Dec. 9, 1969 J. R. EWING 3,482,969

FIXING OF DEFORMATION IMAGES

Filed June 3, 1963

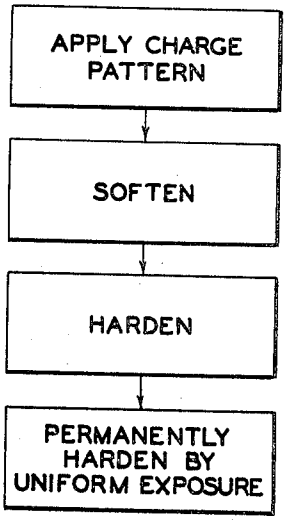

FIG. 1

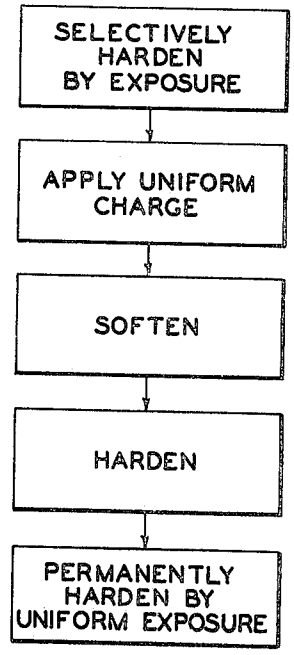

FIG. 2

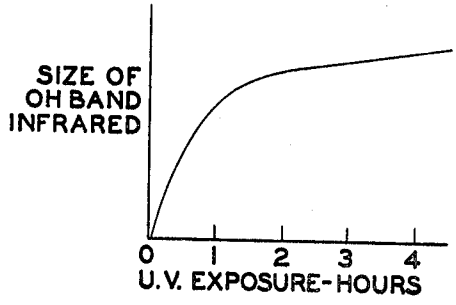

FIG. 3

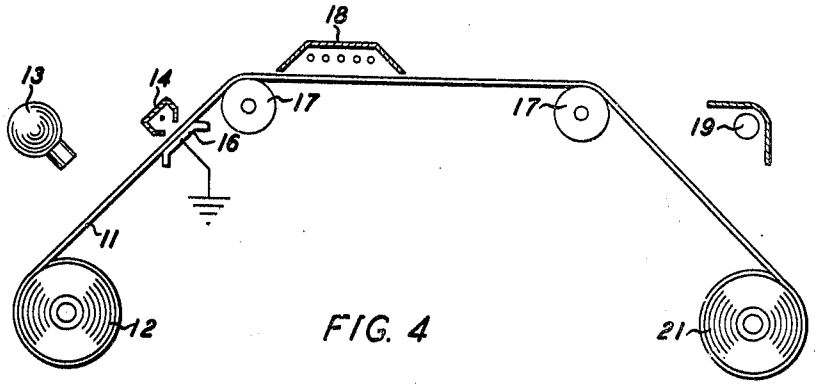

FIG. 4

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FIXING OF DEFORMATION IMAGES

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Int. Cl. G03g 13/20
U.S. Cl. 96—1.1 29 Claims

ABSTRACT OF THE DISCLOSURE

A process and apparatus is disclosed for permanently hardening a deformation image established on a layer of photohardenable insulating material.

This invention relates generally to xerography and more specifically to novel electrostatic techniques for the formation of visible images.

In the most commonly practiced forms of xerography, an electrostatic latent image is formed by the combined action of an electric field and a pattern of electromagnetic radiation, such as visible light, on a photoconductive insulating layer. The latent electrostatic image is then generally converted to a visible image by utilizing the electrostatic image to control the deposition of finely-divided colored electroscopic developing material on the surface bearing the latent eletcrostatic image. After the visible image is formed, it is usually fixed in place on the surface of the photoconductive insulator or transferred to a second surface and fixed thereon depending upon whether or not the photoconductive insulator is reuseable. Reference is made to U.S. Patent No. 2,297,691 to Carlson for a more detailed description of the basic process.

