May 21, 1968 D. A. NEWMAN 3,384,015

THERMOGRAPHIC METHOD

Filed March 11, 1966

Fig. 1

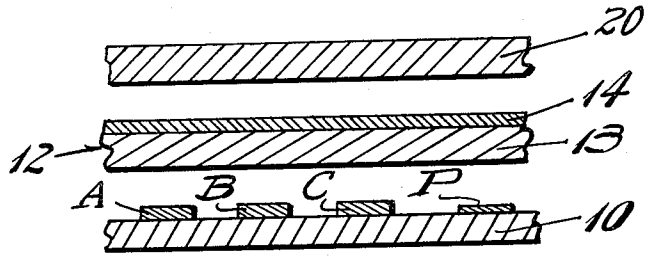
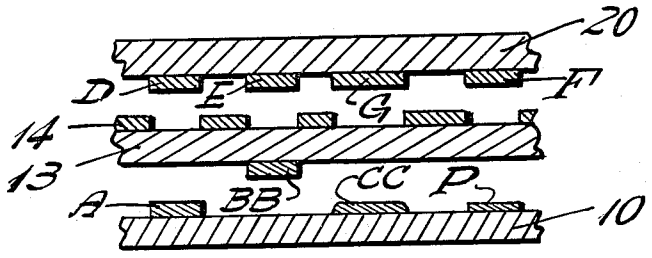


Fig. 2



INVENTOR.
Douglas A. Newman
BY
Johnson and Kline
ATTORNEYS

United States Patent Office 3,384,015 Patented May 21, 1968

3,384,015

THERMOGRAPHIC METHOD

Douglas A. Newman, Glen Cove, N.Y., assignor to Columbia Ribbon and Carbon Manufacturing Co., Inc., Glen Cove, N.Y., a corporation of New York

Continuation-in-part of application Ser. No. 442,126, Mar. 23, 1965. This application Mar. 11, 1966, Ser. No. 533,498

10 Claims. (Cl. 101—467)

ABSTRACT OF THE DISCLOSURE

In the thermographic process for copying original images present on an original sheet in which the original sheet is superposed with a transfer sheet and a copy sheet and subjected to infrared radiation, the improvement whereby the original images are applied from a pressure transfer sheet and consist of a resinous composition which absorbs infrared radiation to a predetermined substantial degree and which contains a porous extender.

This application is a continuation-in-part of my copending application Ser. No. 442,126, filed Mar. 23, 1965, now abandoned.

Methods of thermographically imaging copy sheets such as hectograph master sheets have been known for some time. According to the known methods, an original sheet bearing infrared radiation absorbing images is superposed with an unimaged master sheet and a hectograph transfer sheet carrying a layer of transfer material which does not absorb infrared radiation. The superposed sheets are exposed to infrared radiation which is absorbed by the images on the original sheet, converted to heat and melts the transfer material in corresponding areas on the transfer sheet. The melted transfer material flows onto or adheres to the master sheet in contact therewith and upon separation of the sheets, a hectograph master sheet is formed bearing reproducible hectograph images corresponding directly or in reverse to the images on the original sheet.

Many difficulties have been encountered in carrying out such processes. The length of time of exposure of each different original sheet to infrared radiation will vary depending upon the radiation-absorbing properties of the composition comprising the image. To determine the correct exposure time and intensity, it is necessary to experiment by exposing the imaged original, copy sheet and transfer sheet to radiation. Insufficient exposure results in insufficient transfer of the imaging composition, and since the sheets cannot be precisely and accurately superposed more than once, a waste of the transfer sheet and copy sheet results. Excessive exposure to the radiation results in the same waste of time and materials due to excess transfer caused in part by the high ambient temperature generated and in some cases causes a contamination of the equipment due to the melting and flowing of the hectograph composition.

Another difficulty is encountered in the case of preprinted original forms wherein the forms are first printed in blank using infrared radiation-absorbing printing ink and the blanks are periodically and systematically typed in using carbon papers on which the transfer composition also absorbs infrared radiation. Such forms are popularly used for billing purposes whereby charges, credits and balance are recorded on the original and copies are sent monthly as debit notes.

