

[54] **PHOTOELECTROSOLOGRAPHIC IMAGING
METHOD UTILIZING POWDER PARTICLES**

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[22] Filed: **Oct. 20, 1972**

[21] Appl. No.: **299,531**

Related U.S. Application Data

[63] Continuation of Ser. No. 32,597, April 28, 1970,
abandoned, which is a continuation-in-part of Ser.
No. 679,774, Nov. 1, 1967, abandoned.

[52] U.S. Cl. **96/1 PS, 96/1.2, 96/1.5,**
117/17.5

[51] Int. Cl. **G03g 13/00, G03g 5/02**

[58] Field of Search **96/1 PS, 1.2, 1.5;**
252/501; 117/17.5

[56] **References Cited**

UNITED STATES PATENTS

3,512,968 5/1970 Tulagin 96/1 X

3,547,627	12/1970	Amidon et al.	96/1
2,940,847	6/1960	Kaprelian.....	96/14 X
3,212,887	10/1965	Miller et al.	96/1
3,520,681	7/1970	Goffe.....	96/1
3,556,781	1/1971	Levy et al.	117/17.5 X
3,723,113	3/1973	Goffe.....	96/1 PS X

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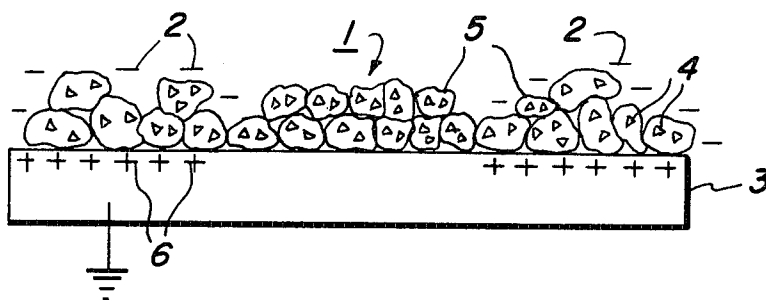
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Petre; Ronald L. Lyons

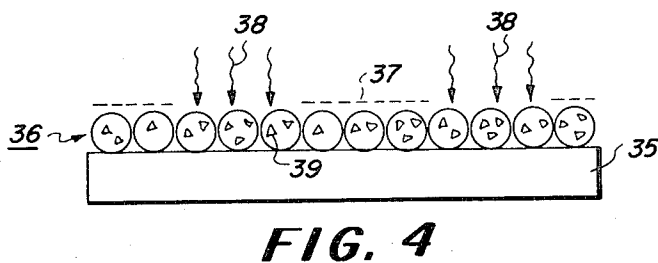
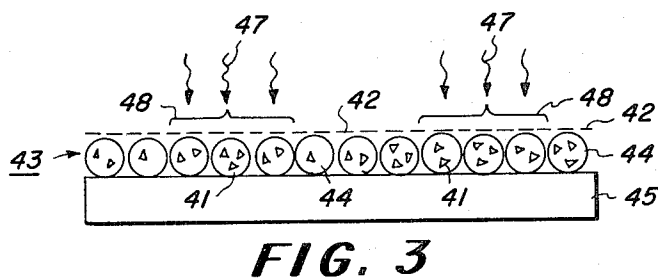
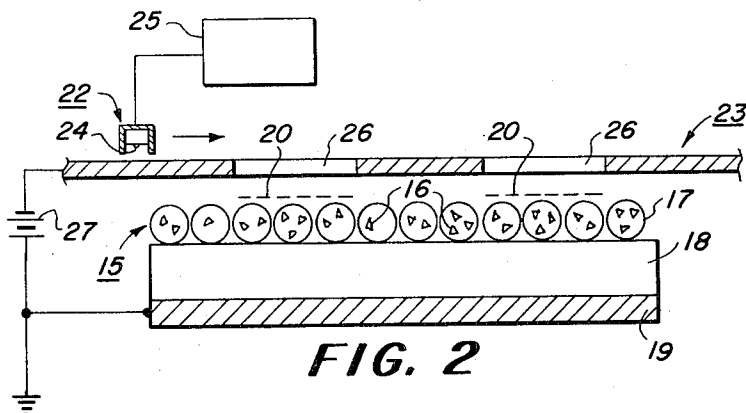
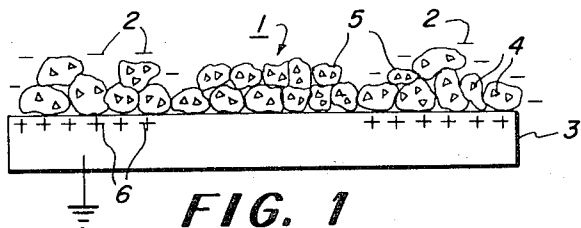
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ABSTRACT

A migration imaging method using a structure made from a plurality of powder particles each including a marking material and a softenable material. Charge is deposited on the powder particles and effects migration of the marking material upon softening the softenable material.

21 Claims, 6 Drawing Figures





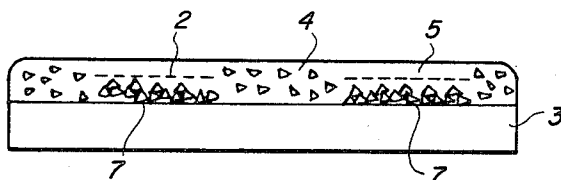


FIG. 5

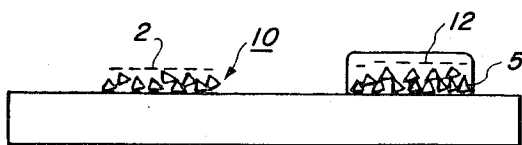


FIG. 6

PHOTOELECTROSOLOGRAPHIC IMAGING METHOD UTILIZING POWDER PARTICLES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation application of my copending U.S. patent application Ser. No. 32,597, filed Apr. 28, 1970, now abandoned, which is a continuation-in-part of a copending application under the same title filed Nov. 1, 1967 in the names of William L. Goffe and Robert W. Gundlach, Ser. No. 679,774 now abandoned. This disclosure of Ser. No. 679,774 is hereby incorporated by reference into the present application.

