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PATENT SPECIFICATION

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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, U.S.A. (Assignees of WILLIAM JAMES DULMAGE, STERLING SCOTT SWEET and WILLIAM ANDREW 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 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.

[Price 4s. 6d.]

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 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.

The use of means such as solid inert particles incorporated in the heat-sensitive layer and having an average diameter greater than the layer, or porous overcoats, which regulates the said transfer, and materials therefor, are described and claimed in our spec. No. 1,015,962 (23939/65).

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



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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

5 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
10 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
15 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
20 (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 requirements can be found without difficulty among
25 polyhydrocarbons, especially among polyvinyl compounds, polyacrylic compounds, polyesters, polyamides, polyesteramides, polycarbonates, polyethers, polyurethanes and polyureas. Examples of substances are poly-
30 (2,2 - dimethyltrimethylene succinate) and isotactic poly(butene-1) and poly(1,4-cyclohexanedimethylene adipate) and poly(pentamethylene carbonate) and poly(1,4-cyclohexanedimethylene adipate-azelaate [3:1]).
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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
40 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
45 between glass transition temperature and the tackifying point it increases with temperature through a maximum value. Polymeric compositions with recrystallization times from
50 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.
55 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
60 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.

65 If the rate of recrystallization causes the

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

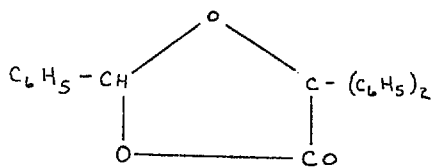
The heat-sensitive layers employed in the present invention can be prepared using either crystalline or amorphous polymers chosen from
80 a wide variety of linear, film-forming polymers and co-polymers.

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

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.

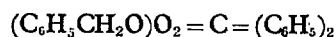
The non-polymeric crystalline substances which may be used are compounds which melt in the range of 50° to 200°C. and are miscible with the amorphous polymer. By "miscible" as used herein we mean that they are miscible at the fusion point of the mixture, and on cooling into the range below the fusion 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; bezoin acetate; N - pentyl - 1,8-naphthalimide; bis(*o*-methoxyphenyl)carbonate eugenol cinnamate; 2,5,5 - triphenyl - 1,3-dioxolan - 4 - one; bis(benzoyloxy)diphenylmethane; 4-cyclohexylphenyl benzoate; 4-biphenyl benzoate; pentachlorophenyl benzoate; anthraquinone - 2 - carboxyethyl; camphor.

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



and

Bis(benzoyloxy)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, that 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 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 chlorhydrocarbon such as
 benzene, toluene, methylene chloride, ethylene
 chloride or carbon tetrachloride, or a ketone
 10 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 cellu-
 lose acetate or polyethylene terephthalate. Sub-
 15 stances 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
 20 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), di-
 butyl fumarate, menthol, diethyl phthalate,
 eugenol, isoeugenol, dibutyl phthalate, eugenol
 25 methyl ether, isoeugenol methyl ether, clay,
 glass beads, ground quartz, crosslinked poly
 (methyl methacrylate) beads, 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
 30 in Part II thereof where available. The Colour
 Index is published jointly by the Society of
 Dyers and 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	

Usually the heat-sensitive layer should be coated for use in the transfer process to a maximum coating rate of 0.05 to 0.3 grams per square foot since heavier coatings may cause excessive transfer to first copies and consequent loss of image definition.

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, crystallisation 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 increase 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 exposure 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 facilitates 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.

For low viscosity compositions less transfer pressure is needed than for transfer of more viscous compositions.

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.

EXAMPLE 1.

This Example illustrate heat-sensitive material prepared for use in making a lithographic printing plate.

A 10 per cent solution of a heat-sensitive component, namely poly(2,2-dimethyltrimethylene succinate) having an inherent viscosity of 0.34 and a tackifying point of 79°C., was prepared in a 4:1 mixture of acetone and methylene chloride. To the solution was

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added Azo Oil Blue Black B Dye at a concentration to give 5 per cent (by weight) dye in the dry coated composition. The composition was then coated onto a parchment paper support. After drying, the layer was annealed at 70°C. for 6 hours to give a final coating thickness of 0.1 mil (2.5 microns).

