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[54] **METHOD OF PROTECTING IMAGES**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 854,324, Aug. 29, 1969, abandoned.

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[51] **Int. Cl.** **G03g 13/20**, G03g 13/22

[58] **Field of Search** ..... 96/1 R, 67; 117/17.5, 37 LE, 93.31; 204/181

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[57] **ABSTRACT**

A method is disclosed for applying a protective overcoat to developed images, such as a developed electrostatic charge pattern. The protective overcoat is applied electrophoretically from a dispersion of transparent resin particles in an electrically insulating carrier liquid. The process involves the formation of a developed image on an image-bearing member having associated therewith a conductive backing. An external electrical source is then provided. Next, an electrical field and a resulting electrical bias potential is provided between the electrical source and the conductive backing. While the bias potential is applied, a dispersion of transparent charge-bearing resin particles in an electrically insulating carrier liquid is applied to the member with the result that the resin particles are uniformly deposited over the image-bearing surface of the member.

17 Claims, No Drawings

METHOD OF PROTECTING IMAGES

This application is a continuation-in-part application of U.S. Pat. application Mosehauer et al. Ser. No. 854,324, filed Aug. 29, 1969, now abandoned entitled "Method of Protecting Images."

This invention relates to electrography, and in particular, it relates to a method of fixing developed electrostatic charge patterns.

Electrographic and particularly electrophotographic imaging processes and techniques have been extensively described in both the patent and other literature, for example, U. S. Pat. Nos. 2,221,776; 2,277,013; 2,297,691; 2,357,809; 2,551,582; 2,825,814; 2,833,648; 3,220,324; 3,220,831; 3,220,833 and many others. Generally, these processes have in common the steps of employing a normally insulating photoconductive element which is prepared to respond to imagewise exposure with electromagnetic radiation by forming a latent electrostatic charge image. The electrostatic latent image is then rendered visible by a development step in which the charged surface of the photoconductive element is brought into contact with a suitable developer mix.

A particularly useful procedure for developing electrostatic latent images is through the use of a liquid developer as described, for example, by Metcalfe in LIQUID DEVELOPERS FOR XEROGRAPHY, Journal of Scientific Instruments, Vol. 32 (1955), pages 74 and 75. Developers of this type are comprised basically of a simple dispersion of pigment. Because no binder is present in the developer, the resultant images must be separately fixed. It was later proposed, for example, by Metcalfe and Wright, Journal of Oil and Color Chemists' Associations, 39 (1956), pages 851–853, that liquid developers containing a resin be used. The resultant images are then self-fixing because of the presence of the resin. These self-fixing developers are very useful for preparation of a limited number of images from a single batch of developer. However, problems often arise where it is desired to make a large number of copies from a single batch of developer. It appears as if the developer and the resin are not always depleted at the same rate. In view of the differing depletion rates, replenishment is often difficult or impossible. Thus, for certain applications, it is more desirable to use the simple developers disclosed earlier by Metcalfe or a variation containing only a small amount of resin and fix the resultant image by a subsequent procedure.

One useful procedure for subsequent fixing of developed images is the application of a lacquer overcoat. Various procedures have been suggested for applying such a lacquer overcoat. The most popular method has been to spray a resin solution onto the developed image. Another method has been to apply a resin solution from an applicator roller. Both of these systems have the disadvantage that the resin solution is exposed to the air which causes drying of the solution. This in turn results in the applicating apparatus becoming "gummed up." A further disadvantage with such systems utilizing a resin solution is that the solvent for the resin is different from and generally incompatible with the liquid carrier vehicle of the developer used. Because of this incompatibility, it is necessary to dry a liquid developed image prior to applying the resin solution. In addition, there if often a problem of venting any toxic or dangerous solvent vapors.

Accordingly, there is a need for a method of fixing developed images which is clean and does not require previous drying of the developed image.

It is, therefore, an object of this invention to provide a novel method of fixing developed images.

It is a further object of this invention to provide a novel method of protecting developed images which is clean and which does not require elaborate venting of solvent vapors.

It is still another object of this invention to provide a novel process for fixing liquid developed images which does not require previous drying of the developed image.