BACKGROUND OF THE INVENTION

This invention relates to imaging systems and in particular to novel migration imaging processes and structures.

New migration imaging systems are disclosed in copending applications Ser. Nos. 837,780 and 837,591 both filed June 30, 1969 and the disclosures of those applications are expressly incorporated by reference into the present application. Briefly, the migration imaging systems employ an imaging structure that includes a marking material and a continuous layer of softenable material. Typically, in embodiments in which the marking materials are responsive to light, a visible image is created by uniformly charging the imaging structure, exposing it to a pattern of activating electromagnetic radiation to form a latent electrical image and developing the latent image to form the visible image. In embodiments in which the marking material is not responsive to light, the latent electrical image is an electrostatic charge image created on the surface of the imaging structure by known techniques before or simultaneously with the developing step. The developing step entails softening the softenable layer to allow electric forces associated with the latent electrical image to effect migration of marking particles through the bulk of the softenable material. In other embodiments or migration imaging systems, the marking material includes particles arranged as a layer in, on or between softenable layers or randomly dispersed throughout the bulk of the softenable layer. One feature common to all embodiments is the relatively smooth, continuous surface of the imaging structure that supports electrostatic charge comprising the latent electrical image. The broader term "latent electrical image" is used in preference to "latent electrostatic image" because the latter denotes latent images of the type known in xerography, as an example, wherein electrical potential differences between adjacent areas define an image. In certain embodiments of the migration imaging process using photosensitive marking particles, the latent image is not characterized by any readily detectable differences in surface potential between image and non-image areas.

The developing step includes heat or solvent softening the imaging structure. When developing by solvent softening, both the softenable material and marking particles may be washed away in non-migrated areas leaving the migrated marking particles, i.e., image, on the substrate. If not all the softenable material is washed away, the remainder is available for fixing the marking particle image to the substrate. When develop-

ing by heat softening or exposure to solvent vapors or liquids the migrated and unmigrated particles form complementary positive and negative images. Both these images are usable when separated by splitting the softenable layer at a level between the migrated and unmigrated particles.

Both positive and negative images can be made from a positive original by the migration imaging systems by varying parameters such as charge polarity and/or magnitude and the nature of the materials, e.g., by substituting materials with different photosensitive characteristics. A positive image is one in which the density of the marking particles, i.e., the number of marking particles per unit area, is directly proportional to the density of corresponding areas in the original and a negative image is one in which the marking particle density is inversely proportional to the density of corresponding areas in an original.

"Softenable" as used herein is intended to mean any material which can be rendered more permeable to migration material migrating through its bulk. Conventionally, changing permeability is accomplished by dissolving, melting, and softening as by contact with heat, vapors, partial solvents and combinations thereof.

The density, resolution, tone range and other characteristics of images produced by migration imaging methods are controlled by varying parameters that include: marking material particle size; marking material to softenable material ratios; the arrangement of the marking material (e.g., whether layered or randomly dispersed); exposure pattern, intensity and/or wavelength; charge polarity and/or magnitude, and; the type of development employed (i.e., whether heat or solvent softening or a combination of both).

The present invention is based on the discovery that migration imaging can be performed using an imaging structure composed of a plurality of individual particles rather than a continuous layer. The individual particles are hereafter called "powder particles" and include a marking material and a softenable material. The term powder particle is chosen because it is descriptive of the appearance and mechanical properties of the imaging structure.

Accordingly, it is an object of the present invention to enhance the migration imaging systems described in the above mentioned copending applications and related applications. Specifically, it is an object to develop a migration imaging method employing a particularized imaging structure.

Another object of the invention is to devise new embodiments of migration imaging methods that facilitate the handling and storage of migration imaging materials.

It is also an object of this invention to devise methods and apparatus that lend themselves to recycling of materials used in migration imaging systems.

Still another object of this invention is to devise an imaging system for making images with materials not normally adaptable to electrical imaging processes.

The powder particle imaging structure of the present invention greatly expands the versatility of migration imaging systems. Continuous imaging structures are commonly used in consumable web configurations wherein the non-migrated marking material is not readily reclaimable. With the present invention, the imaging structure is formed when needed on generally any substrate. For example, the powder particles are cascaded

or sprayed onto a substrate forming an imaging structure on which a latent electrical image is formed. The powder particles in non-image areas may be separated from the substrate prior to development of the image and the separated powder particles may be used in the formation of a subsequent image, i.e., the separated powder particles are recycled. The recycling is particularly important where expensive photosensitive marking particles are used. Furthermore, powder particle imaging structures can be readily formed on irregularly shaped substrates since the powder can flow into or penetrate the irregular contours of a surface. In addition, powder particles can be piled atop one another to increase the number of marking particles over a unit area. The denser structure yields images of greater density. The thickness of a continuous layer can be increased to pack more marking particles over a unit area for the same reason. However, as the thickness of a continuous layer bonded to a web is increased it becomes brittle and may fracture, i.e., crack, when rolled onto a spool.

