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[54] **MANIFOLD IMAGING PROCESS USING ELECTRICALLY PHOTOSENSITIVE MATERIAL SUBJECT TO LIGHT FATIGUE**

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Related U.S. Application Data

[63] Continuation of Ser. No. 186,125, Oct. 4, 1971, abandoned, which is a continuation-in-part of Ser. No. 798,094, Feb. 10, 1969, abandoned.

[52] **U.S. Cl.** ..... **96/1 M;** 96/1 R; 96/1.3

[51] **Int. Cl.** **G03g 13/14;** G03g 13/22

[58] **Field of Search** ..... 96/1 R, 1 PE, 1 M, 1.3, 96/1.5

[56] **References Cited**

UNITED STATES PATENTS

2,979,403	4/1961	Giaimo	96/1 R
3,005,707	10/1961	Kallmann et al.	96/1 R
3,072,542	1/1963	Johnson et al.	96/1 R X
3,384,566	5/1968	Clark	96/1 PE X
3,595,770	7/1971	Luebbe et al.	96/1.3
3,707,368	12/1972	Van Dorn	96/1 M

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[57] **ABSTRACT**

A manifold imaging process wherein a cohesively weak electrically photosensitive imaging layer is exposed to electromagnetic radiation to which the imaging layer is sensitive and subsequently subjected to an electric field while the imaging layer is sandwiched between a donor sheet and a receiver sheet. Upon separation of the sheets, the imaging layer fractures so as to provide a positive image on one of the sheets and a negative image on the other sheet.

10 Claims, 2 Drawing Figures

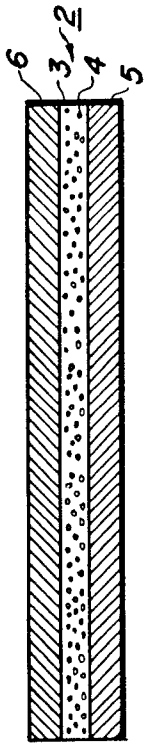


FIG. 1

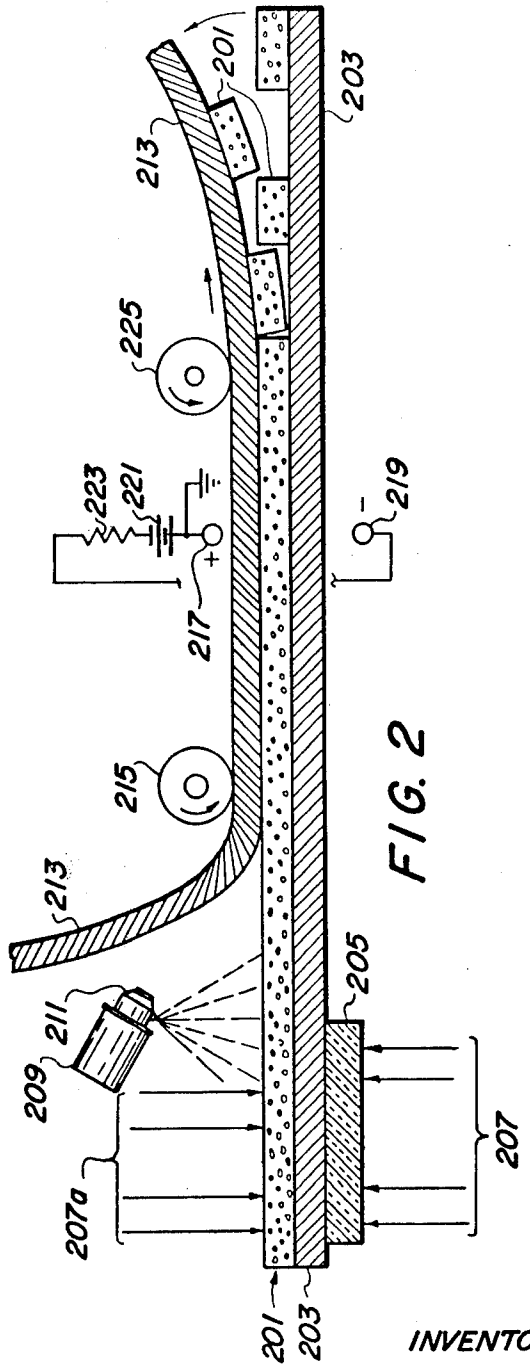


FIG. 2

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MANIFOLD IMAGING PROCESS USING ELECTRICALLY PHOTOSENSITIVE MATERIAL SUBJECT TO LIGHT FATIGUE

CROSS REFERENCE TO RELATED APPLICATIONS

This is a continuation of Ser. No. 186,125, filed Oct. 4, 1971.

Said application Ser. No. 186,125, now abandoned, is a continuation-in-part application of our application Ser. No. 798,094, filed Feb. 10, 1969 now abandoned.

BACKGROUND OF THE INVENTION

The present invention relates in general to imaging systems and, more particularly, to an improved manifold imaging process.

There has recently been developed a manifold imaging technique based upon the transfer of an imaging layer comprising a cohesively weak electrically photosensitive material sandwiched between a pair of sheets. Under the influence of electromagnetic radiation to which the imaging layer is sensitive and an electric field, the imaging layer fractures in imagewise configuration when the sandwich is separated under an electrical field. In the most common embodiment of this imaging technique, a layer of cohesively weak electrically photosensitive imaging material is coated onto a substrate. This coated substrate is called a donor. In one form the imaging layer comprises a photosensitive material such as metal free phthalocyanine dispersed in a binder. When needed, in preparation for the imaging operation, the imaging layer is activated as by contacting it with a swelling agent, solvent, or partial solvent for the imaging layer or by heating. This step may be eliminated, of course, if the layer retains sufficient residual solvent after having been coated on the substrate from a solution or paste or is sufficiently cohesively weak to fracture in response to the application of electromagnetic radiation and electrical field. After activation, a receiver sheet is laid over the surface of the imaging layer. An electrical field is then applied across this manifold sandwich while it is exposed to a pattern of light and shadow representative of the image to be reproduced. Upon separation of the donor substrate or sheet and receiver sheet, the imaging layer fractures along the line defined by the pattern of light and shadow to which the imaging layer has been exposed. Part of the imaging layer is transferred to one of the sheets while the remainder is retained on the other sheet so that a positive image, that is, a duplicate of the original, is produced on one sheet while a negative image is produced on the other.

