United States Patent Office 3,261,023 Patented July 12, 1966

3,261,023

THERMOGRAPHIC RECORDING PROCESS WHEREIN THE HEAT-SENSITIVE SHEET IS USED IN PLURAL PROCESSES

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No Drawing. Filed Aug. 7, 1963, Ser. No. 300,641
5 Claims. (Cl. 117—37)

This invention relates to thermographic methods and to materials used in such methods.

The present invention employs a matrix comprising a sheet support having coated thereon a layer of thermoplastic material in a normally non-tacky state of at least partial crystallization. This layer of heat-sensitive material has the property of undergoing transition from its partially crystalline to its tacky amorphous state at a temperature called the original tackifying temperature (preferably between 50° C. and 200° C.) and of remaining in a state having a tackifying temperature substantially lower than the original tackifying temperature for a period of time at least long enough to permit transfer of tackified material from the matrix to produce a transfer print on a receiving surface at a transfer temperature below said original tackifying temperature. The heat sensitive material has a melt viscosity at the original tackifying temperature between 10 and 100,000 poises and preferably from about 50 to 500 poises. Heat-sensitive elements of the kind just described, and thermographic methods for their use, are described in more detail in the copending U.S. patent application Serial No. 211,927 of Dulmage, Sweet and Light, filed June 27, 1962.

In the particular heat sensitive matrix for use in accordance with the present invention, the heat-sensitive material has the further property, after transition to its amorphous state, of recrystallizing at ordinary room temperatures (15°–35° C.) to a state having a tackifying temperature substantially higher than a selected temperature at which transfer of thermoplastic material to a receiving surface is to be made. Preferably the period for this recrystallization is in the magnitude of a few seconds to a few minutes, though a longer period will be suitable for some embodiments.

An object of the invention is to provide a thermographic process for producing transfer prints wherein a single heat-sensitive matrix of the kind described is used for making at least one copy each of a plurality of different documents.

Another object is to provide a thermographic process wherein a single matrix of the kind described is activated thermographically more than one time and, after each activation, at least one transfer print of the last-imposed thermographic image is made.

Accordingly, the invention comprises a process wherein a matrix of the kind described is activated only in selected image areas by preferentially heating only those image areas, by any suitable means, to a temperature above the original tackifying temperature of material in the heat-sensitive layer, and then at a selected transfer temperature substantially lower than the original tackifying temperature of said material but above the tackifying temperature of activated material in the image areas, the heat-sensitive layer is pressed against a receiving surface with sufficient pressure to transfer tackified material from image areas of the matrix and thereby print an image on the receiving surface. After activated material in the heat-sensitive layer has recrystallized at room temperature to a state having a tackifying temperature substantially above the temperature selected for making succeeding transfers (preferably to nearly the same as the original tackifying temperature) the matrix is again activated by

again selectively heating only image areas thereon (which may be and usually will be different from the image of the first activation) to a temperature above the original tackifying temperature and the transfer step is repeated at a selected transfer temperature above the tackifying temperature of the newly activated material in the image areas and below the tackifying temperature of the recrystallized material in the heat sensitive layer. Thus a series of transfer prints of different documents can be made with a single matrix. In most embodiments the selected transfer temperature will be the same for the first and all succeeding transfers, though this is by no means necessary.

The invention can be more readily understood by reference to a specific example.

Example 1

A heat-sensitive element suitable for use in the process of the invention is prepared as follows. On a sheet of a map-overlay tracing paper (Rhinelander Folio Transparent Copy Paper) is coated at 30% solution of a 95:5 mixture of poly(1,4-cyclohexanedimethylene adipate) and Azo Oil Blue Black B dye in ethylene dichloride. The homopolymer has an inherent viscosity, measured in a 1:1 mixture of phenol and chlorobenzene, of 0.47.

After drying overnight at 72° C., the dried thermoplastic coating is about 0.1 mil thick and has crystallized to a non-tacky, non-viscous state having an original tackifying temperature of about 110° C. At this original tackifying temperature, the polymer coating will undergo transition to an amorphous state, in which state it will be tacky at temperatures at least as low as room temperature. However, as the amorphous material cools to temperatures below the original tackifying temperature, it begins to recrystallize rapidly and as recrystallization proceeds the tackifying temperature increases rapidly. About five minutes after the activated material has cooled to room temperature, its tackifying temperature has increased to a value higher than room temperature (20–25° C.) which is the temperature we have selected for making transfer prints.

