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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Thermographic Process and Materials

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America (Assignees of WILLIAM JAMES DULMAGE, STERLING SCOTT SWEET and WILLIAM ANDRES LIGHT) do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to thermographic processes of document copying and to heat-sensitive materials therefor.

The invention is concerned with the copying of documents of the kind having areas of relatively high infra-red absorption and areas of no or relatively low infra-red absorption.

In one form of the present invention there is provided a thermographic process of making copies of a document of the kind referred to by a transfer process employing a heat sensitive material comprising a flexible support having coated thereon a heat-sensitive layer comprising a polymer in a crystalline form said polymer having in the temperature range from 50° C to 200° C a tackifying point (as herein defined) at which it becomes adhesive and remains adhesive when reduced in temperature below its tackifying point and being transferable to a receiving sheet by pressure thereonto while at said reduced temperature and the material being provided with integral means which regulates the transfer of the heat sensitive layer when in its tacky state at said reduced temperature wherein said material is placed in contact with the document to be copied, exposed to infra-red radiation until a tacky image has been formed in the sensitive layer, then the material is separated from the document and, while still in its tacky state, is pressed against a receiving sheet with sufficient pressure to cause the surface of the tacky areas to adhere thereto

and then the material is separated from the receiving sheet carrying at least a stratum of the tacky areas and if desired the transfer step is repeated on a further receiving sheet or sheets to produce a further copy or copies.

In an alternative form of the present invention there is provided a thermographic process of making copies of a document of the kind referred to by a transfer process employing a heat sensitive material comprising a flexible support having coated thereon a heat sensitive layer comprising an amorphous polymer in admixture with a non-polymeric crystalline substance miscible therewith which melts in the temperature range from 50° C to 200° C and the mixture has a tackifying point (as herein defined) at which it becomes adhesive and remains adhesive when reduced in temperature below its tackifying point and being transferable to a receiving sheet by pressure thereonto while at said reduced temperature and the material being provided with integral means which regulates the transfer of the heat sensitive layer when in its tacky state at said reduced temperature wherein said material is placed in contact with the document to be copied, exposed to infra-red radiation until a tacky image has been formed in the sensitive layer, then the material is separated from the document and, while still in its tacky state, is pressed against a receiving sheet with sufficient pressure to cause the surface of the tacky areas to adhere thereto and then the material is separated from the receiving sheet carrying at least a stratum of the tacky areas and if desired the transfer step is repeated on a further receiving sheet or sheets to produce a further copy or copies.

In the first form of the present invention there is employed a heat-sensitive material comprising a flexible support having coated thereon a heat-sensitive layer comprising a polymer in a crystalline form said polymer having in the temperature range from 50° C to 200° C a tackifying point at which it becomes adhesive and remains adhesive when

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reduced in temperature below its tackifying point and being transferable to a receiving sheet by pressure there onto while at said reduced temperature, the material being provided with integral means which regulates the transfer of the heat sensitive layer when in its tacky state at said reduced temperature.

In the second form of the present invention there is employed a heat-sensitive material comprising a flexible support having coated thereon a heat-sensitive layer comprising an amorphous polymer in admixture with a non-polymeric crystalline substance miscible therewith which melts in the temperature range from 50°C to 200° C and the mixture becomes adhesive and remains adhesive when reduced in temperature below its tackifying point and being transferable to a receiving sheet by pressure thereonto while at said reduced temperature, the material being provided with integral means which regulates the transfer of the heat sensitive layer when in its tacky state at said reduced temperature.

The said regulating means may be for instance, as will be described hereinafter, glass beads in the heat-sensitive layer or an outer porous layer.

The processes of the present invention are a modification of those described and claimed in our Specification No. 1,015,925 (27283/62).

In order to produce directly good visible transfer copies the heat sensitive layers used in the present invention are preferably made with colouring matter incorporated in them.

A crystalline polymeric substance used in the present invention should be one which is crystalline and non-tacky at temperatures below the tackifying point and when heated above the tackifying point becomes amorphous and remains in this state, i.e. without crystallizing, when the temperature of the layer is allowed to fall, for at least a few seconds so that when the material is employed in the aforesaid processes there is time to carry out the transfer.

The tackifying point of a polymer or composition is the temperature at which the polymer or composition becomes tacky when its temperature is raised. By "tacky" we mean that a layer thereof or a stratum of such layer can be transferred by mere pressure on to a receiving sheet.

Generally, the crystalline polymers used in the present invention have a glass transition temperature below the tackifying temperature. The term "glass transition temperature" is used in the sense in which it is used in the polymer art, see for instance, "Textbook of Polymer Chemistry" by F. W. Billmeyer (Interscience Publishers Inc.—New York) 1957, pages 40—45.