The difficulty in producing satisfactory copies of such printed forms is due to the difference in the infrared radiation-absorbing properties of the printed and typed

portions thereof. Printing ink has a high content of carbon black whereas conventional transfer layers cannot contain such large amounts of carbon black without losing frangibility. Thus the heat-generating properties of the printed portions of the original are much higher than the typed portions. If the time of exposure to infrared radiation is calculated so as to be proper for the printed images, then it is insufficient to permit reproduction of the typed images, and if the time of exposure is prolonged to bring the typed images to a sufficient temperature, then the printed images are overexposed and they generate an excess amount of heat causing excess transfer to the copy sheet in the form of broadened images which are sometimes illegible.

I have found that although it is necessary to start with typed original images which have uniform high infrared radiation-absorbing heat-generating properties and which are sharp, it is equally important that the original images are stable and do not lose their sharpness or become tacky or adhesive at the range of temperatures generated in the thermographic method. In the case of ordinary wax binder transfer materials, such materials cannot contain very large amounts of infrared radiation-absorbing pigments and the images formed therefrom become melted when they absorb infrared radiation. When they melt, they spread on the original sheet and contaminate the carrier sheet or the thermographic apparatus. However, more important is the fact that the heat pattern which is generated by the images conforms to the configuration of the melted, spread original images so that the melting of the transfer layer and the transfer thereof to the copy sheet is in the form of spread, uneven images. In the case of ordinary resinous or cellulosic transfer materials, the images formed therewith are resistant to melting or spreading due to the heat generated by absorbed infrared radiation but have the critical disadvantage of becoming tacky or adhesive whereby they bond to the sheet or element with which they are in contact during the exposure step. In cases where the original sheet has poor retentive powers for the original images, such as where a plastic film original is used, the original images sometimes strip completely from the original sheet onto the rear surface of the transfer sheet or copy sheet or carrier sheet or onto portions of the thermographic exposure device, depending upon the superposition and use of the various sheets.

It is the main object of the present invention to overcome the critical time-temperature relationship of prior thermographic transfer processes through the use of original images which are capable of being applied where desired by typing or the like, which contain a predetermined high amount of infrared radiation-absorbing material so that even brief exposure is sufficient to generate a sufficient heat pattern, and which are based upon frangible transfer compositions which resist becoming tacky and are stable over the wide range of temperatures encountered in the thermographic process so that picking, melting and spreading thereof at such temperatures is avoided.

It is another object of this invention to provide a method for insuring the formation of uniformly-imaged copy sheets from original sheets such as forms on which some of the images are preapplied, such as by printing, and on which some of the images are later applied, such as by typing, but resist picking, melting and spreading due to exposure to infrared radiation.

These and other objects and advantages are accomplished as more fully set forth in the specification and drawing, in which:

FIGURE 1 is a diagrammatic cross-section, to an enlarged scale, of an original sheet bearing a conventional wax-base carbon image A, non-smear images B and

printed image P, superposed together with a master sheet and a hectograph transfer sheet prior to irradiation.

FIG. 2 shows the arrangement of FIG. 1 after treatment with infrared radiation.

The objects and advantages of the present invention are accomplished by imaging the original sheet using solvent-applied frangible transfer compositions which produce infrared radiation-absorbing images which contain a predetermined high amount of an infrared radiation-absorbing material and which resist picking, melting and spreading at the thermographic temperatures. The present frangible transfer compositions are heat-resistant due to the fact that they are based upon resinous or plastic binder materials and resist becoming tacky at high temperatures due to the fact that they contain large amounts of solid particulate extender. Also, they contain a high amount of infrared radiation-absorbing material such as carbon black because they are applied as solutions, similar to printing inks, and contain a large amount of volatile solvent which renders the composition coatable but is then evaporated and forms no part of the transfer layer.

Whereas conventional resinous transfer compositions resist melting and spreading at thermographic temperatures, the compositions used in the present invention have the critical advantage that they remain non-tacky at such temperatures and thus will not pick or transfer to sheets or elements with which they make contact during the thermographic exposure. This requirement is necessary not only from the point of view of avoiding contamination of the other sheets, the carrier and the exposure device, but also because it is necessary in most cases to preserve the original sheet either for record purposes or for the systematic production of additional thermographic copies as needed.

The frangible transfer compositions of the present invention are preferably based upon cellulosic binder materials such as ethyl cellulose, hydroxyethyl cellulose, ethyl hydroxyethyl cellulose and the like, although other normally thermoplastic resinous binders may be used such as polystyrene, acrylic and methacrylic acids and esters and copolymers thereof, polyvinyl butyral, polyvinyl acetate, and the like. The use of natural and synthetic thermoplastic resinous binder materials to produce heat-resistant frangible transfer compositions is well known to the carbon paper art.

