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[54] **ELECTROTHERMOGRAPHIC DUPLICATING SHEET AND PROCESS**

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[57] **ABSTRACT**

Electrothermographic reproduction sheet and process in which the latent image is both electrostatic and tacky to achieve more uniform and higher image densities, lower background densities and better resolution.

20 Claims, No Drawings

ELECTROTHERMOGRAPHIC DUPLICATING SHEET AND PROCESS

This is a division, of application Ser. No. 863,365, filed on Oct. 2, 1969 now Patent No. 3,672,981.

SUMMARY OF INVENTION

Electrophotographic reproduction, i.e., xerography, has been widely used in recent years. This technique involves applying an electrostatic charge to an electrostatically chargeable, photo-conductive layer of material containing photo-semiconductors, which are sensitive to light to reduce the electrical resistance of the layer (increase its electrical conductance) and thereby cause the charge to leak away at the light struck areas. The charged layer is exposed to light under a pattern to form a latent electrostatic image of such pattern, which is converted to a visible image by the application of colored toner particles, which may or may not be triboelectrically charged (i.e., they may or may not be electrotropic) and which selectively adhere either to the latent electrostatic image area (positive image) or the latent electrostatic background area (negative image), followed by (1) fixing of the visible image as by heat fusion of the toner particles to the layer or by solvent vapors or (2) transferring the visible image by transfer of the toner particles to another sheet and fixing it on the transfer sheet. The photo-conductive layer may be in the form of a selenium drum which, when toner developed, functions as printing plate to transfer the visible toner image to a transfer sheet, i.e., paper, or the layer may be in the form of a photoconductive coating over a substrate sheet such as paper.

Over the past 10 years in order to overcome certain disadvantages in xerography, including the relatively high cost thereof particularly when a large number of duplicates of a single master are required, there have been a number of proposals and attempts to modify this process to produce the electrostatic image by the influence of heat rather than by light. This technique is sometimes referred to as electrothermography or thermoxerography and embodies an electro-statically chargeable layer of material which is sensitive to heat, rather than to light, to reduce its electrical resistance (increase its conductivity) to thereby cause the charge to leak away at the heat struck areas. The material is electrostatically charged and is exposed to radiant energy, e.g. infra red rays produced in a Thermofax machine, while under a pattern or master. The infra red rays are absorbed by the darker areas, e.g. the print, of the pattern and thereby preferentially heat these dark areas whereas they pass through the light areas, e.g. the non-printed areas, without heating them. The heat absorbed by the dark areas of the pattern is transmitted to the areas of the charged, heat sensitive, thermographic material opposite such dark areas to decrease the electrical resistance and increase the electrical conductance of the material at such areas and thereby cause the charge to leak away at these heat-struck areas. On the other hand, the non-heat struck areas of the material opposite the light areas of the pattern remain electrically charged so that an electrostatic image is formed on the material, from which a visible image is made by conventional xerographic toner development followed by conventional xerographic fixing or transfer.

Such proposals and attempts are described in U.S. Pat. Nos. 3,205,354, 3,132,963, 3,363,099, 3,128,198, 3,161,529 and 3,368,892.

Although these electrothermographic or thermoxerographic techniques have important advantages over the xerographic electro-photographic techniques, particularly with respect to lower cost, none of them have achieved commercial success for a number of reasons. Resolution is not as good as with electrophotographic techniques; also image densities are not as uniform or as high and background densities are not as low.

These disadvantages of known electrothermographic techniques are in the most part overcome in accordance with the present invention by the use of a normally non-conductive electrostatically chargeable material (i.e., material having a sufficiently high electrical resistance at normal temperatures to hold an electrostatic charge), which is not only sensitive to radiant electrothermographic energy or heat to change its electrical resistance (usually to lower such resistance and increase its conductivity to cause discharge of the electrostatic charge in the heat struck areas) and thereby provide a latent electrostatic image, but which is also at the same time activated by such energy or heat to change from a normal non-tacky state to a soft tacky state at the heat struck areas and thereby provide a latent tacky, as well as a latent electrostatic, image. This provides better selective adherence of the toner particles to the latent image during toner development, thereby increasing density of the image and decreasing density of the background to provide a sharper image with better resolution and less background fog. At the same time the lower cost advantages of the electrothermographic technique are preserved.

