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FROST IMAGING PROCESS

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ABSTRACT OF THE DISCLOSURE

The invention relates to a frost imaging process wherein the surface deformable film comprises a thermoplastic material and an additive to improve the frostability of the film. The additive has a viscosity greater than the bulk thermoplastic material at the softening temperature of said bulk material.

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 of which 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. Pats. 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 wherein 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 for 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.

The thermoplastic 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 methods may be used and are included in this term. Generally, the frost imaging process of this invention includes the step of applying a latent electrostatic image or charge pattern to an insulating film which is softenable as by the application of heat or solvent vapor. The film is softened until the electrostatic 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 spontaneously formed on the film surface, the depth of the wrinkles in a particular area of the film being generally dependent upon the intensity of charge in that area, and the film thickness. This gives the image a frosted appearance. Alternatively, the film may be softened prior to the application of the charge pattern if the film remains sufficiently insulating in a softened state to hold the charge. The frost image is set or fixed by allowing the film to harden. In a reusable frost system, it is usually desirable to later erase the fixed images after use by resoftening the thermoplastic film and maintaining a sufficiently low viscosity for an appropriate period of time to permit surface tension forces to smooth the film surface.

It has been found that many thermoplastic materials, while having desirable physical characteristics, would relief but not frost. In addition, it has been found that many thermoplastic materials will not frost in the 0.5 to 10 micron thickness range and will frost only to a comparatively small degree with thicknesses of 10 microns and above. It is desirable, for economic and other reasons, in many instances to avoid the use of thicker films and utilize thinner films in the 0.5 to 10 micron range.

Recently, it has been found that these non-frostable materials could be made frostable by forming on the surface of the film a very thin coating of higher viscosity material. This process is described in detail in copending applications 388,322, 388,323 and 388,324 all filed Aug. 7, 1964 and all now abandoned. In application Ser. No. 388,322, there is disclosed a process of improving the frostability of thermoplastic films having the thickness of from 0.5 to 300 microns which comprises forming on the surface thereof a coating of a material having a higher viscosity, the thickness of said coating being about 0.3 micron. A method for fixing a frost image is disclosed and claimed in application Ser. No. 388,324. This process comprises the steps of forming a frost image, then forming a surface coating on the film, which coating exceeds the critical thickness and renders the film non-frostable thereafter. A method of frosting materials which were previously thought to be non-frostable is disclosed in application 388,323. In this process, a film having a thickness of from about 0.5 to about 10 microns has deposited thereon a surface coating of a higher viscosity material. The film is then frostable where the coating thickness is up to about 0.3 micron. As disclosed in these applications, when a coating thickness of appreciably greater than 0.3 is used, a film is substantially non-frostable.

While the processes as disclosed in said copending applications result in high quality frost, these processes are limited by the necessity of providing a separate coating of relatively critical thickness. Application of this second, very thin, film requires elaborate and carefully controlled apparatus. Producing frostable films having a 0.3 micron or thinner surface coating is both difficult and expensive.

It is, therefore, an object of this invention to provide novel frostable materials devoid of the above-noted disadvantages.

Another object of this invention is to make available materials for frost imaging which were previously thought non-frostable.

Another object of this invention is to provide a method which will permit a substantially wide selection of relatively thin materials and films for frost imaging.

Still another object of this invention is to provide a novel method of converting heretofore substantially non-frostable materials to desirable frostable materials.

Yet another object of this invention is to provide a novel method for frost imaging prior non-frostable materials.

Yet another object of this invention is to provide a method of frost imaging on materials which were previously non-frostable without the addition of a surface coating thereover.

Still another object of this invention is to provide a method of frost imaging a film which contains a dispersed photoconductive material.

The foregoing objects and others are accomplished in accordance with this invention, generally speaking, by providing a method of converting a substantially non-frostable insulating thermoplastic layer to a frostable layer. This method comprises mixing with the molten or dissolved thermoplastic material a small proportion of an additive having higher viscosity than the bulk of said thermoplastic material at the softening temperature of

said bulk material, then coating the mixture onto a substrate and hardening the coating.

