# United States Patent [19]

**Bean**

[11] **3,926,626**

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[54] **CIRCULATION IMAGING METHOD**


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[52] **U.S. Cl.** ..... **96/1 R;** 96/1 PS; 96/35; 96/36; 96/35.1; 250/315; 346/74 EB

[51] **Int. Cl.²** ..... **G03G 13/22**

[58] **Field of Search** ..... 96/1 R, 1 PS, 1.1



[56] **References Cited**

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*Primary Examiner*—Roland E. Martins, Jr.



[57] **ABSTRACT**

Images are formed by the selective electrical mixing of materials to alter physical and/or chemical properties in imagewise configuration. The materials are conveniently provided in an imaging member having a circulation layer, and one or more layers of materials the mixing of which results in a physical and/or chemical property which is distinct from that of at least one of the individual materials.


**27 Claims, 3 Drawing Figures**

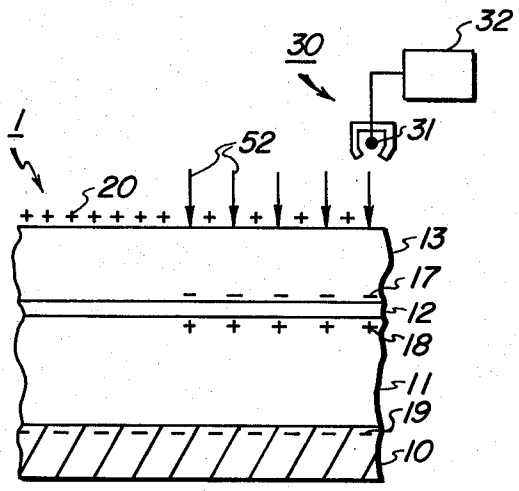



FIG. 1

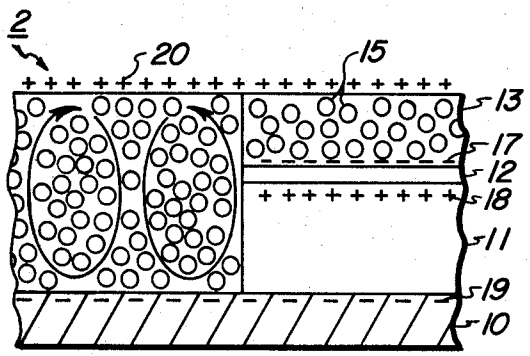



FIG. 2

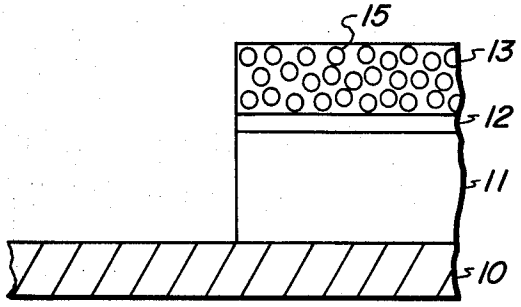



FIG. 3

# CIRCULATION IMAGING METHOD

## BACKGROUND OF THE INVENTION

This invention relates to imaging systems and in particular to a novel imaging system utilizing selective electrical mixing of materials to form the image.

## SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide a novel imaging system.

It is another object of the invention to provide a novel imaging system which forms images by the imagewise mixing of materials in the imaging member.

The foregoing objects and others are accomplished in the present invention, generally, by providing an imaging member having a circulation layer and one or more layers of materials the mixing of which results in a physical and/or chemical property which is distinct from that of at least one of the individual unmixed materials; and selectively mixing such layers in imagewise configuration.

The process steps of this invention include creating an electrical latent image on the free surface of the novel imaging member which has electrical fields associated therewith and softening the layer or layers of materials and circulation layer by exposing them to heat, partial solvent liquid or solvent vapors or combinations thereof. The softening step reduces the viscosity of the layer sufficiently to allow circulation of one or more layers and therefore mixing of the layers in areas where electrical fields are present. The phrases "circulation", "circulate" and variations thereof are used herein to mean the movement of material, generally in a circular convection pattern, in response to a charge density at or above the "threshold level of circulation". The latter phrase is used herein to mean the charge density at which the circulation layer begins to circulate. After mixing, the property differential between mixed portions of the imaging member and unmixed portions is in imagewise configuration and is utilized for image creation. For example, if the property differential is solubility, then either the mixed or unmixed portions of the imaging member is removed with a suitable solvent. If the property differential is color, then a visible image is created upon mixing, and so forth.

## DESCRIPTIONS OF THE DRAWINGS

Other objects and features of the present invention will be apparent from further reading of the specification and from the drawings which are:

FIG. 1 is a partial schematic illustration of a cross-section of the preferred embodiment imaging member employed in this invention.

FIG. 2 is a partial schematic illustration of a cross-section of an imaging member according to this invention which shows selective mixing via selective circulation and further illustrates the inclusion of either an initiator or inhibitor in polymerizable embodiments of the invention.

FIG. 3 partially schematically illustrates in cross-section the developed FIG. 2 member where mixed portions of the member were removed during development.