This heat-sensitive material was exposed to an original document by means of infra red radiation. After separation from the original, the exposed element was then passed between pressure rollers exerting 30 lbs per linear inch of roller length, the rollers having diameters of 2½ inches, with the coated side of said material in contact with a hydrophilic-type paper support to form a lithographic printing plate which was used in an offset press. About 150 good copies were run off on the press.

EXAMPLE 2.

This Example illustrate a heat-sensitive material prepared for use in making a spirit duplicating master. 7.5 grams of a heat-sensitive component namely poly(1,4-cyclohexanedimethylene adipate), having an inherent viscosity of 0.38 and a tackifying point of 92°C. were added to a solution comprising 2.5 grams of methyl violet dye in 5 grams of ethanol and 25 grams of ethylene chloride. The resulting composition was blended in a Waring Blendor for 5 minutes and then coated on a sheet of smooth lightweight Transparent Copy Greaseproof Paper at a thickness of 3 mils (75 microns). After drying the layer was annealed at 75°C. for 1 hours. This heat-sensitive material was placed with its support side in contact with the printed characters of a document to be copied and exposed by directing infra-red radiation on to the heat-sensitive side. After separation it was then passed between pressure rollers with the heat-sensitive side in contact with a receiving sheet of parchment paper. The rollers for use in the transfer process had a roller diameter of 2 1/2 inches and exerted 100 pound pressure per linear inch of roller length. The resulting reverse-reading image was then used as a spirit duplicating master in a conventional process of this type wherein successive sheets of a spirit duplicating copy paper, dampened with methanol, brought into pressure-contact with the master. 25 Violet copies of good quality were obtained.

EXAMPLE 3.

A heat-sensitive material was prepared by the addition of 95 grams of the amorphous resin obtained as the condensation product (melting at 105° to 115°C.) of polymerized linoleic acid and a diamine (sold under the trade name Versamide 930 by General Mills), and 142 grams of benzoin acetate (m.p. 82°C.) to 83 grams of isopropanol and 667 grams of benzene which contained 13 grams of Azo

Oil Blue Black B dye. The polymer of said composition had a tackifying point in the range from 105 to 115°C.

After thoroughly mixing the above composition while holding at a temperature of 50°C., the composition was coated on a sheet of a smooth light weight paper as used in Example 2 at a thickness of 2 mils (50 microns). The coating was then dried. The crystallized coating was next overcoated with a 2-mil wet thickness aqueous layer of 5 weight per cent of polyvinyl alcohol containing as a coating aid less than 0.1 weight per cent of an aryl sulphonate surfactant. The overcoated material was then dried at 50°C., for 10 minutes. The purpose of the protective overcoat was to stabilize the heat-sensitive layer and to facilitate packaging, thermographic exposure and transfer. The resulting thermographic sheet material was then exposed and a transfer to a paper receiving sheet of highly absorbent wet-strength paper moistened with water was made by passing the two sheets together between pressure rollers exerting 60 lbs per linear inch of roller length. The rollers had diameters of 2.1/2 inches. A good copy of the original was obtained.

EXAMPLE 4.

A heat-sensitive material was prepared by coating onto a smooth light weight paper as used in Example 2, a composition consisting of 9.0 grams of a heat-sensitive component namely poly(1,4 - cyclohexanedimethylene adipate-azelaate [3:1]) having an inherent viscosity of 0.42 and a tackifying point of 92°C., 1.0 gram of Isosol Black dye, and 30 grams of ethylene chloride. After coating, the layer was dried and annealed at 80°C. to yield a layer of 1.1 gram per square foot. This heat-sensitive material was overcoated with a 2 1/2 percent by weight solution of medium viscosity carboxymethyl cellulose to form an overcoat to protect the heat-sensitive layer during handling and storage. The overcoat was dried to yield a layer of 0.1 gram per square foot. The resulting thermographic material was then exposed and a transfer to a paper receiving sheet was made substantially as in Example 1 to produce a copy of the original having good quality, with the exception that the water-soluble overcoat required softening before transfer by wiping the surface of the exposed matrix with a damp sponge or by dampening each receiving sheet.