The natural tendency of these binder materials to become tacky when heated to temperatures in the thermographic range, i.e. between about 200° F. and 350° F., is avoided according to the present invention by the incorporation of a major amount by weight, based upon the total weight of the solid transfer layer, of a solid particulate extender which is preferably an inert filler such as clay, bentonite, talc, barium sulphate, calcium carbonate, ultramarine, or the like, but which may also be an infrared radiation-absorbing pigment such as graphite or carbon black. The only requirement for the extender is that it must be a material which has interior and/or surface porosity and does not destroy the infrared radiation-absorbing property of the composition. The porosity is necessary to permit the resinous binder to be absorbed and/or adsorbed sufficiently so that its tackiness is destroyed or reduced below the level of the dry feel which the extender gives to the composition. The adsorption and/or adsorption of resin by the extender also destroys the bright color which the extender normally may have and therefore avoids the reflection of radiation by the original images. The extender must be present in an amount in excess of the weight of the binder material and is preferably present in an amount equal to at least three times the weight of the binder.

The following examples are given to illustrate different types of carbon papers which may be used to apply original images according to this invention. The ingredients are thoroughly intermixed to a coatable consistency, spread evenly on a flexible paper foundation such as paper or plastic film and allowed to set by evaporation heat-tackification of the binder material. In such cases of the solvent to form pressure-sensitive stencilling-type transfer sheets suitable for the placing of non-melting, non-tackifying original images according to this invention.

Example 1

Ingredients:	Parts by weight
Polystyrene (Styron)	1.2
Ethyl cellulose (N–7)	1.2
Clay	7.6
Graphite	10.0
Toluol	80.0

Example 2

Ingredients:	
Polymethyl methacrylate emulsion (45% solids)	1.0
Styrene-butadiene emulsion (50% solids)	1.0
Clay	25.0
Carbon black	17.0
Water	56.0

Example 3

Ingredients:	
Polystyrene (Styron)	1.5
Ethyl cellulose (N–7)	1.5
Polybutene resin (Vistanex)	0.5
Lanolin	0.7
Clay	21.0
Graphite	17.0
Toluol	45.0
Methyl isobutyl ketone	12.8

Example 4

Ingredients:	
Polyvinyl acetate	2.5
Castor oil	13.0
Dibutyl phthalate	7.0
Tannic acid	8.0
Clay	10.0
Titanium dioxide	15.0
Carbon black	7.0
Ethanol	37.5

The infrared radiation-absorbing material of the pressure-transfer composition is preferably a carbonaceous pigment such as graphite, carbon black or the like, although other materials such as the complex azine dyes and dissolved infrared-absorbing dye salts such as disclosed in copending application Ser. No. 488,498, filed Sept. 20, 1965, may be used in mixture with carbon pigments. The amount of the infrared-absorbing material used depends upon its infrared-absorbing ability and its function but in general where it is a carbonaceous pigment, it is present in amounts of at least about 10% by weight of the total weight of the resinous imaging composition. In cases where the infrared radiation-absorbing material is a solid porous pigment, such as graphite or carbon black which have surface porosity, it may also function or assist as an extender to destroy the normal heat tackification of the binder material. In such cases the graphite or carbon black must be present, either alone or in combination with another extender, in a total or combined amount in excess of at least about 50% of the total weight of the transfer composition.

Transfer sheets produced according to the foregoing examples may be attached along one edge to any suitable original sheet using a weak adhesive or weakened severing lines or the like so that the imaged original sheet may be easily separated from the transfer sheet after being suitably imaged.

One of the novel advantages of the present method and the heat stable original images used therein is the elimination of the criticality with respect to the time and temperature of exposure to the radiation. When using conventional wax-base original images, the time and temperature must be closely regulated so that the images generate

sufficient heat to cause transfer of the imaging material but insufficient heat to cause melting and spreading. The images used in the present invention may be heated to very high temperatures of about 350° F. and for long periods of time without melting and spreading. Thus, in the case of preprinted master sheets or original sheets, the images of the present invention may be placed thereon to provide excellent results regardless of the nature of the printing ink used so long as it absorbs radiation to some degree. The radiation-absorbing properties of the printing ink determine the minimum amount of radiation which must be applied, and the original images placed according to this invention are sufficiently heat stable to provide excellent sharpness of copy even though they are heated to temperatures in excess of that necessary to cause heat-transfer of the imaging layer and up to temperatures of about 350° F.