Crystalline polymeric heat-sensitive substances which may be used in the present invention and satisfy the aforesaid require-

ments can be found without difficulty among polyhydrocarbons, especially among polyvinyl compounds, polyacrylic compounds, polyesters, polyamides, polyesteramides, polycarbonates, polyethers, polyurethanes and polyureas. Examples of substances are poly(2,2-dimethyltrimethylene succinate) and ~~isotactic~~ poly(isotactic butene-1) and poly(1,4-cyclohexanedimethylene adipate) and poly(pentamethylene carbonate) and poly(1,4-cyclohexanedimethylene adipate - azelate [3:1]).

After thermographic exposure of the heat-sensitive layers used in the present invention, the amorphous condition of the image areas and the attendant properties of tackiness remain until the layer recrystallizes. The crystallization rate is independent of the tackifying point, and glass transition temperature. It varies according to the chemical structure of the polymer, and within the range between glass transition temperature and the tackifying point it increases with temperature through a maximum value. Polymeric compositions with recrystallization times from a few seconds to several hours can be used in the thermographic materials of this invention, according to whether the required copies are to be made rapidly after the exposure and further copies in rapid succession, say in an automatic machine, or more leisurely by hand. For example, the thermographic materials for use in a simple hand operated office document copying thermographic process, should have a recrystallization rate slow enough to permit thermographic exposure, separation of the heat-sensitive element from the original, and the preparation of several copies by pressure transfer without undue haste. In this case a recrystallization time of say 5 to 10 minutes would be suitable.

If the rate of recrystallization causes the image areas to lose their tackiness rapidly, a general heat treatment may be applied. The image and non-image areas at this stage have different tackifying points because the former have been heated by the exposure and the latter have not. The whole element is heated rapidly to a temperature between the tackifying points of the image and non-image portions, e.g., by re-exposing to infra-red radiation without the original but, if desired, in contact with a receiving sheet. This causes the image areas to regain sufficient tackiness for additional transfers to be made whereas the non-image areas remain non-tacky.

The heat-sensitive layers employed in the present invention can be prepared using either crystalline or amorphous polymers chosen from a wide variety of linear, film-forming polymers and copolymers.

The following representative examples of amorphous polymers which can be used in admixture with non-polymeric crystalline substances to prepare the heat-sensitive layers of the present invention:

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isotactic

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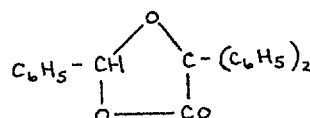
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1. Atactic polystyrene.
2. Poly(vinyl acetate), medium-viscosity grade.
3. Butadiene-styrene copolymer of 45:55 ratio (Goodyear Tire and Rubber Co.'s "Pliolite S-7"). "Pliolite" is a registered trade mark.
4. Poly(alkyl acrylates), low- and medium-viscosity grades, such as polyethyl acrylate, polypropyl acrylate or polybutyl acrylate.
5. Poly(alkyl methacrylates), low- and medium-viscosity grade, such as polymethyl methacrylate, polyethyl methacrylate or polybutyl methacrylate.
6. Poly(terpenes), softening point range 70°—110° C. (Schenectady Resins Co.; Pennsylvania Chemical Co.).
7. Poly(vinyl butyral) and other polyacetals of low-viscosity grade.
8. Cellulose butyrate.
9. Cellulose acetate butyrate, low-viscosity grade.
10. The resin product formed by condensation of polymerised linoleic acid and a diamine (melting at 105° C to 115° C), sold under the trade name Versamide 930 by General Mills.
11. Polyethylene terephthalate, polyethylene isophthalate mixed copolymer of 60:40 ratio (Goodyear Tire and Rubber Co.'s "Vitel PE-101-X").
12. Vinyl chloride, vinyl acetate copolymer of 87:13 ratio (Union Carbide's "Vinylite VYLF").
13. Phenol-formaldehyde resins (noncross-linked) softening point range 70°—110° C. (Union Carbide's "Novolacs"). "Vitel," "Vinylite" are registered trade marks.

The non-polymeric crystalline substances which may be used are compounds which melt in the range of 50° to 200° C. and are miscible with the amorphous polymer. By "miscible" as used herein we mean that they are miscible at the fusion point of the mixture, and on cooling into the range below the fusion point but above the glass transition temperature of the mixture, form an unstable amorphous homogeneous composition exhibiting surface tackiness as long as the temperature remains between the tackifying temperature and the glass transition temperature of the composition and until the crystalline substance recrystallizes. Suitable non-polymeric crystalline substances can be chosen from the following representative examples, the specific composition and the ratio of

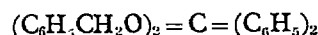
polymer to non-polymeric crystalline substance depending on the properties of the polymer with which it will be admixed, the desired tackifying point and the rate of recrystallization; pentaerythritol tetra-isobutyrate; 2,6-di*tert*.butyl-4-methylphenol; eugenol benzoate; triphenyl orthoformate; benzoin acetate; N - pentyl - 1,8 - naphthalimide; bis(*o*-methoxyphenyl)carbonate; eugenol cinnamate; 2,5,5 - triphenyl - 1,3 - dioxolan - 4 - one; bis - (benzyloxy) diphenylmethane; 4-cyclohexylphenyl benzoate; 4-biphenyl benzoate; pentachlorophenyl benzoate; anthraquinone-2-carboxyl-ethyl; camphor.

