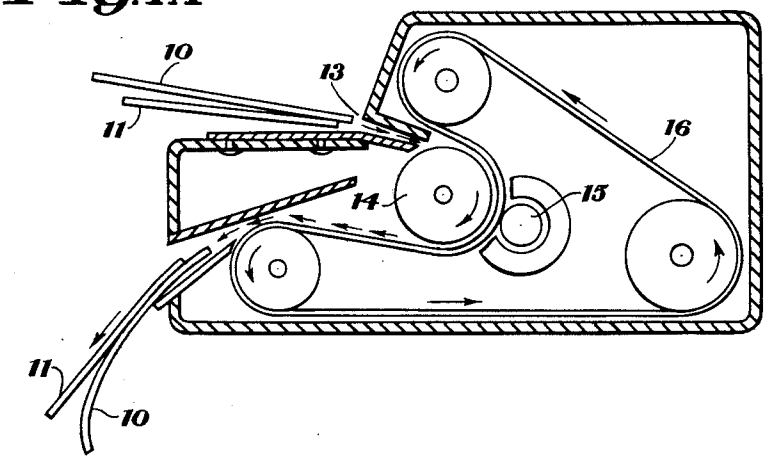
April 7, 1964 W. J. DULMAGE ETAL 3,128,198

THERMOXEROGRAPHY

Filed June 21, 1961

Fig. 1A



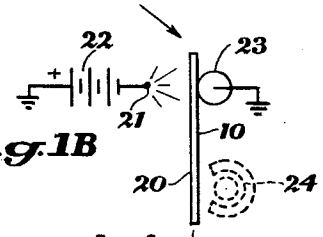


Fig. 1B

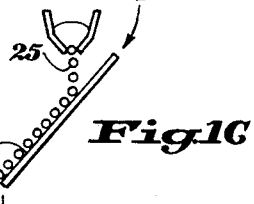


Fig. 1C

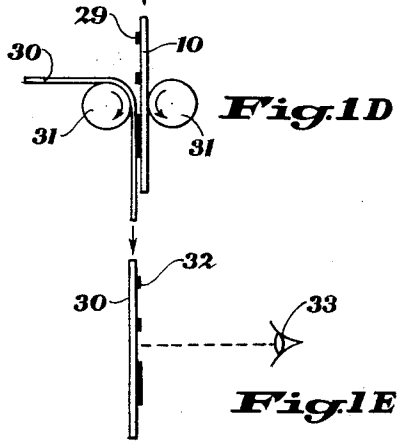


Fig. 1D

Fig. 1E

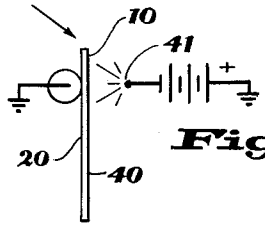


Fig. 2B

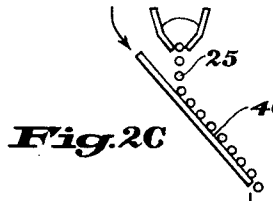


Fig. 2C

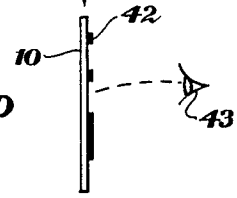


Fig. 2D

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3,128,198

Patented Apr. 7, 1964

3,128,198

THERMOXEROGRAPHY

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Filed June 21, 1961, Ser. No. 118,593

5 Claims. (Cl. 117—17.5)

This invention relates to xerography in the sense that it uses certain standard xerographic steps for some of its steps. However, it establishes the electrostatic image by thermographic methods.