These and other objects and advantages are accomplished in accordance with this invention by electrophoretically applying a uniform layer of transparent resin over a visible developed image on an image-bearing member having an electrically conducting backing. It is readily apparent that the present invention can be utilized for the provision of protective coatings to typical silver or other images as well as electrographic images. However, for ease of presentation, we will refer only to images prepared by electrographic means with the understanding that the image-bearing member could bear a silver image, for example.

The image-bearing members used in the present invention can take a variety of forms. A particularly useful member is in the form of an electrophotographic element. Such elements are typically comprised of a conducting support having coated thereon a photoconductive composition. Such elements are well known in the art and particularly useful ones employ a photoconductive layer comprised of an organic photoconductor in an electrically insulating resin binder. An element of this type is given a uniform surface charge and then exposed to a pattern of actinic radiation. This exposure causes reduction in the surface potential in accordance with the relative energy contained in the radiation pattern. This charging and exposing sequence results in the formation of an electrostatic charge pattern on the photoconductive element. Another useful image-bearing member is comprised simply of a sheet of an electrically insulating material such as poly(ethylene terephthalate). An electrostatic charge pattern can be placed on such a member by charge transfer of a pattern carried on a photoconductive element as described above. In addition, an electrostatic charge pattern can be applied by placing a stencil over the insulating sheet and subjecting it to a corona discharge. The insulating sheet in this instance can be provided with a permanent conductive backing or it can be simply placed in contact with a separable conductive backing. In any case it will be recognized that the image-bearing surface of the image-bearing member has a contiguous electrically conducting backing associated with a surface of the member opposed to the image-bearing surface.

The resultant electrostatic charge pattern formed on the image-bearing member is then ready for development. The pattern can be readily developed by the now well-known liquid development techniques as disclosed for example in U. S. Pat. No. 2,907,674. In general, liquid developers useful for developing the electrostatic charge pattern are comprised of a colorant dispersed in an electrically insulating carrier vehicle. These colorants can be pigment particles or colored resin particles which are electrostatically deposited in accordance

with the charge pattern carried on the image-bearing member. In addition, the charge patterns can be developed by dry development techniques which utilize dry particles of coloring material such as pigment particles and/or pigmented resin particles.

After development of the electrostatic charge pattern to form a visible image, the resultant image is fixed in accordance with this invention by the electrophoretic deposition of a uniform layer of resin over the entire image surface of the image-bearing member. The electrophoretic deposition is accomplished by subjecting the member to an externally applied electric field and applying a suitable resin dispersion to the image-bearing surface on the member while this member is under the influence of the external electric field. The externally applied electric field utilized is a direct current field. Various means may be used as an external source to generate this field. For example, a counter electrode may be used as described hereinafter. In addition, various types of corona-charging devices such as a corona charging needle or corona charging wire may be used. The externally applied field passes through the applied resin suspension and creates a potential difference (i.e., a bias voltage) between the conductive backing of the image-bearing member and the external field source (eg. the corona charging device, etc.). Generally, regardless of the type of external electrical source used to establish the field, the strength of the field used to establish an electrical bias voltage between the conductive backing of the image-bearing member through the applied resin dispersion to the external field source should be sufficient to provide a suitable protective coating. Generally, a useful bias voltage lies within the range of from about 200 to about 50,000 volts, a preferred voltage range being between about 500 and 20,000 volts. Of course, the voltage will vary depending on the particular resin suspension used and the spacing between the image-bearing member and the external field source. For example, using a counter electrode as the means for generating the externally applied field, the counter electrode is closely spaced from the image-bearing surface of the image-bearing member and an electrical bias potential is established between the counter electrode and the conductive backing of the image-bearing member. In such case, the counter electrode is usually spaced about one-fourth mm. to about 6 mm. from the image-bearing member, with a preferred spacing of from about one-half mm. to about 2 mm. Using such a closely spaced counter electrode, a voltage in the range of about 500 to about 5,000 volts, preferably 800 to about 2,000 volts may be applied. However, the spacing and voltage can be varied to suit particular needs. Where a corona charging device such as a corona charging needle is used to establish the externally applied field, a preferred spacing between the needle and the image-bearing member is larger, generally within the range of from about 2 mm. to 10 cm., with a preferred range of from about 0.8 cm. to about 4.0 cm., and a voltage in the range of about 2000–50,000, preferably 3,000–12,000, volts is applied. Corona charging needles, as well as other types of corona charges, are well-known. Detailed information concerning corona charging devices is therefore unnecessary. However, for additional information, reference may be made to Electrophotography, by R. M. Schaffert, Focal Press, 1965, hereby incorporated by reference thereto. Useful as a corona charging needle is a No. 6, "Sharps" sewing needle manufactured by Leo Lammertz of London, England. A corona charging needle made from such a sewing needle was used in Example 7 hereinafter.

