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DUPLICATION WITH HEAT-MELTABLE SOLVENT
FOR HECTOGRAPHIC COLORING MATERIAL
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Fig. 1

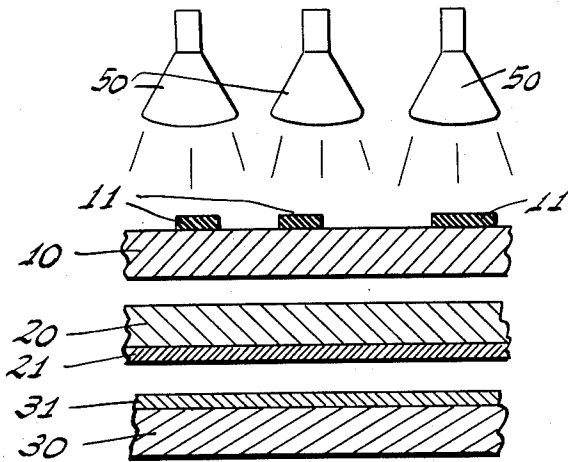
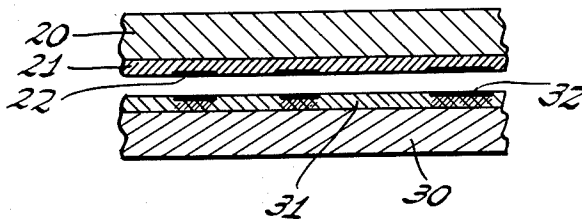


Fig. 2



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DUPLICATION WITH HEAT-MELTABLE SOLVENT FOR HECTOGRAPHIC COLORING MATERIAL

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6 Claims. (Cl. 250—65)

This invention relates to the process of imaging copy 10 sheets having thereon normally solid coatings comprising heat-meltable material which in its melted form is a solvent for hectograph coloring material by means of heat.

Heretofore hectograph copies have been made by re- 15 production processes which have been carried out by systems generally referred to in the art as either the gelatin system or as the spirit duplicating system. In the gelatin system, a master sheet is imaged by typing, writing or otherwise inscribing with an ink composition including a water-soluble dye. This image is then transferred in reverse from the master by absorption during contact against a gelatin layer. The water-soluble dyestuff is then transferred from the moist gelatin layer to a super- 20 positioned copy sheet impressed on the imaged gelatin printing medium.

In prior known spirit duplicating systems, the image is formed on the master by transfer from a carbon type sheet coated with a composition containing a high pro- 25 portion of a spirit-soluble or water- and spirit-soluble dye. The image on the master is then partially dissolved and transferred from the master to successive copy sheets, the surfaces of the copy sheets having been wetted with an alcohol or an alcohol and water fluid. This image reproduction on the copy sheet is effected by contacting the fluid dampened surface of the copy sheet with the imaged surface of the master sheet while processing the thus assembled sheets between the compression cylin- 30 ders of a rotary duplicating machine. In this spirit duplicating system, the image is formed on the master generally in mirror reverse, in order to produce a direct reading copy when reproduced on the copy sheet.

These known hectograph processes have numerous disadvantages which make their use impractical where it is desired to produce only a few copies. For instance, since the master sheet must be imaged manually, it is just as simple to type the desired copies in duplicate rather than employ the hectograph duplicating process.

It is an object of this invention to avoid these and other shortcomings of the prior known spirit duplicating systems, and this is accomplished by providing a dry hecto- 35 graph printing process.

It is another object of this invention to provide for the imaging of novel copy sheets with a hectograph dye transfer sheet through the use of infrared radiation in the absence of any hectograph master sheet and in the absence of the usual spirit duplicating fluids.

It is another object of the present invention to provide for the imaging of novel copy sheets by complementary chemical reagents through the use of infrared radiation and in the absence of imaging pressures.

It is a still further object of the present invention to provide for the automatic imaging of a copy sheet directly corresponding to an imaged original sheet and in the absence of combustible volatile solvents.

These and other objects are accomplished in the manners hereinafter described.