In the prior art manifold imaging process, the manifold sandwich was placed on a transparent conductive electrode. Then a second conductive electrode was placed over the receiver sheet. Conventionally, the transparent conductive electrode was a NESA glass plate and the receiver side electrode was a flexible conductive black paper or aluminum foil. These electrodes were then connected to a source of potential difference resulting in the application of an electrical field across the manifold sandwich. The electrical field was maintained during the step of exposing the imaging layer to electromagnetic radiation. Ordinarily, one of these electrodes was transparent and the image to be reproduced was projected onto the imaging layer through the transparent electrode.

In the usual manifold imaging process, at least one of the donor sheet and receiver sheet is at least partially transparent to permit exposure of the imaging layer to the electromagnetic radiation through the sheet.

The prior art process, as described above, produces high quality, high contrast images. However, several disadvantages are apparent in the prior art process. For example, it was necessary to have an electric field applied across the sandwich during the exposure of the imaging layer to electromagnetic radiation. It was, therefore, conventional to use a transparent conductive electrode which was at least as large as the desired image. Conductive transparent materials are expensive and usually fragile. Also, at least one of the donor or receiver sheets were at least partially transparent to the electromagentic radiation employed in order to permit the exposure of the imaging layer which was sandwiched between the sheets and electrodes. Thus, the prior art manifold imaging process employed transparent components and also required means for subjecting the manifold sandwich to an electric field at or near the location at which the imaging layer was exposed to electromagnetic radiation.

SUMMARY OF THE INVENTION

It is, therefore, an object of this invention to provide a manifold imaging process which overcomes the above-noted disadvantages.

It is another object of this invention to provide a sequential manifold imaging process capable of providing relatively high quality images.

It is another object of this invention to provide a manifold imaging process which does not require the use of transparent components.

It is another object of this invention to provide a manifold imaging process wherein the application of an electric field across the manifold sandwich is not required during the exposure step.

It is another object of this invention to provide a manifold imaging process wherein the exposure step is accomplished prior to forming the manifold sandwich.

The foregoing objects and others are accomplished in accordance with this invention by a manifold imaging process wherein a cohesively weak electrically photosensitive imaging layer is exposed to electromagnetic radiation to which it is sensitive and subsequently charged or subjected to an electric field while sandwiched between two sheets. The imaging layer is placed between two sheets conventionally referred to as donor and receiver sheets, either before or after exposure but prior to being subjected to an electric field. After the manifold sandwich is subjected to an electric field, the sandwich is separated. Upon separation of the donor and receiver sheet, the imaging layer fractures along the lines defined by the electromagnetic radiation to which the imaging layer has been exposed. Part of the imaging layer is transferred to one of the sheets while the remainder is retained on the other sheet so that a positive image, that is, a duplicate of the original is produced on one sheet while a negative image is produced on the other. Of course, if the imaging layer is placed between the donor sheet and receiver sheet thus forming a manifold sandwich prior to the exposure step then at least one of the donor or receiver sheets must be at least partially transparent to the electromagnetic radiation employed. If the exposure step occurs prior to forming the manifold sandwich comprising the imaging

layer between a donor and a receiver sheet, then there is no need that the sheets be transparent to the electromagnetic radiation employed.

In the prior art, exposure of the imaging layer to electromagnetic radiation to which it is sensitive was accomplished while an electric field is maintained across the manifold sandwich. The electrical field was applied through conductive electrodes or was present as an electrostatic charge on the surface of the insulating donor and receiver sheets which were in contact with the imaging layer. It has now been learned that imaging layers can be prepared wherein simultaneous electric field and exposure to electromagnetic radiation is not required. The amount of time which can be allowed between exposure of the imaging layer to electromagnetic radiation and the charging step depends upon the electrically photosensitive material in the imaging layer, the amount of exposure and the strength of the electric field.

The characteristic of the electrically photosensitive particles in a manifold imaging layer which allows image development by sandwich separation under an electric field subsequent to imagewise exposure is referred to as fatigue. One skilled in the art may easily determine this characteristic by using an apparatus similar to that shown in FIG. **2.** The apparatus is described in detail later. In general, the experiment is performed as follows: an electrically photosensitive imaging layer is coated on an electrically insulating substrate or donor sheet and exposed to imagewise electromagnetic radiation to which the imaging layer is sensitive. Image exposure is discontinued and a receiver sheet is then placed over the imaging layer. The donor substrate and the receiver are charged after the manifold sandwich is formed. Upon separation of the sandwich the imaging layer fractures in imagewise configuration, part of the imaging layer is transferred to the receiver sheet while the remainder is retained on the donor sheet. The allowable time interval between discontinuance of the exposure and the charging of the manifold sandwich is defined as the fatigue characteristic for the particular imaging layer. The fatigue characteristic for a particular imaging layer may be determined under various operating conditions by varying the amount of exposure and also be varying the strength of the field across the manifold sandwich. In addition, the fatigue characteristics of some electrically photosensitive materials are affected by electromagnetic radiation to which it may be exposed after the imagewise exposure and before charging. Thus, the allowable time between imagewise exposure and charging is decreased if general exposure such as room light is allowed prior to charging. The amount of time which can elapse between exposure and charging may vary from a few hundredths of a second to hours. For those electrically photosensitive materials having a very short fatigue characteristic the embodiment of FIG. **2** should be modified to eliminate as much as possible the amount of time elapsed between exposure, sandwich formation and charging.

