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HEAT DEFORMABLE RECORDING MATERIALS CONTAINING PHOTOCONDUCTIVE RESINOUS CHARGE TRANSFER COMPLEXES

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ABSTRACT OF THE DISCLOSURE

Photoconductive materials are prepared from phenol-aldehyde resins and Lewis acids. The materials are charge transfer complexes. The materials are used in conjunction with heat deformable materials to form a recording medium. Methods of using the recording medium are disclosed.

This invention relates to an electrophotographic process and more specifically, to a novel electrostatic process for the formation of images on deformable thermoplastic materials.

It is known to record on deformable dielectric materials by the use of two distinct methods; the first is known as "frost" imaging and is defined in detail in a publication "A Cyclic Xerographic Method Based on Frost Deformation" by R. W. Gundlach and C. J. Claus, Journal of Photographic Science and Engineering, January-February edition, 1963. The other method is "relief" imaging and is described in U.S. Patents 3,055,006; 3,063,872; and 3,113,179. A fundamental distinction between "frost" and "relief" is that frost occurs on uniformly charged areas whereas relief responds to electrostatic charge gradients but not to uniform charge distribution. This is an important difference, not only from the viewpoint of application, but also because it definitely indicates a different mechanism in the two systems. It is also interesting to note that a frost structure can be created without informational input whereas relief has no structure, that is, it does not exist without informational input. The distinction in the two systems is further established by the fact that certain materials will relief but not frost.

It is an object of this invention to provide a photoconductive material which is adapted for use in both frost and relief systems.

Another object of this invention is to provide a novel organic photoconductive material useful in the preparation of heat deformable recording media.

Another object of this invention is to provide a novel method for the preparation of a heat deformable recording medium.

Another object of this invention is to provide a novel transparent photoconductive material adapted for use in frost and relief systems and for later viewing in projection display devices.

Still another object of this invention is to provide a novel method for forming an image on a deformable photoconductive recording medium.

Still another object of this invention is to provide a material which acts both as the heat-deformable material and the photoconductor in a recording medium.

The foregoing objects and others are accomplished in accordance with this invention, generally speaking, by providing a method for recording an image on a heat deformable surface which comprises charging a thermoplastic layer obtained by a process which comprises mixing under charge transfer complexing conditions a phenol-aldehyde resin and a Lewis acid; exposing said layer to a pattern of light and shadow; and deforming said layer either subsequent to or concurrently with said exposure step, thereby forming an image pattern comprising raised

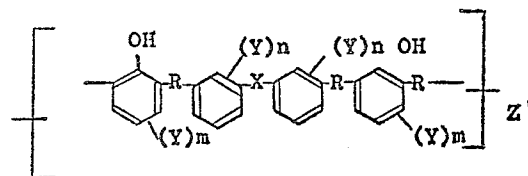
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and depressed portions corresponding to said pattern of light and shadow.

The resinous layer which deforms in charge pattern configuration may be deformed by heat, vapor or other suitable means. The invention will hereinafter be discussed with reference to a "heat deformable" member, but it is understood that other deformation means may be used and are included in this term. Generally in utilizing the process of this invention in frosting the steps involve applying a latent electrostatic image or charge pattern to an insulating film as defined above which is softenable, as by the application of heat or solvent vapor. The film may then be softened until the electrostatic attraction forces of the charge pattern exceed the surface tension forces of the film.

When this threshold condition is reached, a series of very small surface folds or wrinkles are formed on the film with the depth of the folds in any particular area of the film being dependent upon the amount of charge in that area, thus giving the image a frosted appearance. The film may be softened prior to the application of the charge pattern if it is sufficiently insulating to hold the charge. The frost image formed may then be "frozen" by allowing the film to harden by permitting it to return to its prefrosted condition. In a reusable frost system it is usually desirable to erase these images after hardening by resoftening the thermoplastic film and maintaining a low enough viscosity for a sufficient period of time for surface tension forces to smooth the surface.