The conductive backing of the image-bearing member is usually nagative with respect to the external electrical field source; however, this will vary depending on the polarity of the charge-bearing resin particles in the resin suspension. As noted above, a suitable resin dispersion is introduced in the space between the external field source and the surface bearing the developed image while the external field is applied. The presence of the field induces the migration of the charge-bearing resin particles of the resin dispersion to the image-bearing surface of the image-bearing member. Thus, a uniform coating of these charge-bearing particles is obtained on the image-bearing surface of the image-bearing member. As is apparent, the polarity of the charge-bearing resin particles in the liquid carrier is not particularly critical. That is, if the polarity of the charge-bearing particles is such that in the presence of the externally applied field the net migration of the particles is away from the image-bearing surface, one need only reverse the polarity of the external field and the migration of the particles will be reversed, ie. the particles will be attracted to the image-bearing surface and deposited thereon as described above. The resin dispersion can be flowed through this space or the various parts can be immersed in a suitable resin dispersion. The image-bearing member may then be removed, the external field may be turned off, and the member may then be subsequently heated or otherwise treated to eliminate any excess carrier liquid and more firmly fix the resin which is uniformly deposited over the entire surface of the image-bearing element.

Many resin dispersions are useful in the instant procedure and in general they are comprised of an electrically insulating carrier liquid having dispersed therein particles of a transparent resin material. Conductive liquids such as water can be used if desired; however, dispersions using insulating liquids are often simpler to prepare. Useful carrier liquids generally have an electrical volume resistivity in excess of 10^9 ohm-cm and a dielectric constant of less than about 3. A further property of the carrier liquid which is desirable is that the liquid be of relatively high volatility in order to facilitate drying after application of the protective resin overcoat. Volatility may be considered in a relative manner as the time required for 0.5 cc. of a liquid to evaporate from filter paper at room temperature and atmospheric pressure. Kerosene is found to have an evaporation rate of an excess of 300 minutes in accordance with this test and thus represents the lower limit of volatility of useful liquids. In addition, preferred liquids should have a high flash point, preferably above about 30°C. (Tag Open Cup Test), in that an explosion danger is present with highly volatile materials having a lower flash point. Of course, liquids having a low flash point can safely be used when mixed with a liquid having a higher flash point. Additionally, in the case of prior liquid development, the carrier liquid in the resin dispersion should be compatible with the electrically insulating liquid vehicle of the developer. Thus, the carrier should be soluble in or miscible with this vehicle and the two liquids should not be reactive. Furthermore, the carrier liquid should have no substantial solvent effect on the previously deposited toner particles.

Still another property which the carrier liquid should have is a relatively low solvent power with respect to a particular dispersed resin. The solvent power of a liquid must be such that the resin does not dissolve in the liquid in order to prevent the liquid and resin from forming a solution such that the resin no longer exists as a dispersion. Useful carrier liquids include a variety of relatively volatile organic liquids. Suitable liquids useful alone or in mixtures include many aliphatic hydrocarbons such as cyclohexane, n-hexane, n-heptane, n-decane; halogenated hydrocarbons such as carbontetrachloride, chlorinated fluorinated lower alkanes; isoparaffinic hydrocarbons such as Isopar G (Humble Oil & Refining Co.); aromatic hydrocarbons such as Solvesso 100 which is a narrow cut aromatic solvent obtained from Humble Oil & Refining Co.; as well as mineral oil and the like.