2,5,5 - triphenyl 1,3 - dioxolan - 4 - one has the formula:



and

Bis(benzyloxy)diphenylmethane has the formula:



Representative examples of crystalline polymeric substances useful in the present invention are given in Table I below along with the tackifying points and intrinsic viscosities, or in one case the molecular weight. In the table, the letter A indicates a melt-viscosity in the range from 50 to 500 poises, whereas the letter B indicates a melt-viscosity in the range from 500 to 100,000 poises. In Table I the intrinsic viscosity is given as a measure of the degree of polymerization of the polymer. Intrinsic viscosity, accordingly, also is a reflection of the molecular weight of the polymer; that is to say as intrinsic viscosity goes up the molecular weight of the polymer is also higher.

Intrinsic viscosity was measured according to the formula:

$$\text{limit } \frac{\eta_s}{C} \text{ as } C \text{ approaches zero}$$

wherein η_s is the viscosity in a dilute phenol-chlorobenzene-(1:1) solution of the polymer divided by the viscosity of the phenol-chlorobenzene mixture per se measured in the same units at the same temperature, and C is the concentration in grams of the polymer per 100 cc. of solution.

TABLE I

Heat-Sensitive Component	Tackifying Point (°C.)	Melt Viscosity at Tackifying Point	Intrinsic Viscosity
Poly(butene-1)	96	B	0.24
Poly(pentene-1)	80	B	0.26
Poly(tert-butyl acrylate)	197	B	0.58
Poly(tetramethylene carbonate)	60	B	0.66
Poly(pentamethylene carbonate)	72	B	0.66
Poly(2,2-dimethyltrimethylene succinate)	78	A	0.29
	80	B	0.35
	82	B	0.45
Poly(1,4-cyclohexane-dimethylene succinate)	120	A	0.24
Poly(1,4-cyclohexanedimethylene adipate), Sample I.	115	A	0.30
Poly(1,4-cyclohexane-dimethylene adipate), Sample II.	115	B	0.45
Poly(ethylene succinate)	100—102	B	0.40
Poly(nonamethylene succinate)	65	A	0.39
Poly(pentamethylene terephthalate)	136—139	B	0.52
Poly(ethylene 1,4-cyclohexanedicarboxylate)	165—171	A	0.30
Poly(ethylene glycol) (6000—7500, mol wt.)	60—63	A	

5 In order to coat a heat-sensitive layer used in the present invention, the heat-sensitive composition to be employed is dispersed or dissolved in a suitable solvent, usually a hydrocarbon or chlorohydrocarbon such as benzene, toluene, methylene chloride, ethylene chloride or carbon tetrachloride, or a ketone such as acetone, 2-butanone, or 4-methyl-2-pentanone, or a mixture thereof, and coated in any well-known manner on a support such as a paper or film, for instance such as cellulose acetate or polyethylene terephthalate. Substances may be included in the heat-sensitive layer to decrease the amount of polymer or modify the surface or bulk of the heat-sensitive layer or for modifying the flexibility of the layer or its adhesion to the support or for preventing too close contact (often referred to as optical contact) when the finished layer is

pressed in contact with a document. Examples of such additional substances are:— tricresyl phosphate, poly(alkyl acrylates), dibutyl fumarate, menthol, diethyl phthalate, eugenol, isoeugenol, dibutyl phthalate, eugenol methyl ether, isoeugenol methyl ether, clay, glass beads, crosslinked poly(methyl methacrylate) beads, ground quartz, titanium dioxide, zinc oxide.

Colouring matters, when incorporated in the heat-sensitive layer should be those which do not unduly absorb infra-red radiation such as those in the following list where the second and third columns give the names in Part I of the new Colour Index and the numbers in Part II thereof where available. The colour index is published jointly by the Society of Dyers & Colourists and the American Chemical Society.

	Part I	Part II
	New C. I.	New C. I.
Azo Oil Black	Solvent Black 12	
Azo Oil Blue Black B	Solvent Black 12	
Oil Black BT	Solvent Black 3	26150
Alizarin Blue G. R. L.	Solvent Blue 12	62100
Oil Scarlet 6G	Solvent Orange 7	26150
Oil Red O	Solvent Red 27	12140
Oil Orange 2311	Solvent Yellow 14	12055
Iosol Black	Solvent Black 13	

The heat-sensitive layer may be formed in one or more coats. For most purposes a total finished thickness of 0.05 to 1.0 mil (1.25 to 25 microns) is required, but preferably 0.1 to 0.3 mil (2.5 to 7.5 microns).