The most important feature of the present invention is the novel method of preparing duplicate copies of an original sheet without the necessity of first preparing a hectograph master sheet, and without the necessity of 40

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employing solvents as required by the known spirit duplicating processes.

Other features and advantages will hereinafter appear.

In the accompanying drawing:

FIGURE 1 is a fragmentary sectional view showing an original sheet, a transfer sheet bearing a layer containing coloring matter, and a copy sheet bearing a layer of heat-fusible solvent material, said sheets being superposed under the influence of radiation but being shown out of contact for purposes of clarifying the illustration.

FIG. 2 is a fragmentary sectional view of the transfer and copy sheets of FIG. 1 after irradiation and separation of the sheets, demonstrating the imaged areas on the copy sheet and the affected portions of the transfer sheet.

As illustrated by the drawings, the present invention is concerned with a method of selectively activating certain portions of a heat-fusible solvent layer 31 of a copy sheet 30 so that only those portions which are fused and melted function as active solvents for a color donor layer 21 of a transfer sheet 20 in contact therewith. The selective activation is accomplished through the use of infrared radiation 50 and an original sheet 10 bearing images 11 comprising infrared radiation-absorbing material.

In this manner, when infrared radiation is applied against the original it is absorbed by the images thereon and converted to heat. This heat pattern, corresponding to the images on the original sheet, penetrates to the copy sheet, the coating of which becomes melted in the heated areas. The coating on the copy sheet, in its melted liquid state, is a solvent for the coloring matter of the transfer sheet and thereby dissolves this coloring matter from the transfer sheet in areas corresponding to the imaged areas of the original sheet to form a true copy thereof. This procedure may be repeated as many times as necessary, using the same transfer sheet, to produce as many copies as may be desired. It should be made clear at this point that the order of sheets shown in the drawing may be changed where desired. For instance, if an original sheet is to be duplicated but it has imaging on both sides, then it is preferred to place such original sheet on the bottom under the copy sheet with the surface to be duplicated facing the copy sheet. Also in some instances where it is desired to have a convenient self-duplicating transfer sheet which may be copied from time to time, then the original sheet may be omitted and the infrared radiation-absorbing images may be present on the transfer sheet on the side opposite the color-forming layer.

The present invention involves the use of a copy paper free of imaging pigment or dyestuff comprising a paper sheet coated on its printing side with a heat modifiable, heat softenable or a low melting point solid, which when heated softens and becomes variously otherwise modified into a state in which it is a solvent for the coloring material used on the transfer sheet. Any one of a number of fusible solids such as the solid alcohols, fatty acids or esters may be employed for the coating on the copy paper, the essential requirement being that when they are heat-activated they are solvents for the coloring material on the transfer sheet. Examples of materials which may be used are solid alcohols such as cetyl, myristyl and stearyl; solid fatty acids such as stearic, palmitic, lauric and capric; solid esters of various glycols and of organic acids; and solid glycol ethers such as the polyethylene- and polypropylene-glycol ethers. By the term "coating" as used herein is meant a superficial film of heat-modifiable solid material, the major part of which impregnates the paper foundation and is held below the surface thereof. Such 70

coating is applied in an amount just sufficient to wet the surface of the copy sheets and insufficient to result in the formation of a separate frangible layer on the surface of the sheet. It is important to the present process that the coating on the copy sheets be non-transferable to the transfer sheet under the effects of heat or pressure in that such transfer would frustrate any attempt to image the copy sheets and would also result in contamination and destruction of the transfer sheet.