The partial schematic illustrations of the imaging members before, during and after development are not to scale; but rather, illustrate the structural and functional relationships between the imaging member layers, components thereof and the circulation phenomena.



## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Imaging member 1 of FIG. 1 comprises a substrate **10**, a circulation layer **11**, a photoconductive binder layer **12**, and a softenable insulating layer **13**. All three layers are "softenable" as that term is used herein; however, for ease of description they are herein conveniently given different descriptive names. In the imaging method of the invention, an electrical latent image is created on the free surface of the imaging member **1**. This may be accomplished by a wide variety of methods including charging through a stencil, electrostatic transfer of charge and charge induction methods. Preferably, the softenable layer is photoconductive enabling the latent image to be formed by charging and exposing steps. For example, the free surface of layer **13** can be electrostatically charged and exposed to electromagnetic radiation **50** to which the photoconductive binder layer **12** is sensitive; i.e., the electromagnetic radiation is actinic or activating with respect to the layer **12**. As depicted in FIG. **1**, the electrostatic charging step results in the deposition of a charge of one polarity on the free surface of layer **13** and the induction of another charge **19** of opposite polarity in the substrate **10**. As further depicted in FIG. **1**, in dark or non-exposed areas of member **1**, the electrical fields associated with charges **19** and **20** extends across layers **11, 12** and **13**. However, in exposed areas of member **1**, the actinic radiation renders the photoconductive layer **12** conductive and therefore collapses the electrical field previously existing across photocoductive layer **12** and sets up charges **17** and **18**. Charge **17** resides in layer **13** and is of opposite polarity from charge **20**. Charge **18** resides in layer **11** and is of opposite polarity from charge **19**. Thus, in exposed areas of member **1** it can be seen that two electrical fields are present as opposed to the one electrical field in dark areas of imaging member **1**: the electrical field associated with charges **20** and **17** and the electrical field associated with charges **18** and **19**. After exposure, the viscosity of layers **11, 12,** and **13** are reduced sufficiently to allow circulation to preferably occur in all three layers thereby effectively mixing the three layers in areas where the electrical field associated with the charge density of charge **20** extends across all three layers; i.e., in the dark areas of imaging member **1** when charge-expose techniques are used to create the electrical latent image. In exposed areas some circulation may occur in layers **13** and **11** upon viscosity reduction, but typically such circulation is limited substantially to within the respective layers and does not extend across the photoconductive binder layer **12**. Accordingly, in exposed areas of imaging member **1**, upon reducing the viscosity of layers **11, 12** and **13**, these layers normally do not sufficiently mix to provide a physical and/or chemical property distinct from either of the three layers. At this point in the process a property differential has been formed comprising a pattern of physical and/or chemical properties corresponding to dark and exposed areas of imaging member **1**.

However, in those embodiments where layer **12** is dispensed with and either the circulation layer **11** or the insulating layer **13** is rendered photoconductive as discussed below, then process variables can be adjusted

so that circulation occurs substantially within the non-photoconductive layer to either have or lack sufficient effect on the other layer to cause some mixing of the materials in the two layers in exposed areas.

The step of electrostatically charging is preferably one of uniformly electrostatic charging which allows charge-expose creation of the electrical latent image. Charge-expose steps are preferred for convenience and speed of imaging, allowing camera speeds of ASA 0.1 or faster. Referring now to FIG. **1**, the imaging member **1** is uniformly electrostatically charged, generally in the substantial absence of actinic radiation for layer **12**, illustratively by means of a corona discharge device **30** which is shown to be traversing the member **1** from left to right and depositing a uniform charge on the surface of layer **13**. The corotron includes thin conductive wire **31** coupled to a suitable high voltage source **32**. Corona discharge devices of the general description and generally operated as disclosed in Yverberg U.S. Pat. No. 2,836,725 and Walkup U.S. Pat. No. 2,777,957 have been found to be excellent sources of corona useful in the charging of member **1**. Modes of electron charging may also be used. Other charging techniques ranging from rubbing the member, to induction charging for example, as described in Walkup U.S. Pat. No. 2,934,649 are available in the art. Where substrate **10** is an insulating material or where there is no substrate **10**, charging of the member, for example, may be accomplished by placing a conductive surface in contact with the member and charging as illustrated in FIG. **1**. Alternatively, other methods known in the art of xerography for charging xerographic plates having insulating backings may be applied. For example, the member may be charged using double sided corona charging techniques where two corona charging devices on each side of the member **1** and oppositely charged are traversed in register relative to member **1**. Charge densities producing an electric field across layers **11, 12** and **13** from about **10** volts per micron to about 80 volts per micron are satisfactory; a range of from about 30 volts per micron to about 50 volts per micron being preferred.