DESCRIPTION OF THE DRAWINGS

Objects and features of the present invention in addition to the foregoing will be apparent to those skilled in the art from a further reading of the present disclosure and from the drawings which are:

FIG. 1 is a schematic of powder particles of irregular shape arranged in a layer more than one particle thick and having an electrostatic charge pattern on them.

FIG. 2 is a schematic of a powder particle imaging structure on a substrate with a charge pattern deposited on the powder particles by means including a stencil.

FIG. 3 is a schematic of a charged powder particle imaging structure on a substrate illustrating that the charge may not appear significantly disturbed after exposure when the marking material is photosensitive.

FIG. 4 is a schematic of a powder particle imaging structure on a substrate employing photosensitive materials with an electrostatic latent image created by uniformly charging the powder particles and exposing them to imagewise activating electromagnetic radiation to discharge the particles in the exposed areas.

FIG. 5 is a schematic of a powder particle imaging structure after the softenable material is softened and particles have migrated to the substrate.

FIG. 6 is a schematic of a developed image formed with marking material alone or marking material that is fixed to the substrate by that portion of the softenable material not washed away.

The various embodiments known to migration imaging systems using continuous imaging structures are possible with the present invention. With powder particle structures, however, the term "fracturable" used to describe the marking material in the aforementioned patent applications does not have any significant meaning. Fracturable denotes the ability of the marking material to break up during the developing step to provide particles for migration. Obviously, in a powder particle structure the marking material is already broken up into small portions although it is possible that it experience further subdivision in size during development.

Although the mechanisms effecting marking material migration are not fully understood it is fairly safe to say that migration occurs because a material has electrical charge associated with it and the charge is in an electric

field. In practice, the charge deposited on the surface of an imaging structure serves both the function of establishing an electric field and of associating with an individual particle. The imaging structure is normally adjacent a conductive substrate in which charges of opposite polarity are induced by the deposited charge, thereby creating an electric field between the deposited and induced charge. The deposited charge is attracted toward the induced charge and is free to move when the imaging structure is softened. Consequently, if a latent electrostatic image is formed on the imaging structure, wherein charge is present in some areas and not others (at least comparatively), only that marking material between the deposited and induced charge can be expected to migrate either because it already has charge or because the deposited charge somehow associates with it. If the marking material is photosensitive and becomes more receptive to acquiring charge when exposed to activating electromagnetic radiation especially when compared to non-exposed particles, then only the exposed marking material can be expected to migrate, since substantially only they accept or associate with sufficient charge for migration. If the photosensitivity of the marking material and/or the softenable material imparts photoconductivity to the entire particle, then the exposed marking particles can dissipate the deposited charge by effectively creating a conductive link between the deposited charge and a conductive substrate. This means that the non-exposed marking material migrates because only it will be between deposited and induced charge. It has been demonstrated that the photosensitive case, wherein exposed particles migrate because they are more capable of becoming associated with the deposited charge than their non-exposed neighbors, may respond like the photoconductive case if the intensity of the electric fields exceed fairly well defined threshold levels.

The foregoing discussion of migration imaging mechanisms might be expected to predict the failure of powder particle imaging members because for one reason, of their irregular shaped surfaces. Charge deposited on a powder particle structure can reside on both the peaks and depressions of the irregular surface and consequently be on both sides of the marking material. In addition, when the softenable material is softened the irregular surface tends to become level or smooth and the charge might be expected to move laterally.

Generally, the materials comprising the marking material, softenable material and substrates are the same as those known in other migration imaging systems. Naturally, the marking material and substrates are insoluble in the solvent for the softenable material and are capable of withstanding the heat used to soften a material. The solvents on the other hand are generally electrically insulating particularly if used to soften the softenable material to permit migration. If a powder particle is heat softened for image development, i.e., migration, the remaining softenable material can be washed away with a non-insulating solvent. It is also noted that the marking particle need not be photosensitive, conductive, insulating or have any other unique characteristic. On the other hand, the softenable material may be photosensitive, photoconductive or possess some other wanted characteristic, for example, a trait making it particularly suited for fixing the migrated marking material to a substrate.

The substrate may be in any suitable form such as a metallic strip, sheet, plate, coil, cylinder, drum, endless belt, moebius strip or the like. If desired, the conductive substrate may be coated on an insulator such as paper, glass or plastic. Examples of this type of substrate are a substantially transparent tin oxide coated glass available under the trademark NESA from the Pittsburgh Plate Glass Co., aluminized polyester film the polyester film available under the trademark Mylar from DuPont, or Mylar coated with copper iodide.

Electrically insulating substrates may also be used which opens up a wide variety of film formable materials such as plastics for use as a substrate.