A variety of xerographic methods are known which generally conform to the above description and which enjoy widespread commercial use. A new technique for making latent electrostatic images visible known as "frost development" has recently been devised and is more fully described in an article entitled "A Cyclic Xerographic Method Based on Frost Deformation" by R. W. Gundlach and C. J. Claus appearing in the January-February 1963 issue of the Journal of Photographic Science and Engineering. Basically, this new technique involves applying a latent electrostatic image or charge pattern to an insulating film which is softenable as by the application of heat or a solvent vapor and softening the film until the electrostatic repulsion forces of the charge pattern exceed the surface tension forces of the film. When this critical or threshold condition is met, a series of very small surface folds or wrinkles are formed on the film with the depth of these folds in any particular surface area of the film being dependent upon the amount of charge in that area, thus giving the image a frosted appearance. Actually, the film may be softened prior to the application of the charge pattern so long as it is sufficiently insulated to hold the charge, the basic requirement being that the charge pattern be on the film while it is soft. This generally requires highly insulating films; however, in cases where charging may be continued during softening films with relatively low resistivities on the order of about 10^{10} ohm-cm. may be employed. These lower resistivity films are also referred to as insulating for purposes of this description. This "frost" image is then frozen by allowing or causing the film to reharden as by removing the heat or solvent vapors or in the case of a material which at room temperature is sufficiently soft to frost under the influence of a deposited charge pattern by cooling the material. It has also been found possible to erase such images after use by simply resoftening the film and maintaining a low viscosity for a sufficient period of time. Discharge is believed to occur during this resoftening by fluid migration of the ions making up the charge pattern on the top surface of the frosted film whereupon surface tension forces restore a smooth surface to the film.

Now in accordance with the present invention, it has been found that selected frostable materials may be caused to harden by exposure to radiation such as ultraviolet light and that this hardening by exposure may be used to permanently fix frost images, making them nonerasable by significantly raising their resistance to softening agents such as heat or solvents. It has also been found that such frostable materials may be selectively hardened prior to the frosting process and that such hardening may be caused to occur in a pattern of an image which is to be reproduced. For example, the frostable material may be uniformly charged and uniformly subjected to heat, solvent vapor or other softening action in which case frosting occurs only in those areas of the material which have not been previously hardened by exposure. With this latter technique, charge pattern modulating devices such as photoconductive insulators which are used in the ordinary frost process to apply charge to the frostable layer in a pattern which conforms with the image to be reproduced are eliminated from the system, because the charge pattern to be laid down on the frostable resin is uniform.

In addition, the film may be uniformly prefrosted and exposed to an image with hardening radiation whereupon a subsequent softening step erases the frost pattern only in nonimage areas. Although this invention is generally described in terms of the frost process it may also be employed in other types of electrostatic charge-induced plastic deformation. For example, relief imaging is a similar system in which deformation occurs only in lines at areas on the film of high potential gradient, after charging and softening.

Other objects, features, and advantages of the present invention will become apparent upon consideration of the following detailed disclosure of the invention, especially when taken in conjunction with the accompaying drawings wherein:

FIG. 1 is a process flow diagram of a modified form of the xerographic frost process according to one embodiment of this invention;

FIG. 2 is a process flow diagram of a modified form of the xerographic frost process according to a second embodiment of this invention;

FIG. 3 is a graph showing the duration of ultraviolet exposure of a frostable film versus the size of its hydroxyl band on infrared analysis.

FIG. 4 is an apparatus using the FIG. 2 process.

Referring now to FIG. 1 of the drawings where the process steps are illustrated, it is seen that a charge pattern is first applied to the frostable layer. This charge pattern conforms with the image to be reproduced, and may be applied by any of the techniques described in the Gundlach-Claus publication referred to above or in a copending application S.N. 193,277 filed May 8, 1962, and entitled Electrostatic Frosting, now U.S. Patent 3,196,011. Frequently, although not always, the charge deposition technique involves placing the insulating frostable material in close proximity to a photoconductor with a grounded conductive substrate and exposing the photoconductor to the light image to be reproduced. This exposure, by modulating the conductivity of the photoconductor, controls the amount of charge which is reflected through the frostable film. In other techniques, charge patterns are formed on photoconductive insulators as they are in the ordinary method of xerographic reproduction and then transferred to the insulating frostable layer by bringing the two into very close proximity and utilizing breakdown techniques as described, for example, in

U.S. Patents 2,825,814, 2,937,943 to Walkup and 2,982,-647 to Carlson. In addition, charge patterns conforming to selected shaped electrodes or combinations of electrodes may be formed on the insulating frostable layer by the "Tesi" discharge technique as more fully described in U.S. Patents 3,023,731 and 2,919,967 both to Schwertz or by the techniques described in U.S. Patents 3,001,848 and 3,001,849 both to Walkup. The second step in the process is to soften the frostable layer bearing its electrostatic charge pattern to a viscosity at which the repulsive forces of the charge pattern on the frostable layer overcome the surface tension forces of the layer so that the wrinkled frost pattern of ridges and valleys conforming to the charge pattern forms on the surface of the frost layer. This step need not necessarily be carried out subsequent to the application of the charge pattern, but instead the charge pattern may be applied to a simultaneously softened or pre-softened film so that frosting occurs on the film surface simultaneously with charge deposition. As described more fully in the above referenced patent applications and publication, this softening may be accomplished by different techniques which may, for example, include the application of heat if the frostable layer is thermally softenable or by the use of vapors containing a solvent for the frostable film. It should be noted that the film need not be softened through its whole thickness but that it is only necessary to soften the upper portion of the film where the deformation occurs. Of course, as film thickness decreases, this makes up an ever increasing percentage of the film thickness.