With respect to the exposure step, it is appreciated of course that the step is effected with charge-exposure techniques are used to create the electrical latent image and can be dispensed with when other techniques such as stencil charging are used to create the electrical latent image. Similarly, either layer **12** can be dispensed with or its photoconductive nature omitted in such cases. In exposing thhe photoconductive layer **12** to actinic electromagnetic radiation, any suitable actinic electromagnetic radiation may be used. Typical types include radiation from ordinary incandescent lamps, x-rays, beams of charged particles, infrared, ultraviolet and combinations thereof. FIG. **1** illustratively shows charges **17, 18, 19,** and **20** present in previously exposed areas. Prior to exposure, however, only charge **20** and **19** are present as in the representative dark or unexposed area of member **1**. The charges **17** and **18** in FIG. **1** are believed to be injected into layers **13** and **11,** respectively, from the photoconductive layer **12** upon exposure to actinic radiation. It is further believed that the subsequent step of softening the three layers **11, 12** and **13** in reducing their viscosity to allow circulation permits further injection of charges **17** and **20** into layer **13** and charges **18** and **19** into layer **11,** thereby collapsing the electrical fields across these two layers. It is felt that this believed phenomena accounts for the lack of sufficient circulation in layers **11** and **13** during the softening step to permit the development of a distinct physical and/or chemical property as is done in the dark or unexposed areas.

The softening step which reduces the viscosity of layers **11, 12** and **13** sufficiently to allow circulation in the dark areas may be conveniently accomplished by exposing the imaging member **1** to heat, solvent vapors, partial solvent liquid or combinations thereof. "Partial solvent" is used herein to mean a solvent which either in amount or kind only partially dissolves, swells, softens or otherwise reduces viscosity without complete dissolution. Development of the imaging member **1,** where the distinct property of solubility is provided by mixing the three layers, may be satisfactorily accomplished by removing either the mixed or unmixed part of imaging member **1;** and, where mixing produce a distinct color, the mere mixing itself may provide image development, such as a chemical reaction in imagewise configuration.

Substrate **10** may be electrically conductive or insulating. Conductive substrates generally facilitate the charging of the member and typically may be of metals, such as brass, copper, chromium, stainless steel, brass, zinc, or may be conductive plastics and rubbers. The conductive substrate may be coated on an insulator such as plastic, glass or paper; for example, a substantially transparent tin oxide coated glass available under the trademark NESA from the Pittsburgh Plate Glass Company.

The softenable material of insulating layers **11** and **13** may comprise any suitable softenable material. The phrase "softenable material" is used herein to mean any suitable material which is reduced in viscosity in a partial solvent, solvent vapor, or heat, and in addition, is substantially electrically insulating during the imaging process of the invention. Classes of materials falling within this definition include polystyrenes, alkyd substituted polystyrenes, polyolefins, stryene-acrylate copolymers, styrene-olefin copolymers, silicone resins, phenolic resins, and organic amorphous glasses. Typical materials are Staybelite Ester 10, a partially hydrogenated rosin ester, Foral Ester, a hydrogenated rosin triester, and Neolyne 23, an alkyd resin, all from Hercules Powder Co., SR 82, SR 84, silicone resins, both obtained from General Electric Corporation; Velsicol X-37, a poly-styrene-olefin copolymer from Velsicol Chemical Corp.; Hydrogenated Piccopale 100, a higly branched poly-olefin, HP-100, hydrogenated Piccopale 100, Piccotex 100, a copolymer of methyl styrene and vinyl toluene, Piccolastic A-75, 100 and 125, all polystyrenes, Piccodiene 2215, a polystyrene-olefin copolymer, all from Pennsylvania Industrial Chemical Co., Araldite 6060 and 6071, epoxy resins of Ciba; Amoco 18, a poly-alpha-methyl-styrene from Amoco Chem. Corp.; ET-693, and Amberol ST, phenol-formaldehyde resins, ethyl cellulose, and Dow C4, a methylphenylsilicone, all from Dow Chemical; M-140, a custom synthesized styrene-co-n-butylmethacrylate, R50601A, a phenylmethyl silicone resin from Dow Corning; Epon 1001, a bisphenol A-epichlorohydrin epoxy resin, from Shell Chemical Corp.; and PS-2, PS-3, both polystyrenes, and ET-693, a phenolformaldehyde resin, from Dow Chemical; and a custom synthesized 80/20 mole percent copolymer of styrene and hexlmethacrylate having an intrinsic viscosity of 0.179 dl/gm. and Nirez 1085, a polyterpene resin, available from Tenneco Corp. under that trade name. Although any operable

thickness for layers **11** and **13** may be used, a satisfactory range for these two layers have a thickness in the range from about 1 micron to about 12 microns. For reliability, fastness of drying and image resolution, a range of from about 1 micron to about 6 microns is preferred.