In general, the present dispersions of transparent resins can be prepared by dissolving a suitable resin along with a dispersing agent if needed in a solvent such as methylene chloride, etc. The resultant combination is then mixed into a carrier liquid in which the resin is relatively insoluble thereby forming a particulate suspension of resin in the carrier liquid. The resins useful for dispersing in the carrier liquids can also be selected from a wide variety of materials. Desirable properties of the resins useful in the present invention include the following: high gloss and hardness, water-white color and transparency, good dielectric properties, resistance to ultraviolet degradation, high abrasion resistance, resistance to discoloration at reasonably high temperatures, and resistance to water, alcohol, dilute acids and alkalis. In general, the resin concentration in the carrier liquid is kept at a relatively low value of from about one-eighth to about 10 g/l. with a preferred concentration being from about one-fourth to about 5 g/l. The resin concentration is, of course variable with a particular concentration being dependent upon the results desired. It should also be noted that the stability of various resin dispersions is also dependent upon the concentration.

A further useful property of the transparent resin is that after deposition on the image-bearing member, the resin must be capable of being permanently fixed thereto. The resins useful can be ones of which are permanently fixed simply on evaporation of the carrier liquid. In general, however, the resins are heated to cause fusing or crosslinking thereby forming a permanent protective coating. Useful resins include a variety of materials such as alkyd resins including modified alkyd resins, phenol formaldehyde resins, methacrylate resins, various vinyl resins, including styrene-containing resins and the like as well as mixtures of these and other resins. The particular resin used should be substantially insoluble in the carrier liquid and should be capable of forming a particulate dispersion in the carrier liquid.

If necessary or desirable, the resin dispersions can also contain an additional charge control agent to insure that the individual particles of resin contained in the dispersion have the proper electrostatic charge and are thus uniformly deposited on the image-bearing member. A variety of charge control agents are disclosed in the art with heavy metal soaps being particularly useful as disclosed in U. S. Pat. No. 3,417,019.

The following examples are included for a further understanding of the invention.

EXAMPLE 1

A liquid developer is prepared from the following ingredients:

- Carbon black in a soya-modified phthalic alkyd resin (3046 Carbon black paste, Interchemical Corp.) — 0.75 grams
- Alkali blue RR paste (Sherwin Williams Co.) — 0.25 grams
- Cyclohexane — 30 ml.
- Cobalt naphthenate (6% solution) (Uversol Cobalt Liquid, Harshaw Chemical Co.) — 1.2 ml.
- Isopar G (supra) — 970 ml.

The developer is prepared by mixing the two pastes in a solution of cyclohexane and cobalt napthenate liquid to form a developer concentrate. The Isopar G is then added to the concentrate to form the final working developer. This liquid electrophotographic developer is then used to develop an image carried on an electrophotographic element comprised of a conductive support carrying a photoconductive layer comprised of a poly(ethylene terephthalate) film base having an evaporated nickel conducting layer carrying a photoconducting layer comprised of a 4,4'-diethylamino-2,2'-dimethyltriphenylmethane photoconductor in a polycarbonate binder. The electrophotographic element is charged, exposed and developed with the above developer to form a visible image. The resultant image is substantially unfixed as this developer does not fix well to the photoconductive surface. Even the application of a substantial amount of heat does not significantly increase the adhesion of the developed image. The developed image is then electrophoretically coated with a positive polarity resin dispersion containing the following:

- Reactive unmodified phenol formaldehyde — 1.5 g.
- Soya-modified phthalic alkyd resin — 0.5 g.
- Methylene chloride — 25 ml.
- Cobalt naphthenate (6% solution) (as above) — 1.2 ml.
- Isopar G — 975 ml.

This resin dispersion is formed by dissolving the two resins in methylene chloride after which the cobalt naphthenate is added to form the resin concentrate. The resin concentrate is then added to the Isopar G to form the final resin dispersion. The dispersion stability of the resultant material is very good. A developed electrophotographic element as prepared above is placed to and about 1 mm from a counter electrode. A bias potential (positive with respect to the counter electrode) of 1,000 volts is applied between the counter electrode and the conductive support of the electrophotographic element. While this potential is being applied 20 to 30 ml. of the resin dispersion prepared above are flowed through the space between the counterelectrode and the surface of the element carrying the developed image. The electrical bias potential provides a sufficient electric field to cause complete uniform deposition of resin particles over the full surface of the element. After the resin is deposited, the carrier liquid is evaporated using a stream of warm air and the element is then heated to about 120°C on a hot plate to soften and fix the resin to the surface of the element. The resulting image is physically stable with a smooth surface capable of taking much physical abuse. The transparent resin overcoat does not affect the qual-

ity of the image or impair optical readout or printout capability.