The next step in the process is to reharden the frosted layer which may, for example, be accomplished by removal of the solvent vapor or heat so that the frost image is "frozen." It should be noted at this point that a frostable material which is initially soft may be utilized thus eliminating the softening step described above. Thus, material which is relatively soft or viscous at room temperatures, may be frosted by merely applying the charge pattern as desired. It is however, important that the charge pattern be frozen within a relatively short time after the formation of the frost image whether the image is formed on a material which is initially soft or one which is softened during or subsequent to charge deposition, because excessive or overlong softening of the frostable layer permits the charge which forms the charge pattern to flow through the frostable layer so that surface tension forces tend to restore the smooth surface of the layer thereby destroying the image. In fact, this technique may be used for erasing the image after it is utilized and the erased film may be used to reform a new image during a later recycling of the process.

Although erasable films are valuable in some applications, they are undesirable for other applications because they cannot be used with assurance as truly permanent images. In many instances, it is therefore highly desirable to permanently harden the frost images after they have been formed as is indicated by the fourth step of the FIG. 1 process. This permanent hardening is preferably accomplished by exposing the frosted layer to a source of electromagnetic radiation which may for example be light, since such a hardening technique is both simple and inexpensive. Furthermore, hardening by exposure makes the process described below in connection with FIG. 2 feasible.

In this second process, the frostable film is first selectively hardened by exposing the film to a radiation image of the original to be reproduced. Thus, for example, the film is exposed to an ultraviolet image of the original until it is hardened in areas corresponding to nonimage areas of the original. If the process is begun with this selective permanent hardening by exposure, it is unnecessary to apply the charge in a pattern since frosting will take place only in unhardened areas when the film is softened. Instead, the charge is applied uniformly over the surface of the selectively exposure-hardened film. This charging may be accomplished by any one of a number of known techniques including any one of those commonly used in the xerographic reproduction process. More specifically, this charging may be accomplished with a corona generating unit as described in U.S. Patents 2,588,699 to Carlson and 2,778,946 to Mayo. The frostable film is then softened, as for example by the heat or solvent techniques described in connection with the FIG. 1 process until the frost pattern appears on the film. As shall be described more fully hereinafter, the degree of selective hardening by initial exposure may vary depending upon the amount and intensity of exposure, the addition of radiation sensitizers to the frostable film and the like. It should be apparent, therefore, that if the initial selective hardening by exposure has not been sufficient to impart a significant degree of difference between the softening points of exposed and unexposed portions of the film, care should be taken in application of the softening means so that the film is not softened in all areas thereby allowing the formation of a uniform frost pattern over the whole surface of the film. In the case of larger differentials in the degree of initial hardening by selective exposure, it is not necessary to exercise so much care in carrying out the softening step. This softening step is then followed by freezing or "temporary" hardening of the frost image by removal of the softening agents as in the FIG. 1 process and optionally by permanent hardening of the whole film with its frost image by uniform exposure of the whole film with radiation similar to that of the first step of the process.

In an alternative mode of operation of the FIG. 2 process the film may first be uniformly frosted by charging, softening, and freezing. It may then be permanently hardened in image configuration by exposure to an image to be reproduced with an actinic energy source so that when a softening agent such as heat or solvent vapor is applied to the film for a sufficient period, the unexposed areas are erased, leaving the preformed frost wrinkles on the film in the image areas. The advantage of this technique is that the film may be obtained in the prefrosted condition from the manufacturer and the only equipment needed by the customer for forming images is an energy source and a film softening apparatus.

If desired, the last two steps of either the process of FIG. 1 or the process of FIG. 2 may be combined so that hardening is accomplished solely by uniform exposure. In this way, the film need not necessarily be separated from the softening agents in order to achieve hardening. In that instance, for example, the whole process could be carried out while the frostable film was moving through a solvent vapor atmosphere or through a heated chamber.