The invention is based on the discovery that certain materials which are highly resistive to the extent that an electrostatic charge may be stored on the surface thereof, change when heated so that if they are subsequently exposed to a charging device the charge is not established on the areas which have been heated. This, for convenience, may be thought of as a more or less permanent increase in conductivity by the heat but many experiments have shown that this is not the whole story and that actually there may be no change in conductivity at least no change which may be measured by direct conductivity measuring procedures. There is some basis for believing that the effect is a change in the ability of "willingness" of the material to accept or store an electrostatic charge for example from a corona discharge. On this theory the heated areas do not accept the charge or if they do accept it they tend to dissipate it in some way which is only partly due to conductivity. In this same speculative or theoretical vein, it may be that some charge is accepted in all areas but that in the heated areas the first charge resists the acceptance of any further charge.

In any case there are materials which will preferentially accept and store electrostatic charge except in areas which have been heated. This differential exists long after the material has returned to room temperature.

According to the invention, a heat image is applied to such a material either by radiation or preferably by contact with a radiation absorbing document while the sandwich of the recording layer and the document is passed under an intense source of radiation. The recording layer is not charged until after the thermal exposure and this contributes to the high quality of reproduction. This order, exposure followed by charging, as well as the use of heat, distinguishes the present invention from the many forms of xerography, and from xerothermography which is described in copending application, Serial No. 25,108, filed April 27, 1960, by J. G. Jarvis.

The imagewise heated surface is subjected to uniform charging, for example by corona discharge. The charge leaks away in the preheated areas leaving an electrostatic image. Immediately before or preferably immediately after charging the whole sheet may be uniformly heated to hasten the discharging. It has been found that such uniform heating does not appreciably affect the background areas which retain charge but does cause more rapid discharge of the preheated areas. However, even without the uniform heating, the electrostatic image becomes established in a short while, usually less than a minute.

After the electrostatic image has been established on the surface, this image is toned by any of the standard xerographic development processes. Preferably the toner is charged the same as the image so that the toner deposits in the previously heated areas, particularly if these heated areas have been produced by contact with the characters on a document. This preferable system gives a direct positive to positive reproduction.

If the surface in contact with the document is the one which is charged and toned, the image must be transferred to a receiving sheet to be "right-reading" or must be viewed through the recording sheet itself, which in this case must be transparent. Alternatively the other surface of the recording sheet may be the one which is charged and toned. This latter alternative has the disadvantage that the definition and resolution is somewhat reduced because of the thickness of the recording layer between the source of heat and the surface on which the ultimate record is made.

The xerographic toning process may be of any of the usual types such as cascade development, cloud development, liquid development or magnetic brush development. If the toner particles are charged the same as the surface, they tend to deposit in the heated areas and hence form a positive compared to the original document.

Many different materials have been found to display the above-mentioned properties of decreasing in resistance or in charge acceptance when heated, the effect being more or less permanent and persisting after the sheet has cooled. Such materials can be used alone or as coatings on ordinary paper or other materials which if uncoated would conduct surface charges away rapidly. The coating may be on either or both sides of the paper, at least on the side which is to be charged. Such coating includes the hydrophobic polyvinyl acetals and various polymers and copolymers such as vinylidene chloride acrylonitrile and vinyl chloride-vinyl acetate. The latter copolymers in ratios of about 87:13 are known as VYHH and have proven to be particularly satisfactory giving high contrast, high resolution prints when used according to the present invention. When using VYHH, various solvents may be used during the coating operation and some solvents are preferable to others and it has been found that the print quality depends on how much of the solvent remains in the coating. Coating from low boiling solvents such as acetone and chloroform do not give as good prints as those from the higher boiling ketones, such as methylisobutyl ketone; the latter is a preferred solvent. However, even with methylisobutyl ketone, the final image densities are best when the residual solvent is between 2% and 10% preferably between 5% and 8%. The images become faint when the solvent content at the time of the heat exposure is too low. It is also known that vinyl compounds containing a high percentage of certain plasticizers such as dioctyl phthalate do not tend to retain the solvent and hence it is desirable to avoid using such plasticizers as they tend to cause the percentage of solvent normally retained, to fall below 2% say. However, this all has to do with the most preferred embodiments of the invention and it is not too critical if the contrast of the image at lower densities is acceptable.