The heat deformable material of this invention is desirable for use in the presently discussed system since it is not only deformable but is also a photoconductive insulating material. Thus, it may be deposited directly over a suitable conductive substrate without the heretofore required intermediate photoconductive layer. This thermoplastic photoconductive material is obtained by complexing a suitable Lewis acid with a composition wherein:



R is a residue of a member selected from the group consisting of formaldehyde, paraformaldehyde, furfural, amino formaldehyde, acrolein, benzaldehyde, chloral, oxo-aldehydes, acetaldehyde, glyoxal, propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-valeraldehyde, isovaleraldehyde, n-caproaldehyde, n-heptaldehyde, stearylaldehyde, crotonaldehyde, and mixtures thereof;

Y is a member selected from the group consisting of hydrogen, OH, lower alkyl, halogen and mixtures thereof;

X is a member selected from the group consisting of above R and oxygen;

Z is an integer having a value of at least 2;

n is an integer having a value of from 1-4; and

m is an integer having a value of from 1-3.

It is preferable that the above composition have a molecular weight of at least about 300.

It should be noted that neither of the above two components (A and B) used to make the photoconductor of this invention is by itself photoconductive; rather they are each non-photoconductive. After the above substantially non-photoconductive Lewis acid is mixed or otherwise complexed with said substantially non-photoconductive thermoplastic material, a highly desirable photoconduc-

tive insulating material is obtained which may conveniently be coated over a suitable conductive supporting substrate to form the heat deformable recording medium. In lieu of positioning the photoconductive layer on a supporting substrate, it may be cast as a self-supporting layer, and/or the photoconductor may have a second heat deformable overcoating. It is important that the heat deformable layer have a resistivity of about 10^{10} ohms cm. or more and a viscosity of up to about 10^6 poise at its softening point. The heat deformable layer may be up to about 300 microns in thickness; however, best results are obtained in using 5 to 15 microns. While the ratio of resin to Lewis acid may be up to about 1:100, a ratio of up to about 1:5 is preferred for optimum sensitivity.

Any suitable imaging method may be used in the process of the present invention. The following methods have been found to be typical:

- (1) The photoconductive thermoplastic layer is first substantially uniformly charged and selectively exposed to an image to be reproduced. The material is subsequently heated and deformed to form a frost pattern corresponding to the selective exposure. The frost image is then substantially fixed or set by permitting the heat deformable layer to cool.
- (2) In another process the thermoplastic material is selectively charged in imagewise configuration, e.g., by corona charging through a stencil or by transfer of charge from a second photoconductor. The material is heated, thereby obtaining selective heat deformation of the material only in those portions upon which the charge was initially deposited.
- (3) In another process, the photoconductive layer is overcoated with a thermoplastic material. The composite is substantially uniformly charged, exposed to the image to be reproduced, and recharged as before. The composite is heated and deformed to form a frost image, which is negative, i.e., black-for-white.
- (4) In still another process, the photoconductive thermoplastic material is in the form of a self-supporting film. The film is charged by passing it between a pair of corona charging means. The film is selectively exposed to an image to be reproduced, is heated and deformed, forming a frost pattern corresponding to the selective exposure. A light scattering image results on a transparent film which is then suitable for use in projection display devices.
- (5) The imaged layer or film produced by any of the above typical methods is re-heated to the softening point of the film while charge-free. Surface tension forces smooth the surface, thereby erasing the image. The material is then ready for reimaging by any suitable heat deformation method.
- (6) Any of the methods described in detail in copending applications Ser. Nos. 388,323 and 388,322 refiled as application Ser. Nos. 670,824 and 388,324 may be used in the process of this invention.

The methods for forming the frost or relief images may vary depending on the particular requirements. In certain situations the heat deformable electrically insulating layer may be pre-treated before uniformly charging the surface thereof. In addition, various suitable methods may be used to fix and/or erase the material in imagewise configuration.

A "Lewis acid" is defined for the purposes of this invention as any material which is electron accepting relative to the polymer with which it is complexed.

A "charge transfer complex" may be defined as a molecular complex between substantially neutral electron-donor and acceptor molecules, characterized by the fact that photo-excitation produces internal electron transfer to yield a temporary excited state in which the donor is more positive and the acceptor more negative than in the ground state.

It is believed that the donor-type insulating resins of

the present invention are rendered photoconductive by the formation of charge transfer complexes with electron acceptors, or Lewis acids, and that these complexes, once formed, constitute the photoconductive elements of the plates.

Broadly speaking, charge transfer complexes are loose associations between electron donors and acceptors, frequently in stoichiometric ratios, which are characterized as follows:

- (a) Donor-acceptor interaction is weak in the neutral ground state, i.e., neither donor nor acceptor are appreciably perturbed by each other in the absence of photo-excitation.
- (b) Donor-acceptor interaction is relatively strong in the photo-excited state, i.e., the components are at least partially ionized by photo-excitation.
- (c) When the complex is formed, one or more new absorption bands appear in the near ultraviolet or visible region (wave lengths between 3200-7500 angstrom units) which are present in neither donor alone nor acceptor alone, but which are instead a property of the donor/acceptor complex.