EXAMPLE 2

A positive polarity resin dispersion is prepared from the following materials:

n-Butyl/isobutyl methacrylate 50/50 copolymer — 0.5 g.
Trichlorotrifluoroethane (solvent) — 25 ml.
Cobalt naphthenate as in Example 1 — 1.2 ml.
Isopar G — 975 ml.

The copolymer is dissolved in the solvent after which the cobalt naphthenate is added to form the resin concentrate. The concentrate is then added to the Isopar G to form the final resin dispersion. The dispersion stability of this material is very good. This resin dispersion is used in the manner of Example 1 to provide a protective resin overcoat on a developed electrophotographic image. This resin gives excellent protection against abrasion and solvent attack without degrading the quality of the underlying image. The image could not be smudged by hand.

EXAMPLE 3

A positive polarity resin dispersion is prepared using the following ingredients:

Alphaprene A-115 — 1 g.
Cobalt naphthenate as in Example 1 — 1.2 ml.
Isopar G — 1 liter

Alphaprene A-115 is a resin obtained from Reichold Chemicals, Inc., and is based on a vinylidene aromatic-acrylic terpolymer system. The Alphaprene resin and cobalt naphthenate are added to 400 ml. of Isopar G. The Isopar G is heated to approximately 100°C until the resin dissolves and is in solution (Alphaprene resin is not soluble in Isopar G at room temperature). The resultant 100°C concentrate is then added to 600 ml. of Isopar G at room temperature to form the final resin dispersion which has good stability. This resin dispersion is used as in Example 1 to provide a protective overcoat over a developed image carried on an electrophotographic element. The resultant resin coating provides good protection against abrasion and solvent attack while at the same time providing a smooth transparent coating.

EXAMPLE 4

The procedure of Example 1 is repeated using the resin dispersion of Example 3 in place of the resin dispersion of Example 1. An image is developed as previously described and the developed image is allowed to dry completely before application of the resin protective coating. A second element carrying a developed image is prepared as above and in this instance the protective resin overcoat is applied prior to allowing the developed image to dry. No difference in appearance of the two final images could be ascertained either in abrasion resistance or in appearance of the image itself.

EXAMPLE 5

A sheet of poly(ethylene terephthalate) film base is covered with a stencil formed of elastically insulating polymethyl methacrylate having cut out portions such that areas of the underlying film base are left uncovered in an imagewise fashion. The poly(ethylene terephthalate) sheet carrying the stencil is then subjected to a corona discharge as in Example 1 and the stencil is removed to leave an electrostatic charge pattern on the insulating sheet. This insulating sheet is then developed with the liquid developer of Example 1 and the non-image-bearing side of the sheet is placed in contact with a metal plate which serves as a conductive backing. A counter electrode is then placed about 1 mm. from the image-bearing side of the insulating sheet, a positive (with respect to the counter electrode) bias potential of 1,000 v. is applied and a resin dispersion is applied to the surface of the sheet in the manner described in Example 1. The insulating sheet is separated from the conductive backing and the excess carrier liquid is evaporated as in Example 1 whereupon the element is heated to about 120°C on a hot plate to fix the resin to the surface of the element. The resultant image has a smooth surface capable of taking considerable physical abuse. The transparent overcoat does not affect the quality of the image.

The present electrophoretic coating procedure is well suited for use with microimages. In particular, it may be desired to add on additional information to a microfiche card. Consequently, the resin applied over a developed image must not hinder the application or formation of additional developed images. This procedure can be repeated several times applying a resin layer each time. Thus, it would not be uncommon to apply a new image over as many as ten or more resin layers. These various resin layers cannot substantially interfere with the image quality or information contained in a microimage can be lost. The following examples further illustrate the application of a plurality of resin layers by the process of this invention.

EXAMPLE 5

A resin dispersion is prepared by forming a 1:1 mixture of the dispersion of Example 1 with the dispersion of Example 2. A positive to positive 16X reduced microimage is made on each of three 35 mm. photoconductive elements A, B and C using the method and materials of Example 1. The image on Element A is deposited directly on the photoconductive layer and used as a control. The image on Element B is deposited over one resin coating. The image on Element C is applied over 10 resin coatings using the procedure of Example 1. All three images are then overcoated as in the preceding examples. The overall microimage quality was good for the images produced on all three elements.