The non-transferability of the copy sheet coatings of the present invention is effected by controlling the amount of heat-modifiable solid material which is applied to the paper foundation. As will be understood by those skilled in the art, various grades of paper have different degrees of absorbency. Thus a heavy coating may be applied to rough paper stock and will be absorbed thereby while the same amount of coating will form a pressure-transferable layer if applied to high grade or sized paper. The surface of any paper sheet, under magnification, is toothy and shows the presence of fibers, rough spots, interstices and high and low spots. As indicated supra, the degree of roughness depends upon the type and quality of the paper and whether it is sized or otherwise treated. If one wishes to apply a pressure-transfer layer to a paper foundation, it is well-recognized that a certain amount of the transfer material is lost or wasted due to impregnation by the paper sheet and saturation of the surface rough spots and interstices. Such impregnation and saturation is necessary to provide tooth for the transfer coating but, however, the amount of material used up for these purposes is firmly held by the foundation sheet and is not transferable under pressure. Only that amount of the coating, beyond that held by interfacial attraction, is pressure-transferable.

According to the present invention, only that amount of coating material is applied which is necessary to fill the surface interstices and to wet the fibers and form a very thin but continuous film on the paper foundation. Such film is substantially non-transferable in that it is firmly attached to the surface fibers and rough spots. In other words, a given amount of coating must be consumed in wetting and filling the surface inconsistencies of a paper sheet and it is that amount which is workable for producing copies in the present heat process. Just enough material is applied so that there is no transfer to and contamination of the master sheet, but enough material is applied to afford a continuous developing layer on the surface of the paper foundation.

It is also important that the coating on the copy sheets softens and melts at a temperature within the range of approximately 90° to about 150° F. which is the temperature range of the present process. Lower melting coatings tend to tackify at room temperatures causing sticking of the stored copy sheets, while coatings having melting temperatures in excess of about 150° F. are exceedingly hard and resist melting and prevent imaging of the copy sheets.

Besides the above-mentioned fusible or otherwise modified solids, still other compositions may be used for coating a copy sheet. Thus a composition including a low-melting wax which in itself is not a dye solvent for the dye in the master image but which wax includes admixed therewith a substantial amount of a dye solvent may be used as such a copy sheet coating. Then when the copy sheet and the film forming the coating thereon is heated above atmospheric or room temperature, the composition softens. The solubility of the said composition in its softened and modified state will then be effective to dissolve sufficient coloring matter from the imaged master to form a legible copy. An example of such a coating can be prepared by mixing together equal parts by weight of a wax such as microcrystalline wax or beeswax and a liquid solvent or developer such as oleic acid, octadecyl alcohol or ethylene glycol, melting the

mixture and coating it on a sheet of copy paper to form such a film.

When the duplication is to be effected, the normally and comparatively solid (at room temperature) coating on the copy sheet is modified or softened and if necessary even melted by a suitable infrared radiation source such as infrared lamp bank 50 and the modified coating becomes a solvent for the coloring matter present on the transfer sheet. Thus by subjecting the original sheet, the copy sheet and its immediately contiguous transfer sheet to infrared radiation and sufficient pressure to maintain intimate contact therebetween, the contact of the normally solid but now selectively modified solvent on the copying surface of the copy sheet with the layer on the surface of the transfer sheet containing coloring matter dissolves some of the coloring matter from the transfer layer to reproduce the desired copy.

The source of infrared radiation is not critical although the use of an infrared radiation lamp is generally preferred, particularly when incorporated in a convenient apparatus such as the Thermofax machine or conventional flat-bed apparatus. The length of exposure time, of course, depends upon the strength and proximity of the radiation source but, in general, exposure is continued only long enough to provide for a heat generation in the imaged areas of the original sheet sufficiently high to melt the solvent layer on the copy sheet in the corresponding areas, generally between about two and ten seconds. Thus temperatures within the range of about 100° F. to about 200° F. are preferred.

According to the present invention, the layer on the transfer sheet comprises a conventional hectograph dye-stuff, preferably carried by a suitable binder such as wax or ethyl cellulose, the dyestuff being one which absorbs substantially no infrared radiation. Suitable dyestuffs include conventional hectograph dyestuffs from the tri-arylmethane, safranin and rhodamine families. It should be understood, however, that the transfer layer does not transfer bodily to the copy sheet in the present process, due mainly to the fact that the melted surface on the copy sheet is not receptive to the transfer layer. Secondly, the radiation necessary to melt the copy sheet coating is generally much less than that necessary to melt the transfer layer of a hectograph transfer sheet. Although conventional hectograph transfer sheets may be employed in the present process, it should be understood that much thinner dye layers may be used, with or without a wax binder. Also, other known resinous binders may be substituted for the wax such as the cellulosic resins and the vinyl resins. It is generally preferred, though not necessary, that the binder for the dyestuff also be at least partly soluble in the melted solvent of the copy sheet.