A "photoconductive insulator" for the purposes of this invention is defined with reference to the practical application to xerographic imaging. It is generally considered that any insulator may be rendered "photoconductive" by excitation with radiation of sufficiently short wave length of adequate intensity. This statement applies generally to inorganic as well as to organic materials, including the inert binder resins used in binder plates, the electron acceptor type activators presently used, and the aromatic thermoplastic materials used in the present invention. However, this short wave length radiation sensitivity is not useful in practical imaging systems because adequately intense sources of wave lengths below 3200 angstrom units are not available, because such radiation is damaging to the human eye, and because this radiation is absorbed by glass optical systems. Accordingly we restrictively define the use of the term "photoconductive insulators" to include only those which are characterized as follows:

- (1) They may be formed into continuous films which are capable of retaining electrostatic charge in the absence of actinic radiation.
- (2) These films are sufficiently sensitive to illumination of wave lengths longer than 3200 Angstrom units to be discharged by at least one-half by a total flux of, at most, 10^{14} quanta per centimeter² of absorbed radiation.

This definition excludes the resins and Lewis acids of our disclosure, when these are used individually, from the class of "photoconductive insulators."

The thermoplastic material used in the present invention may be generally defined as a phenol-aldehyde type resin. Any suitable phenol-aldehyde resin may be used depending on the immediate needs and required properties. Typical phenols useful in making phenol-aldehyde resins are: phenol, cresol, xylenol, alkyl phenols, such as p-tertiary amyl phenol, p-cyclohexyl phenol; aryl phenols such as p-phenyl phenol, triphenyl-p-hydroxy phenol; alkenyl phenols such as para, and ortho-1,5, di and 1,3 dibutenyl phenol, 1,3,5 tri-butenyl phenol; halogenated phenols such as mono, di, tri and tetra chlorinated phenol, resorcinol, hydroquinone and mixtures thereof; sulfonated phenols such as p-hydroxy-ter-butyl-benzene sulfonic acid, dihydric, trihydric and polyhydric phenols such as resorcinol, catechol, hydroquinone, pyrocatechol, pyrogallol, phloroglucinol, benzenetriol, xylenol; polynuclear phenols such as alpha and beta naphthol anthracene phenol; dihydroxy-di phenyl alkanes such as bisphenol A and mixtures thereof. Any suitable substituted phenol as above noted may also be used to prepare the phenolic type resin useful in this invention. Modified phenol-aldehyde resins may also be used if desired; for example, the phenol-formaldehyde type resins may be modified with

diphenyl-oxide to form a phenol-formaldehyde type resin of the phenol.

Any suitable aldehyde may be used in the reaction with the phenol. Typical aldehydes are: formaldehyde, para-formaldehyde, furfural, amino formaldehyde, acrolein, benzaldehyde, chloral, oxo-aldehydes, acetaldehyde, glyoxal, propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-valeraldehyde, isovaleraldehyde, n-caproaldehyde, n-heptaldehyde, stearaldehyde, crotonaldehyde, and mixtures thereof.

Any suitable Lewis acid can be complexed with the above noted phenol-aldehyde type resins to form the desired heat deformable photoconductive material. While the mechanism of the complex chemical inter-reaction involved in the present process is not completely understood, it is believed that a "charge transfer complex" is formed having absorption bands characteristic of neither of the two components considered separately. The addition to and mixture with one non-photoconductive component and the other seems to have a synergistic effect; that is much greater than additive.

Best results were obtained when using these preferred Lewis acids: 2,4,7-trinitro-9-fluorenone, 4,4-bis (dimethyl-amino) benzophenone, tetrachlorophthalic anhydride, chloranil, picric acid, benz(a)anthracene-7,12 dione and 1,3,5-trinitro-benzene.

