

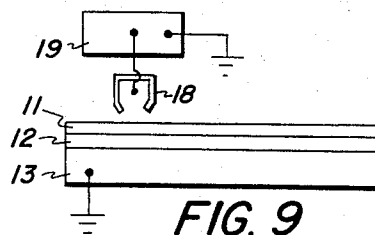
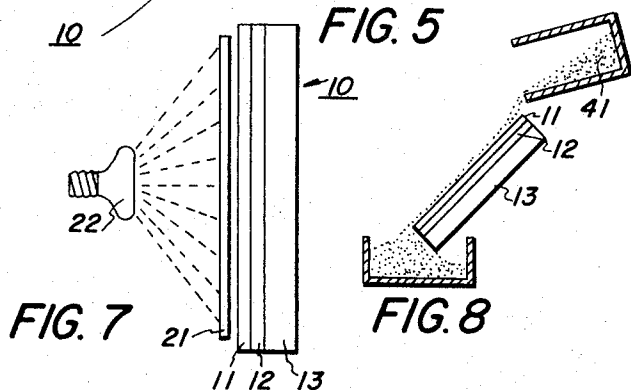
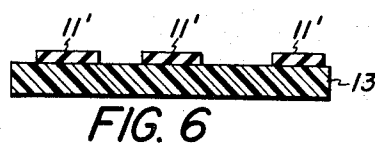
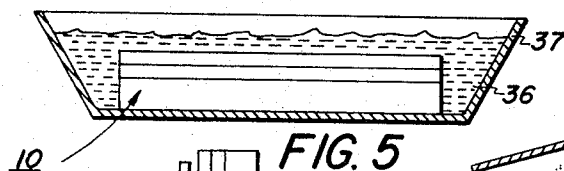
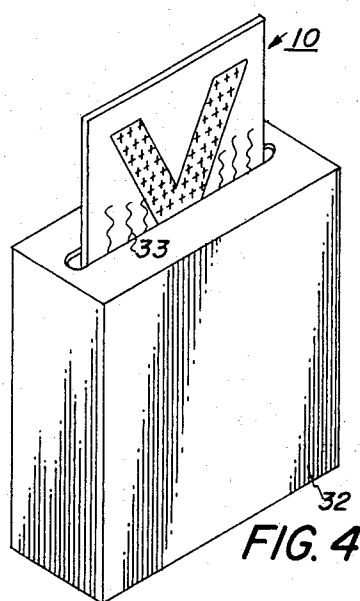
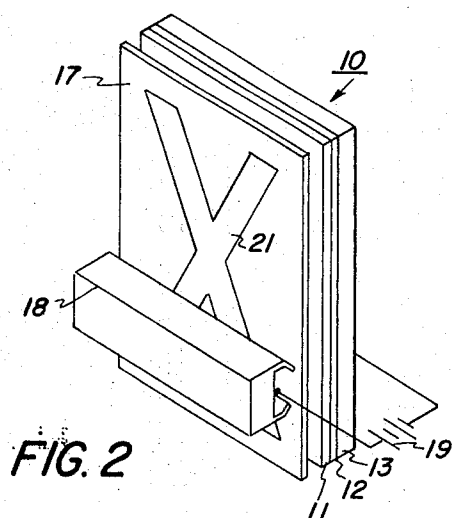
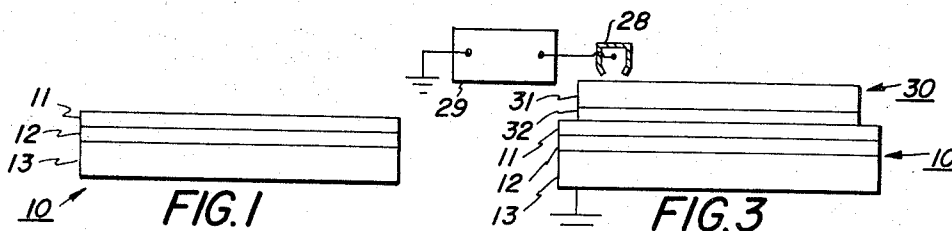
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3,707,391

IMAGING PROCESS

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3,707,391

IMAGING PROCESS

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Continuation of application Ser. No. 483,675, Aug. 30, 1965, now Patent No. 3,656,990, which is a continuation-in-part of application Ser. No. 403,002, Oct. 12, 1964, now abandoned, and a continuation-in-part of application Ser. No. 460,377, June 1, 1965, now Patent No. 3,520,681, which in turn is a continuation-in-part of said application Ser. No. 403,002. This application June 4, 1971, Ser. No. 150,106