Any suitable electrically photosensitive material or mixtures of such materials exhibiting fatigue characteristics may be used in carrying out the invention. The pigments can be made up of one or more components in solid solution or dispersed one in the other whether the particles are made up of multiple layers of different materials or are combined of photosensitive and non-photosensitive materials. Typical highly colored electrically photosensitive materials include materials such as 8,13-dioxodinaphtho-(1,2,2',3')-furan-6-carbox-p-methoxyanilide; Locarno Red, C.I. No. 15865, 1-(4'-methyl-5'-chloroazobenzene-2'-sulfonic acid)-hydroxy-3-naphthoic acid; Watchung Red B, the varium salt of 1-(4'-methyl-5'-chloroazobenzene-2'-sulfonic acid)-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'-methylazobenzene-2'-sulfonic acid)-2-hydroxy-3-naphthoic acid, C.I. No. 15850; Calcium Lithol Red, the calcium lake of 1-(2'-azonaphthalene-1'sulfonic acid)-2-naphthol, C.I. No. 15630; Pyranthrones; Indofast Brilliant Scarlet Toner, 3,4,9,10-bis (N,N'-(p-methoxy-phenyl)-imido)-perylene, C.I. No. 71140; dichloro thioindigo; Pyrazolone Red B Toner, C.I. No. 21120; Methyl Violet, a phosphotungstomolybdic acid lake of a Triphenylmethane dye, C.I. 42535; 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'-npahthanilide, 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-di (C,C'-diphenyl)-thiazole-anthraquinone, C.I. No. 67300; Flavanthrone; Indofast Orange Toner, C.I. No. 71105; 1-cyano-2,3-phthaloyl-7,8-benzopyrrocoline and many other thio indigos, acetoacetic arylides, anthraquinones, perinones, perylenes, dioxazines, quinacridones, azos, diaxos, thoazines, azines and the like. In addition to the aforementioned pigments, other typical organic materials include polyvinyl carbazole; 2,4-bis (4,4'-diethyl-aminophenyl)-1,3,4-oxidiazole; N-isopropylcarbazole; polyvinyl-anthracene; triphenylpyrrol; 4,5-diphenylimidazolidinethione; 4,5-diphenyldiphenylimidazolidinone; 4,5-diphenylimidazolidinethione; 4,5-bis-(4'-amino-phenyl)-imidazolidinone; 1,2,5,6-tetraazacyclooc-tatetraene-(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-tetraaza-cyclooctatetraene-(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-naphthylidene-oxazolone; 2-phenyl-4-diphenylideneoxazolone; 2-phenyl-4-p-methoxybenzylideneoxazolone; 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-aminobenzylideneisonicotinic acid hydrazide; furfurylidene-(2)-4'-dimethylaminobenzhydrazide; 5-benzilidene-amino-acenaphthene-3-benzylideneamino-carbazole; (4,N,N-dimethylamino-benzylidene)-p-N,N-dimethyl-aminoaniline; (2-nitro-benzylidene)-p-bromo-aniline; N,N-dimethyl-N'-(2-nitro-4-cyano-benzylidene)-p-phenylenediamine; 2,4-diphenyl-quinazoline; 2-(4'-amino-phenyl)-4-phenyl quinazoline; 2-phenyl-4-(4'-dimethyl-amino-phenyl)-7-methoxyquinazoline; 1,3-diphenyl-tetrahydroimidazole; 1,3-di(4'-chlorophenyl)-tetrahydroimidazole; 1,3-diphenyl-2,4'-dimethyl aminophenyl)-tetrahydroimidazole; 1,3-di-(p-tolyl)-2-[quinolyl-(2,'-(] tetrahydroimidazole; 2-(4'-dimethylamino-phenyl)-5-(4''-methoxyphenyl)-6-phe-

nyl-1,2,4-triazine; 3-pyridil-(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-tetraphenyl-pyrazoline; 1-phenyl-3-(p-methoxy styrl)-5-(p-methoxy-phenyl)-pyrazoline; 1-methoxy-2-(3',4' -dihydroxy-methylenephenyl)-benzimidazole; 2-(4'dimethylamino 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 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-dichloro-benzoquinone; anthra-quinone-2-carboxylic acid, Bromal, 4-nitro-phenol; 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, zine 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. In addition to the charge transfer complexes, it is to be noted that many additional ones of the above material may be further sensitized by the charge transfer complexing technique and that many of these materials may be dye-sensitized to narrow, broaden or heighten their spectral response curves.

Naphthanilides are preferred because of their excellent fatigue characteristic. Any naphthanilide, if suitable, may be used to prepare the imaging suspension of the present invention. Particularly preferred are naphthanilides complexed with electron acceptors.

Trinitro-9-fluorenones are particularly preferred electron acceptors. Any crystalline phase may be used, if suitable. The combination of trinitro-9-fluorenones with photosensitive materials such as polyvinyl carbazole are exceptionally well-known materials.

Typical naphthanilides include: 1-(2'-methoxy-5'-nitrophenylazo)-2-hydroxy-3''-nitro-3-naphthanilide, 1-(2'-chloro-4'-nitrophenylazo)-3''-nitro-3-naphthanilide, 1-(3',5'-dinitrophenylazo)-2-chloro-3''-naphthanilide, 1-(3,5'-dimethoxyphenylazo)-2-hydroxy-3''-nitro-3-naphthanilide and mixtures thereof.