The photoconductive binder layer **12** when employed, may comprise any suitable photosensitive material in a suitable binder in sufficient quantities to render layer **12** photoconductive. For example, adding 2, 5-bis (p-aminophenyl)-1,3,4-oxadiazole available under the trademark TO 1920 from Kalle and Co., Weisbaden-Biebrich, Germany to Vinylite VYNS, a copolymer of vinly chloride and vinylacetate available from Union Carbide Plastics Co., or, adding 2,4,7-trinitro-9-fluoerenone to polyvinyl carbazole, available under the trademark Luvican 170 from Winter, Wolff and Co., New York, New York. Similarly photoconductive dyes may be added to suitable materials to broaden the photoconductive layer's spectral response; such as, for example, the addition of Rhodamine B dye, a red water-soluble dye available from DuPont, to either TO 1920 and Vinylite VYNS or VYLF (another copolymer of vinylchloride and vinyl acetates). The photosensitive material may consist of any suitable inorganic or organic photosensitive material. Typical inorganic materials are vitreous selenium, vitreous selenium alloyed with arsenic, tellurium, antimony or bismuth, etc.; cadmium sulfide, zinc oxide, cadmium sulfoselenide, and many others. U.S. Pat. No. 3,121,006 to Middleton et al and U.S. Pat. No. 3,288,603 set forth a whole host of typical inorganic pigments and suitable binders therefor which are hereby incorporated by reference. Typical organic materials are: Watchung Red B, a barium salt of 1-(4'-methyl-5'-chloro-azo-benzene-2'-sulfonic acid)-2-hydrohydroxy-3-napthoic acid,C.I. No. 15865, available from DuPont; Indofast double scarlet toner, a Pyranthrone-type pigment available from Harmon Colors; quindo magenta RV-6803, a quinacridones, such as Monastral Red B (E. I. DuPont), Cyan Blue, GTNF the beta form of copper phthalocyanine, C.I. No. 74160, available from Collway Colors; Monolite Fast Blue GS, the alpha form of metal-free phthalocyanine, C. I. No. 74100, available from Arnold Hoffman Co.; Diane Blue, 3,3-methoxy-4,4'-diphenyl-bis (1''azo-2'' hydroxy-3''-naphthanilide), C. I. No. 21180, available from Harmon Colors; and Algol G. C., polyvinyl carbazole 1,2,5,6-di (D,D'-diphenyl)-thiazole-anthraquinone, C. I. No. 67300, available from General Dyestuffs. The above list of organic and inorganic photosensitive materials is illustrative of some of the typical materials, and should not be taken as a complete listing. Preferred volume ratios of photosensitive material to binder material are from about 1.8 to about 7:1, preferred weight ratios are from about 1:6 to about 4:1.

Any operable thickness for the photoconductive binder layer **12** may be utilized; a preferred thickness range for layer **12** is from about 0.5 micron to about 1 micron. A satisfactory range is from about 0.5 micron to about 5 microns. Even in charge-expose imaging techniques, layer **12** may be omitted and either layer **11** or layer **13** rendered photoconductive by the addition of the above materials. However, in charge-expose imaging it is preferred to have a separate photoconductive layer **12** so that wide process latitudes are available in creating a distinct physical or chemical property differential upon mixing layers **11** and **13**. That is, layer **12** acts as a buffer to prevent mixing of layers **11** and **13** when either or both are circulating; and, acts as a chemical buffer when layers **11** and **13** each contain a reagent which combines with the other to undergo a color or other conversion reaction. Without layer **12**, as previously mentioned, circulation of only one layer may or may not cause mixing of the two layers, depending upon process variables which may or may not cause the mixing effect of circulation to be extended beyond the one circulating layer. Thus, without layer **12**, the process variables should be carefully co-ordinated so that the desired mixing effect is achieved. Typically, the desired effect is to have mixing in certain areas (dark areas or areas where the electrical field associated with the electrical latent image extends across the entire imaging member) and no mixing in other areas (exposed areas or areas where the electrical field is discharged across one or more layers). However, such a desired effect is not necessary to the practice of the invention and primarily represents convenience annd clarity of imaging.

Following exposure to activating radiation, the entire imaging structure including the exposed portions of the imaging member is then softened by uniformly subjecting it to either heat, partial solvent, or solvent vapor. Solvent vapor exposure is typically from about 5 to about 15 seconds. Any suitable solvent may be used for partial solvent or solvent vapor softening of the imaging member. Typical solvents are Freon TMC, available from DuPont; trichlorethylene, chloroform, ethyl, xylene, dioxane, benzene, toluene, cyclohexane, 1,1,1-trichloroethane, pentane, n-heptane, Odorless Solvent 3440 (Sohio), Freon 113, available from DuPont; mxylene, carbon tetrachloride, thiophene, diphenyl ether, pcymene, cis-2, 2-dichlorethylene, nitromethane, N,N-dimethyl formide, ethanol, ethyl acetate, methyl ethyl ketone, ethylene dichloride, methylene chloride, 1,1-dichloroethylene, trans 1,2-dichloroethylene, and super naptholite (Buffalo Solvents and Chemicals), and various mixtures thereof.

Upon softening, mixing occurs via the circulation of layers **11, 12** and **13** in nonexposed portions of the imaging member. This is depicted in FIG. **2.** Where the property differential is solubility, the imaging member may be developed by removing either the mixed or unmixed portions thereof by contact with a suitable solvent. FIG. **3** represents the developed FIG. **2** member where mixed portions were removed. Typical suitable solvents include those listed above for the softening step, including mixtures thereof and additionally includes kerosene and discrete fractions thereof, alone, or in combination with the above listed solvents. A suitable technique for solvent removal where kerosene can be used as the solvent involves simple immersion of the imaging member in the kerosene. When the other stronger solvents are used, either alone or in combination with kerosene, it is preferred to use a cotton swab loaded with solvent and to apply the solvent to the imaging member by swabbing the member for a period of from about 2 to 4 seconds. The swabbing prevents the application of too much solvent which can degrade the image if the solubility differential between mixed and unmixed portions of the member is slight with respect to the solvent employed.