This process produces frost images of surprisingly high density and good grain structure on materials which were previously thought to be non-frostable, without the necessity of forming a coating of critical thickness over the deformable film surface.

The effect of the additive is substantially independent of the thickness of the thermoplastic layer. It has been found that excellent frost images may be prepared by this method on films having a thickness of from 0.5 to 300 microns.

The mechanism by which the additive having a higher viscosity and/or a higher softening temperature improves the frostability of a thermoplastic layer is not fully understood. However, it is thought that a large proportion of the additive may migrate to the surface of the thermoplastic layer, forming a layer of higher viscosity and/or higher softening temperature material analogous to the surface skin described in the above-cited copending applications. Theory notwithstanding, the improvement in frostability due to the additive is both surprising and extensive, as pointed out in the examples below. In general, excellent results have been obtained with up to 10% by weight, based on the thermoplastic layer, of additive. Optimum improvement in frostability and image density has been obtained where the thermoplastic layer contains from about 1–3% by weight additive.

The additive which improves frostability may be obtained from a material or composition having the same or different chemical composition as the bulk of the original insulating material to which it is added. It is important that the additive have a viscosity greater than said bulk material at the softening temperature of said bulk material. Thus, the additive may have a higher viscosity and/or a softening temperature greater than said bulk material. The viscosity difference between the thermoplastic material and the phenol formaldehyde additive is not critical as long as the viscosity of the additive is greater than the viscosity of the bulk thermoplastic at the softening temperature of said bulk material. Also, it is important that the additive have a resistivity of 10^{10} ohm centimeters or greater at the frosting temperature. In addition, the bulk of the insulating layer should have a viscosity of about 10^6 poise or less at the frosting temperature. The heat deformable layer may be a self-supporting layer, a layer deposited over a supporting substrate such as a conductive base and/or a layer coated over a photoconductive substrate, or a deformable layer which by itself is both deformable and photoconductive.

Any suitable material may be used as the non-frostable heat deformable layer to be converted to a frostable material. The softening temperature and viscosity of the heat deformable materials employed are not critical and vary with the particular application. Typical non-polymeric materials include esters of abietic acid and related acids made from the condensation of the acids and alcoholic compounds such as ethylene glycol, propylene glycol, butylene glycol, trimethylol propane, pentaerythritol, propane triol, hexane triol, xylylene glycol, amylene glycol, glycerine, diethylene glycol, triethylene glycol, sorbitol, and mixtures thereof. The term "alcohol" as used herein is intended to include mono, di, and poly alcohols. Other typical non-polymeric materials include sucrose esters such as sucrose-octobenzoate, sucrose octaacetate, and mixtures thereof. Typical thermoplastic polymers are low molecular weight polymers or oligomers. Typical polymers include aromatic polymers such as polystyrene, alpha-methylstyrene, copolymers made from styrene and other materials such as vinyl toluene, methyl styrene, alpha methylstyrene, chlorinated styrene, and polymers and copolymers made from petroleum cuts and indene polymers, phenolics such as phenol-aldehyde resins, phenol formaldehyde resins and mixtures thereof; vinyl polymers such as polyvinylacetate, polyvinylalcohol, polyvinylbutyl, butylmethylacrylate-styrene polymers, butylmethyl-acrylate-alkylated styrene copolymers, styrene-methylacrylate-butadiene terpolymers; organo polysiloxanes such as polydiphenyl siloxane; polyesters such as acrylic esters, bisphenol-A type polyesters; bisphenol-A copolymers such as bisphenol-A adipylchloride copolymers; complex hydrocarbon polymers such as hydrogenated Piccopale (a polyethylene polymer available from Pennsylvania Industries Chemical Corporation), Nirez (1085, 1100, 1115, and 1125 which are believed to be polyterpenes (Newport Co.)). Any of the above non-polymeric and polymeric materials may be used where suitable in mixture with each other or copolymerized with each other. In addition, the process of the present invention may be employed in frostable materials to further improve their frosting capability.