Many photosensitive particles may be used in carrying out the invention, regardless of whether the particular particle selected is organic, inorganic, is made up of one or more components in solid solution or dispersed one in the other or whether the particles are made up of multiple layers of different materials. Typical photosensitive particles include organic photoconductive insulating materials such as 8,13-dioxodinanaphtho-(1,2,2'3')-furan-6-carbox-p-methoxyanilide; Locarno Red, C. I. No. 15865, 1-(4'-methyl-5'-chloroazobenzene-2'-sulfonic acid)-2-hydroxy-3-naphthoic acid; Watchung Red B the barium salt of 1-(4'-methyl-5'-chloroazobenzene-2'-sulfonic acid)-2-hydroxy-3-naphthoic acid, C. I. No. 15865; Naphthol Red B, 1-(2'-methoxy-5'-nitrophenylazo)-2-hydroxy-3'-nitro-3-naphthanilide, C. I. No. 12355; Duol Carmine, the calcium lake of 1-(4'-methyl-azobenzene-2'-sulfonic acid)-2-hydroxy-3-naphthoic acid, C. I. No. 15805; Calcium Lithol Red, the calcium lake of 1-(2'-azo-naphthalene-1'-sulfonic acid)-2-naphthol, C. I. No. 15630; Quinacridone and substituted quinacridones such as 2,9-dimethylquinacridone; Pyranthrones; Indofast Brilliant Scarlet Toner, 3,4,9,10-bis(N,N'-(p-methoxyphenyl)-imido)-perylene, C. I. No. 71140; dichloro thioindigo; Pyrazolone Red B Toner, C. I. No. 21120; phthalocyanines including substituted and unsubstituted metal and metal-free phthalocyanines such as copper phthalocyanine, magnesium phthalocyanine, metal-free phthalocyanine, polychloro substituted phthalocyanine, etc.; Methyl Violet, a phosphotungstomolybdic lake of a triphenylmethane dye, C. I. No. 425,535; Indofast Violet Lake, dichloro-9,18-isoviolanthrone, C. I. No. 60010; Diane Blue, 3,3'-methoxy-4,4'-diphenyl-bis(1''-azo-2''-hydroxy-3''-naphthanilide), C. I. No. 21180; Indanthrene Brilliant Orange R.K., 4,10-dibromo-6,12-anthanthrone, C. I. No. 59300; Algol Yellow G.C., 1,2,5,6-di9C,C'-diphenyl)-thiazone-anthraquinone, C. I. No. 67300; Flavanthrone; Indofast Orange Toner, C. I. No. 71105; 1-cyano-2,3-phthaloyl-7,8-benzo-pyrrocoline and many other thio indigos, acetoacetic arylides, anthraquinones, perionones, perylenes, dioxazines, quinacridones, azos, diazos, thiazines, azines and the like; inorganics such as cadmium sulfide, cadmium sulfoselenide, zinc oxide, zinc sulfide, sulphur selenium, mercuric sulfide, lead oxide, lead sulfide, cadmium selenide, titanium dioxide, indium trioxide, and the like. In addition to the aforementioned pigments other organic materials which may be employed in the particles include polyvinylcarbazole; 2,4-bis (4,4'-diethylaminophenyl)-1,3,4-oxidiazole; N-isopropylcarbazole; polyvinylanthracene; triphenylpyrrol; 4,5-diphenylimidazolidinone; 4,5-diphenylimidazolidinone; 4,5-diphenylimidazolidinethione; 4,5-

bis-(4'-amino-phenyl)-imidazolidinone; 1,2,5,6-tetraazacyclo-octatetraene-(2,4,6,8); 3,4-di-(4'-methoxyphenyl)-7,8-diphenyl-1,2,5,6-tetraazacyclooctatetraene-(2,4,6,8); 3,4-di(4'-phenoxyphenyl)-7,8-diphenyl-1,2,5,6-tetraazacyclooctatetraene-(2,4,6,8); 3,4,7,8-tetramethoxy-1,2,5,6-tetraaza-cyclooctatetraene-(2,4,6,8); 2-mercapto-benzthiazole; 2-phenyl-4-alpha-nuphtylidene-oxazolone; 2-phenyl-4-diphenylidene-oxazolone; 2-phenyl-4-p-methoxybenzylidene-oxazolone; 6-hydroxy-2-phenyl(p-dimethyl-amino phenyl)-benzofurane; 6-hydroxy-2,3-di(p-methoxyphenyl)-benzofurane; 2,3,5,6-tetra(p-methoxyphenyl)-furo-(3,2f)-benzofurane; 4-dimethylamino-benzylidene-benzhydrazide; 4-dimethyl-amino-benzylideneisonicotinic acid hydrazide; turfurylidene-(2)-4'-dimethylamino-benzhydrazide; 5-benzylidene-amino-acenaphthene-3-benzylidene-amino-carbazole; (4-N,N-dimethylamino-benzylidene)p-N,N-dimethylaminoaniline; (2-nitro-benzylidene)-p-bromoaniline; N,N-dimethyl-N'-(2-nitro-4-cyanobenzylidene)-p-phenylene-diamine; 2,4-diphenylquinazoline; 2-(4'-amino-phenyl)-4-phenylquinazoline; 2-phenyl-4-(4'-di-methyl-amino-phenyl)-7-methoxy-quinazoline; 1,3-diphenyl-tetrahydroimidazole; 1,3-di-(4'-chlorophenyl)-tetrahydroimidazole; 1,3-diphenyl-2,4'-dimethylamino-phenyl)-tetra-hydroimidazole; 1,3-di-(p-tolyl)-2-[quinolyl-(2'-)]-tetrahydroimidazole; 3-(4'-dimethylamino-phenyl)-5-(4''-methoxy-phenyl)-6-phenyl-1,2,4-triazine; 3-pyridyl-(4')-5-(4''-dimethylaminophenyl)-6-phenyl-1,2,4-triazine; 3-(4'-amino-phenyl)-5,6-di-phenyl-1,2,4-triazine; 2,5-bis[4'-amino-phenyl-(1')]-1,3,3-triazole; 2,5-bis[4'-(N-ethyl-N-acetyl-amino)-phenyl-(1')]-1,3,4-triazole; 1,5-diphenyl-3-methyl-pyrazoline; 1,3,4,5-tetraphenylpyrazoline; 1-phenyl-3-(p-methoxy styryl)-5-(p-methoxy-phenyl)-pyrazoline; 1-methyl-2-(3',4'-dihydroxy-methylene-phenyl)-benzimidazole; 2-(4'-dimethyl-amino phenyl)-benzoxazole; 2-(4'-methoxyphenyl)-benzthiazole; 2,5-bis-[p-amino-phenyl-(1)]-1,3,4-oxidiazole; 4,5-diphenyl-imidazolone; 3-amino-carbazole; copolymers and mixtures thereof.