In the preparation of the heat-sensitive materials of the present invention, particularly those where the heat-sensitive layer is formed from crystalline polymers, crystallization can be promoted in many ways, for instance it is sometimes advantageous to "anneal" the layer after coating, by holding the layer at a temperature well above the glass transition temperature of the polymeric composition but below the initial tackifying temperature of the composition from a few minutes to several hours depending upon the composition involved. The process of annealing appears to have the effect of ripening the crystals to perfect the crystalline phase, although, the mechanism is not clearly understood. Raising the annealing temperature and prolonged annealing also increases the tackifying temperature for the crystalline composition. Since the temperature range between the glass transition temperature and the tackifying temperature for many of the compositions of the present invention, is broad, annealing can usually be carried out during manufacture, for example, while the coated materials are being cut into sheets or wound into rolls.

The heat-annealing process can be used to reclaim "used," that is exposed, matrices from which the number of prior transfers made was sufficiently small not to have removed all of the heat-sensitive coating in the image-areas. By reannealing this coating, the exposed areas slowly recrystallize to their initial crystalline state, i.e., become identical to the background areas, and the whole matrix can then be put to use exactly as a new (unused) matrix.

The infra-red exposure of the heat-sensitive layer to the document to be copied may be made in any of the usual ways. For most of the transfer processes the document is placed with its characters or lines in contact with the layer and the exposure is made through the layer support, as illustrated in most of the Examples given hereinafter. However the ex-

posure may be made with the support side of the heat-sensitive element against the characters of the document, or with the support side of the document against the heat-sensitive layer and in the latter case the exposure is made through the document. Of course when the exposing rays pass through the layer support this support must be infra-red transparent, but otherwise it need not be infra-red transparent.

After the image-wise exposure the transfer of the tacky areas to a receiving sheet can be accomplished by using sufficient contact pressure. Calender rolls may be used to provide the necessary contact pressure. These rolls may be heated in order to raise the temperature of the heat-sensitive element during transfer, thereby to facilitate the transfer. Transfer can be effected by feeding the activated heat-sensitive element, and a receiving sheet in contact with the heat-sensitive layer, through the nip of calender rolls.

If a reflex exposure is to be made, the melt viscosity of the heat-sensitive material should preferably be above 200 poises at the activation temperature and transferred to a receiving sheet by calendering the heat-sensitive element in contact with the receiving sheet through steel rolls having a nip pressure of at least 50 pounds per linear inch.

The means for regulating the amount of material transferred from the heat-exposed layer prevents excessive flow of the composition to the receiving surface during the transfer step, thus conserving it in the matrix for producing more additional copies from a single heat-sensitive layer. This is the more important the lower the melt viscosity. Because the flow is attenuated while the first copies are being made, heavier coats of the sensitive composition can be used without causing excessive transfer while making the first copies. Thus, with heavier heat-sensitive coatings, even more copies are possible from a single heat-sensitive material. Further, the separation of the matrix from the transfer surface after the transfer step is usually facilitated. One useful means is to incorporate in the layer glass beads or other particles of an average diameter or size greater than the

thickness of the heat-sensitive layer such that they will extend outward from the heat-sensitive layer above the surface of the layer.

5 Another and preferred regulating means is to provide a porous, outer layer which is non-thermoplastic at the tackifying temperature of the heat-sensitive layer underneath. This outer layer should be sufficiently thin and porous that at the contact pressures used
10 for the transfer step, the tackified viscous composition of the image areas can permeate the porous outer layer and be transferred to the receiving surface.

By incorporating solid particles, as indicated above, such as glass beads having diameters from 18 to 40 microns, in the heat-sensitive layer, the maximum coating rate can be for instance 0.8—1.1 grams per square foot.

20 A preferred outer porous layer for regulating the transfer comprises a continuous porous layer of polyvinyl alcohol (PVA) overlying the heat-sensitive layer. Such a layer can be coated from an aqueous solution. The porosity of the layer can be chosen to accommodate any of a wide variety of transfer compositions. When employing such a porous outer coating, the heat-sensitive layer is preferably of low melt viscosity material and
25 can be coated to give a finished layer of between 1.5 and 3.0 grams per square foot without causing excessive transfer to first copies. For low viscosity compositions less transfer pressure is needed than for transfer of more viscous compositions.
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35 The necessary porous structure in a polyvinyl alcohol coating is preferably obtained by adding to the coating solution a pore-forming agent, either a metal salt or a surfactant, and preferably both a salt and a surfactant. When a salt is used one may employ up to 60 parts by weight per 100 parts by weight of PVA so long as it does not cause precipitation of the PVA. Usually
40 the amount of surfactant may be up to 3% of the weight of the coating solution.

Fine grain insoluble particles, for example zinc oxide, colloidal silica, titanium dioxide, zirconium dioxide and clays, may be mixed in the porous coating mixture prior to coating. Such substances may be present in amounts up to 10% by weight based on the weight of polyvinyl alcohol, preferably between 5 and 8 1/2%.
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55 The porous structure may be improved by heating the matrix, say to, from 35° F to 75° F as soon as the coating solution has been applied over the heat-sensitive layer.