The original sheet **10** may be a translucent paper or a clear or at least translucent plastic film which is preferably frosted or coated to improve its receptivity for the original images. Receptive coatings which do not absorb infrared radiation, such as ethyl cellulose coatings as disclosed by my U.S. Patent No. 3,002,858 or similar normally-thermoplastic resin coatings containing calcium carbonate or other porous filler materials provide excellent receptivity and yet are resistant to melting and becoming tacky at the thermographic temperatures. Translucency of the original sheet is only necessary in the shoot-through process as illustrated by the drawings. In the reflex process the original may be opaque but the copy and transfer sheets must be translucent, as known to the art.

FIGS. 1 and 2 of the drawing illustrate the use of an imaged original sheet which may be used time and time again to produce sharp and clear master sheet images corresponding to original image A.

For comparison purposes a conventional wax-based image C, a resin-based image B, and a printing ink image P were also placed upon the original sheet. The thus-imaged original sheet was then superposed with a master sheet **20** and a hectograph transfer sheet **12** having a transfer layer **14** which contains hectograph dyestuff such as crystal violet which does not absorb infrared radiation.

The superposed sheets were exposed to infrared radiation focused against the original images in a conventional Thermo-Fax machine to produce sufficient heating of image P, and upon removal from the light source and separation of the sheets, the results were as illustrated in FIG. 2. The sharpness of heat-resistant images A and B and printed images P remained substantially unchanged by the heat so that the corresponding dye images D, E and F were as sharp and clear as the original images and were uniformly identical since the radiation-absorbing properties of original images A, B and P are substantially identical. The wax image C, however, was melted and spread by the heat as illustrated by CC and the corresponding dye image G corresponded to the spread fuzzy image CC rather than to the original image C.

Images D, E and F were duplicated sharply, clearly and uniformly when the master sheet was used in the spirit duplicating process for imaging hectograph copy sheets whereas the spirit prints of image G were very broad and fuzzy in comparison to original image C to which they are supposed to correspond.

While image B has the same resistance to melting and spreading as image A, image B consists of the conventional heat-resistant composition set out in my U.S. Patent No. 2,810,661 and becomes tacky at the temperature generated by the thermographic exposure and becomes bonded to and picked-off by the rear surface of the transfer sheet as image BB, shown in FIG. 2. This contaminates the transfer sheet and destroys the utility of the original sheet for producing additional copies of images B. The contamination problem is more serious in cases where the original sheet is in contact with copy sheet **20**, or a carrier sheet or the thermographic exposure device.

An essential feature of the present invention is the ability of the original images to withstand excessive heating without melting and spreading and thus creating a broadened heat pattern and without becoming tacky or adhesive. Using such original images the original can be subjected to a more intense radiation, either stronger or for a prolonged period, than is necessary to merely cause such images to generate enough heat to cause transfer of the imaging layer. The main advantages of these features are that they remove the previous criticality of the time-temperature relationship, insure that each exposure will be successful and will result in the formation of images on the copy sheet which have the same sharpness and clarity as the original images, insure the formation of sharp, clear and uniform duplicate images on the copy sheet even though the original sheet may also carry printed images and permit the original sheet to be reused as often as necessary to produce as many duplicate thermographic copies as desired.

As shown by FIG. 2, the amount of hectograph transfer material from layer **14** which adheres to and is picked off by the images corresponds to the shape of the heated images rather than to the shape of the original images. In the case of images A, B and P, their shape or sharpness is unaffected by the heat so that the hectograph layer portions D, E and F transferred thereto correspond in shape and sharpness to the original images. However, in the case of the conventional wax-base original image C, it has melted and spread or broadened to form image CC and the portion G of the hectograph layer transferred thereto corresponds to the shape of the melted, spread image CC rather than to the shape of original image C.

Moreover, since printed image P and typed images A and B have similar infrared radiation-absorbing properties, the transfer of the composition of layer **14** is uniform so that the copy formed is of uniform legibility and/or is capable of forming duplicate images of uniform intensity in the spirit or planographic processes. Although printed images P have less mass or bulk than typed images, they contain a major amount of infrared radiation-absorbing pigment and require a shorter exposure time or less intense radiation than the typed hot-melt wax images in order to generate a heat pattern of the intensity necessary to cause heat-transfer of layer **14**. Since typed images A also contain a large amount of carbon pigment and have the necessary heat-stability and dry nature, they react to infrared radiation in the same way as the printed images. Printed images have the required heat-stability and dry nature because they consist of dried printing ink and are free of meltable binders such as wax.