In FIG. 4 there is illustrated a frost imaging apparatus which operates according to the FIG. 2 process. In this embodiment, a frostable film **11** such as one of the Staybelites described below is fed into the system from a supply roll **12**. The film is then exposed to an ultraviolet light projection of the image to be reproduced by projector **13** thus selectively hardening the film in areas which correspond to the transparent sections of the projected image. The film then passes under a charging unit **14** of the corona discharge type described above where a uniform layer of charge is deposited over the whole of the film. As shown in this view, the film is backed by a conductive stationary grounded plate **16** so that charge will deposit upon the film. In the alternative, however, the film may be initially formed on a thin conductive foil such as aluminum or brass. The film then passes over two idle rollers **17** while passing beneath a softening unit which in this instance is an electrical resistance heating unit shown in side section. This heating unit is set so as to generate sufficient heat to soften unexposed areas and consequently unhardened areas of the film **11** to the point where a frost pattern appears on those areas while not generating sufficient heat to soften or burn exposed and hardened film areas. As explained above, a solvent vapor

atmosphere may be provided for the film at this point in the processing cycle in place of the resistance heating unit. After passing under the softening unit, the film begins to harden as its temperature drops, thus causing the frost image to "freeze" whereupon the film passes under a second ultraviolet light exposure source which applies a uniform ultraviolet exposure over the whole of the film serving to harden and permanently fix the image. In simple inexpensive machines, this second ultraviolet light exposure may be accomplished by using the same light source from projector **13** used for the initial exposure of the film by passing the film on the opposite side of projector **13** from its initial exposure position and providing an opening in the back of projector **13**. After uniform exposure, the film then passes onto a take-up roll **21** for further use as desired.

As should be apparent at this point, the two processes described above impose certain limitations upon the selection of materials which may be used in the process. Of course, the prime requisite of the materials utilized in the process is that they be able to form frost patterns. Referennce is again made to the above-mentioned copending application in the names of Gunther and Gundlach for an extensive treatment of selection techniques of frostable materials, their usable thicknesses, frost thresholds, as well as for a detailed description of the process steps and parameters of the frost process. Generally speaking, the most important property of frostable materials is that they be insulating at their melting or softening points so that deposited charge is maintained on them at least until the frost pattern is formed. It is generally also preferable, although not absolutely necessary, that material selected for the frost process be solid at ordinary room temperatures and that they be thermoplastic in nature.

In addition to being capable of forming frost images, the frost films utilized in the processes of this invention must have the additional capability of irreversibly hardening upon exposure to radiation such as ultraviolet light, visible light, beta rays or the like. This exposure-initiated hardening is to be distinguished from the reversible hardening, termed "freezing," and softening of the frostable film with solvents or heat as they are applied upon initial formation of the frost pattern. In contrast, the exposure-initiated hardening acts to effectively diminish the solubility of the exposed layers and/or to increase their melting points. This change in the characteristics of the frost layers is believed to be caused by an actual change in the chemical structure of the materials in which their average molecular weights are increased. It is presently believed that a primary requisite of the material or materials in the layer is that it contain at least one radiation-excitable reactive site in its molecular structure so that exposure to light for example, may cause or initiate, crosslinking of polymer chains, polymerization of small molecules, intermolecular bridging of large molecules or other mechanisms for increasing the average molecular weights of layer materials so as to raise their softening points and/or increase their resistance to solvents. Many materials which meet these requirements contain the ethylenic linkage (>C=<) which is most sensitive to light in the ultraviolet; however as will be more specifically described hereinafter various sensitizers may be added to the materials to increase their sensitivity or extend their spectral response and various combinations of materials may be used. When excited with ultraviolet light the ethylenic linkage opens readily for addition type reactions which leave a single carbon-to-carbon bond at the site of the previous double bond. All these radiation-initiated changes may be included within the purview of the term polymerization when it is thought of in its broadest sense, however, there is no intention to limit the invention to this theory of operation since the operability of the photohardenable frost layers described below has been experimentally verified. Reference is made to the extensive prior art on the specific subject of "hardening" organic resins by radiation which has been treated in patents and other literature.