60 The polyvinyl alcohol composition used for the porous layer may comprise an aqueous solution of 87% hydrolyzed polyvinyl alcohol, namely polyvinyl alcohol made by hydrolysing 87% by weight of the acetate groups of polyvinyl acetate. Other aqueous solutions of polyvinyl alcohol can be used, for instance
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solutions with other volatile surfactants, e.g., methanol, provided they do not attack the heat-sensitive composition during the coating process. The total solids content of the coating solution, including PVA, salt, and insoluble particles is preferably in the range from 5%—9% by weight, based on the total weight of the solution. The remainder consists essentially of solvent.

70 Metal salts which are soluble in the solvent medium can be used as pore-forming agents in the coating solution, for instance, such salts as Na_3PO_4 , Na_2HPO_4 , $\text{KAl}(\text{SO}_4)_2$, and NaCO_3CH_3 . Any of a wide variety of commercially available surface active agents can be used in the coating solution, for example, Aerosol 22, sold by American Cyanamide Company.

75 In order to obtain a good porous structure in the polyvinyl alcohol layer it is preferable that the temperature of the coating solution be raised immediately upon application of the coating solution over the heat-sensitive layer, and held at the raised temperature until the desired porous structure has formed and the coating has dried. This raised temperature which varies depending upon the composition of the solution will in most instances be in the range from 35° to 75° F.

80 The preferred coating density for the porous overcoating layer is in the range from 0.3 to 1.0 gram per square foot, for example 0.7 gram per square foot, when dried.

85 The porous outer layer may range in thickness from 0.0001 inch to 0.002 inch thick and the individual pores may comprise from 25 to 75% of the total area. The openings are preferably evenly distributed over the matrix but some random fluctuation in distribution and size is permissible. The optimum average size of the pores will vary depending on the viscosity of the heat-sensitive composition and the conditions to be used for exposure and transfer. Generally, optimum average pore size will range from 0.1 micron to 500 microns preferably from 1 to 50 microns.
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95 Examples of other porous outer layers which may be used are perforated or porous thin layers of cellulose esters, polyesters, polyamides, polycarbonates, papers, felted webs, woven fabrics and metal.

EXAMPLE 1.

A heat-sensitive material was prepared as follows.

100 Seven grams of a heat-sensitive polymer, namely poly(1,4 - cyclohexanedimethyl succinate), having an inherent viscosity of 0.24 and a tackifying point of 120° C., was added to 30 grams of an ethylene chloride solution containing 1 gram of Azo Oil Blue Black B dye (purchased from the Allied Chemical and Dye Corporation). To the above was added a solid particle extender in the form of 2 grams of glass beads having an average
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diameter in the range from 18 to 40 microns. The resulting mixture was heated to 60° C. and then coated on a glassine support at a 3-mil (75 microns) thickness. After removal of the solvent from the coating by drying, the element was annealed at 100° C. for 40 minutes. The final coating thickness was 0.3 mil (7.5 microns) and contained 0.9 gram of solids per square foot.

The resulting thermographic material was placed in contact with an original document so that the heat-sensitive layer of said material was in contact with the graphic portions of the original. The 2-ply assembly was then exposed to infra-red radiation through the support side of said material. The exposure produced tacky areas in said material corresponding to the image areas in the original. After the exposure, the original and the heat-sensitive material were separated.

The heat-sensitive material having tackiness in the image areas was then passed with a receiving sheet between pressure rollers exerting 30 pounds per linear inch of roller length and having a roller diameter of 2 1/2 inches. In this pressure transfer, the coated side of the heat-sensitive material was in contact with a receiving sheet of highly absorbent wet-strength paper. The transfer produced good blue-black image reproduction of the original on the receiving sheet. By repeating the transfer step with further receiving sheets, several high quality copies of the original were thus produced from the single thermographic exposure. The time which elapsed between the production of these several copies was one minute.

EXAMPLE 2.

8.5 grams of isotactic poly(butene-1) having an inherent viscosity of 0.24 and a tackifying point of 96° C. was dissolved in 50 grams of methylene chloride containing 0.5 gram of Oil Black BT dye and 0.5 gram of glass beads having an average diameter of 18 to 40 microns. This mixture was then coated at a wet thickness of 3 mils (75 microns) on a strip of a smooth light weight Transparent Copy Greaseproof Paper. After the solvent was removed from the coating by drying, the layer, which was approximately 7.5 microns thick, was annealed for 18 hours at 75° C. The resulting heat-sensitive material was exposed in contact with an original document as in Example 1. The layer containing the tacky areas thus produced by the exposure were then pressed in contact with successive receiving sheets of paper as in Example 1 to produce several copies from a single exposure of the heat-sensitive material.

EXAMPLE 3.