The invention may be used to produce unlimited types of images capable of being produced by the mixture of two materials, Where resist images are desired, the layers **11** and **13** each contain a different material.

The material of layer **11** and that of layer **13** are chosen, typically, so that upon mixture thereof the mixture is either more or less soluble than the unmixed materials so that it can be removed from the unmixed materials with a specific solvent. For example, one way to achieve solubility differentials between mixed and unmixed materials is to polymerize selectively. "Polymerize" and variations thereof are used herein to include crosslinking of polymers as well as the formation of polymers from smaller units such as monomers. Such a resist system yields a negative working resist system; i.e., one in which exposed areas (unmixed) remain after removal of nonexposed areas (mixed).

The materials of both layers **11** and **13** can enter in the polymerization upon mixing; or, after being subjected to a separate polymerization step. In the former case polymerization constitutes the property differential; in the latter case, polymerization susceptibility constitutes the differential. Also, one of the layers (such as **13**) can be inert with respect to polymerization (layer **11** being polymerizable) and have dispersed therein an inhibitor **15** (FIG. **2**) which prevents the material in layer **11** from polymerizing. In such cases, after the polymerization step, the mixed areas comprise an unpolymerized layer **11.** This embodiment prevents the troublesome undercutting typically associated with photoresist processes. The same result can be achieved where both layers are normally non-polymerizable but where one layer (such as **13**) contains an initiator which causes polymerization of the other (such as **11**) either upon mixing or after the polymerization step. Here, after the polymerization step, the mixed areas comprise polymerized material and the unmixed areas comprise unpolymerized material. Removing the unmixed areas of the imaging member yields a positive working resist system. Removing the mixed areas of the imaging member yields a negative working resist system.

It is preferred that when inhibitors and initiators are employed, that they be included in a layer other than that residing on the substrate. This configuration diminishes undercutting by solvent or solvent vapor applied during the wash-away or removal step, because layer **11** then becomes polymerized during the polymerization step. Any suitable initiator may be used including, for example, cationic, anionic and free radical initiators. Typical suitable initiators include: aluminum chloride, boron fluoride, sulfuric acid, activated clays; hydro-chloric, hydrobromic, hydrofluoric, perchloric, nitric, phosphoric, acetic, and trichloracetic acids; alkali metals and amides thereof; and acyl and alkyl perchlorates. Any suitable inhibitor may be used. Typical suitable inhibitors include: 2.2′-methylenebis[6-(2-methylcyclohexyl)p-cresol]; bis[2-hydroxy-3-(a-methylcyclohexyl)-5-methylphenyl]methane; 4,4′-ethylidenedi-o-cresol; 1,1-bis(3-methyl-4-hydroxyphenyl)ethane; 4,4′-methylene-bis(2 6-dialkylphenol); 2,6-di-tert-butyl-p-cresol; N,N′-di-2-naphthyl-p-phenylenediamine; salts or amides of 3,3′-triodipropionic acid; bis(dimethylthiocarbamoly)disulfide; tetramethylthiuram disulfide; 1,1′-triodi-2-naphthol; 1,1′-thiodi-2-naphthol; 1,1′-thiobis[N-phenyl-2-naphthylamine]; bis(N-phenyl-2-naphthyl-amine) sulfide; N,N′-(iminodiethylene)bisoctadccanamide; N,N′-dioleoyldiethylenetriamine.

Any suitable polymerizable material may be used in the invention where solubility differential between mixed and unmixed areas is promoted by polymerization; including, for example, suitable softenable materials listed above and KPR (Kodak Photoresist available from Eastman Kodak Company, Rochester, N.Y.), the cinnamate esters of polyvinyl alcohol and cellulose. Any suitable polymerizing step may be utilized, including, for example, thermal polymerization at elevated temperatures and exposure to U. V. light. It is preferred that polymerization be delayed until after mixing via circulation and require a separate process step, to provide best results, although this is not essential.

The process of the invention can be used to produce functional color images. Functional color is employed, for example, in the makeing of charts, posters and projection transparencies for visual aids. For functional color, each of layers **11** and **13** can comprise a differently colored softenable material which, when mixed either produce a third distinct color or form a colorless product. Color can be imparted by the inclusion of any suitable dye or pigment. Color may also be imparted by including in each of layers **11** and **13** reagents which when combined upon mixing chemically produce a color conversion reaction, such as those disclosed in U.S. Pat. No. 3,404,001 which is incorporated herein by reference. It will be appreciated, of course, that the reagents should be placed in layers **11** and **13** with layer **12** serving as the protective buffer barrier.