The additive for use with the above materials may comprise any material having the above described viscosity and softening temperature characteristics. Especially suitable additive materials include Bakelite 2432, Bakelite 2400 and Bakelite 5254, phenol-formaldehyde resin of the resol and/or novolak type and derivatives thereof, more fully described in "Preparative Methods Of Polymer Chemistry," W. R. Sorensen and T. W. Campbell, pages 293–294 (1961) Intersciences Publication, available from Union Carbide, Foster Grant #50 PS, a polystyrene resin available from Foster Grant, and a styrene-butyl methacrylate copolymer available from benzoyl peroxide initiated polymerization.

The following examples will more specifically define the particulars of this invention. While preferred embodiments are described in the examples below, they are illustrative only and are not meant to limit the invention. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE I

The heat deformable material used in this example is Piccotex–100, sold by the Pennsylvania Industries Chemical Corporation, and prepared as follows: one mole of alpha-methyl-styrene and one mole of vinyl toluene are added to sufficient xylene to obtain a 40 percent solution. A catalytic amount of BF_3 etherate is added and the mixture is stirred until polymerization is complete. After polymerization, sufficient methanol is added to decompose any BF_3 and then the polymer is isolated by steam distillation.

About 12 parts of Piccotex–100 is dissolved in about 25 parts of toluene. Five mil aluminum foil sheets are coated from the solution and the coatings are air dried in a 70° C. oven for one hour. Four coated aluminum sheets are prepared having film thicknesses of 5, 10, 15 and 25 microns, respectively. Each of the thus prepared plates is corona charged by the method described in U.S. 2,777,957 by means of a corona unit maintained at about 900 volts. The plates are then placed on a 90° C. hot stage. As the temperature of the plates reaches the softening point of the coating, very low density frosting occurs on the 15 and 25 micron plates. No frosting occurs on the 5 and 10 micron plates.

EXAMPLE II

The plate coating, curing, and developing steps of Example I are repeated. However, the coating solution for this example includes about 2 parts Bakelite 2423, a phenol-formaldehyde resin available from Union Carbide per 98 parts Piccotex–100. As the plates on the hot stage reach the softening point of the Piccotex–100, excellent frost images of high density appear on each of the four plates. Only slight differences in frost quality are observable between the different plates.

EXAMPLE III

About 40 parts Piccotex–100, and about 6 parts 2,5-bis-(p-aminophenyl) - 1,3,4 - oxadiazole, available from Kalle & Co., are dissolved in about 100 parts toluene.

Four plates are coated from this solution as in Example I. These plates are each charged by corona discharge maintained at 1000 v. Each plate is then exposed to a light-and-shadow image. Then the plates are placed on a 90° hot stage and heated to the softening point of the Piccotex–100. No frost is observed on the 5 and 10 micron plates and poor frost images of very low density occurs on the 15 and 25 micron plates.

EXAMPLE IV

Four plates are prepared as in Example III, except that about 1 part Bakelite 2400, a phenol-formaldehyde resin available from Union Carbide is mixed with the 40 parts Piccotex–100. These plates are then charged, exposed and developed as in Example III. Excellent frost images are developed on each plate.

EXAMPLE V

A coating solution is prepared by dissolving about 99 parts Amco 18, poly-alpha-methyl styrene, available from the American Oil Company is dissolved in about 200 parts toluene. Four plates are coated onto aluminum sheets from this solution by means of a Boston-Bradley draw-down coater to dry thicknesses of 5,10,15 and 25 microns, respectively. The plates are dried at about 70° C. for about 1 hour. The plates are then uniformly charged by means of a corona unit maintained at a potential of about 1000 volts. Each plate is then heated to the softening temperature of the Amoco 18. No frosting occurs on the 15 and 25 micron plates.