The heat sensitive electrostatic chargeable material of the invention comprises a resin, preferably a thermoplastic resin, and a heat-activatable tackifying agent which is activated by the electro-static image-forming radiant energy heat to convert the resin tackifying agent composition at the heat struck areas from a normal substantially non-tacky solid state to a soft, tacky or sticky state which causes the toner particles to better adhere thereto. Actually the composition is converted by the heat to a highly viscous, slightly flowable semiliquid. It is believed that the tacky state of the heat activated composition not only improves the final stage by virtue of the fact that its tacky nature causes more toner particles to physically stick to it but also by virtue of the fact that it increases the voltage differential between the heat struck image areas and the non-heat struck background areas, as compared to conventional electro-thermography, by increasing the conductance of the heat struck areas and by making the conductivity thereof more uniform.

The heat-activatable tackifying agent is a plasticizer for the resin. Accordingly, any known heat-activatable plasticizer for the particular resin involved can be used so long as it is heat-activatable by the heat conditions normally encountered in conventional electrothermography to render the resin-plasticizer system soft and tacky without making it soft and tacky under normal conditions.

Preferably the heat sensitive thermographic material of the invention is supported on and adhered to a conductive support or substrate, such as paper, which affords a path for leakage of the charge from the heat struck areas and on which the material is coated.

The ratio of tackifying agent to resin is substantially greater than one, preferably greater than 1.5 and more preferably greater than 2.0.

Preferably a colloidal stabilizer, such as a protein, is incorporated in the heat sensitive electrothermographic material as a coating levelling agent, i.e. to provide a more level uniform coating and to better adhere the coating to the support.

A number of proposals and attempts have been made to form a latent adhesive image in the duplicating art by the use of non-electrostatic thermographic techniques, i.e., by exposing a heat sensitive duplicating material to radiant energy under a pattern to selectively heat the areas thereof under the dark areas of the pattern and thereby cause the material at such areas to become sticky so that the toner particles will adhere thereto. See U.S. Pat. No. 3,383,505, British Pat. No. 1,091,488, Belguim Pat. No. 644,239 and Photographic Science and Engineering, Vol. 10, No. 1, January-February 1966. In one case, the heat sensitive material contains compounds from which the water of crystallization is driven off by the heat to wet the material and in another case the heat sensitive material contains compounds which are melted by the heat and exist in a super-cooled wet condition. None of these proposals and attempts embody electrostatic imaging as in the case of the present invention. None of them have proven commercially successful for a number of reasons, e.g. resolution is poor, image density is low and background density is high.

DETAILED DESCRIPTION

EXAMPLE 1

Particulate polyvinyl acetate (average particle size of less than two microns) and N-cyclohexyl-p-toluenesulfonamide (a solid plasticizer and heat-activatable tackifying agent for the polyvinyl acetate) sold by Monsanto under the name "Santicizer 1-H" were dispersed in water together with α-protein in an amount equal to 1 percent by weight of the dispersion. The ratio of sulfonamide to polyvinyl acetate was 4/1. The total solids content of the dispersion was 28 percent by weight. The mixture was mixed in a ball mill for four hours to fine grind the solids and get a good dispersion of the resin, plasticizer and α-protein particles in the water.

The dispersion was applied to one surface of a conductive bond paper by a meier rod in an amount equal to 1.5 lbs. per ream of paper followed by drying. The resultant dry coating was 0.30 mil thick.

The coated surface of the resulting sheet was negatively charged to 210 volts with a conventional negative corona discharge unit.

The resulting charged sheet was then sandwiched against a mirror image copy of a master with the coated surface against the image side of the mirror image copy and the sandwich was subjected to infra red rays in a conventional Thermofax machine at a setting of 6 with the side of the mirror image copy opposite from the charged sheet facing the infra red lamp so that the infra red rays passed through the mirror image copy to the image thereon (direct imaging). The sandwich was separated and the resultant latent imaged (electrostatic and tacky image) coated surface of the charged sheet was toner developed in conventionl manner to give a visible image with a magnetic brush using a Xerox electrotropic toner (carbon black-thermoplastic resin) of negative polarity (triboelectric) containing iron filings as a carrier and brush.

The coating became tacky and discharged its electrostatic charge in the image areas due to infra red absorption upon exposure to the infra red lamp, whereas the background areas remained non-tacky and retained their negative charge to thereby form a tacky and electro-static positive image. During development, the toner deposited quite densely in the image areas due to the tackiness as well as the reversal electrostatic development of the latent electrostatic and tacky image.