It is also to be understood that the electrically photosensitive particles themselves may consist of any suitable one or more of the aforementioned electrically photosensitive materials dispersed in, in solid solution in, or copolymerized with, any suitable insulating resin whether or not the resin itself is photosensitive. This particular type of particle may be particularly desirable to facilitate dispersion of the particle to prevent undesirable reactions between the binder and the photosensitive material or between the photosensitive and the activator and for similar purposes. Typical resins of this type include polyethylene, polypropylene, polyamides, polymethacrylates, polyacrylates, polyvinyl chlorides, polyvinyl acetates, polystyrene, polysiloxanes, chlorinated rubbers, polyacrylonitrile, epoxies, phenolics, hydrocarbon resins and other natural resins such as rosin derivatives as well as mixtures and copolymers thereof.

The basic physical property desired in the imaging layer is that it be frangible as prepared or after having been suitably activated. That is, the layer must be sufficiently weak structurally so that the application of electrical field combined with the action of electromagnetic radiation on the electrically photosensitive materials will fracture the imaging layer. Further, the layer must respond to the application of field the strength of which is below that field strength which will cause electrical breakdown or arcing across the imaging layer. Another term for "cohesively weak," therefore, is "field fracturable." The imaging layer need not be cohesively weak at the time it is exposed to electromagnetic radiation provided it can be rendered cohesively weak by proper treatment such as activation prior to the separation of the charged sandwich.

The imaging layer serves as the photoresponsive element of the system as well as the colorant for the final image produced. Preferably, the imaging layer is selected so as to have a high level of response while at the same time being intensely colored so that a high contrast image can be formed by the high gamma system of this invention. The imaging layer may be homogeneous comprising, for example, a solid solution of two or more pigments. The imaging layer may also be heterogeneous comprising, for example, pigment particles dispersed in a binder.

One technique for achieving low cohesive strength in the imaging layer is to employ relatively weak, low molecular weight materials therein. Thus, for example, in a single component homogeneous imaging layer, a monomeric compound or a low molecular weight polymer complexed with a Lewis acid to impart a high level of photoresponse to the layer may be employed. Similarly, when a homogeneous layer utilizing two or more components in solid solution is selected to make up the imaging layer, either one or both of the components of the solid solution may be a low molecular weight material so that the layer has the desired low level of cohesive strength. This approach may also be taken in connection with the heterogeneous imaging layer. Although the binder material in the heterogeneous system may in itself be photosensitive, it does not necessarily have this property. Materials may be selected for use as this binder material solely on the basis of physical properties without regard to their photosensitivity. This is also true of the two component homogeneous system where photoinsensitive materials with the desired physical properties can be used. Any other technique for achieving low cohesive strength in the imaging layer may also be employed. For example, suitable blends of incompatible materials such as a blend of a polysiloxane resin with a polyacrylic ester resin may be used either as the binder layer in a heterogeneous system in conjunction with a "homogeneous" system in which the photoresponsive material may be either one of the incompatible components (complexed with a Lewis acid) or a separate and additional component of the layer. The thickness of the imaging layer preferably ranges from about 0.2 microns to about 25 microns

generally about 1 micron to about 10 microns and preferably about 5 microns.

The ratio of photosensitive material to binder by weight in the heterogeneous system may range from about 10 to 1 about 1 to 10 respectively, but it has generally been found that properties in the range of from about 1 to 4 to about 2 to 1 respectively produce the best results and, accordingly, this constitutes a preferred range.

The binder material in the heterogeneous imaging layer or the material used in conjunction with the pigment materials in the homogeneous layer, where applicable, may comprise any suitable cohesively weak insulating material or materials which can be rendered cohesively weak. Typical materials include: microcrystalline waxes such as: Sunoco 1290, Sunoco 5825, Sunoco 985, all available from Sun Oil Co.; Paraflint RG, available from the Moore and Munger Company; paraffin waxes such as: Sunoco 5512, Sunoco 3425, available from Sun Oil Co.; Sohio Parowax, available from Standard Oil of Ohio; waxes made from hydrogenated oils such as: Capitol City 1380 wax, available from Capitol City Products, Co. Columbus, Ohio; Caster Wax L-2790, available from Baker Caster Oil Co.; Vitikote L-304; available from Duro Commodities; polyethylene such as: Eastman Epolene N-11, Eastman Epolene C-12, available from Eastman Chemical Products, Co.; Polyethylene DYJT, Polyethylene DYLT, Polyethylene DYNF, Polyethylene DYDT, all available from Union Carbide, Corp.; Marlex TR 822, Marlex 1478, available from Phillips Petroleum Co.; Epolene C-13; available from Eastman Chemical Products, Co.; Polyethylene AC8, Polyethylene AC612, Polyethylene AC324, available from Allied Chemicals; modified styrenes such as: Piccotex 75, Piccotex 100, Piccotex 120, available from Pennsylvania Industrial Chemical; vinylacetateethylene copolymers such as: Elvax Resin 210, Elvax Resin 310, Elvax Resin 420, available from E. I. DuPont de Nemours & Co., Inc., Vistanex MH, Vistanex L-80, available from Enjay Chemical Co., vinyl chloride-vinyl acetate copolyers such as: Vinylite VYLF, available from Union Carbide Corp.; styrene-vinyl toluene copolymers; polypropylenes; and mixtures thereof. The use of an insulating binder is preferred because it allows the use of a larger range of electrically photosensitive pigments.

A mixture of microcrystalline wax and polyethylene is preferred because it is cohesively weak and an insulator.

Where the imaging layer is not sufficiently cohesively weak to allow imagewise fracture, it is desirable to include an activation step in the process of this invention. The activation step may take many forms such as heating the imaging layer thus reducing its cohesive strength or applying a substance to the surface of the imaging layer or including a substance in the imaging layer which substance lowers the cohesive strength of the layer or aids in lowering the cohesive strength. The substance so employed is termed an "activator." Preferably, the activator should have a high resistivity so as to prevent electrical breakdown of the manifold sandwich. Accordingly, it will generally be found to be desirable to purify commercial grades of activators so as to remove impurities which might impart a higher level of conductivity. This may be accomplished by running the fluids through a clay column or by employing any other suitable purification technique. Generally speaking, the activator may consist of any suitable material having the aforementioned properties. For purposes of this specification and the appended claims, the term activator shall be understood to include not only materials which are conventionally termed solvents but also those which are partial solvents, swelling agents or softening agents for the imaging layer. The activator can be applied at any point in the process prior to separation of the sandwich.