Other typical Lewis acids are: quinones, such as p-benzoquinone, 2,5-dichlorobenzoquinone, 2,6-dichlorobenzoquinone, chloranil, naphthoquinone-(1,4), 2,3-dichloronaphthoquinone-(1,4), anthraquinone, 2-methyl-anthraquinone, 1,4-dimethylantraquinone, 1-chloroanthraquinone, anthraquinone-2-carboxylic acid, 1,5-dichloroanthraquinone, 1-chloro-4-nitroanthraquinone, phenanthrene-quinone, acenaphthenequinone, pyranthrenequinone, chrysene quinone, thio-naphthene-quinone, anthraquinone-1,8-disulfonic acid and anthraquinone-2-aldehyde; triphthaloyl-benzene; aldehydes such as bromal, 4-nitrobenzaldehyde, 2,6-di-chlorobenzaldehyde, 2-ethoxy 1-naphthaldehyde, anthracene-9 aldehyde, pyrene-3-aldehyde, oxindole-3-aldehyde, pyridine-2,6-dialdehyde, biphenyl-4-aldehyde; organic phosphonic acids such as 4-chloro-3-nitro-benzene phosphonic acid, nitrophenols, such as 4-nitrophenol, and picric acid; acid anhydrides, for example; acetic anhydride, succinic anhydride, maleic anhydride, phthalic anhydride, tetrachlorophthalic anhydride, perylene-3,4,9,10-tetracarboxylic acid and chrysene-2,3,8,9 tetracarboxylic anhydride, di-bromomaleic acid anhydride; metal halides of the metals and metalloids of the Groups IB, II through to Group VIII of the periodical system, for example: aluminum chloride, zinc chloride, ferric chloride, tin tetrachloride, (stannic chloride), arsenic trichloride, stannous chloride, antimony pentachloride, magnesium chloride, magnesium bromide, calcium bromide, calcium iodide, strontium bromide, chromic bromide, manganous chloride, cobaltous chloride, cobaltic chloride, cupric bromide, ceric chloride, thorium chloride, arsenic tri-iodide; boron halide compounds, for example: boron trifluoride, and boron trichloride; and ketones, such as acetophenone, benzophenone, 2-acetyl-naphthalene, benzil, benzoin, 5-benzoyl-acenaphthene, biacene-dione, 9 acetyl-anthracene, 9-benzoyl anthracene, 4-(4-dimethylamino-cinnamoyl)-1-acetylbenzene, acetoacetic acid-anilide, indandione-(1,3), (1,3-diketo-hydrindene), acenaphthene-quinone-dichloride, anisil, 2,2-pyridil and furil.

Additional Lewis acids are mineral acids such as the hydrogen halides, sulphuric acid and phosphoric acid; organic carboxylic acids, such as acetic acid and the substitution products thereof, monochloro-acetic acid, dichloroacetic acid, trichloroacetic acid, phenylacetic acid, and 6-methyl-coumarinylacetic acid (4); maleic acid, cinnamic acid, benzoic acid, 1-(4-diethylamino-benzoyl)benzene-2-carboxylic acid, phthalic acid, and tetrachlorophthalic acid, alpha beta-di-bromo-beta-formyl-acrylic acid (mucobromic acid), dibromo-maleic acid, 2-bromo-benzoic acid, gallic acid, 3-nitro-2-hydroxyl-1-benzoic acid, 2-nitro-

phenoxy acetic acid, 2-nitro benzoic acid, 3-nitrobenzoic acid, 4-nitrobenzoic acid, 3-nitro 4-ethoxy-benzoic acid, 2-chloro-4-nitro 1-benzoic acid, 2-chloro-4-nitro-1-benzoic acid, 3-nitro-4-methoxy-benzoic acid, 4-nitro-1-methyl-benzoic acid, 2-chloro-5-nitro-1 benzoic acid, 3-chloro-6-nitro-1-benzoic acid, 4-chloro-3-nitro-1 benzoic acid, 5-chloro-3 nitro-2-hydroxy-benzoic acid, 4-chloro-2 hydroxy-benzoic acid, 2,4-dinitro-1-benzoic acid, 2-bromo-5-nitro-benzoic acid, 4-chlorophenyl acetic acid, 2-chloro-cinnamic acid, 2-cyano-cinnamic acid, 2,4-dichlorobenzoic acid, 3,5-dinitro benzoic acid, 3,5-dinitro-salicylic acid, malonic acid, mucic acid, acetosalicylic acid, benzilic acid, butane-tetracarboxylic acid, citric acid, cyano-acetic acid, cyclo-hexane-dicarboxylic acid, cyclo-hexene-carboxylic acid, 9,10-dichloro-stearic acid, fumaric acid, itaconic acid, levulinic acid (levulic acid), malic acid, succinic acid, alpha-bromo-stearic acid, citraconic acid, dibromo-succinic acid, pyrene-2,3,7,8-tetra-carboxylic acid, tartaric acid; organic sulphonic acids, such as 4-toluene-sulphonic acid, and benzene sulphonic acid 2,4-dinitro-1-methyl-benzene-6-sulphonic acid, 2,6 dinitro-1-hydroxybenzene-4 sulphonic acid, 2-nitro-1-hydroxy-benzene-4-sulphonic acid, 4-nitro-1-hydroxy-2-benzene sulphonic acid, 3-nitro-2-methyl-1-hydroxy-benzene-5-sulphonic acid, 6-nitro-4-methyl-1-hydroxy-benzene-2-sulphonic acid, 4-chloro-1-hydroxy-benzene-3-sulphonic acid, 2-chloro-3-nitro-1-methyl-benzene-5-sulphonic acid and chloro-1-methyl-benzene-4-sulphonic acid.