EXAMPLE VI

The tests of Example V are repeated, except that here about 1 part of Bakelite 2432 is dissolved in the toluene with the 99 parts Amoco 18. The plates are coated, charged and developed as in Example V. Excellent frost is observed on each plate.

EXAMPLE VII

About 79 parts Piccotex–100, and about 12 parts 2,5-bis-(p-aminophenyl) - 1,3,4 - oxadiazole are dissolved in about 200 parts toluene. Four plates are coated onto alumium sheets from this solution to dry thicknesses of about 5, 10, 25 and 50 microns, respectively. Each plate is charged to a positive potential by means of a corona unit maintained at about 900 volts. Each plate is then contact exposed to a black-and-white transparency for one minute by means of an Hanovia ultraviolet lamp (available from the Hanovia Lamp Division of Englehard Industries, Lamp Catalog No. 30600) held about 7 inches from the plate. The plates are developed by heating them to about 95° C. No frost is observed on the 5 and 10 micron plates. Poor frost images are observed on the 25 and 50 micron plates.

EXAMPLE VIII

Four plates are prepared as in Example VII, except that the solution contains about 9 parts Staybelite Ester 10, the glyceryl tri-ester of 50% hydrogenated wood resin, available from the Hercules Powder Company in addition to the 79 parts Piccotex–100. Each plate is charged, imaged and developed as in Example VII. An excellent frost image, conforming to the original, is observed on each plate.

EXAMPLE IX

A coating solution is prepared by dissolving in about 250 parts toluene about 100 parts Piccotex–100, about 1 part triphenylamine and about 0.5 part 2,4,7-trinitro-9-fluorenone. Four aluminum plates are coated to dry thicknesses of 5, 10, 25 and 50 microns, respectively. Each plate is charged, exposed to an image and developed as in Example VII. No frost develops on the 5 and 10 micron plates and poor frost images are observed on the 25 and 50 micron plates.

EXAMPLE X

The test of Example IX is repeated, except that here about 2.5 parts Bakelite 2432 is added to the coating solution. Excellent frost images corresponding to the original are observed on the plates.

EXAMPLE XI

The experiment of Example X is repeated, except that about 2.5 parts Foster Grant #50 PS, a polystyrene resin available from Foster Grant, Inc. is dissolved in the coating solution in place of the Bakelite 2432. Again, with the additive excellent frost images result.

EXAMPLE XII

A polydiphenylsiloxane resin is prepared as follows:

About 600 parts octaphenylcyclotetrasiloxane is placed in a flask under nitrogen and is heated to about 230° C. About 1 part cesium hydroxide is added and the mixture is stirred while the temperature is slowly raised to about 260° C. for about 1 hour. A second portion of about 0.5 part cesium hydroxide is added, and heating is continued at about 260° C. for about 1½ hours longer. At this time a small amount of iodine is added to the hot reaction mixture until the purple color is no longer present, showing that the cesium hydroxide is completely neutralized. Excess iodine is allowed to sublime. The reaction mixture is then cooled to about 125° C. About 430 parts toluene is then added and stirred into the viscous melt. The resulting solution is allowed to stand for about 72 hours. The crystalline material that forms is filtered off. Residual solvent is then removed from the polymer by distillation at atmospheric pressure, followed by vacuum evaporation at about 125° C.

About 98 parts of the thus produced polydiphenylsiloxane is dissolved in about 200 parts toluene. Four aluminum sheets are coated with this solution to dry thicknesses of about 5, 10, 25 and 50 microns, respectively, and dried. Each plate is uniformly electrostatically charged by corona means held at a positive potential of about 1000 volts. Each plate is then heated to the softening point of the resin. No frost occurs on the 5 and 10 micron plates, while poor frost occurs on the 25 and 50 micron plates.