The toner developed sheet was then cleaned with fresh carrier, i.e. iron filings, to clean the background areas followed by fixing the visual, cleaned image by heat in conventional manner to fuse the toner to the coating and thereby give a permanent image of excellent quality.

The image was a "right reading" image of the master.

The resolution of the final image was excellent with very high and uniform image density and low background density. The filling of the image area was excellent.

When compared with an image made in the identical manner except that charging of the sheet was omitted to thereby provide a tacky but non-electrostatic latent image, the resolution and sharpness of the Example 1 image was much better with higher image density and lower background density.

When compared to an image made in the identical manner except that the sulfonamide was omitted to thereby provide an electrostatic but not a tacky latent image, the sharpness and resolution of the Exhibit 1 image was much better, image density was higher and back-ground density was lower.

EXAMPLE 2

Example 1 was repeated except that the coating was charged within ten seconds after exposure of the sandwich to infra red instead of before such exposure. The resulting image had even better resolution and sharpness with higher image densities and lower background densities than the image of Example 1. The heat activated coating had a delay tack of 30 seconds before reverting back to a non-tacky state which is adequate for charging and developing.

EXAMPLE 3

Example 2 was repeated except that (1) conductive transparent onionskin paper was used instead of bond paper and (2) exposure to infra red was a reflex exposure in which the uncoated surface of the coated sheet in the sandwich was facing the infra red lamp so that the infra red rays passed through such sheet. The results were comparable to Example 2.

EXAMPLE 4

Example 2 was repeated except that (1) the master was used instead of the mirror image copy and (2) the uncoated surface of the coated sheet was held against the image surface of the master, so that the heat was transmitted from the dark image areas of the master through the coated sheet to the coated surface thereof to image the coated surface. The image on the coated surface was a "right reading" image. The resolution and sharpness of the visible image was not nearly as good as in Example 2. Also the image density was less and the background density was greater.

EXAMPLE 5

Example 2 was repeated except that (1) the master was used in place of the mirror image copy and (2) instead of fixing the developed toner image, it was transferred to a transfer bond paper sheet by pressing the transfer sheet against the toner image and the transferred image was fixed. The image on the coated sheet was a mirror image of the master but the transferred image was a "right reading" image. The transferred image was lighter than the image of Example 2.

EXAMPLE 6

Example 2 was repeated except that (1) the master was used instead of the mirror image copy thereof and (2) a conductive transparent mylar sheet was used instead of paper. The results were comparable to Example 2 and the image was "right reading" through the mylar.

EXAMPLE 7

Example 2 was repeated except that (1) the ratio of plasticizer to resin was 2 to 1 and (2) the Thermofax setting was 6. The sharpness, resolution, image density and background density of the resulting image was not as good as in Example 2. Also the latent tacky image was less tacky than in Example 2.

EXAMPLES 8 & 9

Example 2 was repeated except that in one case triphenyl phosphate and styrene-butadiene rubber was used instead of the sulfonamide and polyvinyl acetate, respectively, with a Thermofax setting of 6 and in the other case, dioctyl phthalate was used in place of the sulfonamide with a Thermofax setting of 6. The sharpness, resolution, image density and background density in both cases were good but not quite as good as in Example 2.

EXAMPLE 10

Example 2 was repeated except that an aluminum substrate was used in place of the paper. The results were satisfactory but not as good as in Example 2.

EXAMPLE 11

Example 2 was repeated except that conductive gift wrap paper was used in place of bond paper. The results compared favorably with those of Example 2.

DESCRIPTION OF CLASSES OF MATERIALS, PROPORTIONS AND CONDITIONS

Any thermoplastic resin can be used which has the following physical properties: (1) it must be an electrostatic chargeable thermoplastic resin which, by itself or when admixed with the plasticizer or tackifying agent, (a) has a relatively high electrical resistance, e.g. specific resistance of 10^{10} ohm-cm to 10^{19} ohm-cm, and hence is non-conductive at normal temperatures to thereby take and hold an electrostatic charge at such temperatures, but (b) is sensitive to the elevated temperature and heat conditions encountered in conventional electrothermography, e.g., 100° F – 250° F, to reduce its electrical resistance and become conductive and thereby cause discharge of the charged resin. Resins having these properties are well known in electrothermography (2) it, itself or when admixed with the plasticizer or heat activatable tackifying agent, must be non-tacky at normal temperatures but sensitive to such conventional electrothermographic elevated temperature and heat conditions to become soft and slightly tacky or sticky. In a sense, the resin plasticizer mix is a heat sensitive or heat activatable weak adhesive.