A heat-sensitive material with a rapid rate of recrystallization was prepared as follows.

To 20.3 grams of a heat-sensitive polymer, poly(1,4-cyclohexanedimethylene adipate) hav-

ing an inherent viscosity of 0.36 and a tackifying point of 115° C., in 75 grams of ethylene chloride, were added 1.25 grams of Azo Blue Black B dye, 2.5 grams of glass-beads (18—40 microns), and 1 gram of poly(ethyl acrylate) as flexibilizer. The resulting dispersion was coated on a smooth light weight paper as used in Example 2. After coating, the layer was dried to yield a coating of 0.9 grams per square foot and thickness approximately 8 microns. After drying, the layer was annealed for one hour at 80° C.

After annealing, the resulting thermographic material was placed in contact with an original document and the 2-ply assembly was then exposed and after separation the tacky image areas were transferred rapidly to a receiving sheet. The transfer operation was begun within 3 to 5 seconds after exposure and completed within the subsequent 5 to 7 seconds. A copy of excellent quality was obtained.

EXAMPLE 4.

A heat-sensitive material was prepared by the addition of 57 grams of the condensation product of polymerized linoleic acid and a diamine (sold under the trade name Versamide 930 by General Mills), 133 grams of bis-(*o*-methoxyphenyl) carbonate, 47 grams of *n*-dodecyl-amine and 12 grams of glass beads (18—40 microns), to 51 grams of isopropanol and 700 grams of benzene. The polymer of said composition had a tackifying point in the range from 105° to 115° C. and the bis(*o*-methoxyphenyl) carbonate had a melting point of 87° C. The resulting dispersion was coated on a smooth light weight paper as used in Example 2. After coating the layer was air-dried for 4 hours to yield a colourless matrix.

EXAMPLE 5.

A dispersion for coating a porous outer layer was prepared as follows. 8.6 grams of a 25% solution of sodium sulphate in water was stirred into 100 grams of a 5% solution of 87% hydrolysed polyvinyl alcohol (made from polyvinyl acetate as indicated above) in water which contained as a coating aid 0.1 gram of a surfactant, Aerosol OT. 1.8 gram of zinc oxide was dispersed in the resulting solution. After the dispersion had defoamed, it was coated over a dyed heat-sensitive layer on a support of map overlay paper. The heat-sensitive layer comprised a 1.5 gram per square foot coating of 85 parts of poly(1,4-cyclohexanedimethylene adipate-azelate [3:1] having a melt viscosity of 16,000 poises at 70—75° C., 5 parts of polyethyl acrylate, and 10 parts of azo Oil Blue Black B dye. The porous polyvinyl alcohol overcoating coverage was 0.5 gram per square foot. During application and drying of the overcoating, it was maintained at 40°C. After drying, the resulting matrix was annealed for 1 hour at 75° C.



The resulting thermographic matrix was placed in contact with an ordinary lithographic document and the 2-ply assembly was then exposed and then separated. The tacky image areas were transformed successively to receiving sheets of paper to produce ten high quality transfers. The two-ply assemblies were passed at a rate of 0.172 in./sec. between transfer rolls which were maintained at a temperature of 70—75° C. and at a pressure of 52 pounds per lineal inch.

The present invention may be employed to produce copies of an original by the aid of a colour forming reaction. For example, separate colour-forming components of a two-component system may be employed, one being incorporated in the heat-sensitive layer and the other in the receiving sheet. An example of a colour-forming reaction of this type comprises, for example, incorporating ferric stearate in the heat-sensitive layer and propyl gallate in a polymeric layer on the receiving sheet. A number of copies may be made by successive transfers of a stratum of the layer containing ferric stearate.

WHAT WE CLAIM IS:—

1. A thermographic process of making copies of a document of the kind referred to by a transfer process employing a heat-sensitive material comprising a flexible support having coated thereon a heat-sensitive layer comprising a polymer in a crystalline form and having in the temperature range from 50° C. to 200° C. a tackifying point (as herein defined) at which it becomes adhesive and remains adhesive when reduced in temperature below its tackifying point and is transferable to a receiving sheet by pressure thereonto while at said reduced temperature and the material being provided with integral means which regulates the transfer of the heat-sensitive layer when in its tacky state at said reduced temperature wherein said material is placed in contact with the document to be copied, exposed to infra-red radiation until a tacky image has been formed in the sensitive layer, then the material is separated from the document and, while still in its tacky state, is pressed against a receiving sheet with sufficient pressure to cause the surface of the tacky areas to adhere thereto and then the material is separated from the receiving sheet carrying at least a stratum of the tacky areas, and if desired the transfer step is repeated on a further receiving sheet or sheets to produce a further copy or copies.