The following conditions should be observed during imaging in accordance with this invention: the softenable material of layers **11** and **13** should be insoluble in, and not a good solvent for, photoconductive layer **12;** in removing either mixed or unmixed areas of the imaged member from the other by solvent, the application of solvent should substantially result in removal of only the desired areas and should therefor be a good solvent only for that area; and the relationship of the electrical field, in dark areas of the imaging member and associated with the charges **19** and **20,** with the softenable materials of layers **11, 12,** and **13** should be such that the softenable materials in their softened state have a viscosity sufficiently low enough to allow circulation with the use of any particular change density for charge **20.**

Notably, many materials suitable for frost and relief deformation imaging are also suitable as the softenable material in the circulation and other layers. Surface deformation imaging systems are described in a paper by R. W. Gundlach and C. J. Claus titled "A Cyclic Xerographic Method Based on Frost Deformation" in Photographic Sciences and Engineering, Vol. 7, No. 3, pp. 14–19, January – February 1963. Additional descriptions are given in U.S. Pat. Nos. 3,196,011 to K. W. Gunther and R. W. Gundlach and 3,113,179 to W. E. Glen, Jr. Two distinct surface deformation imaging systems have evolved: relief imaging and frost imaging. Both imaging systems employ a softenable film (hereafter called a deformable material) overcoating a conductive substrate. Surface deformations occur in both relief and frost systems due to electrical forces exerted on the deformable material when its viscosity is reduced. The deformations in relief imaging are highly regular in shape because they are caused by forces lateral to the surface associated with abrupt changes in charge density. The deformations in frost imaging include randomly shaped depressions generally uniformly spaced over an area of the frostable material having constant or continuously charging charge densities above threshold levels for frosting. The threshold level for frosting is presently believed related to such

parameters on ion mobility, viscosity, bulk conductivity, surface conductivity and thickness of the frostable material. During the frost deforming process, the frostable material circulates or flows in a manner similar to convection currents. Selective circulating action including selective frost circulation is employed in the present invention to form novel images by the mixture of at least two materials; that is, the selective circulation is herein made to cause mixing or intermixing of two or more layers in areas of circulation. Any softenable material which will circulate will suffice, even though it does not deform; for example silicone oil.

Preferably, the imaging member layers **11, 12** and **13** are dissimilar so that mixing by diffusion and other non-bulk mixing mechanisms does not occur in the absence of circulation. This provides greater stability to the imaging member when not being subjected to the imaging process; but, the bulk-mixing properties may be chosen for creating the desired property differential so that relatively slow mixing phenomena, such as diffusion, are of minor consequence to the final image.

The degree of dissimilarity which is preferred is any dissimilarity which prevents the mixing of imaging member layers under imaging process conditions in the absence of at least the circulation layer circulating. In this regard, immiscible layers or materials are an example of the degree of dissimilarity which calls for circulating the circulation layer. "Immiscible layers or materials" are used herein to include two or more layers or materials which can be cast such that a distinct interface or interfaces, including viscosity gradients, exists therebetween even though the layers or materials can be cast to have no distinct interface or interfaces under other conditions; and include materials which initially have a distinct interface but which diffuse into one another either in time or under certain conditions outside those in the imaging process.

The circulation mechanism generally requires that the circulation layer be sufficiently thin so that the charge density required to initiate circulation will not cause dielectric breakdown. Further, the resistivity of the circulation layer should be sufficiently great so that ohmic discharge does not occur before elapse of the development time for the imaging member. It has been empirically found that development time for the imaging members disclosed herein can be approximated by the factor $N10^{-4}$ sec/poise where N is the viscosity in poises of the softenable material of the circulation layer. Accordingly, since viscosity is temperature dependent, the selection of softenable material for the circulation layer and other layers is made with a view of contemplated process variables such as charge density levels, operating temperatures, the circulation layer viscosity at such temperatures and the circulation layer resistivity.

The following examples further specifically define the present novel imaging system, its material and methods for making the imaging members. The parts and percentages are by weight unless otherwise indicated. The examples below are intended to illustrate various preferred embodiments of the instant invention. The imaged multiple layered imaging members herein may have softenable material removed from one or more layers by immersion in discrete kerosene fractions such as Sohio Odorless Solvent 3440, Sohio Odorless Solvent 3456 and other discreet kerosene fractions. Furthermore, the background removal and splitting techniques described in copending application U.S. Ser. No. 784,164, filed Dec. 16, 1968 and U.S. Pat. No. 3,664,834, hereby incorporated by reference, may be utilized after imaging according to the instant invention to split apart the imaged member or to remove one or more layers from the circulation or lower softenable layer (or vice versa) or to split apart unmixed layers of material or to cause one layer or material to be removed as by washing away or abrasion and other modes taught therein.

## EXAMPLE I

The imaging member in FIG. **1** is prepared as follows: An about 3 mil "Mylar" film, available from E. I. DuPont and vacuum coated with a thin layer of aluminum, forms an opaque highly reflective conductor and is used as the substrate. The circulation layer is made of Dow Resin PS-2, a polystyrene available from the Dow Chemical Corp., and is coated upon the substrate at about 6 microns in thickness out of a solution of the resin and toluene. The photoconductive layer is coated upon the circulation layer at about 1 micron in thickness out of a dispersion of about 1 part phthalocyanine particles in a solution of about 2 parts "Nirez **1085**" dissolved in kerosene. A softenable insulating layer is coated upon the photoconductive layer at about 3 microns thickness out of a solution of "Nirez 1085" in kerosene.