It is generally preferable that the activator have a relatively low boiling point so that fixing of the resulting image can be accomplished upon evaporation of the activator. If desired, fixing of the image can be accomplished more quickly with mild heating at most. It is to be understood, however, that the invention is not limited to the use of these relatively volatile activators. In fact, very high boiling point non-volatile activators including silicone oils such as dimethyl-polysiloxanes and very high boiling point long chain aliphatic hydrocarbon oils ordinarily used as transformer oils such as Wemco-C transformer oil, available from Westinghouse Electric Co., have also been successfully utilized in the imaging process. Although these less volatile activators do not dry off by evaporation, image fixing can be accomplished contacting the final image with an absorbent sheet such as paper which absorbs the activator fluid. In short, any suitable volatile or non-volatile activator may be employed. Typical activators include Sohio Odorless Solvent 3440, an aliphatic (kerosene) hydrocarbon fraction, available from Standard Oil Co. of Ohio, carbon tetrachloride, petroleum ether, Freon 214 (tetrafluorotetrachloropropane), other halogenated hydrocarbons such as chloroform, methylene chloride, trichloroethylene, perchloroethylene, chlorobenzene, trichloromonofluoromethane, tetrachlorodifluoroethane, trichlorotrifluoroethane, ethers such as diethyl ether, diisopropyl ether, dioxane, tetrahydrofuran, ethyleneglycol monoethyl ether, aromatic and aliphatic hydrocarbons such as benzene, toluene, xylene, hexane, cyclohexane, gasoline, mineral spirits and white mineral oil and begetable oils such as coconut oil, babussu oil, palm oil, olive oil, castor oil, peanut oil and neatsfoot oil, decane, dodecane and mixtures thereof. Sohio Odorless Solvent 3440 is preferred because it is odorless, nontoxic and has a relatively high flash point.

Although the imaging layers may be prepared as self-supporting films, normally these layers are coated onto a sheet referred to as the donor sheet or substrate. For convenience, the combination of imaging layer and donor sheet is referred to as the donor. When employing a binder, the pigment can be mixed in the binder material by convention means for blending solids as by ball milling. After blending the ingredients of the imaging layer, the desired amount is coated on a substrate. In a particularly preferred form of the invention, an imaging layer comprising the electrically photosensitive pigment dispersed in a binder is coated onto an electrically insulating donor sheet.

The donor sheet and receiving sheet may comprise any suitable electrically insulating or electrically conducting material. Insulating materials are preferred since they allow the use of high strength polymeric materials. Typical insulating materials include polyethylene, polypropylene, polyethylene terephthalate, cellulose acetate, paper, plastic coated paper, such as polyethylene coated paper, vinyl chloride-vinylidene chloride copolymers and mixtures thereof. Mylar (a polyes-

ter formed by the condensation reaction between ethylene glycol and tetephalic acid available from E. I. DuPont de Nemours & Co., Inc.) is preferred because of its durability and excellent insulative properties. Not only does the use of this type of high strength polymer provide a strong substrate for the positive and negative images formed on the donor substrate and receiver sheet but, in addition, it provides an electrical barrier between the electrodes and the imaging layer which tends to inhibit electrical breakdown of the system while subjecting the manifold sandwich to an electrical field. The donor sheet and receiver sheet may each be selected from different materials. Thus, a manifold sandwich can be prepared by employing an insulating donor sheet while a conductive material is employed as a receiver sheet.

As stated above, according to the process of this invention, the manifold sandwich comprising the donor sheet, receiver sheet and the imaging layer is subjected to an electrical field. The electrical field can be applied in many ways. Generally, the sandwich is placed between electrodes having different electrical potential. Also, an electrical charge can be imposed upon one or both of the donor sheet and receiver sheet before or after forming the sandwich by any one of several known methods for inducing a static electrical charge into a material. Static charges can be imposed by contacting the sheet or substrate with an electrically charged electrode. Alternatively, one or both sheets may be charged using corona discharge devices such as those described in U.S. Pat. No. 2,588,699 to Carlson, U.S. Pat. No. 2,777,957 to Walkup, U.S. Pat. No. 2,885,556 to Gundlach or by using conductive rollers as described in U.S. Pat. No. 2,980,834 to Tregay et al., or by frinctional means as described in U.S. Pat. No. 2,297,691 to Carlson or other suitable apparatus.

Thus, the electrical field can be provided by means known to the art for subjecting an area to an electrical field. The electrodes employed may comprise any suitable conductive material and may be flexible or rigid. Typical conductive materials include: metals such as aluminum, brass, steel, copper, nickel, zinc, etc., metallic coatings on plastic substrates, rubber rendered conductive by the inclusion of a suitable material therein, or paper rendered conductive by the inclusion of a suitable material therein or through conditioning in a humid atmosphere to insure the presence therein of sufficient water content to render the material conductive. Conductive rubber is preferred because of its flexibility. In the process of this invention wherein the imaging layer is exposed to electromagnetic radiation while positioned between electrodes, one of the electrodes must be at least partially transparent. The transparent conductive electrode may be made of any suitable conductive transparent material and may be flexible or rigid. Typical conductive transparent materials include cellophane, conductively coated glass, such as tin or indium oxide coated glass, aluminum coated glass, or similar coatings on plastic substrates. NESA, a tin oxide coated glass available from Pittsburgh Plate Glass Co., is preferred because it is a good conductor and is highly transparent. Although not preferred, in the process of this invention wherein the donor and/or receiver is composed of conductive material each may also be employed as the electrodes by which the imaging layer is subjected to an electrical field. This is, either one or both of the donor sheet and receiver sheet may serve a dual function in the process of this invention.