EXAMPLE 6

The entire procedure of Example 5 is repeated only the images are prepared using a positive to negative mode of development. The quality of each of the resultant images is similar to that obtained in Example 5.

EXAMPLE 7

This Example (parts I and II) is presented to illustrate a comparison between the method of forming a protective overcoat for developed images according to the present invention with certain previous methods known in the art for bonding or fixing developed images. One previous method used in the art is illustrated in Canadian Pat. No. 709,348 issued May 11, 1965. This patent describes a method for bonding the visible image-forming particles to an electrostatic charge image carried on an electrographic element by co-depositing the bonding medium and the marking particles medium

from an electrically insulating carrier liquid. According to the co-deposition method described in the above-noted Canadian patent, finely divided particles of a pigment material and finely divided particles of a resinous bonding material are co-deposited onto the latent electrostatic charge image of an electrographic support to form a visible image bonded to said support and, in certain cases, overcoated with a layer of the resinous bonding medium. The bonding medium and pigment are both co-deposited on the electrostatic charge image due to the charge differential existing between the pigment and bonding medium particles ad the latent imagewise electrostatic charge pattern obtained by conventionally charging and exposing the electrographic element. Thus, deposition of the bonding medium and the pigment particles takes place only in areas bearing an imagewise electrostatic charge pattern. The amount of bonding medium applied and the areas to which it is applied is dependent on the original imagewise electrostatic charge pattern placed on the electrophotographic element.

In the present invention, as described hereinbefore, it will be appreciated that the protective overcoat applied to a developed image is applied, in the usual case, over the entire surface of a developed image-bearing element. Deposition is accomplished electrophoretically making use of an external electrical field applied to an image-bearing surface after it has been developed. Thus, the amount of and the thickness of the applied protective coating is not dependent on the original, latent electrostatic charge image on the element. As the following tests demonstrate, the protective overcoat obtained using the method of the present invention exhibits significant improvements over the method described in Canadian Pat. No. 709,348.

PART I

The following example illustrates the limitations on the maximum color transmission density resulting from use of the co-deposition method of applying a resinous bonding medium described in the above-mentioned Canadian patent. These limitations occur because the original latent imagewise electrostatic charge pattern on the electrographic element is used to deposit both pigmented marking particles and the resinous bonding particles on the element. In this example, the following materials are used:

MATERIALS:

Film: A homogeneous organic photoconductor film.
Toner A
Blue colored toner containing:
Alkali Blue RR (Sherwin Williams CP1568) — 0.5 g
Cobalt Naphthenate (6% solution) (Uversol Cobalt Liquid, Harshaw Chemical Co.) — 1.2 ml
Cyclohexane — 30 ml
Isopar G — 970 ml
Toner B
Black-colored toner used was commercially available O.G. Chroma Black from OptoGraphics Inc. Chemical analysis of this material indicates that it is similar to Toner A above, but also includes some carbon black.
Resin Suspension
Rosin modified phenol formaldehyde resin (Beckosol 7) — 0.25 g
Soya-modified phthalic alkyd resin (Ambersol ST-137) — 0.75 g
Cobalt Naphthenate (6% solution) (Uversol Cobalt Liquid, Harshaw Chemical Co.) — 1.20 ml
Dichloromethane — 25.00 ml

The above concentrate is added dropwise to 500 ml of Isopar G. After the concentrate has all been added, an additional 500 ml of Isopar G is added with stirring. The colorless resin particles are of positive polarity.

In this example the following test procedure was utilized:

Test Procedure

Samples of the photoconductor element were charged negatively to 600 volts, camera exposed at 23x reduction to a positive-appearing original and developed using either Toner A or Toner B. The exposure provided an image-wise charge pattern having a maximum ΔV (maximum voltage difference between exposed and unexposed areas) of 350 to 400 volts. The following results were obtained at different development times.

Development Time	Density* (transmission) (Toner A)	Density** (transmission) (Toner B)
2.0 seconds	0.70	0.70
5.0 seconds	1.12	1.20
10.0 seconds	1.17	1.39

* to red light since toner is blue
** to white light since this toner is black

The above data illustrate that development has gone nearly to completion after 5 seconds but that there is still unsatisfied or developable electrostatic charge available after 2 seconds.