As discussed in more detail below, the exposure latitude may be increased by using multilayer coatings consisting of different heat sensitive materials having sensitivities in slightly different ranges.

The operation of the invention and some of its advantages will be more fully understood when read in connection with the accompanying drawing in which:

FIGS. 1A to 1E constitute a schematic flow chart illustrating the preferred embodiment of the invention.

FIGS. 2B to 2D similarly show an alternative embodiment of the invention, the first step of which is the same as in FIG. 1A.

In FIG. 1A a document 11 to be copied is placed in contact with a recording sheet and the sandwich is passed into a thermal exposing device through an entrance slit 13 and over a roller 14. The sandwich is held tight to the roller 14 by a moving belt 16, while the sandwich is exposed to the thermal radiation from a high intensity tungsten filament lamp 15. After exposure the document 11 is separated from the recording sheet 10, the latter as shown in FIG. 1B is charged by a corona discharge from

a wire **21** which is held at high potential by a source indicated schematically at **22** with respect to a grounded roller **23**. Negative potential is used in the example illustrated, but positive potential could be used with appropriate change in the toner polarity. The arrangement shown places negative charges on the surface **20** which had been in contact with the document **11**. Other forms of xerographic charging may be used for this step. After so charging there is an electrostatic image on the surface **20**. This image is not formed instantaneously or at least does not reach its full potential instantaneously. However, after a few moments the charges are concentrated in the areas which have not been heated and there is considerably less charge in the heated areas. It is not necessary that this charging take place while the film remains hot.

Toner particles may be applied by any standard xerographic system. In FIG. 1C particles **25** are cascaded across the imagewise charged surface **20**. Due to triboelectrification in well known manner the toner is charged to the same polarity as the wire **21** of FIG. 1B so that the toner particles **25** are repelled by the charge image of the surface **20** but attracted to the areas which are not so charged. That is, the toner is attracted to the areas which correspond to the characters on the original document **11**. However, the toner as it appears on the surface **20** is wrong reading when viewed from the side **20** of the recording sheet **10**. These deposited toner particles **29** are transferred by pressure to a receiving sheet **30** by passing both the sheet **10** and the receiving sheet **30** between rollers **31**. The final image **32** on the receiving sheet **30** is stabilized, for example by fusion, and may be viewed "right-reading" by an observer whose eye is illustrated at **33**. High resolution, high quality prints have been obtained by this process. If the image **29** were left on the surface **20** it would be wrong reading unless viewed through the sheet **10** which would require the sheet **10** to be transparent.

Alternatively, a corona from a wire **41** may be applied to the rear surface of the coated paper **10** as shown in FIG. 2B. The sheet **10** is preferably a white opaque paper, coated on one or both sides, and if coated on one side only, the uncoated surface is the one placed in contact with the document **11**. The coated surface **40** of the sheet **10** is thus opposite to the surface which had been in contact with the document **11** during heat exposure. Accordingly, the distribution of heat at the surface **40** is slightly diffused compared to the distribution at the surface **20**. However, good quality prints can be obtained by this process if the sheet **10** is thin. Again, as shown in FIG. 2C, toner particles **25** of negative polarity (by triboelectric effects) are cascaded across the surface **40** of the sheet and adhere to the uncharged areas to form an image **42** on the "back" surface of the sheet **10**. This image **42**, is "right-reading," when viewed by the eye **43** of an observer. After fusing, the sheet is ready for use.

This process is referred to as thermoxerography as distinguished from xerothermography, particularly because in this process none of the xerographic steps are applied, at least in the preferred form, until after the thermographic exposure. There is no recording of the thermal exposure due to the heat itself but only due to the effect of the heat on the charge acceptance and storing ability of the sheet. Since the charging and toning takes place entirely after the exposure, the possibility of the various rollers and other surfaces necessarily involved in the thermal exposing step interfering with the charge is eliminated. If the charge were placed on the surface before exposure as is common in many xerographic processes, all subsequent contacts with any surfaces introduce the possibility of disturbing the uniformity of the charge. In the present invention, however, the charge is not placed on the layer until after the image exposure and such

sources of difficulty with uniformity of charge, are eliminated.