A primary function of the resin is as a binder to bind the heat-activatable plasticizer or tackifying agent particles to each other when such agent is in the form of particulate solids, and to bond or adhere the resin-plasticizer system to the support sheet. It acts as a film former. Furthermore, the resin functions to control the tackiness achieved by the heat activatable tackifying agent at elevated temperatures, to reduce tackiness at normal temperatures and to contribute the desired electrostatic properties to the system. Without the resin, it is difficult to form a cohesive layer which will adhere to the support sheet, and tackiness in response to heat may become excessive.

Resins which have the aforesaid properties and which may be used in the present invention include, in addition to polyvinyl acetate and sytrene-butadiene rubber, other vinyl resins and polyesters such as polyvinyl chloride, after chlorinated polyvinyl chloride, copolymers of vinyl chloride and butadiene, copolymers of vinyl chloride and vinyl acetate, e.g. VYHH, polystyrene, polyterephthalic acid ester, polyethylene, maleic acid resins, such as copolymers of styrene and maleic acid, copolymers of polyvinyl chloride and vinul isobutyl ether (the polyethers), polyethylene, polypropylene, acrylonitrile, polyesters of isophthalic acid and ethylene glycol, natural rubber lattices, acrylic resins such as polymethacrylates and poly-acrylates, waxes, etc. Hygroscopic resins which absorb moisture from the fingers or air, such as gelatin or polyvinyl alcohol, are not preferred.

Any known plasticizer for the particular resin can be used as a heat activatable tackifying agent so long as (1) when it is admixed with the resin, the system is dry and non-tacky at normal temperatures but is sensitive to electrothermographic heat to become soft and slightly tacky to thereby provide a tacky latent image and (2) when it is admixed with the resin, the system is non-conductive and hence electrostatically chargeable at normal temperatures but is sensitive to electrothermographic heat to become conductive to thereby provide an electrostatic latent image. Normally solid particulate crystalline plasticizers are preferred in the form of discrete particles in the coating but normally liquid plasticizers may be used so long as when they are compounded with the resin, the system is dry and non-tacky.

Preferred plasticizers for use in the present invention are those which impart to the resin-plasticizer system a delayed tack after heating and cooling, e.g. 30 seconds to a minute or more.

Plasticizers or tackifying agents which are heat activatable under electrothermographic temperature conditions and which provide a delayed tack are known. See page 7 of Monsanto's Technical Bulletin O/PL 1-H and U.S. Pat. Nos. 2,462,029, 2,608,542, 2,608,543, 2,613,191 and 2,613,156.

The delayed tack has the advantage that when the coated electro-thermographic sheet and master (hereinafter the mirror image copy of a master and from which the images of the invention are made, as well as the master, will both be referred to as the master) are exposed to infra red followed by electrostatic charging,

the latent tacky image is retained during charging and toning and during charging, toning and transfer when transfer techniques are used. Also this permits repetitive charging, toning and transfer or repetitive toning and transfer without repeating the exposure step.

The heat activatable tackifying agent should have a softening temperature, i.e., activation temperature, within the range of conventional thermographic temperatures created by infra red absorption, i.e., between 100° F and 250° F, more usually between 100° F and 200° F.

Preferred tackifying agents are those which themselves are electrostatically chargeable at normal temperatures and are sensitive to heat to reduce the electrical resistance thereof, but this is not essential so long as the resin-plasticizer system has this property.

Suitable delay tack heat activatable tackifyers or plasticizers are the organic amide type plasticizers such as the sulfonamides, particularly alkyl, aryl and alicyclic sulfonamides, e.g. N-cyclohexyl-p-toluene sulfonamide and N-ethyl p-toluene sulfonamide, and acetanilid, organic phosphate esters, particularly the triaryl, trialicylic and tri (alkyl aryl) phosphates, such as triphenyl phosphate, tricresyl phosphate, dicyclohexyl phosphate and tri(p-tert.-butyl phenyl) phosphate, the phthalate esters, particularly the higher dialkyl and dialicyclic phthalates, such as diocytl, dinonyl, didecyl, didodecyl phthalates and dicyclohexyl phthalate, and the terphenyls, such as o-terphenyl. All of these exhibit delayed tack characteristics when subjected to heat. The sulfonamides are best for the polyvinyl ester resins whereas the phosphates are best for the rubbers, e.g. natural rubber and butadiene styrene, and the phthalates are best for polystyrene.