A further series of tests were then made wherein portions of the resin suspension were mixed with the toner to provide a monobath comprising both toner and resin particles, and then imagewise codepositing these on the photoconductor element during development. Development time was 10 seconds to insure complete development of the electrostatic charge pattern. The following results were obtained.

MONOBATH (ml. of Toner and ml. of Resin Suspension)		Net Maximum Density (Transmission Density)
Toner	Resin Suspension	
40 ml Toner A	0 (control)	1.05 (to red light)
40 ml Toner A	10 ml	0.69 (to red light)
40 ml Toner A	20 ml	0.65 (to red light)
40 ml Toner A	30 ml	0.57 (to red light)
40 ml Toner A	40 ml	0.48 (to red light)
40 ml Toner B	0 (control)	1.28 (to white light)
40 ml Toner B	10 ml	0.72 (to white light)
40 ml Toner B	20 ml	0.56 (to white light)
40 ml Toner B	30 ml	0.45 (to white light)
40 ml Toner B	40 ml	0.41 (to white light)

The above data illustrates that when the marking particles and the fixing particles are codeposited, they compete for the available image charge resulting in a lower density than if no resin particles were added to the toner. Therefore, the development of electrostatic charge patterns to an acceptable density would require a much larger ΔV which is usually not practical. In addition, the time required to achieve that density would probably be significantly longer than desired. The other technique wherein the electrostatic charge pattern is developed for a short period of time followed by sequential attraction of the fixing resin to the undeveloped, residual electrostatic image exhibits similar disadvantages since the development of the charge pattern is only partial in nature, low density images are ob-

tained. Furthermore, the residual electrostatic charge pattern is not large enough to attract sufficient resin particles to provide a good protective coating, as is evident in the following example.

PART II

In this example, the photoconductor element and Toners A and B are those described in Part I. The resin suspension comprised Lucite 2046 (a poly(methylmethacrylate)) isopolymer in Isopar G. The resin particles were of positive polarity.

A series of images were recorded on each of three strips (1 to 2 feet in length) of 35mm film in the following manner:

Sample (*a*) The image recording cycle comprised charging the element negatively with a corona needle while simultaneously exposing the element. The electrostatic charge pattern was then developed for two seconds, dried and heat fused. No overcoat was applied over this sample.

Sample (b) A series of images were made on a second strip of film as in (a) above, except that immediately after development, the resin suspension was flowed over the image area for 2 seconds so that unsatisfied charge in the image areas attracted resin particles according to the method of Canadian Pat. No. 709,348. The images were then dried and heat fused.

Sample (c) A series of images were made on a third strip of film as in (a) above except that after development and drying, each image was electrophoretically coated according to the present invention using the corona needle to provide the external field. A positive polarity potential was applied to the needle. The images were heat fused.

Strips of 35mm leader material were taped to the above strips so that each sample could be run through the gate of a Recordak PE-1A reader/printer. In the gate of this reader/printer, the film sample travels through two flat glass plates which subject the organic photoconductor surface to a substantial amount of abrasion. Each film strip was run through the gate a total of 100 times. Prints of one specific image on the film were made after 1, 5, 10, 20, 50 and 100 passes to provide a record of abrasion resistance. The following results were noted.

Sample (a) Some surface scratches and abrasion were evident after 5 passes through the gate and this defect gradually increased until some of the information, especially in the solid areas was practically eliminated after 100 passes through the gate. The toner that rubbed off collected on the glass plate.

Sample (b) This imagewise coated sample performed similar to sample (a), in that abrasion was evident after 5 passes through the gate and parts of the image were obliterated after 100 passes through the gate.

Sample (c) Only a very few surface scratches were evident on this sample after 5 passes through the gate. Scratching became more evident after 100 passes through the gate but was considerably lower than that observed on Samples (a) and (b). Substantially no toner had been lost from the sample due to abrasion, thus demonstrating the superiority of the electrophoretically coated sample.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

We claim:

1. An image add-on process for applying a plurality of transparent protective coatings and at least one additional visible developed image to an image-bearing member having a visible developed image on one surface thereof and a contiguous electrically conducting backing associated with a surface of said member opposed to said one surface, said process comprising

a. subjecting said member to a direct current electrical field established between said conducting backing and an external electrical source to create a potential difference between the conducting backing and the external source;

b. applying a dispersion of transparent charge-bearing resin particles in an electrically insulating carrier liquid to said image-bearing member while said member is under the influence of said field to obtain a uniform coating of said particles over the image-bearing surface of said member;

c. removing said member from the influence of the external electrical source;

d. permanently fixing said uniform coating to said member;

e. forming an additional visible developed image on the surface of said uniform coating; and

f. repeating steps (a) to (d) whereby said image-bearing member has at least two visible developed images, one overlying the other, fixed thereon.