After drying overnight, the coated matrix is placed in contact with a document having infrared absorbent image areas and relatively non-absorbent background areas. The heat-sensitive coating of the matrix is placed against the face of the document, and the composite is exposed to infrared radiation by feeding it through a thermographic machine of the type described in U.S. Patent No. 2,891,165 to Kuhrmeyer et al. In image areas of the document, heat is generated by infrared absorption and this heat is transmitted to adjacent image areas on the matrix, raising the temperature of those areas above the original tackifying temperature of the polymer layer. The matrix is separated from the document and immediately is placed in contact with a receiving sheet of ordinary office stationery with the coated surface of the matrix against the receiving sheet. This composite is fed between a pair of steel rolls loaded to exert 50 pounds force per lineal inch along the line of contact, and activated polymer is transferred from image areas of the matrix to the receiving sheet at room temperature. The matrix and receiving sheet are separated and a printed facsimile of the original document is observed on the receiving sheet.

After about five minutes, during which the used matrix is held at room temperature, the matrix is again fed through the transfer rolls at room temperature in contact with another receiving sheet and no polymer transfer is observed. This is not a necessary step but is done to demonstrate that the activated polymer has recrystallized to a state having a tackifying temperature higher than the selected transfer temperature. After this, using a second printed document, but using the same matrix again, a sec-

ond infrared exposure is made as before followed by another transfer as before through the same transfer rolls. A clear printed facsimile of the second document is observed on the receiving sheet.

Using the same matrix again with a third document, after again allowing five minutes for activated polymer to recrystallize at room temperature, a third exposure is made as before, followed immediately by a transfer as before to produce printed facsimile of the third document.

The steps of activation and transfer after room-temperature recrystallization can be repeated using a single matrix with different documents until so much activated polymer has been transferred from the matrix that bare areas begin to appear in the polymer coating of the matrix. The number of good quality transfers available from a single matrix can be increased by increasing thickness of the polymer coating and by incorporating in the matrix some means for regulating the rate of transfer of thermoplastic material. For example, tiny glass beads or other solid particles dispersed in the thermoplastic layer, or a porous, permeable layer coated over the thermoplastic layer, and in some cases both, may be employed for this purpose. Various means for regulating transfer of activated material are discussed in more detail in the copending application Serial No. 211,927, mentioned above.

Example 2

A solution is prepared of 30 parts by weight poly(1,4-cyclohexanedimethylene adipate) having an inherent viscosity of 0.42, one part by weight National Aniline Azo Oil Blue Black B dye, and 0.5 part by weight 1,3-diphenyl-4-(p-methoxyphenylazo)-5-pyrazolone in sufficient methylene chloride to make 100 parts.

After the dyes and resin have uniformly dissolved in the solvent, 1.8 parts by weight of glass beads having an average size of 10–30 microns are added with continuous agitation.

This material is coated on Rhinelander Greaseproof Stock paper to a dry weight of 1.5 g./ft.^{2} and the coating is held for five minutes at 50° C. in a heated ventilated chamber to evaporate solvent and permit crystallization of the polymer coating. A porous layer is then coated over the first at a dry coverage of 0.4 g./ft.^{2} of the following composition: 47.7 g. of poly(vinyl alcohol) (Du Pont Elvanol 50–42) in a 6.5% aqueous solution, 33 ml. of 1.5% aqueous solution of Aerosol OT as a spreading agent, 60 ml. of Ludox AM, a 30% suspension of colloidal silica in water, 25 g. of sodium sulfate, and 71 ml. of water. This coating is dried to a porous film by evaporation at room temperature. The overcoated matrix is then used for making transfer prints of several documents from a single matrix, as described in Example 1 but using a selected transfer temperature of 70° C. Transfer rolls are heated to 70° C. in order to heat the matrix to the selected transfer temperature as the matrix and receiving sheet are fed through.

More than one transfer can be made after any single activation if there is sufficient time for additional transfers in the period before the tackifying temperature of the activated material rises above the transfer temperature.

In preferred embodiments we may use heat-sensitive materials that recrystallize at room temperature in a period ranging from about 30 seconds to about 10 minutes to a non-transferrable state, i.e., to a state whose tackifying temperature is above the transfer temperature selected for making the next succeeding transfer. The length of this recrystallization period is not critical beyond the requirement that it must be at least long enough to allow time to make at least one transfer print. However, the matrix can be reused in another exposure and transfer process only after the previously activated material has recrystallized to a non-transferrable state, and so it is advantageous for the period for recrystallization at room temperature to be brief. For use in an automatic machine for rapid copying, a matrix having an extremely short room temperature recrystallization period, in the magnitude of 2–10 seconds, might be preferred.

The most suitable polymers we have found for making the heat-sensitive layer of a matrix for use in the process of the invention are poly(cyclohexanedimethylene adipates) having inherent viscosities of about 0.25 to about 0.6, measured as described in Example 1. However, one may use other thermoplastic materials having the necessary tackifying, melt viscosity, recrystallizing, etc., properties as described above.