The imaging member has positive charge deposited on it sufficient to create an electrical field strength of a value of about 30 volts/micron using a corotron described by Vyrerberg in U.S. Pat. No. 2,836,725. The charged surface is imagewise exposed to radiation from a 45 watt tungsten lamp at f/32 for about 1 second through a transparency. In exposed areas, the field within the photoconductive layer collapses.

The charged and exposed imaging member is softened by subjecting it to trichloroethylene vapors for about 10 seconds.

During softening, the circulation, photoconductive and softenable insulating layer circulate and mix with one another in nonexposed or dark portions of the imaging member. The mixed materials in these nonexposed areas are dissolved and removed from the imaging member in a solution of about 15% toluene and about 85% Sohio 3440, applied with a cotton swab by rubbing the swab for about 3 seconds, leaving behind the unmixed layers in an image configuration corresponding to exposed areas of the imaging member.

## EXAMPLE II

Example I is repeated with the following exception: Dow PS-3, a polystyrene available from Dow Chemical Corp., is substituted for the Dow PS-2 in the circulation layer.

## EXAMPLE III

Example I is repeated with the following exception: MA-140, a copolymer of n-butyl methacrylate and polystyrene is substituted for the Dow PS-2 in the circulation layer.

## EXAMPLE IV

Example I is followed with the following exception: an about 80/20 mole percent copolymer of styrene and hexylmethacrylate having an intrinsic viscosity of about 0.179 dl/gm is substituted for the Dow PS-2 in the circulation layer.

EXAMPLE V

Example I is followed except that the softenable insulating layer of "Nirez 1085" additionally contains about 5% by volume 2,6-di-tert-butyl-p-cresol and, prior to application of the toluene — Sohio solvent, the imaging member is uniformly exposed to ultra-violet light for about 5 minutes. The mixed areas of the imaging member have no crosslinking but the circulation layer in unmixed areas is crosslinked and resistant to undercutting by the removal solvent upon subsequent removal of the mixed areas.

EXAMPLE VI

The same substrate as in Example I is used. The circulation layer is made of KPR and is coated upon the substrate at about 5 microns out of a solution of KPR and trichloroethylene and allowed to dry. The photoconductive layer of Example I is overcoated onto the circulation layer; and, the softenable insulating layer of Example V is coated over the photoconductive layer. The imaging member has positive charge deposited on it sufficient to create an electrical field strength of a value of about 50 volts/micron using the corotron of Example I; and, is exposed as in Example I. The charged and exposed imaging member is softened by subjecting it to trichloroethylene vapors for about 10 seconds. During softening, the circulation, photoconductive and softenable insulating layer circulate and mix with one another in non-exposed or dark portions of the imaging member. After mixing, the imaging member is uniformly exposed to a light source rich in ultraviolet. This results in the crosslinking and consequent insolubilizing or the KPR in unmixed areas, while the KPR in mixed areas has no crosslinking. The KPR and other materials in mixed areas are removed as in Example I. The crosslinked KPR in unmixed areas has excellent resistance to undercutting by the solvent used to remove mixed areas. Charging and developing in all the above Examples is carried out in the absence of activating radiation for the photoconductive layers.

Other modifications and ramifications of the present invention will occur to those skilled in the art upon a reading of the disclosure; including various changes to the details, materials, steps and arrangement of parts which have been herein described. These are intended to be included within the scope. It may be that other substances exist or may be discovered that have some or enough of the properties of the particular substances described herein and may be suitable for use in their place; these too are intended to be included within the principal and scope of the invention. One modification is to make the circulation and/or deformation referred to herein to occur in a well ordered and defined pattern. This may be accomplished by various mechanical, electrical and/or optical (i.e. by screened exposure) techniques disclosed in U.S. Pat. No. 3,436,216 and two separate copending applications of Lloyd F. Bean and John Heurtley, each filed on or about Sept. 19, 1970 and having the same title "Method of Organized Thermoplastic Xerography and Photoreceptor Structure Therefor". Broadly, the technique is to modulate the electric field across a frostable material spacially related to the natural special response of the material. The charge densities capable of initiating circulation and/or deformation may be below the normal respective threshold values for circulating or deforming the member. Consequently, the charge of the electrical latent image employed in the present invention should be "capable of circulating and/or deforming" means that the charge density is above the respective threshold level, spacially modulated and/or otherwise effectively employed.

While the preferred embodiment including polymerization has been discussed herein in detail with respect to the imaging member shown and described, it will be understood that less than three layers or more than three layers can be employed in the practice of this invention. That is, in non-charge-expose electrical latent imaging only the circulation layer and one more softenable layer is required; in even charge-expose electrical latent imaging either of the two layers can be made photoconductive and layer **12** dispensed with; and that more than three-layered imaging members can be employed. The object sought being the selective circulation and intermixing of at least any two materials which produce a distinct physical or chemical property. The presence of layer **12** constitutes a preferred imaging member upon which to practice the invention because its presence affords a layer intermediate the circulation and softenable layer to be mixed which provides a buffer in chemical reaction embodiments of the invention.