Also, substantially colorless conventional complementary chemical color formers may be employed in place of hectograph dyestuffs. For instance, the transfer sheet may contain one color-forming chemical such as an organic acid, such as gallic or tannic acid; a thiocyanate derivative such as the potassium, ammonium or sodium salts, trimethyl thiocyanate or tolyl thiocyanate; or a sodium, potassium or ammonium salt of ferrocyanide or ferricyanide; etc., while the heat-fusible copy sheet contains the corresponding chemical which when brought into liquid contact with the chemical of the master sheet reacts therewith to form a sharp colored image on the copy sheet. The corresponding chemical on the copy sheets may be an iron salt such as ferric chloride, ferric ammonium sulfate or iron benzoate, etc.; a copper salt such as cupric chloride, copper acetate or cupric potassium sulfate, etc.; and the corresponding salts of manganese, lead, silver, mercury, nickel and others well known to the art. In this embodiment, the heat-fusible solid material on the copy sheets liquefies under heat and appears to function in a twofold manner. In the first place, it melts in areas corresponding to the imaged areas of the original sheet and absorbs and dissolves some of the

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chemical from the transfer master sheet in these areas; secondly, it serves as a liquid reaction medium for the complementary chemical reagents, namely the chemical originally present on the copy sheets and the chemical dissolved and absorbed from the transfer sheet, thereby causing the chemicals to react and form a sharp colored copy corresponding to the imaged areas of the original sheet. To aid in the reaction it is preferred to have a humectant present on the copy sheets, which absorbs humidity and renders the chemicals more completely ionically available for reaction. Materials such as ethylene glycol and the Carbowaxes function particularly well as humectants.

Other variations using complementary chemical reagents may be employed. For instance both chemicals may be present on either the fusible copy sheet or the transfer sheet in substantially colorless unreacted form. The corresponding transfer or fusible copy sheet is provided with an acidic or alkaline catalyst which, when contacted in liquid form with the chemical reagents on the corresponding sheet, causes them to react and form colored images in the preselected areas corresponding to the imaged areas of the original sheet.

The fused, melted or otherwise heat modified coating almost immediately after forming the duplicate copy from the master sheet solidifies or returns to its normal and comparatively solid state and readily separates from its contiguous transfer sheet.

In preparing the copy sheets of this invention, one of the preferred coatings of the heat modifiable or meltable kind for the copy sheets has a plasticizing agent included therein. Such a coating when subjected to heat causes the solvent to ooze out over the coated surface. A specific example of such a coating mixture would be made up of equal parts by weight of dibutyl phthalate and cetyl alcohol coated on the surface or impregnated into the copy sheet web. When subjected to heat the solvent migrates to the surface and when contacted with the transfer sheet produces a legible copy by dissolving and absorbing coloring matter therefrom.

After being subjected to sufficient radiation and sufficient pressure to maintain intimate contact between the original, transfer and copy sheets, the completed copy cools down to room temperature, and the heat modified portions of the coating on the copy sheet almost immediately return to their original unmodified state to produce a copy of the imaged original sheet. Thereafter other copy sheets can be continuously processed in a similar manner using the same transfer sheet until the desired number of copies is produced.