The strength of the electrical field applied across the manifold sandwich depends on the structure of the manifold sandwich and the materials used. For example, if highly insulating receiver and donor substrate materials are used, a much higher field may be applied than if relatively conductive donor and receiver sheets are used. The field strength required may, however, be easily determined. If too large a potential is applied, electrical breakdown of the manifold sandwich will occur allowing arcing between the electrodes. If too little potential is applied, the imaging layer will not fracture in imagewise configuration. By way of example, if a 3 mil. Mylar receiver sheet and a 2 mil. Mylar donor sheet are used, potentials as high as 20,000 volts may be applied between the electrodes. The preferred field strengths across the manifold sandwich are, however, in the range of from about 1,000 volts per mil. to about 7,000 volts per mil. Since relatively high potentials are utilized, it is desirable to insert a resistor in the circuit to limit the flow of current. Resistors on the order of from about 1 megohm to about 20,000 megohms are conventionally used.

Whether the positive image is formed on the donor sheet or the receiver sheet depends on the imaging layer materials used and the polarity of the applied field. It has been found, in general, however, that if the donor side electrode is held at a positive potential in respect to the receiver side electrode, that the positive image is formed on the donor sheet and a negative image is formed on the receiving sheet, that is, the illuminated portions of the imaging layer adhere to the receiver sheet and the non-illuminated areas of the imaging layer adhere to the donor sheet.

It has also been found, in general, that when the imaging layer is coated onto a donor sheet the best quality images are produced by exposing through the donor sheet.

A visible light source, an ultraviolet light source or any other suitable source of electromagnetic radiation may be used to expose the imaging layer of this invention. The electrically photosensitive material is chosen so as to be responsive to the wavelength of the electromagnetic radiation used. It is to be noted that different electrically photosensitive materials have different spectral responses and that the spectral response of many electrically photosensitive materials may be modified by dye sensitization so as to either increase and narrow the spectral response of a material to a peak or to broaden it to make it more panchromatic in its response.

The imaging layer can be exposed to electromagnetic radiation at any point in the process including prior to charging the manifold sandwich. For example, one embodiment of the process of this invention are the steps of (1) exposing the imaging layer on a donor sheet to electromagnetic radiation to which it is sensitive, (2) placing the receiver on the imaging layer forming a manifold sandwich (3) subjecting the sandwich to an electrical field and (4) separating the sandwich. Alternatively, when employing either a donor or a receiver sheet which is at least partially transparent to the electromagnetic radiation employed, the process of this invention can include the steps of (1) forming the manifold sandwich of the donor and receiver (2) exposing the imaging layer to electromagnetic radiation (3) im-

posing an electrical charge on the donor and receiver as by corona discharge and (4) separating the sandwich.

The sequence of steps of the process of this invention including the optional activation step can be further varied by those skilled in the art without departing from the scope of this invention. For example, the imaging layer can be activated by the application thereon of a swelling agent either before or after the exposure step. Also, activation can take place after the manifold sandwich is formed by means such as heating the sandwich. Thus, when required, the imaging layer can be activated at any point in the process prior to the separation of the manifold sandwich.

BRIEF DESCRIPTION OF THE DRAWINGS

The advantages of this improved method of imaging will become apparent upon consideration of the detailed disclosure of the invention, especially when taken in conjunction with the accompanying drawings wherein:

FIG. **1** is a side sectional view of a manifold sandwich for use in the process of this invention.

FIG. **2** is a side sectional view diagramatically illustrating the process steps of this invention.

Referring now to FIG. **1**, imaging layer **2** comprising electrically photosensitive material **4** dispersed in binder **3** is deposited on the surface of donor sheet **5.** Receiver sheet **6** rests upon imaging layer **2** to complete the manifold sandwich.

Referring now to FIG. **2,** there is shown a manifold imaging process capable of producing positive to positive copy on transparent or opaque receiver sheets or on transparent or opaque donor sheets. In FIG. **2,** imaging layer **201** containing an electrically photosensitive material supported by transparent plate **205** is exposed to electromagnetic radiation such as light image **207** through transparent donor sheet **203.** In those instances wherein donor sheet **203** is desirably opaque to the electromagnetic radiation employed imaging layer **201** can be exposed to electromagnetic radiation and as light image **207***a*. The optical activation step is shown in FIG. **2.** Although the activator may be applied by any suitable technique such as with a brush, with a smooth or rough surface roller, by flow coating, by vapor condensation or the like, FIG. **2** shows the activator fluid **209** being sprayed onto imaging layer **201** from container **211.** Following the deposition of the activator fluid, receiver sheet **213** is brought into contact with imaging layer **201** and the sandwich is closed by roller **215** which also serves to squeeze out any excess activator fluid which may have been deposited. In certain instances, the activation step may be omitted. Thus, for example, a manifold sandwich may be supplied wherein imaging layer **201** is initially fabricated to have a low cohesive strength so that activation may be omitted and receiver **213** may be placed on the surface of imaging layer **201** directly after the exposure step. It is generally preferable, however, to include an activation step in the process for most imaging layers.

After receiver sheet **213** has been placed on imaging layer **201,** an electrical field is applied across the manifold sandwich through electrodes **217** and **219** which are connected to potential source **221** and resistor **223.** Although FIG. **2** shows the manifold sandwich not coming in contact with either of the electrodes **217** and **219,** they may contact one or both electrodes when the electrical field is applied. Preferably, the sandwich will contact at least one electrode to serve as a guide and be spaced 1 to 3 mils from the other electrode to prevent binding.

Alternatively, the charging electrodes may be a corona discharge device or roller **215** may be conductive, for example, and be used in place of electrodes **217.** Additionally, the electrodes may consist of a sharp edge or a friction charging device such as a fur covered roller.