The following examples further define the specifics of the present invention. Parts and percentages are by weight unless otherwise indicated. The examples below should be considered to illustrate various preferred embodiments of the present invention.

EXAMPLE I

About a five gram sample of a diphenyl-oxide modified Novolak resin No. ET-395-1300 (manufactured by The Dow Chemical Company), is put into a 100-ml. beaker containing about 45 grams of a solvent mixture consisting of about 25 grams acetone and about 20 grams toluene. The mixture is agitated using a magnetic stirrer until the resin is fully dissolved in the solvent.

About two hundred and fifty mg. of 2,4,7-trinitro-fluorenone are added to about a 10-gram portion of the diphenyl-oxide modified Novolak resin solution prepared as above (contained in a two-ounce jar). The mixture is stirred as before until solution of the 2,4,7-trinitro-fluorenone is achieved.

The above solution is coated onto an aluminum plate (0.005" x 11" x 16" flat rectangular sheet of bright finished 1145-H19 aluminum foil made by the Aluminum Company of America) by suitable means such as a wire wound bar, or the plate may be dip coated, flow coated, whirler coated, etc. and the plate is dried. The solution is coated onto the plate until the thickness of the dried layer amounts to about 5 microns. The coated sheet is then charged negative to about 300 volts in the dark by means of a corona discharge, exposed for about 15 seconds by projection using a Simmon Omega D3 enlarger equipped with an f4.5 lens and a tungsten light source of 2950° K. color temperature. Illumination level at the exposure plane is four foot candles as measured with a Weston Illumination Meter Model #756. The plate is then developed by placing the plate on a heated platen maintained at 100° C. As the plate is heated, an image corresponding to the projected image forms on the plate. This image is characterized by its light scattering ability and solid area coverage. The plate is removed from the heated platen immediately upon development of the image and cooled to fix the image.

EXAMPLE II

About 1 gram of a phenolic resin (CKM5254) manufactured by Union Carbide Plastics Company, obtained by reacting about 1 mole of p-phenylphenol with less than

about 0.9 mole of formaldehyde, is put into a 50-ml. (Pyrex) glass beaker containing about 9 grams of a 1:1 solvent blend of acetone and toluene. The mixture is agitated by a stirrer until the resin is fully dissolved in the solvent.

About 250 milligrams of 2,4,7-trinitro-9-fluorenone is added to the resin solution prepared above and stirred as before until all of the materials are well dispersed.

The above prepared solution is applied onto an aluminum substrate, dried and the plate processed as described in Example II. As the plate is heated, an image corresponding to the projected image forms on the plate. This image is characterized by its light scattering ability and solid area coverage. The plate is removed from the heated platen immediately upon development of the image and cooled to fix the image.

EXAMPLE III

A coating solution is prepared as described in Example II above except that about 1 gram of a phenolic resin (CKR 2103) manufactured by Union Carbide Plastics Company, obtained by reacting about 1 mole of p-tertiary-butyl-phenol with less than about 1 mole of formaldehyde is used in place of the phenolic resin (CKM 5254). Trinitrofluorenone is added to the above prepared solution, stirred, coated onto an aluminum substrate and dried.

The above plate is processed as described in Examples I and II and the image obtained has the same characteristics as therein described.

EXAMPLE IV

An aluminum plate is coated with about a four micron layer of the composition described in Example II above. The coating is dried and then an overcoating of a non-photoconductive heat deformable resin is applied. The overcoating composition consists of about a 10% by weight solution of Staybelite ester No. 10 (Hercules Powder Company), dissolved in super naphthalite solvent. The overcoating layer thickness is about three microns. The coated sheet is then dried.

