liquid development of any visible image thereon a liquid medium selected to provide a layer on said surface as a barrier substance, said barrier substance consisting of an electrically insulating liquid possessing a solvent power higher than that of the developer liquid later used by a number of at least 8 expressed in terms of the KB (Kauri Butenol) value, then while the barrier substance is still wet rendering the image visible by applying thereto a liquid developer which liquid developer comprises an electrically insulating carrier liquid in which is suspended a pigment medium, whereby the developer pigment is attracted and held to the said layer only under influence of the electrical field defining the image or pattern.

6. In a method of developing an electrically defined image on an electrophotographic layer on a copy sheet, and wherein said image is rendered visible by subsequent application of a liquid toner in the form of an insulating hydrocarbon liquid carrying a color and attracted by the polarity of the image, the step of treating said layer with a material selected from the group consisting of linseed oil in n-heptane; safflower oil in n-heptane; safflower oil in an aliphatic hydrocarbon of boiling range 180–207° C.; safflower oil in cyclohexane; dehydrated castor oil in n-heptane; tung oil in n-heptane; sunflower oil in n-heptane; sandalwood oil in n-heptane; cedarwood oil in n-heptane; clove oil in n-heptane; clove oil in cyclohexane; clove oil in an aliphatic hydrocarbon of boiling range 180–207° C.; paraffin oil in n-heptane; automotive oil in n-heptane; automotive oil in cyclohexane; automotive oil in an aliphatic hydrocarbon of boiling range 58–140° C.; automotive oil in an aliphatic hydrocarbon of boiling range 180–207° C.; automotive oil in trichlorotrifluoroethane; chlorinated diphenyl in n-heptane; silicone oil in n-heptane; silicone oil in cyclohexane; silicone oil in an aliphatic hydrocarbon of boiling range 58–140° C.; sodium oleate in n-heptane; zinc oleate in cyclohexane; copper oleate in an aliphatic hydrocarbon of boiling range 58–140° C.; aluminum stearate in an aliphatic hydrocarbon

of boiling range 58–140° C.; zinc stearate in cyclohexane; nonyl alcohol in an aliphatic hydrocarbon of boiling range 180–207° C.; cetyl alcohol in n-heptane; iso-propyl alcohol in an aliphatic hydrocarbon of boiling range 58–140° C.; paraffin wax in an aliphatic hydrocarbon of boiling range 58–140° C.; lauric acid in n-heptane; stearic acid in cyclohexane; myristic acid in an aliphatic hydrocarbon of boiling range 58–140° C.; Paralac 10 in an aliphatic hydrocarbon of boiling range 58–140° C.; Desmalkyd RS165 in n-heptane; Desmalkyd RS165 in an aliphatic hydrocarbon of boiling range 58–140° C.; Desmalkyd RS165 in cyclohexane; Desmalkyd in trichlorotrifluoroethane; Desmalkyd RS165 in an aliphatic hydrocarbon of boiling range 180–207° C.; hydrogenated rosin in n-heptane; ester gum in an aliphatic hydrocarbon of boiling range 58–140° C.; Pentacite P-423 in cyclohexane; oleic acid in n-heptane; naphthenic acid in an aliphatic hydrocarbon of boiling range 58–140° C.; dibutyl phthalate in n-heptane; triethyl phosphate in n-heptane; cumene in n-heptane; cumene in cyclohexane; cumene in trichlorotrifluoroethane; cumene in an aliphatic hydrocarbon of boiling range 180–207° C.; tetralin in n-heptane; dipentene in n-heptane; and a liquid having a solvent power higher than that of the developer liquid by a number of at least 8 expressed in terms of KB value; said material being applied to inhibit the deposition of said toner liquid in the non-image areas of the sheet, and wherein the liquid toner is applied while the material is still wet.

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U.S. Cl. X.R.

117—37; 252—62.1