One specific material which may be used as the frostable film according to this invention is a partially hydrogenated rosin ester sold under the trade name Staybelite Ester–10 by the Hercules Powder Company of Wilmington, Delaware. More specifically, this resin is made by the esterification of three acid molecules with glycerol. The major component, making up approximately 87% of the acid mixture is dihydroabietic acid. This acid may be said to be 50% hydrogenated derivative of abietic acid since two hydrogen atoms are added to it on average thus saturating one of the double bonds in the abietic acid. The remainder of the acid mixture comprises approximately 11% dihydroabietic acid and 2% abietic acid. For purposes of this explanation, dihydroabietic acid may be considered as fully saturated since all its double bonds go to make up one aromatic ring in the acid molecule which then will not readily add substituents while abietic acid may be considered as unsaturated since its two carbon double bonds may more readily add four hydrogen atoms in hydrogenation. It is thus seen that the major component of this resin is the glycerol ester of dihydroabietic acid which because of the three hydroxyl groups in glycerol will be referred to as a triester. The Staybelite Ester–10 resin and an additional resin of closely related structure which is a viscous liquid at room temperatures and is sold under the trade name of Staybelite Ester–3 (a triethylene glycol ester of partially hydrogenated rosin) have been found to form excellent frost images according to the technique of the above referenced copending application. It has also been found that these Staybelite resins in addition to having excellent frost properties may be hardened by exposure to ultraviolet light. Thus although the resins form good frost images and may be readily erased by resoftening for a sufficient period as described more fully above, they may be permanently fixed or hardened by ultraviolet light exposure, which both reduces the resin solubility in ordinary solvents for them (such as other esters, ketones, higher alcohols, glycol ethers, aliphatic and aromatic hydrocarbons, and chlorinated solvents) and significantly increases their melting point, with the degree of hardening depending upon the length of ultraviolet exposure. Although there is no intention to limit this invention to the following theory of operation, it is presently believed that the ultraviolet light exposure accelerates an aging process which occurs when the aforementioned Staybelite Esters are exposed to air for periods from about two weeks to a month or more. This is accomplished because the ultraviolet exposure excites the remaining unhydrogenated double bonds in the abietic and dihydroabietic acid triesters so that ambient oxygen is added to form an epoxide at the double bonds followed by the addition of oxygen and/or hydrogen from ambient moisture to form OOH or OH groups. This is believed to be followed by linking of rosin molecules through the oxygen of these groups so that a dimer, trimer or other short polyester is formed through the oxygen bridges. This theory has been verified to some extent by tests in which a number of samples of the Staybelite resin were formed in thin films and subjected to the same ultraviolet exposure source for varying lengths of time and then subjected to infrared analysis. As is indicated by the graph in FIG. 3 which compares the amount of ultraviolet exposure of the Staybelite samples with the size of the response at the hydroxyl band on infrared analysis, there is a very sharp increase in the number of hydroxyl groups formed in the early periods of ultraviolet exposure with the number of hydroxyl groups tapering off asymptotically after about 1½ to 2 hours of exposure. The increase in the hydroxyl band correlated well with increasing hardness in the films. This exposure was made with a high pressure quartz mercury vapor arc lamp manufactured by the Hannovia Lamp Division of Englehard Industries, Newark, New

Jersey, Lamp Catalogue No. 30620 containing a 100 watt 1.2 amp lamp with the samples about 6" from the lamp. The lamp transmits the complete ultraviolet spectrum from about 1849 to 4,000 angstrom units.

In addition to the Staybelite esters of partially hydrogenated rosin described above the rosin pentaerythritol tetraester sold under the trade name of Pentalyn-H by the Hercules Powder Company, was also found to be frostable and permanently hardenable by exposure to ultraviolet light. This resin is soluble in most aromatic and aliphatic hydrocarbons as well as in most esters and ethers. It is believed that this tetraester hardens by same mechanism explained above in connection with the above esters, since the tetraester is also only 50% hydrogenated. Further verification of the theory of hardening of the frost layers by oxidation or other reaction at reactive double bonds or other unsaturated sites in the resin molecules was given when an attempt was made to harden two saturated frostable materials (sucrose diacetate hexaisobutyrate and a low molecular weight polystyrene). These materials showed no permanent hardening after extensive intense ultraviolet light exposure and failed to show any increase in the hydroxyl band upon infrared analysis after the exposure. When the resins used are esters of abietic acid, it is preferable that the acid be at least partially hydrogenated since the esters of polyunsaturated abietic acid are subject to relatively rapid oxidation under ordinary atmospheric storage conditions, thus making them unsuitable for fixing according to this invention.

A wide variety of other frostable materials containing reactive unsaturated sites are usable in this invention, for example, a resin marketed by Velsicol Corporation under the trade name EG–11, as well as the Nirez series 1,000 resins including grades 1040, 1085, 1100, 1125, and 1115 marketed by the Newport Industries Division of Heyden Newport Chemical Company were found to be operable in the process of this invention as was Nevillac soft, a phenol modified coumarone-indene resin. The Nirez resins mentioned above are polyterpenes. These resins are also believed to include reactive double carbon-to-carbon bonds and to harden by the same process as that described in connection with the Staybelite resins described above. The Velsicol resin also has favorable frost characteristics and contains the required unsaturated reactive site which is believed to make exposure hardening possible. The Velsicol EG–11 resin is essentially a terpolymer formed from styrene, indene and isoprene monomers and its cross linking is believed to take place principally at the unsaturated double bond in the isoprene group of the polymer. The irradiation hardenability of the above described films may be improved by the addition of small amounts of cross linking monomers such as divinylbenzene.