The coated sheet is charged negative to about 450 volts in the darkness by means of a corona discharge and exposed for about 15 seconds by projection using a Simmon Omega D3 enlarger equipped with an f4.5 lens and a tungsten light source of 2950° K. color temperature. Illumination level at the exposure plane is four foot candles as measured with a Weston Illumination Meter, Model No. 756. The plate is then recharged negative as before and the room lights turned on. The plate is developed by placing the plate on a heated platen maintained at about 70° C. As the plate is heated, an image corresponding to a negative, i.e., black for white, of the projected image forms on the plate. This image is characterized by its light scattering ability and solid area coverage. The plate is removed from the heated platen immediately upon development of the image and coated to fix the image.

EXAMPLE V

An aluminum plate is coated with about a five micron layer of the composition described in Example II above and processed to yield an image characterized by its light scattering ability and solid area coverage. The image is fixed by removing the plate from the heated platen.

The above imaged plate is replaced on the heated platen and so maintained until the heat erases all traces of the image. The plate is cooled to ambient conditions and then processed as described in Example II to yield a new image. Thus, the coated plate may be recycled.

EXAMPLE VI

A coating solution is prepared containing about 1.0 grams of a diphenyloxide modified Novolak resin (ET-395-480, manufactured by the Dow Chemical Company), dissolved in a 1:1 solvent blend consisting of acetone and toluene. About 0.25 gram of 2,4,7-trinitrofluorenone is added to the above mixture. The mixture is stirred until

all of the materials are in solution. The solution is coated onto an aluminum substrate by dip coating and dried to produce a dry film thickness of about 10 microns.

The coated sheet is charged negative to about 150 volts in the dark by means of a corona discharge, and exposed for about 15 seconds by projection, as described in Example I above. The plate is developed on a heated platen maintained at about 45° C. As the plate is heated, an image corresponding to the projected image forms on the plate and this image is characterized by its "relief" outline and lack of solid area coverage. The plate is removed from the heated platen immediately upon development of the image and coated to fix the image.

EXAMPLE VII

A 0.003 x 6 x 20 inch polyethylene terephthalate film sold as Mylar by E. I. du Pont de Nemours and Company is coated with a layer of aluminum on one surface by vacuum evaporation techniques to yield a product which has a surface conductivity of about 500 ohms/square and a light transmission characteristic of at least 65%. The above film is gravure roll coated on the aluminized surface with the charge transfer complex composition described in Example I above and dried to yield a dry film thickness of about 15 microns. The above film is processed in the manner described in Example I above to yield an image which is characterized by its light scattering ability and solid area coverage and when projected gave well defined images.

EXAMPLE VIII

A charge transfer complex coating solution is prepared as described in Example II above and gravure roll coated onto a 0.003 inch thick Mylar substrate and dried. Dry film thickness is about 10 microns. The coated surface of the prepared film is charged negative in the dark by means of a corona discharge device which simultaneously deposits a positive charge on the uncoated Mylar surface. The film is exposed and processed as described in Examples I and II; the image obtained has the same characteristics as therein described and when projected gave well defined images.

The materials used in the above examples illustrate the specific embodiments of the present invention. Other suitable materials, as above listed, may be used with similar results. Also, a separate photoconductive or inert layer may be placed intermediate the supporting substrate and the phenol-aldehyde Lewis acid complex if desired. In addition other materials may be added to said complex or synergize, enhance or otherwise modify its properties.

The photoconductors of this invention may be dye sensitized if desired or may be mixed or otherwise combined with other photoconductors and/or other materials both organic and inorganic. Where the frost imaged plate is transparent, as in Examples VII and VIII, it is suitable for viewing in projection display devices. In addition, the heat deformable media of this invention may be used in intaglio printing or microprinting and other similar applications.

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. A heat deformable recording medium which comprises a first layer comprising a photoconductive charge transfer complex material, said material comprising a phenol-aldehyde resin and a Lewis acid and a second layer overcoating said first layer, said second layer comprising a heat deformable material, said photoconductive charge transfer complex having at least one new absorption band within the range of from about 3200 to about 7500 angstrom units.