The sign of the charge as shown on electrodes **217** and **219** may also be reversed, electrode **217** being made the negative electrode and electrode **219** being made the positive electrode. In a continuous operation, the light image preferably is projected through a slit in such a manner that there if little or no relative movement between the projected light image and the donor sheet. The manifold sandwich after passing electrodes **217** and **219** then passes roller **225** which acts as a guide for the manifold sandwich and as a bearing point for the stripping apart of the sandwich. Alternatively, roller **225** may be a sharp edge, a rod or a wire. Upon separation of the manifold sandwich, imaging layer **201** fractures along the edges of exposed areas and leaves the surface of donor sheet **203** which was exposed to light image **207** or **207***a*. Accordingly, once separation is complete, exposed portions of imaging layer **201** are retained on one of sheets **203** and **213** while unexposed portions are retained on the other sheet. The portions thus provide a positive image on one sheet and a negative image on the other sheet. Various fixative procedures can be employed on the image to be preserved after separation of the sandwich.

DESCRIPTION OF PREFERRED EMBODIMENTS

The following Examples further specifically illustrate the present invention. The Examples below are intended to illustrate various preferred embodiments of the improved imaging method. The parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

An imaging layer comprising electrically photosensitive materials dispersed in a binder is first prepared. About 100 parts of Naphthol Red B, code 20-7575 available from American Cyanamide Company is dissolved in reagent grade ethylenediamine. The solution is filtered immediately through coarse filter paper and the filtrate mixed with an equal volume of reagent grade isopropanol. The Naphthol Red B precipitates in the alcohol and is removed by means of a centrifuge. After separating the ethylenediamine and alcohol, the electrically photosensitive material is washed and filtered with successive amounts of isopropanol, a 2:1 volume mixture of isopropanol and de-ionized water and five washings with de-ionized water until the filtrate is neutral. Finally, the material is washed with dimethylformamide and methanol in succession until the filtrates have a pale yellow color. The Naphthol Red B is then dried at 40°C. under vacuum. About 2.5 parts of the purified Naphthol Red B is combined with about 0.5 parts of Benz Yellow, code 30-0535 available from the Hilton Davis Chemical Company. The Benz Yellow is purified by solvent extraction in an organic solvent. The Naphthol Red B and Benz Yellow are combined with about 45 parts of naphtha and ball milled for 4 hours.

A binder material is prepared by combining about 2.5 parts of Paraflint RG, a low molecular weight parafinic material available from the Moor and Munger Co., New York City; about 3 parts of Polyethylene DYLT available from Union Carbide Corporation; about 0.5 parts of a vinyl acetate-ethylene copolymer available as Elvax 420 from E. I. DuPont de Nemours Inc. and about 2.5 parts of a modified polystyrene available as Piccotex 100 from Pennsylvania Industrial Chemical Co. with about 15 parts of Sohio Ordorless Solvent 3440 a kerosene fraction available from the Standard Oil Company. The mixture is heated until dissolved and then cooled. The binder and pigment mixtures are then ball milled for a period of about 18 hours. About 45 parts of isopropyl alcohol is added to the mixture and the mixture is milled in the ball mill for 15 minutes. The resulting imaging material is then coated on 3 mil Mylar with a doctor knife set at a gap of 4.4 mil to produce a donor. The donor is dried at a temperature of about 115°F.

The donor is then placed on the tin oxide surface of a NESA glass plate with the imaging layer facing away from the tin oxide. The imaging layer is activated by applying Sohio Odorless Solvent 3440 by means of a brush and a sandwich is formed by placing a transparent film of polypropylene over the activated donor as a receiver. The imaging layer is exposed to a pattern of light from an incandesent white light source of 45 ft. candles for a period of 3 minutes through the transparent receiver. After exposure a black paper electrode is laid over the receiver sheet and a 10,000 volt DC potential is applied across the sandwich between a NESA glass plate and the black paper electrode. With the potential still connected, the sandwich is separated yielding a pair of images with a positive image adhering to the donor sheet and a negative image on the receiver sheet.

EXAMPLE II

The procedure of Example I is repeated except that the sandwich is inverted with the transparent polypropylene film adjacent to the NESA glass plate and the imaging layer is exposed through the transparent donor sheet. Upon separation of the sheets, a pair of images are observed with the positive image adhering to the receiver sheet and a negative image adhering to the donor sheet.

EXAMPLE III

An imaging layer comprising electrically photosensitive materials dispersed in a binder is first prepared. About 100 parts of Naphthol Red B, code 20-7575 available from American Cyanamide Company is dissolved in reagent grade ethylenediamine. The solution is filtered immediately through coarse filter paper and the filtrate mixed with an equal volume of reagent grade isopropanol. The Naphthol Red B precititates in the alcohol and is removed by means of a centrifuge. After separating the ethylenediamine and alcohol, the electrically photosensitive material is washed and filtered with successive amounts of isopropanol, a 2:1 volume mixture of isopropanol and de-ionized water and five washings with de-ionized water until the filtrate is neutral. Finally, the material is washed with dimethylformamide and methanol in succession until the filtrates have a pale yellow color. The Naphthol Red B is then dried at 40°C. under vacuum. About 2.5 parts of the purified Naphthol Red B is combined with about 0.5 parts of Benz Yellow, code 30-0535 available from the Hilton Davis Chemical Company, and 0.0025 parts of 2,4,7-Trinitro-9-fluorenone (TNF) available from Eastman Organic Chemicals. The Benz Yellow is purified by solvent extraction in an organic solvent. The Naphthol Red B, Benz Yellow and TNF are combined with 45 parts of naptha and ball milled for 4 hours.