2. A thermographic process of making copies of a document of the kind referred to by a transfer process employing a heat-sensitive material comprising a flexible support having coated thereon a heat-sensitive layer comprising an amorphous polymer in admixture with a non-polymeric crystalline substance miscible therewith which melts in the temperature range from 50° C. to 200°

C. and the mixture has a tackifying point (as herein defined) at which it becomes adhesive and remains adhesive when reduced in temperature below its tackifying point and being transferable to a receiving sheet by pressure thereonto while at the said reduced temperature and the material being provided with integral means which regulates the transfer of the heat-sensitive layer when in its tacky state at said reduced temperature wherein said material is placed in contact with the document to be copied, exposed to infra-red radiation until a tacky image has been formed in the sensitive layer, then the material is separated from the document and, while still in its tacky state, is pressed against a receiving sheet with sufficient pressure to cause the surface of the tacky areas to adhere thereto and then the material is separated from the receiving sheet carrying at least a stratum of the tacky areas and if desired the transfer step is repeated on a further receiving sheet or sheets to produce a further copy or copies.

3. A thermographic process according to Claim 1 wherein the polymer is selected from: poly(butene-1), poly(pentene-1), poly(tetramethylene carbonate), poly(pentamethylene carbonate), poly(2,2-dimethyl trimethylene succinate), poly(1,4-cyclohexanedimethylene succinate), poly(1,4 - cyclohexanedimethylene adipate), poly(ethylene succinate), poly(pentamethylene terephthalate), poly(ethylene 1,4-cyclohexane dicarboxylate), poly(ethylene glycol), and cyclohexanedimethylene adipate-azelaate copolymers.

4. A thermographic process according to Claim 2 wherein the amorphous polymer is any of those described herein by way of example.

5. A thermographic process according to any of Claims 1, 2, 3 or 4 wherein the regulating means consists of solid inert particles incorporated in the heat-sensitive layer and having an average diameter greater than the thickness of the layer.

6. A thermographic process according to Claim 5 wherein the inert particles are glass beads.

7. A thermographic process according to any of Claims 1, 2, 3 or 4 wherein the regulating means consists of a layer coated over the heat-sensitive layer, the overcoated layer being porous to the heat-sensitive layer in its tacky state.

8. A thermographic process according to Claim 7 wherein the porous overcoated layer is formed by coating a solution of polyvinyl alcohol and containing metal salts as pore-forming agents.

9. A thermographic process according to any of the preceding claims wherein the heat-sensitive layer contains a black or strongly coloured infra-red transparent colouring matter, or a colour former.

10. A thermographic process according to

The resulting thermographic matrix was placed in contact with an ordinary lithographic document and the 2-ply assembly was then exposed and then separated. The tacky image areas were transformed successively to receiving sheets of paper to produce ten high quality transfers. The two-ply assemblies were passed at a rate of 0.172 in./sec. between transfer rolls which were maintained at a temperature of 70—75° C. and at a pressure of 52 pounds per lineal inch.

The present invention may be employed to produce copies of an original by the aid of a colour forming reaction. For example, separate colour-forming components of a two-component system may be employed, one being incorporated in the heat-sensitive layer and the other in the receiving sheet. An example of a colour-forming reaction of this type comprises, for example, incorporating ferric stearate in the heat-sensitive layer and propyl gallate in a polymeric layer on the receiving sheet. A number of copies may be made by successive transfers of a stratum of the layer containing ferric stearate.

WHAT WE CLAIM IS:—

1. A thermographic process of making copies of a document of the kind referred to by a transfer process employing a heat-sensitive material comprising a flexible support having coated thereon a heat-sensitive layer comprising a polymer in a crystalline form and having in the temperature range from 50° C. to 200° C. a tackifying point (as herein defined) at which it becomes adhesive and remains adhesive when reduced in temperature below its tackifying point and is transferable to a receiving sheet by pressure thereonto while at said reduced temperature and the material being provided with integral means which regulates the transfer of the heat-sensitive layer when in its tacky state at said reduced temperature wherein said material is placed in contact with the document to be copied, exposed to infra-red radiation until a tacky image has been formed in the sensitive layer, then the material is separated from the document and, while still in its tacky state, is pressed against a receiving sheet with sufficient pressure to cause the surface of the tacky areas to adhere thereto and then the material is separated from the receiving sheet carrying at least a stratum of the tacky areas, and if desired the transfer step is repeated on a further receiving sheet or sheets to produce a further copy or copies.

2. A thermographic process of making copies of a document of the kind referred to by a transfer process employing a heat-sensitive material comprising a flexible support having coated thereon a heat-sensitive layer comprising an amorphous polymer in admixture with a non-polymeric crystalline substance miscible therewith which melts in the temperature range from 50° C. to 200°

C. and the mixture has a tackifying point (as herein defined) at which it becomes adhesive and remains adhesive when reduced in temperature below its tackifying point and being transferable to a receiving sheet by pressure thereonto while at the said reduced temperature and the material being provided with integral means which regulates the transfer of the heat-sensitive layer when in its tacky state at said reduced temperature wherein said material is placed in contact with the document to be copied, exposed to infra-red radiation until a tacky image has been formed in the sensitive layer, then the material is separated from the document and, while still in its tacky state, is pressed against a receiving sheet with sufficient pressure to cause the surface of the tacky areas to adhere thereto and then the material is separated from the receiving sheet carrying at least a stratum of the tacky areas and if desired the transfer step is repeated on a further receiving sheet or sheets to produce a further copy or copies.