2. The recording medium of claim 1 wherein said Lewis acid is selected from at least one member of the group consisting of 2,4,7-trinitro-9-fluorenone, 4,4-bis (dimeth-

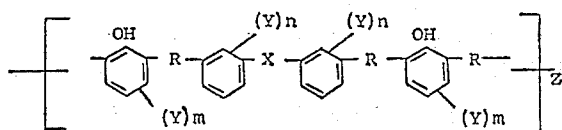
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ylamino) benzo phenone, tetrachlorophthalic anhydride, chloranil, picric acid, benz(a) anthracene-7,12 dione and 1,3,5-trinitrobenzene.

3. The recording medium of claim 2 wherein said Lewis acid is 2,4,7-trinitro-9-fluorenone.

4. The recording medium of claim 1 wherein said first layer comprises from about 1 to about 100 parts of said resin for one part of Lewis acid.

5. The recording medium of claim 1 wherein said resin comprises a composition having the following formula:



wherein:

R is a residue of a member selected from the group consisting of formaldehyde, paraformaldehyde, furfural, amino formaldehyde, acrolein, benzaldehyde, chloral, oxo-aldehydes, acetaldehyde, glyoxal, propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-valeraldehyde, isovaleraldehyde, n-caproaldehyde, n-heptaldehyde, stearaldehyde, crotonaldehyde and mixtures thereof;
Y is a member selected from the group consisting of hydrogen, OH, lower alkyl, halogen and mixtures thereof;
X is a member selected from the group consisting of above R and oxygen;

Z is an integer having a value of at least 2;
n is an integer having a value of from 1 to 4; and
m is an integer having a value of from 1 to 3.

6. A method of forming a frosted image on the surface of the heat deformable recording medium of claim 1 which comprises uniformly charging the surface of said recording medium, selectively exposing said charged surface, and softening said surface until it deforms to form a frost pattern corresponding to the selective exposure.

7. The method as disclosed in claim 6 wherein said exposing and softening steps are carried out concurrently.

8. The method as disclosed in claim 6 further including the step of fixing said frost pattern in situ.

9. The method as disclosed in claim 8 further including the steps of resoftening the recording medium so as to erase the frosted image and reimaging.

10. The method as disclosed in claim 6 wherein said Lewis acid is selected from at least one member of the group consisting of 2,4,7-trinitro-9-fluorenone, 4,4-bis(dimethylamino) benzophenone, tetrachlorophthalic anhydride, chloranil, picric acid, benz(a) anthracene-7,12 dione and 1,3,5-trinitrobenzene.

11. The method as disclosed in claim 10 wherein said Lewis acid comprises 2,4,7-trinitro-9-fluorenone.

12. The method as disclosed in claim 6 wherein said first layer comprises from about 1 to about 100 parts of said resin for one part of Lewis acid.

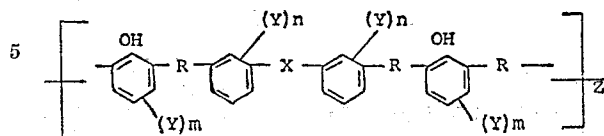
13. A frosted product comprising a support substrate having fixed to the surface thereof a photoconductive charge transfer complex material comprising a Lewis acid and a phenolaldehyde resin, a portion of which is deformed in an imagewise configuration, said charge transfer complex material having at least one new absorption band within the range of from about 3200 to about 7500 angstrom units.

14. The frosted product of claim 13 wherein said Lewis acid is selected from at least one member of the group consisting of 2,4,7-trinitro-9-fluorenone, 4,4-bis(dimethylamino) benzophenone, tetrachlorophthalic anhydride, chloranil, picric acid, benz(a) anthracene-7,12 dione and 1,3,5-trinitrobenzene.

15. The frosted product of claim 14 wherein said Lewis acid comprises 2,4,7-trinitro-9-fluorenone.

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16. The frosted product of claim 13 wherein said resin comprises a composition having the following formula:



wherein:

R is a residue of a member selected from the group consisting of formaldehyde, paraformaldehyde, furfural, amino formaldehyde, acrolein, benzaldehyde, chloral, oxo-aldehydes, acetaldehyde, glyoxal, propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-valeraldehyde, isovaleraldehyde, n-caproaldehyde, n-heptaldehyde, stearaldehyde, crotonaldehyde and mixtures thereof;

Y is a member selected from the group consisting of hydrogen, OH, lower alkyl, halogen and mixtures thereof;

X is a member selected from the group consisting of above R and oxygen;

Z is an integer having a value of at least 2;

n is an integer having a value of from 1 to 4; and

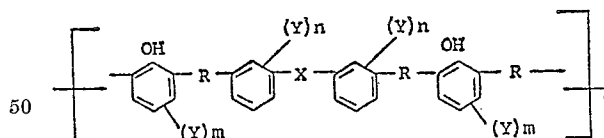
m is an integer having a value of from 1 to 3.