Other materials which may be included in the particles include organic donor-acceptor (Lewis acid-Lewis base) charge transfer complexes made up of donors such as phenolaldehyde resins, phenoxies, epoxies, polycarbonates, urethanes, styrene or the like complexed with electron acceptors such as 2,4,7-trinitro-9-fluorenone; 2,4,5,7-tetranitro-9-fluorenone; picric acid; 1,3,5-trinitro benzene; chloranil; 2,5-dichlorobenzoquinone; anthraquinone-2-carboxylic acid, 4-nitrophenol; maleic anhydride; metal halides of the metals and metalloids of groups I-B and II-VIII of the periodic table including for example, aluminum chloride, zinc chloride, ferric chloride, magnesium chloride, calcium iodide, strontium bromide, chromic bromide, arsenic triiodide, magnesium bromide, stannous chloride etc.; boron halides, such as boron trifluorides; ketones such as benzophenone and anisil, mineral acids such as sulfuric acid; organic carboxylic acids such as acetic acid and maleic acid, succinic acid, citroconic acid, sulphonic acid, such as 4-toluene sulphonic acid and mixtures thereof.

Typical inorganic photoconductors include amorphous selenium; amorphous selenium alloyed with arsenic, tellurium, antimony or bismuth, etc.; amorphous

selenium or its alloys doped with halogens; cadmium sulfide, zinc oxide, cadmium sulfoselenide, cadmium yellows such as Lemon Cadmium Yellow X-2273 from Imperial Color and Chemical Dept. of Hercules Powder Co., and many others. Middleton et al. U.S. Pat. No. 3,121,006 lists typical inorganic photo-conductive pigments.

As stated above, any suitable particle may be employed. The particles should be substantially insoluble in the matrix material (the softenable material) and in the solvent used to develop the member after exposure. Typical particles include those which are made up of only the pure photosensitive material or a sensitized form thereof, solid solutions or dispersions of the photosensitive material in a matrix such as thermoplastic or thermosetting resins, copolymers of photosensitive pigments and organic monomers, multi-layers of particles in which the photosensitive material is included in one of the layers and where other layers provide light filtering action in an outer layer of a fusible or solvent softenable core of resin or a core of liquid such as dye or other marking material or a core of one photosensitive material coated with an overlayer of another photosensitive material to achieve broadened spectral response. Other photosensitive structures include solutions dispersions, or copolymers of one photosensitive material in another with or without other photosensitively inert materials. Other particle structures which may be used, if desired, include those described in U.S. Pat. No. 2,940,847 to Kaprelian.

The softenable material may be any suitable material which is soluble or softenable in a solvent liquid or vapor or heat or combinations thereof to permit selective migration of portions of the particles to the substrate, and in addition is substantially electrically insulating during the latent image forming and developing steps hereof. Where the softenable material is to be dissolved away either during or after imaging it should be soluble in a solvent which does not attack the particles. Typical softenable materials include polyolefins such as polyethylene and polypropylene; organic amorphous glasses; vinyl and vinylidene resins such as polymethylmethacrylate and polyvinylcarbazole; polyamides; polyurethanes; polypeptides; polysulfides; polycarbonates; cellulosic polymers; polysulfones; phenolic resins; amino resins; epoxy resins; silicone resins; and mixtures and copolymers thereof.

Specifically, typical softenable materials include Staybelite Ester 10, a partially hydrogenated rosin ester, Foral Ester, a hydrogenated resin triester, and Neolyne 23, an alkyd resin, all from Hercules Powder Co.; SR type silicone resins available from General Electric Corporation; Sucrose Benzoate, Eastman Chemical; Velsicol X-37, a polystyrene-olefin copolymer from Velsicol Chemical Corp.; Hydrogenated Piccopale 100, a highly branched polyolefin, Piccotex 100 a polystyrene-vinyl toluene copolymer, Piccolastic A-75, 100 and 125, all polystyrenes, Piccodiene 2215, a polystyrene-olefin copolymer, all from Pennsylvania Industrial Chemical Corp.; Araldite 6060 and 6071, epoxy resins from Ciba; R5061A, a phenylmethyl silicone resin, from Dow Corning; Epon 1001, a bisphenol A-epichlorohydrin epoxy resin, from Shell Chemical Corp.; PS-2, PS-3, both polystyrenes, ET-693, a phenol-formaldehyde resin, and Dow C4 a methylphenyl silicone all from Dow Chemical; a custom synthesized 80/20 mole per cent copolymer of styrene and hexyl-

methacrylate having an intrinsic viscosity of about 0.179 dl/gm, a custom synthesized polydiphenylsiloxane; a custom synthesized polyadipate; acrylic resins available under the trademark Acryloid from Rohm & Haas Co., and available under the trademark Lucite from DuPont; Amoco 18 a poly aliphatic-methylstyrene from Amoco Chemical Corp.; thermoplastic resins available under the trademark Pliolite from the Goodyear Tire & Rubber Co.; a chlorinated hydrocarbon available under the trademark Aroclor from Monsanto Chemical Co.; thermoplastic polyvinyl resins available under the trademark Vinylite from Union Carbide Co. and blends thereof.