The portion of the term of the patent subsequent to July 14, 1987, has been disclaimed

Int. Cl. G03g 13/00, 5/02

U.S. Cl. 117-17.5

25 Claims

ABSTRACT OF THE DISCLOSURE

An imaging member comprising a fracturable layer contacting a solvent soluble layer overlying a substrate, said fracturable layer spaced apart from said substrate is imaged by forming an electrostatic image on said member and then contacting said member with a solvent for said solvent soluble layer to form an imagewise pattern of material from said fracturable layer on said substrate.

CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuing application of my copending application Ser. No. 483,675 filed Aug. 30, 1965 now U.S. Pat. 3,656,990 which in turn is a continuation-in-part of copending application Ser. No. 403,002, filed Oct. 12, 1964, now abandoned and a continuation-in-part of copending application Ser. No. 460,377 filed June 1, 1965 (now Goffe Pat. 3,520,681) which is a continuation-in-part of 403,002, and relates to a new imaging technique in which recording material is selectively moved through a softenable medium under the influence of electrical forces.

BACKGROUND OF THE INVENTION

In the above-mentioned application and copending application Ser. No. 460,377, filed June 1, 1965, the imaging process disclosed employs a plate comprising an easily fracturable (usually particulate) photosensitive layer overlying a softenable plastic layer on a support substrate. According to one embodiment of that invention the plate is first uniformly electrostatically charged in darkness and then exposed to an optical image to cause selective charge flow in the photosensitive layer. Upon solvent or heat softening of the plastic layer, the photosensitive layer is selectively moved to the substrate surface in accordance with the optical image. Ordinarily, the plate is immersed in a liquid solvent resulting in, in addition to the selective particle migration, the washing away of the photosensitive material in non-image areas along with the plastic layer itself.

Thus, the aforementioned process requires the use of a consumable layer which is photosensitive, and it also requires control of activating radiation during certain steps of the process. The uniform electrostatic charge must usually be applied in darkness, and exposure to activating radiation is controlled until the image is developed. In addition, the degree of photosensitivity of the particular materials used must be taken into consideration in determining a suitable duration and intensity of exposure.

A somewhat similar plate structure is used in the present invention, but its fracturable layer need not be photosensitive. Controlled migration of conductive or insulat-

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ing particles may be effected without regard to lighting conditions. The present invention is also adaptable for use with reusable photoconductive layers and conventional xerographic plates, and other means for forming an electrostatic image on the consumable layer.

Briefly summarizing the present invention in terms of a preferred embodiment: The imaging plate used comprises a fracturable layer of conductive or insulating particles on or near the surface of a softenable plastic layer coated on a conductive substrate. An electrostatic charge pattern is formed on the fracturable layer in image configuration. Upon softening of the plastic layer, for example by application of a solvent therefor, portions of the fracturable layer migrate to the substrate surface in image configuration. Ordinarily, the nonimaging portions of the fracturable layer are then removed along with the plastic layer. Many variations of this process are within the scope of the present invention which is disclosed in detail in connection with the accompanying drawing.

In the drawing:

FIG. 1 is a schematic representation in cross-section of the imaging plate used in the present invention;

FIG. 2 is a schematic representation of electrostatic image formation on the imaging plate;

FIG. 3 is a schematic representation of an alternate method of electrostatic image formation;

FIG. 4 illustrates image development;

FIG. 5 illustrates dissolving away undesired plate materials;

FIG. 6 is a schematic representation in cross-section of an image produced in accordance with the present invention;

FIG. 7 illustrates selective exposure of the softenable layer to ultraviolet radiation;

FIG. 8 illustrates cascading a particle-carrier mixture across the surface of the softenable layer; and,

FIG. 9 illustrates the application of a substantially uniform electrostatic charge to an imaging plate.

Referring to the drawing, FIG. 1 shows a cross-section of plate 10 according to the invention comprising a thin easily fracturable layer 11 overlying a softenable layer 12 in intimate contact with conductive substrate 13.