17. A frosted product comprising a support substrate having fixed to the surface thereof a heat deformable recording medium, said medium comprising a first layer of a photoconductive charge transfer complex material comprising a phenol-aldehyde resin and a Lewis acid, said charge transfer complex having at least one new absorption band within the range of from about 3200 to about 7500 angstrom units, and a second layer of surface deformable material overlying said first layer, the composite being surfaced deformed in an imagewise pattern.

18. The frosted product of claim 17 wherein said Lewis acid is selected from at least one member of the group consisting of 2,4,7-trinitro-9-fluorenone, 4,4-bis(dimethylamino) benzophenone, tetrachlorophthalic anhydride, chloranil, picric acid, benz(a) anthracene-7, 12 dione and 1,3,5-trinitrobenzene.

19. The frosted product of claim 18 wherein said Lewis acid comprises 2,4,7-trinitro-9-fluorenone.

20. The frosted product of claim 17 wherein said resin comprises a composition having the following formula:



wherein:

R is a residue of a member selected from the group consisting of formaldehyde, paraformaldehyde, furfural, amino formaldehyde, acrolein, benzaldehyde, chloral, oxo-aldehydes, acetaldehyde, glyoxal, propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-valeraldehyde, isovaleraldehyde, n-caproaldehyde, n-heptaldehyde, stearaldehyde, crotonaldehyde and mixtures thereof;

Y is a member selected from the group consisting of hydrogen, OH, lower alkyl, halogen and mixtures thereof;

X is a member selected from the group consisting of above R and oxygen;

Z is an integer having a value of at least 2;

n is an integer having a value of from 1 to 4; and

m is an integer having a value of from 1 to 3.

21. A method for forming an image on a heat deformable photoconductive charge transfer complex material said complex material comprising a phenol-aldehyde resin and a Lewis acid which comprises charging the surface of said charge transfer complex material, exposing said surface to a pattern of light and shadow and softening said

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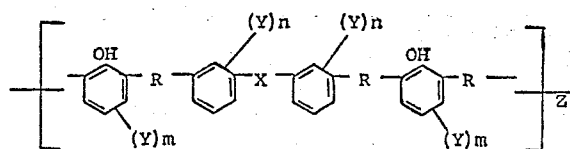
surface until it deforms to form an image corresponding to the exposed pattern of light and shadow, said photoconductive charge transfer complex having at least one new absorption band within the range of from about 3200 to about 7500 angstrom units.

22. The method of claim 21 wherein said Lewis acid is selected from at least one member of the group consisting of 2,4,7-trinitro-9-fluorenone, 4,4-bis (dimethyl-amino) benzophenone, tetrachlorophthalic anhydride, chloranil, picric acid, benz(a) anthracene-7, 12 dione, and 1,3,5-trinitrobenzene.

23. The method of claim 22 wherein said Lewis acid is 2,4,7-trinitro-9-fluorenone.

24. The method of claim 21 wherein said complex comprises from about 1 to about 100 parts of said resin for one part of Lewis acid.

25. The method of claim 21 wherein said complex comprises a resin having a composition of the following formula:



wherein:

R is a residue of a member selected from the group consisting of formaldehyde, paraformaldehyde, furfural,

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amino formaldehyde, acrolein, benzaldehyde, chloral, oxo-aldehydes, acetaldehyde, glyoxal, propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-valeraldehyde, isovaleraldehyde, n-caproaldehyde, n-heptaldehyde, stearylaldehyde, crotonaldehyde and mixtures thereof;

Y is a member selected from the group consisting of hydrogen, OH, lower alkyl, halogen and mixtures thereof;

X is a member selected from the group consisting of above R and oxygen;

Z is an integer having a value of at least 2;

n is an integer having a value of from 1 to 4; and

m is an integer having a value of from 1 to 3.

26. The method as disclosed in claim 21 wherein said exposing and softening steps are carried out concurrently.

27. The method as disclosed in claim 21 further including the step of fixing said resulting image in situ.

28. The method as disclosed in claim 27 further including the steps of resoftening the imaged material so as to erase the deformation image and reimaging.

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