The above group of materials is not intended to be limiting, but merely illustrative of materials suitable for a softenable material.

The powder particles may be formed by dispersing the marking material in the softenable material and then forming beads or particles by any conventional methods such as grinding or spray drying as described in copending application Ser. No. 380,080, filed July 2, 1964, now U.S. Pat. No. 3,338,991. The marking particles may have any suitable diameter. If photosensitive, the highest photosensitivity has been obtained with particles in the range of from about 0.02 to about 2 microns in size with optimum results for particles in the submicron range of from about 0.03 to about 0.5 microns. The powder particles of softenable material containing the marking material also may have any suitable diameter. Generally, it is preferred that the powder particles have a diameter of 0.5 to 30 microns. Of course, the finer the powder particles the higher the resolution and density of the final image. Excellent results have been obtained with particles having diameters from 1 to 10 microns.

The powder particles may be spread across a substrate by any suitable, conventional method. The particles may be formed in layers several particles thick as illustrated in FIG. 1 or in monolayers as illustrated in FIGS. 2-4. One method of forming a substantially uniform monolayer of particles on a substrate is described by Vyverberg U.S. Pat. No. 2,759,450. In this method, the beads are electrostatically charged and blown in an air stream across the substrate. Due to electrostatic attraction forces, a substantially uniform layer of the particles is formed on the substrate. A thick layer of particles can be formed, for example, by pouring or cascading the powder particles over a substrate.

The drawings in FIGS. 1-6 illustrate various modes of practicing the instant invention. The relative sizes of the various elements such as the marking material, softenable material and substrates are exaggerated for clarity. The powder particles in FIG. 1 are irregularly shaped as might be expected when formed by a grinding process whereas the powder particles in FIGS. 2-4 are spherically shaped as might be expected when formed by spraying the marking material into a chamber containing the vapors of the softenable material which condense around the marking material. It should be understood, however, that the various drawings are illustrative and that the powder particles imaging member of this invention may be composed of spherically or irregularly shaped particles, or both, arranged in monolayers or multiple layers.

In FIG. 1, the irregularly shaped powder particles 1 include the marking material 4 and softenable material 5. The powder particles are substantially uniformly de-

posited over the surface of conductive substrate 3 in a layer more than one particle thick. The minus signs 2 represent electrostatic charge residing on the free surfaces of the powder particles in imagewise arrangement of the charge 2 may be accomplished by several well known electrostatic charging techniques including using a corotron and shield as explained in connection with FIG. 2. In addition, the powder particles may be photoconductive and the charge pattern can be formed in a manner explained in connection with FIG. 4. The polarity of charge deposited on the powder particles is generally optional but the imaging process is enhanced by selecting a charge polarity that the marking and softenable material are naturally more efficient in handling. The minus signs 2 represent electrons and/or negative ions and they induce the positive charge on the surface of the substrate represented by the plus signs 6. It is understood, however, that the polarities illustrated in the various drawings are intended to represent charge generally and charge of the opposite polarity may be substituted for that shown.

When the softenable material 5 is softened, e.g., by heat and/or solvent, the deposited charge 2 associates with the marking material 4 between it and the induced charge 6 (it is believed) and causes the marking material to migrate to the substrate. FIG. 5 illustrates, in a general manner, the powder particles after they have been softened and migration has occurred. Broadly speaking, the softened material 5 swells and flows together allowing the marking particles in the areas of charge to migrate through its bulk to the substrate 3. The migrated marking particles are arranged in imagewise configuration (as represented by particles 7) on the substrate and the particles in the non-charged areas are randomly dispersed in the softened material. If the marking particles are conductive, the deposited and induced charge is neutralized when the marking material comes into contact with the conductive substrate. If the marking material is non-conductive the deposited charge is not neutralized and tacks the marking material to the base. If now the softenable material is dissolved away by a solvent the marking material appears substantially like material 10 on the left hand side of substrate 11 in FIG. 6. The marking material 10 may be permanently fixed to the substrate by any suitable means. If less than all the softenable material is dissolved away the marking material is fixed to the substrate by the remaining softenable material as represented by the material 12 on the right hand side of the substrate in FIG. 6. Controlled amounts of the softenable material can be dissolved away because the dissolving process is time dependant.

FIG. 2 illustrates an embodiment of this invention wherein a powder particle imaging member resides on a softenable layer which may be desirable to insure a particular minimum dimension for the imaging member. The monolayer of powder particles 15 composed of marking material 16 and softenable material 17 are carried on the surface of the layer 18 of softenable material which in turn overlies the conductive substrate 19. The softenable materials 17 and 18 may be the same or different materials but preferably are soluble in the same solvent. Development of the latent electrical image represented by charge 20 is similar to the development of the charge bearing structure in FIG. 1 as illustrated in FIGS. 5 and 6. The powder particles 15 and softenable layer 18 are softened by appropriate

means to permit the marking material in the areas of charge 20 to migrate to substrate 19 while the marking material in the non-charged areas are randomly dispersed in the softened materials 17 and 18. FIG. 6 is illustrative of the marking material image formed on substrate 19 when the softenable materials 17 and 18 are dissolved completely and mostly away.