Furthermore the fact that the exposing step is entirely preliminary to the charging and toning step, allows the latter two steps to be greatly simplified. It is preferable not to have the toner particles applied at the same time or immediately following the image charging step since the image obtains greater contrast a few moments after the charge is first applied. As mentioned above, even this slight delay can be shortened by uniform heating.

Example 1

A two-sided coating of VYHH on map overlay paper was exposed thermographically at setting 9 of a commercially available thermal exposing machine, charged negatively under a high potential negative corona wire, and then developed with a cascade developer containing negatively charged toner particles. A good quality reproduction, with high image density and low background density, resulted.

Example 2

A Vinylite recording layer consisting of 0.6 mil of VYHH on one side of "onionskin" paper and containing 6% of residual methyl isobutyl ketone solvent was thermographically exposed at setting 9 in a commercially available thermal exposing machine. The paper surface of the layer was in contact with the document. The recording layer was separated from the document and the coated side was charged as in FIG. 2B under a negative corona wire which was set at a potential of about 12,000 volts. The resulting electrostatic image was then developed with a cascade developer, giving a "right-reading" print with good image density and negligible background.

Example 3

A VYHH coating which consisted of 0.5 mil of VYHH on one side of map overlay paper with 5.2% of residual methyl isobutyl ketone solvent after 4 hours' drying at 70° C. was thermographically exposed at setting 4 of a commercially available thermal exposing machine, with the power consumption of the lamp set at 620 watts. The recording layer was then separated from the document and charged as in FIG. 1B under a rotating wire spiral corona charge of the type described in the copending application by J. G. Jarvis, et al., Serial No. 126,393, filed June 7, 1961, which wire was at a potential of about 15,000 volts. The resulting electrostatic image was then developed with a cascade developer and the image was electrostatically transferred to a piece of bond paper and stabilized by heating. The final copy had well defined images with good density and very low background density.

Example 4

A single-sided coating of VYHH on onionskin was prepared. This had been made by coating two layers, .25 and .35 mil on the same side. This was accomplished by coating at a speed of 5 feet per minute and drying at 50° C. The coating was redried at 5 feet per minute at a temperature of 80° C. This layer contained about 6% of residual methyl isobutyl ketone solvent. This layer was then thermographically exposed with the polymer surface in contact with a document having solid black areas and adjacent all-white areas. The recording layer was separated from this document and charged with the high-speed rotating spiral wire charger. The recording layer charged very rapidly and the surface potentials of the recording layer, where it had been in contact with the solid black areas, and with the white area, were measured without waiting for decay. This procedure was repeated several times and it was observed that the area which contacted the black section attained a surface potential of about 1850 volts whereas the area which contacted the white attained a surface potential of about 2400 volts. In every instance the initial difference in surface potential

after charging was 500 volts or greater. This difference increased with time so that after two minutes it was 1000 volts. As would be expected from these measurements, this recording layer gave good results in the present process. For example, this layer was given a thermographic exposure in contact with a document at setting 6 of a commercially available thermal exposing machine but with power consumption of the lamp reduced to 620 watts. The recording layer was charged and immediately developed and the image electrostatically transferred to a sheet of bond paper. The resulting image had very good density and very low background.

Example 5

A recording layer consisting of 0.5 mil of a copolymer of vinylidene-chloride and acrylonitrile of about 85:15 ratio was coated on one side of onionskin paper from a dope containing 21% of the polymer in methyl isobutyl ketone. The coating was dried 4 hours at 70° C. With the paper surface of the recording layer in contact with a document, the 2-ply combination was exposed at setting 7 of a commercially available thermal exposing machine. The recording layer was separated from the document and the coated side was charged under a negative corona wire. The resulting electrostatic image was developed with a negatively charged developer which was cascaded over the surface. The copy was stabilized by heating and had fair density and negligible background.