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





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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, 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 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 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 ~~melt~~ 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 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(~~pentane~~-1), poly(tetramethylene carbonate), poly(pentamethylene carbonate), poly(2,2 - dimethyl trimethylene succinate), poly(1,4 - cyclohexanedimethylene succinate), poly(1,1 - cyclohexanedimethylene adipate), poly(ethylene succinate), poly(pentamethylene terephthalate), poly(ethylene 1,4-cyclohexane dicarboxylate), poly(ethylene glycol), and cyclohexanedimethylene adipate-azelate 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 one 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.

6. A thermographic process according to any of the preceding claims wherein the heat sensitive layer contains an infra-red transparent dye or colour former.

7. A thermographic process according to Claim 6 wherein the layer contains a black or blue-back dye.

8. A thermographic process according to any of the preceding claims wherein the material has a protective overcoat layer not porous to the heat sensitive layer when in its tacky state.

9. A thermographic process according to Claim 8 wherein the protective overcoat layer comprises polyvinyl alcohol.

10. A thermographic process according to Claim 8 wherein the protective overcoat comprises carboxymethyl cellulose.

11. A thermographic process according to any of Claims 1 to 6 wherein the receiving sheet is hydrophilic and a copy obtained thereon is used as a lithographic printing plate.

12. A thermographic process according to Claims 5 or 6 wherein the dye is spirit soluble and a copy so obtained is used as a spirit duplicating master.

13. A thermographic method of making copies of a document of the kind referred to, wherein a heat sensitive material, which has been used according to the method claimed in any of the preceding claims without all of the sensitive layer in the image-areas having been removed, is annealed by means of a heat treatment until the image-areas have recrystallised and the layer is then used again according to the method claimed in any of the preceding claims.

L. E. T. BRANCH, B.Sc., F.R.I.C.,
Patent Agent.



employing a heat sensitive material

melts



Dr.



1,015,925

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pentene
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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, 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 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 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 ~~melt~~ 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 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(~~pentane~~-1), poly(tetramethylene carbonate), poly(pentamethylene carbonate), poly(2,2[^] dimethyl trimethylene succinate), poly(1,4 - cyclohexanedimethylene succinate), poly(1,1 - cyclohexanedimethylene adipate), poly(ethylene succinate), poly(pentamethylene terephthalate), poly(ethylene 1,4-cyclohexane dicarboxylate), poly(ethylene glycol), and cyclohexanedimethylene adipate-azelate 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 one 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.

6. A thermographic process according to any of the preceding claims wherein the heat sensitive layer contains an infra-red transparent dye or colour former.

7. A thermographic process according to Claim 6 wherein the layer contains a black or blue-back dye.

8. A thermographic process according to any of the preceding claims wherein the material has a protective overcoat layer not porous to the heat sensitive layer when in its tacky state.

9. A thermographic process according to Claim 8 wherein the protective overcoat layer comprises polyvinyl alcohol.

10. A thermographic process according to Claim 8 wherein the protective overcoat comprises carboxymethyl cellulose.

11. A thermographic process according to any of Claims 1 to 6 wherein the receiving sheet is hydrophilic and a copy obtained thereon is used as a lithographic printing plate.

12. A thermographic process according to Claims 5 or 6 wherein the dye is spirit soluble and a copy so obtained is used as a spirit duplicating master.

13. A thermographic method of making copies of a document of the kind referred to, wherein a heat sensitive material, which has been used according to the method claimed in any of the preceding claims without all of the sensitive layer in the image-areas having been removed, is annealed by means of a heat treatment until the image-areas have recrystallised and the layer is then used again according to the method claimed in any of the preceding claims.

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Dr.

employing a heat sensitive material

melts