Layer 11 is desirably sufficiently permeable to permit applied solvent vapor to soften layer 12. Layer 11 should be easily fracturable, nevertheless, and most conveniently comprises a thin layer of finely divided particles which may be either electrically conductive or nonconductive.

Fracturable layer as used herein refers to any layer 11 and specifically all the layer 11 forms disclosed herein, including those layers comprising discrete particles and those comprising apparently more mechanically continuous layers with a microscopic network of lines of mechanical weakness or which are otherwise fracturable and not completely mechanically coherent in the process hereof, which in the imaging member configurations hereof and their equivalents; in response to having an electrostatic image formed thereon followed by solvent contact are caused to selectively deposit in image configuration on a substrate.

Layer 12 is preferably a plastic which may be easily softened to permit selective migration of portions of layer 11 to the surface of substrate 13 under the influence of electrical forces. Also, layer 12 is preferably electrically nonconductive.

Substrate 13 of plate 10 is normally an electrical conductor, but procedures adapted from the xerographic art permit the use of nonconductive substrates as well. Substrate 13 may conveniently be a metallic sheet, web, foil, cylinder or the like; a sheet of glass with an electrically conductive coating, preferably transparent; or a conduc-

tively coated sheet of paper or stable plastic such as polyethylene terephthalate.

Starting with substrate 13, any known method may be used to apply layer 12 of substantially uniform thickness. For example, layer 12 may be formed by dip coating, roll coating, or vacuum evaporation, as well as other well-known techniques. For most applications of the present invention, it has been found preferable to use a layer 12 having a thickness of between 1 to 4 microns.

For use in the present invention, layer 11 is preferably about 0.2 to 10 microns in thickness and may be deposited on the plastic layer in various ways. For example, particles may be ground up and dusted onto layer 12, or finely divided particles may be mixed with larger granules of the type known as xerographic carrier and poured or cascaded over the surface of layer 12. If thicker coatings are desired, layer 12 may be softened slightly by heating, for example, to permit particles deposited on its surface to sink a short distance into the plastic after which additional particles may be cascaded across or dusted over the plate. Other techniques may also be used for applying layer 11, such as softening plastic layer 12 slightly to make it tacky, and then adhesively transferring imaging particles from a substantially uniformly coated donor sheet.

As layer 11 must retain an electrostatic charge during part of the instant process, it conveniently comprises particles that are electrically insulating. Conductive particles may be used, however, if lateral conductivity is minimized by loose packing, for example, or by partly embedding only a thin layer of particles in layer 12 so that neighboring particles are in poor electrical contact.

Layer 11 may comprise any conductive or insulating particles (preferably micron or submicron sized) which do not dissolve in the solvent applied during the development step and which do not react with layer 12 in a way that would prevent particle migration to the substrate surface. Moreover, photosensitive particles, such as disclosed in the aforementioned application Ser. No. 460,377, may be used in the instant process if it is carried out in the substantial absence of actinic radiation. Generally, subdued lighting would meet this requirement.

The thickness of layer 12 is not extremely critical. However, for a given material, thicker layers require the application of a higher charging voltage in carrying out the instant imaging process, and are, therefore, less desirable from the standpoint of employing the process with equipment of minimum cost and complexity. On the other hand, extremely thin layers are difficult to form with a suitable degree of uniformity. Two microns has proven to be a generally suitable thickness for layer 12.

Any one of a variety of softenable materials may be used for layer 12, including thermoplastic type materials which have been used in electrostatic deformation imaging as described, for example, in application Ser. No. 193,277, filed May 8, 1962 (now U.S. Pat. 3,196,011). Representative of suitable materials are: Staybelite Ester 10, a 50 percent hydrogenated glycerol rosin ester of the Hercules Powder Company; Piccotex 100, a styrene-type resin of Pennsylvania Industrial Chemical Company; Araldite 6060 and 6071, epoxy resins of Ciba; and Velsicol X-37 (Velsicol Chemical Corp.).

The basic process steps of the present invention are schematically represented in FIGS. 2-5. In general, an electrostatic charge pattern conforming to the image to be reproduced is formed on layer 11 of plate 10, and layer 12 is then softened to permit selective migration of portions of layer 11 to the surface of substrate 13. Optionally, but preferably for most applications of the present invention, layer 12 and the nonimaged portions of layer 11 are removed after the development step, whereby an image 11' resides on the surface of substrate 13 as shown in FIG. 6.