Clearly, this invention is not limited to any one single type of photosensitive hardening mechanism. Rather the only requirements of the system are that the selected material be frostable and hardenable by irradiation with actinic energy such as ultraviolet light, visible light, or the like. For example, one other group of photohardenable polymers include the cinnamate esters of polyvinylalcohol and of cellulose which may be further sensitized by the presence of anthrones and their derivatives, polynuclear quinone derivatives and certain ketones such as Michler's Ketone. Hardening by photopolymerization may thus be accomplished either directly as by excitation of a pi electron in the monomer or by radiation activation of an included polymerization initiator. These materials are commercially available from the Eastman Kodak Company of Rochester, New York, under the trade name KPR or Kodak Photoresist. This type of polymerization system is more fully described in U.S. Patent 2,670,285, 2,670,286 and 2,670,287 and although they don't form good frost images with facility it has been found that mixed systems employing them are operable to great advantage in the process of this invention, where the two materials are compatible. Thus, for example, it was found that a one-to-two mixture by weight of the Staybelite Ester–10 described above with KPR was capable of frosting and had significantly faster irradiation hardening capabilities than Staybelite alone. It is believed that this was due principally to the much faster cross linking through the unsaturated side groups of the KPR rather than through the cross linking mechanism described in connection with the Staybelite resin, since hardening took place at speeds on the order of a few minutes, which is comparable to the hardening speed of KPR alone, rather than in the generally longer times which are required for hardening the unsensitized Staybelite. In this combination then, the high photosensitivity of the KPR is combined with the very good frost image forming capability of the Staybelite. It thus becomes apparent that resins which work well in the frost process but which are even incapable of hardening upon irradiation with ultraviolet light or the like may be mixed with other photosensitive polymers or polymer systems so that they may be used in the hardening mode of operation of this invention. Two examples of this type of combination comprise mixtures of Piccolastic A–50 with KPR and Piccolastic A–75 with KPR in equal parts by weight. The Piccolastics are low molecular weight polystyrenes available from the Pennsylvania Industrial Chemical Company of Clairton, Pennsylvania. These two mixed systems were tested and found to be capable of forming frost images and were permanently fixable with ultraviolet light exposures as short as 1–3 minutes. Further testing of films composed of only one of the constituents of the mixed films showed that the Piccolastics although capable of forming frost images could not be fixed by ultraviolet light exposure while with the KPR film it was virtually impossible to form a frost image but the film could be hardened by a short period of ultraviolet light exposure.

Another photosensitive polymer system which may be employed alone or in combination with other of the systems described heretofore, employs nonphotosensitive polymers in the presence of photosensitive, low molecular weight compounds which react with themselves upon exposure to form a physical network throughout the exposed portions of the polymer, which network retards the rate at which solvents attack these portions relative to the unexposed portions. The system is operable with ethylcellulose, polymethyl methylacrylate, polystyrene, coumarone-indene resins and many other commercial plastics containing photosensitive chalcone or unsaturated ketone derivatives as more fully described in U.S. Patents 1,965,710 and 2,544,905.

It should be noted that permanent hardening according to this invention need not necessarily increase both the softening or melting point and the insolubility of the frostable resin layer, since if one of the properties may be affected by exposure to actinic irradiation, the proper softening technique may be selected for use with this layer in the system. Thus, for example, Piccoflex 100A, and Piccopale 70, which are polyvinyl chloride, and unsaturated hydrocarbon resins respectively, available from the Pennsylvania Industrial Chemical Company are not very suitable for heat softening in the frost process even prior to irradiation, but their insolubility to solvent vapors does increase significantly when they are exposed to ultraviolet irradiation and so these resins may be used to advantage in a frost imaging system employing solvent vapor softening. Even if these materials were suitable for heat softening in the frost process and their heat softening points were not materially changed by ultraviolet exposure, they would still be suitable for frost process utilizing the solvent vapor softening technique since ultraviolet light does materially change the solvent vapor softening point of the resin.

The phrase "permanent hardening" as used in this specification and the appended claims is therefore intended to refer to a notable increase in the melting or heat softening points or increase in the degree of insolubility of a frost layer upon exposure to actinic irradiation. Permanent hardening need not take place through the whole thickness of the film but only to the depth to which the frost depressions form so that this hardening will truly fix the image.