A binder material is prepared by combining about 1.5 parts of Paraflint RG, a low molecular weight parafinic material available from the Moore and Munger Co., New York City; about 3 parts of Polyethylene DYLT available from Union Carbide Corporation; about 0.5 parts of a vinyl acetate-ethylene copolymer available as Elvax 420 from E. I. DuPont de Nemours Inc. and about 2.5 parts of a modified polystyrene available as Piccotex 100 from Pennsylvania Industrial Chemical Co. with about 15 parts of Sohio Odorless Solvent 3440 a kerosene fraction available from the Standard Oil Company. The mixture is heated until dissolved and then cooled. The binder and pigment suspension are ball milled for 16–20 hours. About 45 parts of isopropyl alcohol is then added, the mixture which is milled in the ball mill for 15 minutes. The resulting imaging material is then coated on 3 mil Mylar with a doctor knife set at a gap of 4.4 mil to produce a donor. The donor is dried at a temperature of about 115° F.

A donor prepared as described above is placed on the tin oxide surface of a NESA glass plate with the imaging layer facing away from the glass plate and through the NESA and the transparent donor substrate, the imaging layer is exposed to a pattern of light providing a total exposure of 0.14 foot candle seconds. After exposure, the imaging layer is activated by the application of Sohio Odorless Solvent 3440 and a paper receiver is laid over the activated imaging layer. The black paper electrode is placed over the receiver and a potential of 9,000 volts from a DC power supply is placed across the sandwich. With the potential still connected, the sandwich is separated yielding a pair of images with the positive image adhering to the donor sheet and a negative image adhering to the receiver sheet.

EXAMPLE IV

The procedure of Example III is repeated except that the imaging layer is exposed directly on its exposed surface. After exposure, the imaging layer is activated and a sandwich is formed with the receiver placed over the activated imaging layer. Upon separation under an electrical field a pair of images are observed with a positive image adhering to the donor sheet and the negative image adhering to the receiver sheet.

EXAMPLE V

The procedure of Example I is repeated except that Naphthol Red M C.I. No. 12390, available from American Cyanamide (Code 20-7515) is substituted for Naphthol Red B. Upon separation of the sandwich under a electrical field, a pair of images are observed with the positive image adhering to the donor sheet and a negative image adhering to the receiver sheet.

EXAMPLE VI

About 8 parts of quindo magenta, RV6803, 2,9-dimethyl quinacridone as obtained from Harmon Colors Co. is dispersed in about 16 parts of binder material as prepared in accordance with the procedure of Exam-

ple I. The resulting imaging material is coated on 3 mil Mylar with a doctor knife set at a gap of 4.4 mil to produce a donor. The donor is dried at a temperature of 50°C.

The donor is then placed on the tin oxide surface of a NESA glass plate with the imaging layer facing away from the tin oxide. After activating the imaging layer by spraying it with Sohio Odorless Solvent 3440 a manifold sandwich is formed by placing a film of 2 mil Mylar receiver sheet over the imaging layer. The imaging layer is exposed to a pattern of light and shadown for 3 minutes. After exposure is terminated, a black paper electrode is placed on the receiver sheet and a 10,000 volt DC potential is applied across the NESA glass plate and the paper electrode. With the potential still connected, the sandwich is separated yielding a pair of images with a positive image and adhering to the donor sheet and a negative image on the receiver sheet.

Although specific components and proportions have been stated in the above description of preferred embodiments of the invention, other typical materials as listed above as suitable may be used with similar results in addition other materials may be added to the various components of the process to synergize, enhance or otherwise modify the properties of the imaging layer. For example, various dyes, spectral sensitizers, activators or electrical sensitizers such as Lewis acids may be added to the several components of the manifold sandwich.

Other modifications and ramifications of the present invention will occur to those skilled in the art upon a reading of the present disclosure. These are intended to be included within the scope of this invention.

What is claimed is:

1. An imaging method which comprises subjecting an electrically photosensitive imaging layer which exhibits light fatigue to an electrical field while sandwiched between a donor sheet and a receiver sheet said imaging layer comprising an electrically photosensitive material selected from the group consisting of 1-(2'-methoxy-5'-nitrophenylazo)-hydroxy-3''-nitro-3-naphthanilide, 2,9-dimethyl quinacridone and naphthal Red M. C. I. No. 12390, said layer being structurally fracturable in response to the combined effects of an electric field and exposure to electromagnetic radiation to which it is sensitive, and separating said sandwich while subject to the electrical field whereby said imaging layer fractures in image-wise configuration said imaging layer having been imagewise exposed to electromagnetic radiation to which the imaging layer is sensitive prior to being subjected to the electrical field.

2. The method of claim **1** further including the step of rendering said imaging layer structurally fracturable in response to the combined effects of an electric field and exposure to electromagnetic radiation by applying an activating amount of an activator to said imaging layer prior to the separation of the sandwich.

3. The method of claim **2** wherein the activator is heat.

4. The method of claim **1** wherein the imaging layer comprises said electrically photosensitive material dispersed in an electrically insulating binder.

5. The method of claim **2** wherein the imaging layer comprises said electrically photosensitive material dispersed in an insulating binder.

6. The method of claim **1** wherein the donor sheet is at least partially transparent to the electromagnetic radiation and said imaging layer is exposed through said donor sheet.

7. The method of claim **1** wherein the imaging layer is coated onto a donor sheet which is opaque to actinic electromagnetic radiation and said imaging layer is exposed to the electromagnetic radiation on its side opposite the donor sheet.

8. The method of claim **1** wherein the imaging layer is sandwiched between a donor sheet and a receiver sheet at least one of said sheets being at least partially transparent on the electromagnetic radiation employed and said imaging layer is exposed to the electromagnetic radiation to which it is sensitive through the transparent sheet.

9. The method of claim **5** wherein the electrically photosensitive material is 1-(2'-methoxy-5'-nitrophenylazo)-hydroxy-3''-nitro-3-naphthanilide.

10. The method of claim **5** wherein the electrically photosensitive material is 2,9-dimethyl-quinacridone.

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