No particular criticality exists with respect to the thermographic transfer sheets **12** which may be used other than the fact that the transfer composition must not absorb infrared radiation to any significant extent as is recognized by those skilled in this art. The term "dyestuffs" is used herein and in the claims to cover non-absorbing colored dyestuffs such as those of the rhodamine, safranine and triarylmethane families which provide excellent results, as well as the colorless color-forming dye bases such as disclosed in U.S. Patent No. 2,743,191. Also it is preferred to employ non-melt plastic binder materials such as ethyl cellulose rather than wax, as taught by U.S. Patent No. 3,054,692. Wax-base heat-transfer compositions generally become melted and transferable at temperatures as low as from about 150° F. up to about 200° F. Heat-transfer compositions based upon thermoplastic resinous binder materials do not melt to a fluid state at the thermographic temperatures but become tacky and bond to the copy sheet at temperatures of from about 200° F. up to about 350° F. transferring thereto when the copy and transfer sheets are separated. The foundation **13** of the transfer sheet may be any

flexible sheet such as paper or plastic film which transmits infrared radiation.

Likewise any suitable source rich in infrared radiation may be used such as infrared lamps, carbon arc lamps, photoflash bulbs and the like. It is in most cases convenient to use a suitable apparatus such as a Thermo-Fax machine or a flat bed apparatus.

Variations and modifications may be made within the scope of the claims and portions of the improvements may be used without others.

I claim:

1. In the thermographic process for copying infrared radiation-absorbing images comprising the steps of applying infrared radiation-absorbing images to an original sheet, superposing the original sheet, a copy sheet and a transfer sheet carrying a layer of heat-transferable composition which does not absorb infrared radiation, the surface of the copy sheet being in contact with said layer, and applying sufficient infrared radiation for a sufficient period of time to heat the original images and cause the corresponding areas of the transfer layer to transfer to the copy sheet, the improvement which comprises applying the infrared radiation-absorbing images to the original sheet by superposing the original sheet with the pressure-transferable layer of a transfer sheet and applying imaging pressure thereto to effect transfer of infrared radiation-absorbing images to the original sheet, said pressure-transferable layer consisting of a resinous composition which absorbs infrared radiation to a predetermined substantial degree and comprising less than 50% by weight of a thermoplastic resinous binder material and over 50% by weight of an extender having surface porosity to absorb sufficient amounts of the binder material to render the composition resistant to becoming melted or tacky at the temperature generated by the absorbed infrared radiation, whereby the original images can be exposed to excess amounts of infrared radiation for prolonged periods of time without melting or adhering to elements in contact therewith.

2. The method according to claim 1 in which the resinous composition absorbs radiation to such degree because of the presence of a porous carbonaceous pigment which comprises at least 10% by weight of the resinous composition and also functions as at least a portion of the extender.

3. The method according to claim 1 in which the said resinous binder material comprises a cellulosic resin.

4. The method according to claim 1 in which the said extender is clay.

5. The method according to claim 1 in which the extender is present in a weight which is at least three times greater than the weight of the binder material.

6. The method according to claim 1 in which the original sheet also carries infrared radiation-absorbing printed images.

7. The method according to claim 1 in which the said layer of heat-transferable composition is a hectograph composition and the said copy sheet is a hectograph master sheet.

8. The method according to claim 1 in which the said layer of heat-transferable composition is an oleophilic composition and the said copy sheet is a planographic printing plate.

9. The method according to claim 1 in which the said layer of heat-transferable composition is based upon a resinous binder material and becomes tacky but unmelted in the heated image areas.

10. The method according to claim 1 in which the original sheet carries a layer of resinous composition which does not absorb infrared radiation and which is receptive to said infrared radiation-absorbing images and which does not melt or become tacky at the temperatures generated by exposure to infrared radiation.

References Cited

UNITED STATES PATENTS

3,122,998 3/1964 Raczynski et al. ____ 101—149.2

DAVID KLEIN, *Primary Examiner.*

ROBERT E. PULFREY, *Examiner.*

J. A. BELL, *Assistant Examiner.*