The term "polymerization" as used in this specification and the appended claims is intended to be read in its broadest sense, regardless of the length of the polymer formed and to include cross linking of molecules, branching and the like as well as the formation of straight chain polymers of recurring molecular units.

By the term "actinic" as used in this specification and in the appended claims it is intended to mean electromagnetic radiation of sufficiently short wavelength to excite at least one ethylenic linkage or other reactive site in the molecular structure of film materials thus causing them to polymerize. For direct excitation of the linkage in most film materials this requires the use of electromagnetic radiation having a wavelength approximating that of the ultraviolet light range (below about 4000 A.). It is to be noted, however, that indirect excitation with electromagnetic radiation ranging into the wavelength of visible light may be employed when one of the sensitizers described above is present in the film although ultraviolet is generally the most efficient in this regard. Thus actinic radiation is to be distinguished from the application of heat or heat producing radiation such as infrared since the energy applied in this manner tends to be shared by all of the vibrational modes of the material, rather than opening reactive sites within the material by selective excitation at these sites. Accordingly, by actinic radiation, in its broad sense, it is intended to refer to radiation having a wavelength equal to or less than that of visible light.

What is claimed is:

1. A method of image recording comprising depositing a charge pattern conforming to an image to be reproduced on a softenable layer which is insulating at its melting point, which deforms in charge pattern configuration when softened and which is permanently hardenable by irradiation with actinic energy, softening said layer until it deforms in the configuration of said charge pattern, and then irradiating said layer with radiant actinic energy until it is permanently hardened whereby the image formed by said deformation is fixed.

2 A method according to claim **1** in which said layer is permanently hardened by exposure to an actinic light source.

3. A method according to claim **1** in which said layer is permanently hardened by exposure to an ultraviolet light source.

4. A method of image recording comprising depositing a charge pattern conforming to an image to be reproduced on a softenable insulating layer including an organic material in which each molecule contains, on average, at least one unsaturated reactive photoexcitable site, and which deforms in charge pattern configuration when softened, softening said layer until it deforms in the configuration of said charge pattern, and then irradiating said layer with actinic energy until it is permanently hardened whereby the image formed by said deformation is fixed.

5. A method of imaging comprising depositing a charge pattern conforming to an image to be reproduced on a softenable insulating layer containing an organic material in which each molecule contains, on average, at least one ethylenically unsaturated reactive site, and which deforms in charge pattern configuration when softened, softening said layer until it deforms in the configuration of said charge pattern, and then irradiating said layer with ultraviolet light until it is permanently hardened whereby the image formed by said deformation is fixed.

6. The method of imaging comprising depositing a charge pattern conforming to an image to be reproduced and of sufficient field intensity on a viscous insulating layer deformable by such a charge pattern and which is permanently hardenable by irradiation, with actinic energy, to deform said layer in the configuration of said charge pattern and then irradiating said layer with actinic energy until it is permanently hardened whereby the image formed by said deformation is fixed.

7. The method according to claim **6** further including the step of reducing the temperature of said viscous layer after it has been deformed by the deposition of said charge pattern to temporarily fix the image formed by said deformation by freezing prior to permanently hardening said layer by exposure.

8. The method of imaging comprising depositing a charge pattern conforming to an image to be reproduced, on a layer which is capable of forming a deformation image corresponding to said deposited charge pattern when it is softened and which is polymerizable by exposure to an actinic energy source, softening said layer until it deforms in the configuration of said charge pattern and then exposing said layer to an actinic energy source until it polymerizes sufficiently to permanently harden and fix the image formed by said deformation.

9. The method of forming an image comprising exposing a layer capable of forming an image by plastic deformation upon the coincidental softening of and charge deposition on said layer which layer is softenable and insulating at its melting point and permanently hardenable by exposure to actinic energy, to an image with an actinic energy source until it is permanently hardened in image configuration, uniformly charging said layer, softening said layer until those areas on said layer which have not been permanently hardened deform and then finally hardening said layer.

10. The method according to claim **9** in which said layer is finally hardened by the exposure of at least those areas which have not been hardened in the initial exposure step to an actinic energy source until those areas are permanently hardened.

11. The method according to claim **9** including employing an ultraviolet light source as said actinic energy source.

12. The method of forming an image comprising exposing a layer which is softenable, insulating at its melting point capable of deforming in response to a deposited charge pattern upon softening and which includes a photohardenable material containing molecules with at least one reactive, unsaturated site to an image with an actinic energy source until it is permanently hardened in image configuration, uniformly charging said layer, softening at least those areas of said layer which have not been permanently hardened until said areas deform and then hardening at least said softened areas of said layer.