The plasticizer may contribute to some extent to the cohesion of the coating and the adhesion thereof to the substrate.

Upon heating the resin-plasticizer system the change in physical condition of the coating to a tacky highly viscous liquid condition increases the conductivity of the heat struck areas to thereby provide an improved latent electrostatic image as well as a latent tacky image.

The heat-activatable tackifying agent should be one which renders the non-charged coating sufficiently tacky when exposed to conventional electrothermographic infra red heat conditions to provide good adherence of the non-charged toner particles to the heat struck areas but not so tacky that such areas stick to the master against which the coating is held in contact during infra red exposure. The heat activated tackiness achieved by any particular tackifying agent will vary depending on the particular resin used, the ratio thereof to the resin and the intensity of the infra red source. The tackifying agent should not render the system tacky under normal conditions, should not under normal conditions unduly decrease the electrical resistance of the resin-tackifying agent system, and should not interfere with decrease in such resistance in response to electrothermographic heat.

The heat activated tackiness of the resin-plasticizer system can be controlled by controlling the weight ratio of the tackifying agent or plasticizer to the resin. Increasing such ratio increases the tackiness achieved and decreasing it decreases the tackiness achieved since the tackiness is imparted to the system by the tackifying agent and not by the resin. Such ratio will depend on the particular tackifying agent and resin being used. Generally, such ratio should be greater than one to achieve adequate tackiness. A preferred weight ratio is between 1.5 and 6, a more preferred ratio being between 2 and 6. Excellent results have been achieved with a ratio of four although a ratio of three has also given satisfactory tackiness. As aforesaid, tackiness is in direct proportion to this ratio.

The minimum ratio is that at which minimum tackiness is achieved when the non-charged, resin-tackifying agent system is subjected to conventional electrothermographic heat. Minimum tackiness can be observed by toner developing the infra red exposed non-charged coating with non-charged toner particles. Any substantial adherence of the non-charged toner particles to the heat struck areas of the non-charged coating will provide advantages to thereby provide a minimum tackiness. Optimum tackiness and hence the optimum ratio is that at which the greatest amount of non-charged toner particles will adhere to the heat struck areas of the non-charged coating without such areas sticking to the master when they are in conventional electrothermographic contact with each other during exposure. The maximum tackiness and hence the maximum ratio is that beyond which the heat struck areas will stick to the master during exposure. Tackiness which results in sticking to the master will render the latent and visible images indistinct because the coating materials run too much. Thus, the limits of such ratio and the optimum ratio can be obtained by routine testing.

Plasticized resins have been suggested in the past for electrothermographic coatings but in all cases either the plasticizer was not one which is a heat activatable tackifying agent or the ratio of plasticizer to resin was too small to achieve a tacky latent image in addition to an electrostatic latent image.

To a limited extent, tackiness can be controlled by the setting of the Thermofax machine. Increased heat in most, but not all, cases provides increased tackiness. There is usually an optimum setting for any particular resin-tackifying agent combination, which can be observed by routine experiment.

The protein functions as a colloid stabilizer and a coating levelling and bulking agent, i.e., it provides bulk and a more even,level coating layer on the support sheet. It also promotes adhesion of the resin-plasticizer system to the base paper support.

Any protein can be used, such as dextran or starch. It can be omitted. When used, a preferred amount is between 0.57 and 2 percent or 3 percent by weight of the dispersion and between 0.11 and 0.8 or 1.2 percent by weight of the dried coating. The minimum amount is the minimum which will give the coating levelling effect desired. The maximum amount is determined by the fact that after optimum coating levelling is achieved, a greater amount contributes nothing to the electrothermographic properties of the coating and reduces the percentage of the resin and tackifying agent in the dried coating which do contribute to such properties. Accordingly, the desired electrothermographic effect is reduced. It is preferred to use the minimum amount which will give an even, level coating.

If desired, a small amount of pigment, such as a white titanium oxide pigment, can be added to the coating in amounts up to 2 or 3 percent by weight of the coating.

The resin and plasticizer may be applied to the support base from an aqueous dispersion or emulsion as in

the aforesaid examples or from a solution of the resin and/or plasticizer in an organic solvent, such as toluene, alcohols and aromatic solvents, for one or both, the non-dissolved component when only one is dissolved being dispersed in the solution. When solutions are used, it is preferred to use a solution of the resin with the plasticizer dispersed therein.