The formation of an electrostatic image on layer 11 is schematically shown in FIG. 2. According to the method

illustrated, a surface electrostatic charge pattern is applied through stencil 17 by means of corona discharge device 18. Illustratively, corona device 18 is raised to a high potential with respect to the substrate 13 by means of power supply 19 as it is moved back and forth a few times in charging proximity with layer 11 to apply a sufficient charge. The configuration of the electrostatic image formed on layer 11 is determined by the perforations in stencil 17, as represented by the X at reference numeral 21.

Another method for forming an electrostatic image is shown in FIG. 3. According to this method, a xerographic plate 30, comprising substrate 31 and photoconductive layer 32, on which an electrostatic image has been formed by conventional xerographic techniques is brought into direct contact with layer 11 while a substantially uniform electrostatic charge is applied to substrate 31 by means of corona device 28 connected to power supply 29. The polarity of the electrostatic charge applied by corona device 28 may be the same as or opposite to that of the latent electrostatic image on the surface of xerographic plate 30. This will depend upon whether a negative or positive image (in the photographic sense) is to be formed on the surface of substrate 13.

Other methods of forming an electrostatic charge pattern on layer 11 of plate 10 may also be used. For example, a shaped electrode may be positioned in close proximity to layer 11 and then pulsed with a high voltage with respect to substrate 13. The charge pattern may also be formed by means of a low energy electron beam. Still other methods such as those known to the art of xerography may also be applied.

After the electrostatic image has been formed on layer 11, layer 12 is softened to permit selective migration of portions of layer 11 to the surface of substrate 13.

FIG. 4 illustrates image development with a solvent for layer 12. As illustrated, solvent vapor 33 from container 32 is applied to the electrostatic image-bearing plate 10. As a result, the charged portions of layer 11 are found to adhere to the surface of substrate 13. As long as the solvent does not dissolve the material comprising layer 13, plate 10 may be exposed to the solvent vapor for an indefinite period of time without deleterious effect on image quality. Hence, development time is not critical.

At this stage in the instant process, portions of layer 11 remain on the surface of layer 12 and other portions, having selectively migrated, reside on the surface of the substrate. However, as layer 12 is relatively thin, the resultant image, although useful in certain applications, is not readily discernible without special viewing means. Therefore, it is ordinarily desirable to remove the non-imaged portions of layer 11 along with plastic layer 12. This can be done, for example, by abrading away the unwanted materials, or, more conveniently, by immersing the plate in a liquid solvent for layer 12, as illustrated in FIG. 5.

FIG. 5 shows plate 10 immersed in liquid solvent 36 contained in tray 37. Layer 12 is dissolved away and, deprived of mechanical support, the non-imaged portions of layer 11 disperse in the liquid leaving only the migrated portions of layer 11 on the substrate surface in image configuration.

It is noted that the electrostatic image formed on layer 11 may be developed by immersing the latent image-bearing plate in the liquid solvent directly. However, the liquid solvent should then be sufficiently electrically insulating to permit the charged portions of layer 11 to migrate to the surface of substrate 13 before the charge is dissipated by the liquid. If, on the other hand, vapor development precedes immersion in the liquid, the liquid need not be insulating. Migration having taken place before immersion, the washing away of unwanted materials by a conductive liquid will not deleteriously affect the image.

The solvent used should be a solvent for layer 12, but

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not for layers 11 or 13. Typically suitable solvents include for example: cyclohexane, pentane, heptane, toluene, trichloroethylene, Sohio odorless solvent 344° (Standard Oil of Ohio). Freon 113 (E. I. du Pont de Nemours Co., Inc.) and the like.

FIG. 6 schematically represents the developed image in accordance with the present invention after removal of layer 12, and unwanted portions of layer 11. Thus, the migrated portions of layer 11, designated 11', are shown residing on the surface of substrate 13.

The basic process can be further illustrated by means of the following examples.

EXAMPLE I

A plate 10 is made by first roll-coating a sheet of aluminized Mylar polyester film (E. I. du Pont de Nemours Co., Inc.) with a layer of Piccotex 100 (Pennsylvania Industrial Chemical Company) approximately 2 microns in thickness. A mixture of air spun graphite particles (Type 200-19, The Joseph Dixon Crucible Co., Jersey City, N.J.) and 50 micron glass beads is then cascaded across the surface of the resin layer to form a layer 13 (FIG. 1) approximately 1 micron in thickness.