The latent electrical image represented by charge 20 is deposited on the powder particles 15 in imagewise configuration by means of corotron 22 and shield 23. The corotron is a corona discharge device such as shown in U.S. Pat. No. 2,777,957 to Walkup. It includes a corona wire 24 which in this example is coupled to a high negative potential source 25. The shield is made from a conductive material such as aluminum and has holes 26 cut out in imagewise configuration. The shield is coupled to a negative potential source 27 (of less magnitude than potential 25) that is substantially the potential to which the powder particles are to be charged. The conductive substrate 19 is coupled to ground potential. As the corotron is moved over the shield with the foregoing potentials applied, electrons and/or negative ions form around the corona wire and flow toward substrate 19. The shield intercepts the generated charge except in the areas of the holes or cut-outs 26 resulting in the collection of charge on the powder particles in imagewise configuration. A complementary charge pattern, i.e., latent electrical image, can be made by first uniformly charging the powder particles negative while the stencil is removed and then passing the corotron over the powder particles with the stencil interposed. This time, however, the corotron generates positive charge which neutralizes the earlier deposited negative charge opposite the cut-outs.

The embodiment illustrated in FIG. 4 is similar to that in FIG. 2 in that a marking material image is created on substrate 35 from the marking material in the powder particles 36 residing under the electrostatic charge 37. Charge 37 comprises a latent electrical image, specifically an electrostatic image, created by uniformly charging the powder particles and discharging the particles in areas exposed to light represented by arrows 38. In this case, the marking material 39 is photoconductive, experiences an increase in conductivity when exposed to light, and is packed into the softenable material in substantial quantities such as to render the particles insulating in dark and conducting in light. The charge residing on the exposed powder particles is therefore substantially dissipated since they form a conductive link with the conductive substrate 35. When the powder particles 36 are heat or solvent softened they assume, at least generally, the appearance of the materials in FIG. 5. That is, the marking material beneath the charge 37 migrates to the substrate 35 while the remaining marking material remain randomly dispersed within a substantially continuous layer of softened, softenable material. The photoconductive embodiment represented by FIG. 4 may be practiced with either or both the marking and softenable materials comprising the powder particles 36 being photoconductive. The prime consideration is to render the powder particle photoconductive, that is, sufficiently insulating in dark to support charge 37 and sufficiently conductive in light to discharge the charge in exposed areas.

The embodiment of FIG. 3 illustrates the case where the latent electrical image is not a latent electrostatic

image. Here the marking material 41 is a photosensitive material which includes photoconductive materials. The main requirement of the photosensitive marking material is that it be highly insulating in the dark and that it become more susceptible to acquiring the charge 42 uniformly deposited on the powder particles 43 when exposed to light than its unexposed neighbors. If the marking material is photoconductive, the charge in the exposed areas can remain substantially undisturbed if the percentage of marking material is so low as to be incapable of providing a conductive path through an insulating softenable material 44 to the substrate 45 and if no charge injection takes place from the marking particles into the softenable material.

The arrows 47 and brackets 48 denote the activating electromagnetic radiation e.g., light, and the powder particles exposed to it. As mentioned, the exposure leaves the charge 42 substantially undisturbed. However, when the powder particles 43 are subjected to heat or solvent the charge 42 is able to move and substantially greater quantities associate with the exposed particles rather than the unexposed. These charged particles then migrate in imagewise configuration (in the configuration of the light pattern to which the particles are exposed). Again, FIG. 5 is generally illustrative of the materials in FIG. 3 when the powder particles are softened and sufficient time has elapsed to allow the charge bearing marking particles to migrate to the substrate. Also, the softenable material can be completely or substantially removed to yield generally the situation illustrated in FIG. 6.

In all the foregoing embodiments, the softenable material may be hardened after the marking material has migrated to the substrate without dissolving it away, i.e., when the materials are in the condition illustrated in FIG. 5. The migration image, represented by the marking material 7 on substrate 3, can be separated by once again softening the material 5 but this time only to the extent to permit the material to be split. That is, the softenable material 5 and marking material not on the substrate are removed by severing the softenable material at an elevation above the marking material 7 on the substrate.

The advantages offered by this invention include being able to readily construct a migration imaging structure on a wide variety of surfaces in a wide variety of environments. For example, to form a marking material image on a work of art such as a sculpture the powder particles provide a convenient form for storing and handling the marking material. One way to cover an area on the sculpture with a uniform layer of powder particles is to produce a cloud of charged powder particles around the desired area and to couple a potential to the sculpture. If the sculpture is non-conductive it can be placed between the cloud and a conductive plate coupled to the proper potential. The latent electrical image may be created by the methods including those described in connection with FIGS. 1-4. Thereafter, the powder particles may be substantially simultaneously softened and dissolved away by exposing at least the particles in the area of the latent electrical image to a suitable solvent.

The marking material used in the above example may be a chemical etchant for the sculpture, a dye or some other material not easily arranged in imagewise configuration. The marking material may be selected from a wide variety of materials and the marking material

image formed by this invention may be used in a wide variety of processes. For example, the marking material may be water or oil repellent and as such the marking material image may be used as a master in a lithography printing process.

The following examples describe specific embodiments and methods of the present invention. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

A powder particle material is prepared as follows: About two parts Monolite Fast Blue GS, a mixture of alpha and beta form metal-free phthalocyanine, available from Arnold Hoffman Co. is dispersed in a solution of about six parts Piccotex 100 in about 50 parts Isopar G, a long chain saturated aliphatic hydrocarbon liquid boiling point 315°-350° F. from Humble Oil Co. The dispersion is spray dried as by the process described in copending application Ser. No. 380,080, filed June 2, 1964, forming powder particles of Piccotex 100 softenable material having the photosensitive pigment particles uniformly distributed therethrough. A uniform, substantial monolayer of the powder particles is then formed on an aluminum substrate by the powder cloud loading process described in Gundlach U.S. Pat. No. 3,166,432. The thus prepared plate is then uniformly electrostatically charged to a negative potential of about 200 volts by corona discharge as described in Carlson U.S. Pat. No. 2,588,699. The plate is then exposed to a light image using a conventional transparency. Total exposure is about 260 f.c.s. in illuminated areas. The exposed plate is then developed by dipping it in a container containing trichloroethylene. After a few seconds in the solvent, the plate is removed. An image consisting of migrated particles is seen on the plate conforming to the original. Unneeded particles and most of the resin is removed by the solvent.