Example 6

While two different polymers coated on opposite sides of a paper support have been found to have the exposure characteristics of the material on the exposed side, with no interaction between the two polymers, improved results and extended exposure latitude was obtained in the following example by superimposing two different polymers on the same side of a paper support. A highly thermal sensitive material was coated directly on the onionskin paper support and consisted of VYHH polymer layer (Bakelite Company) coated 0.5 mil thick. Such material has an exposure range between 3.5 and 5.5 inches per second in a commercially available thermal exposing machine. On top of this VYHH layer, a second layer was coated consisting of polyvinyl formal 0.5 mil thick. This material alone has an exposure range, i.e., gives satisfactory exposures, at 2.5 to 3.5 inches per second exposure. It should be noted that the polymers are decreasing in thermal sensitivity and although they are the same thickness in this example, they could with advantage, also decrease in thickness from the support upward. With the document and recording sheet held in contact on a vacuum plate the sample was charged to −1500 volts D.C. It was exposed under an infrared lamp and developed by xerographic techniques. Such material yielded prints of acceptable quality with exposures ranging from 1.5 to 6.5 inches per second and in fact some images were obtained with exposures as slow as 0.8 inch per second and as fast as 7.5 inches per second. Thus this example has an exposure range extending beyond the ranges of the separate layers.

The advantage of adopting this type of recording sheet is in the simplified design and use of either xerothermographic or the present thermoxerographic process machines. Such material is useful in either process. Due to the greater exposure range, there is less need to adjust the exposure for each type of document. That is, the exposure is less critical. Furthermore a document having a wider than normal density range can be copied.

Example 7

This example is the same as Example 6 above consisting of an onionskin paper support with VYHH coated thereon and Formvar coated on top of the VYHH layer. In this Example 7, a third, heat sensitive, material namely BPA polycarbonate (bis-phenol-A-polycarbonate) with an exposure range of 0.8 to 1 inch per second is coated on top of the Formvar layer. Such a coating extends the exposure range giving good prints down to 0.8 inch per second. As with Example 6, this triple coated material can be used in both xerothermography and in the present invention having to do with thermoxerography.

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. A copying process comprising imagewise heating so as to produce a pattern of heated and unheated areas thereon, the outer surface of a high electric resistance layer coated on a sheet of paper which outer surface at room temperature accepts and stores an electrostatic charge except after being heated, then substantially uniformly applying electrostatic charges to said outer surface to deposit charges on the unheated areas, and then with said surface cooled at least to the temperature at which xerographic toner will not fuse to the areas to which it is not electrostatically attracted xerographically toning the surface in accordance with the charge image.

2. A process according to claim 1 in which the high electric resistance layer comprises a polymer selected from the group consisting of hydrophobic polyvinyl acetals, vinylidene chloride-acrylonitrile copolymers and vinyl chloride-vinylacetate copolymers.

3. A process according to claim 1 in which the high electric resistance layer comprises essentially a vinyl chloride-vinyl acetate copolymer of about 87:13 ratio containing between 2% and 10% of methyl isobutyl ketone.

4. A copying process comprising imagewise heating so as to produce a pattern of heated and unheated areas thereon, the surface of a sheet material which surface at room temperature accepts and stores an electrostatic charge except after being heated, then substantially uniformly applying electrostatic charges to said surface to deposit charges on the unheated areas, and then with said surface cooled at least to the temperature at which xerographic toner will not fuse to the areas to which it is not electrostatically attracted xerographically toning the surface in accordance with the charge image.

5. A process according to claim 4 in which the xerographic toning step is performed with toner electrostatically charged to the same polarity as the charge image so as to be attracted substantially only to the uncharged areas.

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