An electrostatic image is applied to the plate by means of a corona discharge device and a stencil, as illustrated in FIG. 2. The image areas are positively charged to about 60 volts. The latent image-bearing plate is then treated with cyclohexane vapor resulting in migration of the charged areas of layer 13 to the surface of the polyester film. Non-imaged portions of layer 13 and the layer of Piccotex 100 are then removed by immersing the developed plate in liquid cyclohexane for about 10 seconds. The result is a faithful visible replica of electrostatic image.

EXAMPLES II-V

The procedure of Example I was carried out with a series of plates to which were applied electrostatic images of 2, 20, 40, and 160 volts, respectively, instead of 60 volts as in Example I. Faithful visible replicas of the electrostatic images were produced.

EXAMPLES VI-XXII

A series of seventeen plates was prepared by cascading a mixture of graphite particles (as used in Example I) and 50 micron glass beads several times across the surface of a two micron layer of Staybelite 10 (Hercules Powder Company) overlying aluminized Mylar polyester film (E. I. du Pont de Nemours Co., Inc.). An electrostatic image was then formed on each plate by means of a corona discharge device and mask (as illustrated in FIG. 2), and the plates were developed by immersion in liquid solvents to form faithful replicas, in accordance with the following:

Applied potential, volts:	Solvent
+40 -----	Sohio odorless solvent 3440.
+60 -----	Do.
+90 -----	Do.
+110 -----	Do.
+180 -----	Do.
+40 -----	Cyclohexane.
+50 -----	Do.
+60 -----	Do.
+70 -----	Do.
+80 -----	Do.
+100 -----	Do.
+60 -----	Freon 113.
+150 -----	Do.
-40 -----	Sohio odorless solvent 3440.
-50 -----	Cyclohexane.
-180 -----	Do.
-300 -----	Do.

The instant imaging process has also been carried out with the materials and values shown in Table I. In each instance, the substrate comprised aluminized Mylar over

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which layer 12 was roll coated. Layer 11 was formed by the cascade method described above. Development was by immersion in solvent liquid. The garnet particles used had an average diameter of about 5 microns.

TABLE I

Layer 11	Layer 12	Applied potential	Solvent 36
Neo Spectra carbon black (Columbian Carbon Co.)	Piccotex 100...	+160	Cyclohexane.
Do	do	+160	Freon 113.
Do	Staybelite 10...	+160	Cyclohexane.
Do	do	+160	Freon 113.
Garnet	do	+7	Cyclohexane.
Do	do	+30	Do.
Do	do	+80	Do.
Do	do	+95	Do.
Do	do	+250	Do.
Do	do	+140	Freon 113.
Do	do	-260	Sohio odorless solvent 3440.
Do	Piccotex 100...	+6	Cyclohexane.
Do	do	+30	Do.
Do	do	+40	Do.
Do	do	-125	Do.
Do	do	+70	Freon 113.
Iron oxide	Staybelite 10...	+90	Cyclohexane.

Thus, the magnitude of the electrostatic image applied to the imaging plate is not critical as long as it is above the threshold to produce migration with the particular combination of materials used. As a practical matter, however, the magnitude of the electrostatic image applied will conveniently be far in excess of the threshold value. Generally, it is preferred to apply a potential of at least about 20 volts to assure high quality images. Below that value image contrast diminishes, but useful results are nevertheless produced.

According to another aspect of the present invention, particle migration is controlled by an imagewise modification of the softenable layer prior to the above described development process. This approach obviates the formation of an electrostatic image and permits, instead, the use of a substantially uniform charge to impart the electrical forces required for particle migration. It also permits the use of electrically conductive particles without regard to lateral conductivity of layer 11.

Reference is made to FIG. 7 showing the modification of the softenable layer by means of ultraviolet radiation. Illustratively, layer 12 of Staybelite 10 (two microns in thickness) overlying aluminized Mylar substrate 13 is exposed for several minutes through image mask 21 to an image pattern of ultraviolet radiation from lamp 22.

Layer 11 is then formed on layer 12 by cascading across it a mixture 41 of finely divided zinc oxide, or other marking particles and glass beads of the type suitable for xerographic carrier, as schematically illustrated in FIG. 8. The three-layer structure thereby formed is ready for the charging and developing steps for forming a visible image.