2. The method as described in claim **1** wherein said developed images are microimages.

3. The method as described in claim **1** wherein the carrier liquid has a volume resistivity of greater than about 10^9 ohm.-cm. and a dielectric constant of less than about 3.

4. The method as described in claim **1** wherein the image-bearing member is an electrophotographic element comprised of a photoconductive layer carried on an electrically conductive support.

5. The method as described in claim **1** wherein the developed image is formed using a liquid developer comprised of colored marking particles contained in an electrically insulating liquid vehicle.

6. The method as described in claim **1** wherein the uniformly deposited transparent resin particles are heated to permanently fix said particles to the image-bearing member.

7. The method as described in claim **1** wherein the image-bearing member is comprised of an electrically insulating material having a separate electrically conductive backing in contact therewith.

8. The method as described in claim **1** wherein said dispersion of transparent charge-bearing particles in an electrically insulating carrier liquid comprises from about one-fourth to about 5 grams of said particles per liter of carrier liquid.

9. A microimage add-on process wherein a plurality of transparent protective coatings and at least one additional visible developed microimage are applied to an electrographic element having a visible, substantially unfixed, developed electrostatic microimage on one surface thereof and a contiguous electrically conductive backing associated with a surface of said element opposed to said one surface, said process comprising

a. subjecting said member to a direct current electrical field established between said conducting back-

ing and an external electrical source to create a potential difference between the conducting backing and the external source;

b. applying a dispersion, comprising about one-fourth to about 5 grams of transparent charge-bearing resin particles admixed in each liter of a carrier liquid having a volume resistivity greater than about 10^9 ohm.-cm. and a dielectric constant less than about 3, to said microimage-bearing member while said element is under the influence of said field to obtain a uniform coating of said particles over the micro image-bearing surface of said element;

c. removing said member from the influence of the external electrical source;

d. drying exces carrier liquid from the element and permanently fixing said uniformly deposited transparent resin particles to said element;

e. forming an additional visible, substantially unfixed, developed electrostatic microimage on the surface of said uniform coating; and

f. repeating the cycle defined by steps (a) – (e) from 1 up to 10 more times with the proviso that in the last repetition of said cycle step (e) is omitted, whereby a series of visible, fixed, microimages superimposed one over the other are produced on the surface of the resultant electrographic element.

10. The method as described in claim **9** wherein the developed microimages are formed using a liquid developer composition comprising colored marking particles dispersed in an electrically insulating liquid vehicle.

11. The method as described in claim **9** wherein the developed microimages are formed using a liquid developer composition comprising colored marking particles dispersed in an electrically insulating liquid vehicle comprised of the same liquid as said carrier liquid.

12. The method as described in claim **9** wherein said element is an electrophotographic element comprised of an organic photoconductor-containing layer carried on an electrically conductive support.

13. The method as described in claim **9** wherein the external electrical source is a closely spaced electrode which is spaced about one-half to about 2 mm. from said image-bearing element and wherein the potential difference created between said electrode and said conducting backing is from about 800 to about 2,000 volts.

14. The method as described in claim **9** wherein said resin is selected from the group consisting of an alkyd resin, a phenol-formaldehyde resin, a methacrylate resin, a vinyl resin and mixtures thereof.

15. The method as described in claim **9** wherein said resin dispersion contains a heavy metal soap as a chrage control agent.

16. The method as described in claim **9** wherein the potential difference between said conducting backing and said external source is within a range of from about 200 to about 50,000 volts.

17. The method as described in claim **9** wherein the external electrical source is a corona charging needle which is spaced from about 0.8 cm. to about 4.0 cm. from said electrophotographic element and wherein the potential difference created between said needle and said conducting backing is from about 3,000 to about 12,000 volts.

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