EXAMPLE XIII

Four plates are prepared, charged and developed as in Example XII, except that here about 2 parts Bakelite 2432 is added to the coating solution before the plates are coated. Excellent frost is observed on each plate.

Any suitable imaging method may be used with the frostable materials of the present invention. The methods are typical:

(1) A thermoplastic layer which incorporates a photoconductive substance in conjunction with the additive of the present invention is first substantially uniformly charged and then exposed to a light-and-shadow image to be reproduced. The charge dissipates in the light-struck areas. The material is then heated until it deforms to form a frost pattern corresponding to the light-and-shadow image. The frost image thus formed is subsequently fixed or set by permitting the heat deformable layer to cool below its softening point. The image may be erased by reheating the layer in charge-free condition to its softening point.

(2) A thermoplastic layer incorporating special additive materials is selectively charged in imagewise configuration. Subsequently, the thermoplastic material is heated, thereby producing a frost image only in those areas upon which the charge was initially deposited. The material is then cooled to fix the image. The image may be erased by reheating, if desired.

(3) A thermoplastic layer incorporating special additive materials is coated over a photoconductive surface, such as selenium. The composite layer is uniformly charged as by corona discharge and exposed to a light-

and-shadow image. This dissipates the charge in the photoconductive layer where struck by light. The surface of the composite is recharged by corona discharge, thereby depositing a charge of higher density on the non-light-struck areas. The composite is heated until the thermoplastic layer deforms forming a frost pattern corresponding to the light-and-shadow image. The image may be fixed by cooling and erased by reheating, if desired.

(4) Any of the methods described in detail in copending applications, Ser. Nos. 193,277; 232,494; and 338,322, filed May 8, 1962; Oct. 23, 1962; and July 8, 1964, respectively, may be used in the process of this invention. For example, the methods of forming the frost image may vary depending upon the intended use of the resulting product. In certain situations, the heat deformable layer may be pretreated before uniformly charging the surface thereof. In addition, various suitable methods may be used to selectively fix and/or erase the material in image-wise configuration.

Where the frostable thermoplastic layer incorporates both the high viscosity additive material and the photoconductive material, any suitable photoconductor may be used. Organic photoconductors which have given especially good results include 2,5-bis-(p-aminophenyl)-1,3,4-oxadiazole, available from Kalle & Co. and mixtures of aromatic resins and 2,4,7-trinitro-9-fluorenone.

Although specific materials and conditions were set forth in the above examples, these were merely illustrative of the present invention. Various other compositions, such as the typical materials listed above and various conditions, where suitable, may be substituted for those given in the examples with similar results. The deformable layer of this invention may have other materials added thereto to enhance, synergize, or otherwise modify its properties. For example, various spectral and electrical sensitizers may be added to the layer, if desired. The layer described above, having an additive comprising a material having a higher viscosity at the softening temperature of the bulk of the layer may be useful in other systems utilizing charge retention on a thermoplastic layer.

Many other modifications and ramifications of the present invention will occur to those skilled in the art upon a reading of this disclosure. These are intended to be encompassed within the spirit of this invention.

What is claimed is:

1. A frost imaging process comprising depositing a charge pattern in image configuration on the surface of a surface deformable film, said film prepared from a mixture comprising a thermoplastic material having a viscosity of about 10^6 poise or less at the frosting temperature and an additive having a higher viscosity than said thermoplastic material at the softening temperature of said thermoplastic material, said additive comprising a phenol-formaldehyde resin, said resin being selected from the group consisting of resol and novolak types and being present in an amount of up to 10% by weight of said film, and heating said film until it frosts in a configuration of said charge pattern.

2. The method as defined in claim **1** wherein said additive constitutes from about 1 to about 3 percent by weight of said film.

3. The method as defined in claim **1** wherein said film includes an inorganic photoconductive material and said charge pattern is formed by substantially uniformly charging the surface of said film and exposing said surface to a pattern of activating electromagnetic radiation.

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