Depending upon specific materials employed in the plate structure, other forms of actinic radiation may be used (either before or after formation of layer 11) to selectively modify the permeability of layer 12 to particle migration. Suitable methods include: X-ray treatment, Beta ray treatment, Gamma ray treatment and high energy electron bombardment.

As illustrated in FIG. 9, a substantially uniform electrostatic charge may be applied to layer 11 by moving corona discharge device 18 energized by high voltage power supply 19 in charging relation thereto. The corona device preferably applies a potential of at least about 20 volts to layer 11 with respect to substrate 13 to produce images of superior quality, especially as regards contrast. The instant process is operable, however, with much lower voltages, as the foregoing examples indicate. The charged plate may then be developed as described in connection with FIG. 4 and FIG. 5.

The foregoing description set forth for purposes of description and illustration is not intended to limit the invention as defined in the appended claims.

What is claimed is:

1. An imaging method comprising the steps of:
 - (a) providing an imaging member comprising a fracturable layer contacting a solvent soluble layer overlying a substrate, said fracturable layer spaced apart from said substrate;
 - (b) forming an electrostatic image on said member; and
 - (c) applying a solvent for said solvent soluble layer to said member wherein said solvent is sufficiently electrically insulating to prevent fracturable material from losing its charge before reaching said substrate and wherein said fracturable layer and said substrate are not entirely soluble in said solvent, whereby said solvent soluble layer and selective portions of said fracturable layer are substantially removed and whereby selective other portions of said fracturable layer are deposited on said substrate in image configuration.
2. An imaging method according to claim 1 wherein said solvent soluble layer is substantially electrically insulating.
3. An imaging method according to claim 1 wherein said fracturable layer comprises electrically conductive material.
4. An imaging method according to claim 1 wherein said fracturable layer comprises substantially electrically insulating material.
5. An imaging method according to claim 1 wherein said fracturable layer comprises predominantly particles.
6. An imaging method according to claim 1 wherein said substrate is electrically conductive.
7. An imaging method according to claim 1 wherein said fracturable layer comprises a photoconductor.
8. An imaging method according to claim 7 wherein said photoconductor comprises selenium.
9. An imaging method according to claim 8 wherein said selenium comprises amorphous selenium.
10. An imaging method according to claim 7 wherein said photoconductor comprises phthalocyanine.
11. An imaging method according to claim 1 wherein said solvent is applied by immersing said imaging member in said solvent.
12. An imaging method according to claim 1 wherein said fracturable layer is between about 0.2 to about 10 microns thick.
13. An imaging method according to claim 1 wherein said solvent is selected from the group consisting of cyclohexane, pentane, heptane, toluene, trichloroethylene, trichlorotrifluoroethane, kerosene and mixtures thereof.

14. An imaging method according to claim 1 wherein the surface potential of the imaging member in regions of the electrostatic image is greater than about 20 volts.

15. An imaging method according to claim 1 wherein the electrostatic field within the softenable layer in regions of the electrostatic image is greater than about 10 volts/micron thickness of the solvent soluble layer.

16. An imaging method according to claim 1 wherein said solvent soluble layer is between about 1 to about 4 microns thick.

17. An imaging method according to claim 12 wherein said solvent soluble layer is between about 1 to about 4 microns thick.

18. An imaging method according to claim 1 wherein said solvent soluble layer is thermoplastic.

19. An imaging method according to claim 18 wherein said solvent soluble layer comprises a partially hydrogenated rosin ester.

20. An imaging method according to claim 16 wherein said solvent soluble layer is about 2 microns thick.

21. An imaging method according to claim 1 wherein said fracturable layer comprises particles selected from the group consisting of graphite, carbon black, garnet, iron oxide, zinc oxide and mixtures thereof.

22. An imaging method according to claim 6 wherein said substrate comprises a conductively overlayered electrically insulating substrate layer.

23. An imaging method according to claim 22 wherein each of said conductive layer and said electrically insulating substrate layer is at least partially transparent.

24. An imaging method according to claim 23 wherein said electrically insulating substrate layer is a stable plastic.

25. An imaging method according to claim 24 wherein said stable plastic comprises polyethylene terephthalate and said conductive layer comprises aluminum.

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U.S. Cl. X.R.

96-1 R, 1.5; 346-1; 204-181; 117-1.7, 72, 212, 216, 218, 226, 37 R