Where the resin and tackifying agent are applied as a dispersion of resin and plasticizer particles, such resin and plasticizer are present in the resulting dry coating in the form of discrete particles. When the coating is applied as a dispersion of plasticizer particles in a resin solution the resin in the dry coating is in the form of a continuous film having the plasticizer particles disbursed therein.

Where the resin and tackifying agents are applied as a dispersion, a preferred solids concentration is between 20 and 40 percent by weight, a concentration of 25 to 35 percent by weight being more preferred. If the concentration is much less than 20 percent then removal of water becomes a problem and the density of the dried coating is too small. If the solids concentration is much higher than 40 percent, the coating may be uneven and thick and will flake off and crumble. When solutions are used, the combined concentrations of the resin and plasticizer in the solvent is about the same as with a dispersion depending on the solubility characteristics.

An aqueous dispersion is preferred because it is more economical.

The preferred dried coating weight is between 0.6 and 2.0 pounds per ream of paper. Optimum dry coating weight is between 1 to 1.75 pounds per ream of paper. It is advantageous to keep the coating as thin as possible since if it is too thick it may deleteriously affect the feel of the paper, it increases cost and it may decrease resolution of the image and decrease adherence of the toner particles. The reason for this is that the larger mass requires more heat and the heat available with conventional thermographic techniques may not be adequate. Also where reflex imaging is used, the thicker the coating the more difficult it is for the infra red to pass through it. Furthermore where the uncoated side of the duplicating sheet is applied to the master in order to obtain a "right reading" image of the master, it is more difficult for the heat absorbed by the dark areas to penetrate the duplicating sheet to the coating.

A preferred coating thickness is between 0.10 and 0.75 mils, more preferably between 0.20 or 0.25 and 0.5 or 0.65 mils. In Examples 1 and 2, the thickness of the coating was 0.3 mils.

The support sheet should be one which is conductive to provide a path for discharge of the heat struck areas. Any conventional support sheet or substrate used in conventional electrothermography can be used, including conductive paper (treated to make it conductive) such as bond paper, gift wrapping paper and onionskin paper, other conductive cellulosic material such as cellulose hydrate foils, cellulose acetate and cellulose acetobutyrate, conductive plastics (either themselves conductive or treated to make them conductive), such as polyesters, e.g. mylar, polyamides, polyurethanes, polycarbonates, polystyrene, polyvinyl compounds, polyvinylidene chloride, etc., metal foils or plates such as aluminum foil, and glass plates which have been made conductive.

When the coating surface is placed in contact with the source document to be duplicated during exposure, a transparent support such as mylar, together with a transparent coating, should be used so the image can be viewed as a "right reading" image through the support and coating or else the mirror image produced must be transferred to a "right reading" image or else, as preferred, the source document with which the duplicating sheet is exposed should be a mirror image of the original master, which requires a preceding copy to be made from the original master, to thereby provide a "right reading" or non-reversed image. Otherwise, the coated side of the duplicating sheet should be away from the master, i.e., with the support against the master, in which case, the heat from the dark areas of the master must pass through the support and coating to the charged surface to provide a "right reading" image on the coated surface.

When paper is used, it is preferred to coat the smooth side of the paper.

The thickness of the support sheet is not particularly critical unless heat conductance through such sheet is being relied on, i.e., when the support surface is placed against the print of the master during exposure (in such case, the thickness of the support sheet should not exceed 0.005 inch). Also when reflex exposure is to be relied on, the support should not be so thick as to interfere with passage of infra red therethrough. Conventional support sheet thicknesses can be used. A preferred thickness is between 0.4 and 5 mils. In examples 1 and 2, a paper thickness of 2.5 mils was used.

Conventional thermographic machines can be used for infra red exposure, such as the 3M Thermofax machine.

Depending on the components of the coating, any setting over the range of settings of such machines can be used. For each coating, however, there is an optimum setting to provide optimum results.

Electrostatic positive or negative charging is carried out by conventional electrothermographic and electrophotographic xerography charging units and the applied voltage may vary over a wide range.

Any conventional developer toner used in xerography and electrothermography can be used and it is applied to the latent image in any conventional manner, such as by magnetic brush development, cascade development, cloud development, spray development, etc.