The copy sheet of this invention may be made by several diverse methods. For example, the normally solid and heat modifiable solvent may be melted and coated on the web of paper from which the copy sheets are made by hot rolling methods. Alternatively, some of the normally solid and heat modifiable solvent materials, such as the solid alcohols, may be dissolved in suitable volatile solvents and applied to the copy paper by any one of a number of conventional coating methods such as hot melt, emulsion coatings, spraying solvent coatings, dusting and fusing coatings or other means. Thus, for example, by blending granules of the normally solid meltable solvent and dispersing the resultant fine granular materials in a water emulsion and coating the emulsion onto the copy paper, evaporation of the aqueous vehicle leaves a coating suitable for carrying out the process of this invention. The amount of coating applied is generally quite small and only sufficient to wet the surface of the copy sheets. Upon setting or drying, the coating is nearly entirely absorbed by the copy sheets which become impregnated in this manner. The use of an excess amount of coating material is to be avoided in that it remains on the copy sheet surface as a frangible, transferable layer which tends to become mushy during use and contaminate the transfer sheet.

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A number of coating compositions embodying heat modifiable or meltable materials may be coated onto the copy sheet 30. These coatings are such as fuse, otherwise modify or may even become liquid in areas subjected to the increased temperature of the process of this invention and in this modified or fused, or even liquid state, have the necessary dye or chemical solvency to reproduce record data on the surface of copy sheets where selectively heated by infrared lamps while in contact with a dye- or chemical-containing transfer sheet.

The following examples of coating mixtures suitable for use on the copy sheet are merely illustrative and not to be understood as limitative embodiments:

Example I

(Molten state coating)

	Parts by weight
Stearic acid.....	75.0
Cetyl alcohol.....	25.0
	100.0

Example II

(Molten state coating)

Carbowax 4000 (solid polyethylene glycol polymer having an average molecular weight between 3000 and 3700).....	70.0
Colloidal clay.....	30.0
	100.0

Example III

(Water dispersible binder)

Water	100.0
Carboxymethyl cellulose (medium viscosity).....	3.0
Carbowax 4000.....	10.0
	113.0

Example IV

(Emulsion type)

Stearic acid.....	12.0
Oleic acid.....	12.0
Triethanolamine	1.2
Hot water.....	165.0
	190.2

Example V

(Solvent type)

Rosin (wood rosin).....	12.0
Tricresyl phosphate.....	3.0
Ethyl acetate.....	80.0
Colloidal clay.....	5.0
	100.0

Example VI

(Molten state coating)

Carbowax 4000.....	50.0
Colloidal clay.....	20.0
Copper sulfate.....	30.0
	100.0

From the above examples, it is to be noted that several types of coatings can be used to produce the copy sheets. In Examples I, II and VI above, the fusible material itself is hot roll coated or knife coated and absorbed in the molten state by the surface of a web of paper from which the copy sheets are formed. In still another example, a suitable meltable solid dissolved in a volatile solvent is coated on the copy sheet and evaporation of the volatile solvent results in a heat modifiable film containing the solvent for the chemical or dye being absorbed by the copy sheet.

In Examples III and IV, the solid material is held as dispersed particles in a fluid film former such as casein, carboxymethyl cellulose, starch, polyvinyl alcohol or any

water-dispersible colloid such as is commonly used in the paper industry. In the latter case, the solid material is preferably present in discrete particulate form, the particles of which fuse and melt together when subjected to heat as herein described to effect impregnation of the copy sheets and reproduction in accordance with the disclosure herein made.

In Example V, a natural rosin or synthetic resin of similar properties modified with a suitable plasticizer such as castor oil or tricresyl phosphate or the like is dissolved in a suitable solvent such as ethyl acetate and coated on a copy sheet. The evaporation of the solvent leaves the absorbed film having the desirable properties of this invention.

Example VI shows the use of a copper sulfate on the copy sheet. It should be understood that any of the aforementioned copy sheet complementary chemical reagents may be substituted in place thereof, preferably in an amount ranging from about 20-40% by weight, based upon the total weight of the coating composition.

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

This application is a continuation-in-part of application Serial No. 791,770, filed February 6, 1959, now abandoned, and application Serial No. 9,049, filed February 16, 1960.