3. A thermographic process according to Claim 1 wherein the polymer is selected from: poly(butene-1), poly(pentene-1), poly(tetramethylene carbonate), poly(pentamethylene carbonate), poly(2,2-dimethyl trimethylene succinate), poly(1,4-cyclohexanedimethylene succinate), poly(1,4 - cyclohexanedimethylene adipate), poly(ethylene succinate), poly(pentamethylene terephthalate), poly(ethylene 1,4-cyclohexane dicarboxylate), poly(ethylene glycol), and cyclohexanedimethylene adipate-azelaate copolymers.

4. A thermographic process according to Claim 2 wherein the amorphous polymer is any of those described herein by way of example.

5. A thermographic process according to any of Claims 1, 2, 3 or 4 wherein the regulating means consists of solid inert particles incorporated in the heat-sensitive layer and having an average diameter greater than the thickness of the layer.

6. A thermographic process according to Claim 5 wherein the inert particles are glass beads.

7. A thermographic process according to any of Claims 1, 2, 3 or 4 wherein the regulating means consists of a layer coated over the heat-sensitive layer, the overcoated layer being porous to the heat-sensitive layer in its tacky state.

8. A thermographic process according to Claim 7 wherein the porous overcoated layer is formed by coating a solution of polyvinyl alcohol and containing metal salts as pore-forming agents.

9. A thermographic process according to any of the preceding claims wherein the heat-sensitive layer contains a black or strongly coloured infra-red transparent colouring matter, or a colour former.

10. A thermographic process according to



any of the preceding claims wherein the heat-sensitive layer is one which has been annealed after coating, by heating it to a temperature above the glass transition temperature but below its initial tackifying temperature.

11. A heat-sensitive material for producing copies of documents comprising a flexible support having coated thereon a heat-sensitive layer comprising a polymer in a crystalline form said polymer having a tackifying point (as herein defined) in the temperature range from 50° C. to 200° C. and remaining tacky when reduced in temperature below its tackifying point and being transferable to a receiving sheet by pressure thereonto while at said reduced temperature, the material being provided with integral means which regulates the transfer of the heat-sensitive layer when in its tacky state at said reduced temperature.

12. A heat-sensitive material for producing copies of documents comprising a flexible support having coated thereon a heat-sensitive layer comprising an amorphous polymer in admixture with a non-polymeric crystalline substance miscible therewith which melts in the temperature range from 50° C. to 200° C. and the mixture has a tackifying point (as herein defined) at which it becomes adhesive and remains adhesive when reduced in temperature below its tackifying point and being transferable to a receiving sheet by pressure thereonto while at said reduced temperature, the material being provided with integral means which regulates the transfer of the heat-sensitive layer when in its tacky state at said reduced temperature.

13. A heat-sensitive material according to Claim 11 wherein the polymer is selected from: poly (butene-1), poly(pentene-1), poly-(tetramethylene carbonate), poly(pentamethylene carbonate), poly (2,2-dimethyltrimethylene succinate), poly(1,4 - cyclohexanedimethylene succinate), poly(1,4 - cyclohexanedimethylene

adipate), poly(ethylene succinate), poly(pentamethylene terephthalate, poly(ethylene 1,4-cyclohexane dicarboxylate), poly(ethylene glycol), and cyclohexanedimethylene adipate-azelate copolymers.

14. A heat-sensitive material according to Claim 12 wherein the amorphous polymer is any of those described herein by way of example.

15. A heat-sensitive material according to any of Claims 11 to 14 wherein the regulating means consists of solid inert particles incorporated in the heat-sensitive layer and having an average diameter greater than the thickness of the layer.

16. A heat-sensitive material according to Claim 15 wherein the inert particles are in the form of beads.

17. A sensitive material according to Claim 16 wherein the beads are glass beads.

18. A heat-sensitive material according to any of Claims 11 to 14 wherein the regulating means consists of a layer coated over the heat-sensitive layer, the overcoated layer being porous to the heat-sensitive layer in its tacky state.

19. A heat-sensitive material according to Claim 18 wherein the porous overcoated layer is formed by coating a solution of polyvinyl alcohol and containing metal salts as pore-forming agents.

20. A heat-sensitive material according to any of Claims 10 to 16 wherein the heat-sensitive layer contains a black or strongly coloured infra-red transparent colouring matter.

21. A heat-sensitive material according to any of Claims 11 to 20 wherein the heat-sensitive layer in annealed after coating by heating it to a temperature above the glass transition temperature but below its initial tackifying temperature.

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