EXAMPLE II

A xerographic developing toner composed of a plurality of particles consisting of about 40 parts polystyrene, 15 parts poly-n-butyl methacrylate, and five parts carbon black is spread over an aluminum plate forming a multiple particle layer of generally uniform thickness. A conductive stencil like stencil 23 in FIG. 2 is coupled to a negative potential source and the aluminum plate is coupled to ground. A corotron like corotron 22 in FIG. 2 is coupled to a more negative potential and is passed over the layer of toner particles with the stencil interposed. The aluminum plate and the charged toner particles are then dipped into a container of trichloroethylene for about two seconds and withdrawn. The toner in non-charged areas is dissolved away as well as the softenable material in the charged areas leaving a carbon black marking material image on the aluminum plate.

Several modifications can be made to the present invention without departing from its scope or spirit. For example, the powder particle imaging member may include other particles in addition to the powder particles. The "other particles" may be present, for example, to provide a fixing agent for bonding the marking material image to the substrate. These and other modifications are intended as part of the present invention.

What is claimed is:

1. An imaging method comprising:
providing a substrate,
providing on said substrate a layer consisting essentially of powder particles, said powder particles comprising a substantially electrically insulating softenable material containing a particulate migration marking material, said marking material being substantially insoluble in said softenable material, said softenable material capable of having its resistance to migration of said particulate migration marking material decreased sufficiently to allow migration of said marking material through said softenable material toward said substrate,
providing a latent electrical image on the layer of powder particles, and
developing a migration image by decreasing the resistance to migration of the particulate migration marking material through the softenable material at least sufficient to allow migration of the particulate migration marking material through the softenable material to allow imagewise migration of particulate migration marking material through the softenable material towards the substrate.
2. The method of claim 1 wherein development is carried out by heating the imaging member in an amount sufficient to decrease the resistance of the softenable material to migration of particulate migration marking material.
3. The method of claim 1 wherein the step of developing a migration image comprises softening said softenable material by contacting the powder particles with a partial liquid solvent for said softenable material.
4. The method of claim 1 wherein the step of developing the migration image comprises contacting said powder particles with a vaporous partial solvent for said softenable material.
5. The method of claim 1 wherein the step of developing a migration image comprises contacting said powder particles with a liquid solvent for said softenable material whereby imagewise portions of the particulate migration marking material migrate through the softenable material to the substrate and the softenable material and unmigrated particulate migration marking material is removed by said liquid solvent.
6. The method of claim 1 wherein the step comprising providing a latent electrical image on the layer of powder particles comprises electrically charging the layer of powder particles in an imagewise configuration.
7. The method of claim 6 wherein imagewise electrically charging the layer of powder particles comprises electrically charging the powder particles through a stencil having cut-outs in imagewise configuration.
8. The method of claim 1 wherein said particulate migration marking material comprises electrically photosensitive material.
9. The method of claim 8 wherein the step of providing a latent electrical image on the layer of powder particles comprises uniformly electrically charging the layer of powder particles and imagewise exposing the

layer of powder particles with an imagewise pattern of activating electromagnetic radiation.

10. The method of claim 9 wherein the particulate migration marking material exposed to activating electromagnetic radiation migrates to the substrate.

11. The method of claim 9 wherein the powder particles are photoconductive and the layer of powder particles is substantially discharged in the areas exposed with activating electromagnetic radiation.

12. The method of claim 1 wherein said softenable material comprises photoconductive material.

13. The method of claim 12 wherein said particulate migration marking material comprises electrically photosensitive material.

14. The method of claim 12 wherein the step of providing a latent electrical image on the layer of powder particles comprises uniformly electrically charging the layer of powder particles and imagewise exposing said layer with an imagewise pattern of activating electromagnetic radiation.

15. The method of claim 1 additionally comprising providing a layer of substantially electrically insulating softenable material capable of having its resistance to migration of said particulate migration marking material decreased sufficiently to allow migration of said marking material through said softenable layer toward said substrate, said softenable layer located between the layer of powder particles and the substrate, and the developing step comprising decreasing the resistance to migration of the particulate migration marking material through the layer of softenable material as well as the softenable material which comprises the powder particles at least sufficient to allow migration of the particulate migration marking material through the layer of softenable material as well as the softenable material which comprises the powder particles.

16. The method of claim 15 wherein said layer of substantially electrically insulating softenable material is of a thickness in the range of about 1/2 micron to about 16 microns.

17. The method of claim 1 wherein said powder particles are of average diameter in the range of about 0.5 micron to about 30 microns.

18. The method of claim 17 wherein said powder particles are of average diameter in the range of about 1 micron to about 10 microns.

19. The method of claim 8 wherein said particulate migration marking material is of average particle size in the range of about 0.02 micron to about 2 microns.

20. The method of claim 19 wherein said particulate migration marking material is of average particle size in the range of about 0.03 micron to about 0.5 microns.

21. The method of claim 1 additionally comprising after the developing step, the step of increasing the resistance of the softenable material to migration of the particulate migration marking material thereby fixing the migrated image.

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