I claim:

1. The process of preparing duplicate copies of imaged subject matter containing infrared radiation-absorbing material which comprises superposing said imaged subject matter together with a transfer sheet having a layer comprising color-forming material and a copy sheet having a normally solid coating thereon comprising heat-meltable material which, in its melted form, is a solvent for the color-forming material of the transfer sheet, and subjecting the superposed sheets to infrared radiation for a period of time sufficient to cause the solid coating of the copy sheet to melt in areas corresponding to said imaged subject matter and thereby dissolve and absorb color-forming material from the layer of the transfer sheet to produce a duplicate copy of said imaged subject matter.

2. The process of preparing duplicate copies of an imaged original sheet by means of infrared radiation which comprises superposing the original sheet bearing images containing infrared radiation-absorbing material, a transfer sheet having a layer comprising hectograph dyestuff, and a copy sheet having a solid coating thereon comprising heat-meltable material which, in its melted form, is a solvent for the dyestuff of the transfer sheet, and subjecting the superposed sheets to infrared radiation for a period of time sufficient to cause the solid coating of the copy sheet to melt in areas corresponding to the imaged areas of the original sheet and thereby dissolve and absorb dyestuff from the transfer sheet to produce a duplicate copy of said original sheet.

3. The process of preparing duplicate copies of an imaged original sheet by means of infrared radiation which comprises superposing the original sheet bearing images containing infrared radiation-absorbing material, a transfer sheet having a layer comprising a substantially colorless color-forming chemical compound, and a copy sheet having a normally solid coating thereon comprising heat-meltable material which, in its melted form, is a solvent for the chemical compound of the transfer sheet, and which contains a different substantially colorless chemical compound which is reactive with said color-forming

chemical compound upon contact to form a colored reaction product, and subjecting the superposed sheets of infrared radiation for a period of time sufficient to cause the solid coating of the copy sheet to melt in areas corresponding to the imaged areas of the original sheet and thereby dissolve and absorb said color-forming chemical compound from the transfer sheet to produce a duplicate copy of said original sheet.

4. The process of preparing duplicate copies of an imaged original sheet by means of infrared radiation which comprises superposing the original sheet bearing images containing infrared radiation-absorbing material, a transfer sheet having a layer comprising hectograph dyestuff, and a copy sheet having a solid coating thereon comprising a heat-meltable material selected from the group consisting of alcohols, fatty acids, esters and ethers which, in its melted form, is a solvent for the dyestuff of the transfer sheet, and subjecting the superposed sheets to infrared radiation for a period of time sufficient to cause the solid coating of the copy sheet to melt in areas corresponding to the imaged areas of the original sheet and thereby dissolve and absorb dyestuff from the transfer sheet to produce a duplicate copy of said original sheet.

5. The process of preparing duplicate copies of imaged subject matter containing infrared radiation-absorbing material which comprises superposing said imaged subject matter together with a transfer sheet having a layer comprising a first color-forming chemical compound selected from the group consisting of gallic acids, thiocyanates, ferrocyanides and ferricyanides and a copy sheet having a normally solid coating thereon comprising a heat-meltable material which, in its melted form, is a solvent for the color-forming chemical compound of the transfer sheet and contains a second chemical compound which is reactive with said first chemical compound and is selected from the group consisting of salts of iron, copper, manganese, lead, silver, mercury and nickel, and subjecting the superposed sheets to infrared radiation for a period of time sufficient to cause the solid coating of the copy sheet to melt in areas corresponding to said imaged subject matter and thereby dissolve and absorb said first color-forming chemical compound from the layer of the transfer sheet to react with said second chemical compound on the copy sheet to produce a duplicate copy of said imaged subject matter.

6. The process of imaging a copy sheet having a normally solid coating thereon comprising heat-meltable material which, in its melted form, is a solvent for hectograph coloring material, which process comprises superposing said copy sheet with a second sheet having thereon hectograph coloring material, the coating on the copy sheet being in surface contact with said hectograph coloring material, and applying heat for a period of time sufficient to cause the solid coating of the copy sheet to melt and thereby dissolve and absorb said hectograph coloring material from said second sheet to produce a duplicate copy thereof on said copy sheet.

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