13. A method according to claim **12** in which said material containing molecules with reactive unsaturated sites includes ethylenic linkages.

14. The method of forming an image comprising exposing a layer of a viscous electrically insulating liquid which is permanently hardenable by exposure to actinic energy to an image with an actinic energy source until it is permanently hardened in image configuration, uniformly charging said layer until the unexposed areas of said layer deform in image configuration and then hardening at least the deformed areas on said layer.

15. The method of image reproduction comprising plastically deforming a film in its viscous state, which film is deformable at such a viscosity with the application of a charge pattern and which is permanently hardenable by exposure to an actinic energy source, by applying such a charge pattern to said film until it deforms and then fixing the deformation image produced by exposing said deformation image to an actinic energy source until it permanently hardens.

16. The method of forming a plastic deformation image

comprising depositing a charge pattern corresponding in shape to the deformation image to be reproduced on a film consisting essentially of the esterification product of partialy hydrogenated abietic acid and at least one polyhydric alcohol, said charge pattern having a density at least sufficient to overcome the surface tension forces of said film when its viscosity is in the range of about 10^4 to about 10^6 poises, so as to form a surface deformation image on said film and then uniformly exposing said film to an actinic energy source for a sufficient time to permanently harden said film whereby said deformation image is fixed.

17. A method according to claim **16** in which said actinic energy source includes a source of ultraviolet light rays.

18. A method according to claim **16** in which said polyhydric alcohol is glycerol.

19. The method according to claim **16** in which said polyhydric alcohol is triethylene glycol.

20. The method according to claim **16** in which said polyhydric alcohol is pentaerythritol.

21. The method of frost image reproduction comprising forming a uniform frost pattern across the surface of a frostable and photopolymerizable material, exposing said uniformly frosted material to electromagnetic energy of a frequency which causes photopolymerization of said material and in a pattern conforming to an image to be reproduced whereby said material is hardened by photopolymerization in image areas and then uniformly subjecting said film to a softening influence until the frost deformation pattern is erased by surface tension restoring forces of said film in those areas which have not been hardened by photopolymerization.

22. An image forming and processing apparatus comprising means to deposit a charge pattern conforming to the image to be formed on a plastic deformation imaging film, means to reduce the viscosity of said film to the point where it will deform in image configuration when it is bearing said charge pattern, means to expose said film to an actinic energy source of sufficient intensity to permanently harden said deformed film by decreasing its sensitivity to said viscosity reducing means whereby said image is fixed, and means to feed said plastic deformation imaging film past the aforementioned means in the order as stated.

23. The apparatus of claim **22** wherein the means to deposit a charge pattern and the means to reduce the viscosity of said plastic deformation imaging film operate on said film simultaneously.

24. An image forming and processing apparatus comprising means to reduce the viscosity of a plastic deformation imaging film to a point where it will deform in image configuration when it is bearing an electrostatic charge pattern, means to deposit a charge pattern conforming to the image to be formed on said imaging film, means to expose said film to an actinic energy source of sufficient intensity to permanently harden said deformed film, and means to feed said plastic deformation imaging film past the aforementioned means in the order as stated.

25. The apparatus of claim **24** wherein the means to reduce the viscosity of said imaging film and the means to deposit an electrostatic charge pattern operate on said film simultaneously.

26. An image forming and processing apparatus comprising means to deposit a uniform electrostatic charge on a plastic deformation imaging film, means to reduce the viscosity of said film to the point where it will deform when it is bearing said uniform charge to provide a uniform frost pattern across a surface of said plastic deformation imaging film, means to expose said film in a pattern conforming to an image to be reproduced to an actinic energy source of sufficient intensity to permanently harden the exposed portions of said deformed film, means to reduce the viscosity of said film to the point where the deformations will be erased in those areas which have not been exposed to said actinic energy source, and means to feed said plastic deformation imaging film past the aforementioned means in the order as stated.

27. The apparatus of claim **26** wherein the means to deposit a uniform electrostatic charge and the means to reduce the viscosity of said imaging film operate on said film simultaneously.

28. An image forming and processing apparatus comprising means to expose a plastic deformation imaging film to an image with an actinic energy source of sufficient intensity to permanently harden said film in image configuration, means to deposit a uniform electrostatic charge on said imaging film, means to reduce the viscosity of said film to the point where it will deform in those areas which have not been permanently hardened by exposure to said actinic energy source, and means to feed said plastic deformation imaging film past the aforementioned means in order as stated.

29. The apparatus of claim **28** wherein the means to deposit a uniform electrostatic charge and the means to reduce the viscosity of said imaging film operate on said film simultaneously.

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