While development has been described with emphasis on dissolving either the image or non-image area having a solubility differential therebetween it will be understood that any development step suitable to developing the property differential achieved is entirely satisfactory. Those skilled in the art will appreciate that there are a whole host of chemicals having properties suitable for use in accordance with the present invention; that many physical and chemical property differences can be created upon selective imagewise mixing in accordance with the present invention which can be uitilized to develop a visible image in accordance with the disclosure of U.S. Pat. No. 3,518,081 which is incorporated by reference.

Finally, while we have spoken primarily of circulation throughout all layers of the imaging member it will be appreciated that particular combinations of layers can be devised so that circulation limited substantially within one layer is sufficient to achieve the mixing of that layer at least in part with at least portions of two or more layers. That is, mixing of the layers may either be in bulk or restricted to relatively small amounts of material from each layer.

The phrase "electrical latent image" and variations thereof is used herein to include electrostatic charge patterns, patterned electric fields applied by any means including electrodes external to the imaging member, imagewise changes in charge acceptability of the imaging member materials and combinations thereof.

What is claimed is:

**1.** A method for imaging comprising:

a. providing an imaging member comprising on an about 1 to about 12 micron thick softenable circulation layer a softenable photoconductive layer of about 0.5 to about 5 micron thickness; each of said layers comprising electrically insulating softenable material and said photoconductive layer comprising a volume ratio of about 1:8 to about 7:1 photosensitive particles dispersed in softenable material; said softenable layers capable of having their viscosity reduced so as to allow circulation of material therein in response to a charge density, of from about 10 to about 80 volts per micron and cast

from materials sufficiently dissimilar wherein mixing of imaging member layers in bulk in the absence of circulation is prevented;

b. charging the surface of said imaging member at least at said charge density;

c. imagewise exposing said imaging member to activating electromagnetic radiation; and

d. softening said softenable layers by reducing their viscosity wherein circulation of said softenable layers occurs sufficiently to effect bulk mixing of said softenable layers in non-imagewise-exposed portions of said imaging member; the resultant mixture of said layers having at least one chemical or physical property that is distinct from that of at least one of said softenable layers in unmixed portions of said imaging member.

**2.** The method of claim **1** wherein said softenable photoconductive layer is sandwiched in between said circulation layer and a second softenable layer.

**3.** The method of claim **1** wherein the weight ratio of photosensitive material to binder is from about 1:6 to about 4:1.

**4.** The method of claim **1** wherein said photoconductive layer thickness range is from about 0.5 micron to about 1 micron.

**5.** The method of claim **1** wherein said softening step (c) comprises the step of uniformly subjecting said imaging member to solvent vapor.

**6.** The method of claim **1** wherein said imaging member further comprises a substrate adjacent the free surface of said circulation layer.

**7.** The method of claim **1** wherein said at least one physical or chemical property is solubility.

**8.** The method of claim **7** further including the step of removing one of mixed and unmixed portions of said imaging member by contacting said imaging member with a solvent.

**9.** The method of claim **8** wherein said mixed portions are removed.

**10.** The method of claim **8** wherein said unmixed portions are removed.

**11.** The method of claim **8** wherein the remaining portions of said imaging member after the step of removing one of mixed and unmixed portions of said imaging member comprises a resist image.

**12.** The method of claim **8** wherein the step of removing by contacting with a solvent includes swabbing.

**13.** The method of claim **12** wherein said swabbing is for a period of time within the range from about 2 seconds to about 4 seconds.

**14.** The method of claim **1** wherein said at least one physical or chemical property is polymerization.

**15.** The method of claim **14** wherein said insulating layer is nonpolymerizable and said insulating layer contains an initiator which causes polymerization of the circulation layer upon contact therewith.

**16.** The method of claim **14** wherein one of the mixed and unmixed portions of said imaging member is polymerized.

**17.** The method of claim **15** wherein one of the polymerized and unpolymerized portions of said imaging member is removed by further contacting said imaging member with a suitable solvent.

**18.** The method of claim **1** wherein said at least one physical or chemical property is polymerization susceptibility.

**19.** The method of claim **18** wherein said insulating layer contains an inhibitor and said circulation layer is polymerizable upon exposure to U.V. light, further including the step of exposing the mixed and unmixed portions of said imaging member to U.V. light so that the circulation layer in unmixed portions of the imaging member polymerizes.

**20.** The method of claim **19** further including the step of contacting the imaging member with a suitable solvent to remove all but the polymerized portions of the circulation layer.

**21.** The method of claim **1** wherein said at least one physical or chemical property is color.

**22.** The method of claim **21** wherein said circulation layer and said insulating layer each contain a reagent which when combined in mixed portions of said imaging member undergo a color conversion reaction.

**23.** The method of claim **1** wherein said electrical field range is from about 30 volts per micron to about 50 volts per micron.

**24.** The method of claim **1** wherein said circulation layer thickness range is from about 1 micron to about 6 microns.

**25.** The method of claim **1** wherein said softening step (c) comprises the step of uniformly subjecting said imaging member to solvent vapor for a period of time within the range from about 5 seconds to about 15 seconds.

**26.** The method of claim **1** wherein said at least one physical or chemical property is contact electrification susceptibility.

**27.** The method of claim **26** wherein said at least one physical or chemical property is triboelectric charging susceptibility.

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