The toner is preferably in the form of solid toner particles, which are usually made by mixing color pigment, such as carbon black, with a thermoplastic melt, e.g. polystyrene, and grinding the chilled mixture, which is used, as such, or with a carrier such as iron filings, glass beads, etc. However, conventional toners in liquid form can be used also. Xerox toner has been used successfully. Preferred toner particle sizes range from 1 to 5 microns average particle size. The larger the toner particle size the less the background. However, any conventional toner particle sizes can be used. The toner particles may be electrotropic, i.e., triboelectrically charged either negatively or positively. The carrier of the toner carries the charge and the colored toner particles stick or adhere to the carrier particles which act as a brush as well as a carrier. Where the coating has a negative charge, the use of negatively charged toner particles results in a positive image, i.e., the toner particles adhere to the heat struck discharged and tacky

areas and are repelled by the negatively charged background areas.

The cleaning operation with the charged carrier without toner particles, i.e., by brushing with the charged carrier, is conventional and conventional techniques can be used.

The toner is fixed in conventional manner by heat fusion, i.e., thermoplastic of the toner is fused to the coating, or chemically by solvent vapors. However, with the present invention, fixing may not be necessary in all cases because the tackiness of the heat struck coating holds the toner particles and when the coating loses its tackiness, the toner particles are securely bonded to the coating.

The coating is applied from solution or dispersion onto the support in conventional manner such as by coating rollers and meier rod.

If desired, both sides of the support sheet substrate can be coated with the resin-plasticizer coating and either or both surfaces electrostatically charged.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. An electrothermographic reproduction process comprising forming a latent electrostatic and tacky image on a normally nontacky layer of electrostatically chargeable resin which is activatable by electrothermographic radiant energy to both change its electrical conductance and change its state from a normal substantially non-tacky state to a soft and tacky state, said image being formed by exposing said layer to said electrothermographic radiant energy while positioned adjacent a master and electrostatically charging it.

2. A process according to claim **1**, said layer being supported on an electrically conductive support.

3. A method according to claim **1**, said exposure step preceding said charging step, said exposure step forming a latent tacky image, said exposed layer being subjected to said charging step to form said electrostatic image while said latent tacky image is still tacky, said charging step being followed by toner developing said latent image while it is still tacky.

4. A method according to claim **3**, said exposure being a direct exposure by passing said radiant energy through said master.

5. A process according to claim **1**, also including the step of toner developing said latent image.

6. A process according to claim **5**, including fixing said toner developed image.

7. A process according to claim **1**, said layer comprising a resin and an organic heat activatable tackifying agent which is activated by said radiant energy to convert said resin-tackifying agent system form a normally non-tacky state to a soft and tacky state, said resin-tackifying agent system being also sensitive to said energy to change the electrical resistance thereof.

8. A process according to claim **7**, said tackifying agent being a plasticizer for said resin and said resin being a thermoplastic resin.

9. A process according to claim **7**, said tackifying agent being selected from the group consisting of a phosphate ester, a phthalate ester, a sulfonamide and terphenyl.

10. A process according to claim **7**, said tackifying agent being normally non-tacky but being activated by electrothermographic heat to become tacky and thereby render said resin-tackifying agent system soft and tacky.

11. A process according to claim **7**, said resin being electrostatically chargeable and sensitive to electrothermographic heat to change its electrical resistance.

12. A process according to claim **7**, said tackifying agent being electrostatically chargeable and being responsive to heat to change the electrical resistance thereof.

13. A process according to claim **7**, said resin being substantially non-tacky when exposed to said energy, the ratio of tackifying agent to resin being selected so that when the non-charged layer is in contact with said master during said exposure step, the tackiness of said layer developed by said exposure is insufficient to cause the layer to stick to the master but is sufficient to cause substantial amounts of non-charged toner particles to adhere thereto when said toner particles are applied thereto.

14. A process according to claim **7**, said tackifying agent being a heat activatable, delayed tack tackifying agent.

15. A process according to claim **7**, the ratio of said tackifying agent to said resin being at least 1.

16. A process according to claim **15**, said ratio being at least 2.

17. A process according to claim **7**, said layer forming a coating adhered to a conductive support sheet.

18. A process according to claim **17**, including the step of applying said resin and tackifying agent coating to said support from an aqueous dispersion thereof.

19. A process according to claim **17**, said coating also including a coating levelling agent.

20. A process according to claim **19**, said levelling agent being a protein.

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