Suitable polymers and copolymers for this use may be found among a wide variety of synthetic thermoplastic polymer groups, including such polymers as poly(ethylene succinate), poly(tetramethylene fumarate), poly(hexamethylene fumarate), polybutene-1, and other poly α-olefins, to mention a few. A specific example of a copolymer we have found to have suitable properties for use in heat-sensitive layers of this invention is co-poly(tetramethylene fumarate-sebacate) 70/30 wt. percent ratio.

Additives, such as plasticizers, dyes, fine-grain solids, etc., when dispersed in the thermoplastic material of the heat-sensitive layer were found, in some instances, to radically modify the recrystallization properties of the material. For example, by increasing the concentration of Azo Oil Blue Black B dye from 3 to 6% in coatings of poly(1,4-cyclohexanedimethylene adipate) (I.V.—0.47), the period after activation for recrystallization of the material at room temperature to a state having a tackifying temperature above 70° C. could be extended from about 35 seconds to about 1½ minutes. In selecting any particular plasticizer, dye or other additive to be included in the heat-sensitive layer of a matrix for use in the present invention, the effect on recrystallization properties should be considered, as well as its compatibility, effect on tackifying point, etc.

Heat-sensitive materials for a matrix to be used in the present invention may also be selected from the class of heat-sensitive materials that comprise a polymer having dispersed therein a crystalline compound that melts at an activating temperature above 50° C. and blends with the polymer to form an amorphous mixture having a tackifying point substantially lower than the unactivated material in the coating. A material of this class, in order to be useful in the process of this invention, must have the further property of recrystallizing at room temperature, in a suitably short time, to a state having a tackifying temperature higher than the temperature to be used for the transfer step and preferably close to the original tackifying temperature.

For making printed copies of documents, we prefer to have the transferred material colored. Black is a favorite color for printing and we prefer to use a colorant that is both compatible with the thermoplastic material and infrared transparent. An especially suitable black dye mixture that we use consists of about five parts by weight Azo Oil Blue Black B and about two parts by weight of the yellow dye 1,3-diphenyl-4-(p-methoxyphenylazo)-5-pyrazolone. Other compatible yellow dyes may be substituted in the mixture with the blue-black dye to make a compatible black dye. This is only a suggested dye that we have found especially useful. Many other compatible coloring materials of various colors may be selected to color the heat-sensitive layer of the matrix.

Concentration of colorant in the coating usually will be in the range from about 3 to about 20 parts by weight per 100 parts of polymer, the optimum concentration depending upon the image density needed and the amount of polymer to be transferred.

The selected transfer temperature may be any temperature that will tackify heat-sensitive material in activated image areas on the matrix but will not tackify the background areas. In other words, for the first transfer the transfer temperature must be below the original tackify-

ing temperature of the heat-sensitive layer and above the reduced tackifying temperature of activated material that has undergone transition when heated, and for subsequent transfers the transfer temperature must be below the tackifying temperature of material that has recrystallized.

In this specification we use the term "tackifying temperature" to define the lowest temperature at which a thermoplastic material, in the state being described, undergoes change from a non-tacky and non-viscous condition in which the material cannot be transferred by pressure, to a tacky viscous condition in which the material will transfer. A pure crystalline polymer undergoes this change of state at its first-order transition temperature and a pure amorphous polymer undergoes the change at its second-order transition temperature, however, the term "tackifying temperature" was chosen to describe this change of condition for pure and modified polymers in amorphous and crystalline states, as well as polymer compositions in intermediate partially crystallized states, and for modified polymer compositions including those compositions that contain a polymer component and a crystallized non-polymeric component that melts at an elevated temperature to change the condition of the polymeric component.

The process of the present invention may be practiced using a matrix having any suitable support such as paper, photographic film supports, metal foils, cellophane, and the like. When infrared exposure is employed in the activation step, the support must be substantially infrared transparent. A flexible paper support is preferred.

It will be appreciated that with the several variables involved and depending on the particular properties of the selected heat-sensitive material for the matrix to be used, such as original tackifying temperature, reduced tackifying temperature, rate of recrystallization, etc., the operating conditions such as preferential heating, transfer temperature and pressure, etc., may vary considerably within the scope of the invention as described herein and as defined in the following claims.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A method of producing a succession of transfer prints employing a single matrix which comprises a support and coated thereon a heat-sensitive layer of thermoplastic material in a normally non-tacky state of at least partial crystallization, said thermoplastic material having the property of undergoing transition to an amorphous state at an original tackifying temperature in the range from 50 to 200° C. and of remaining in a state having a tackifying temperature substantially below said original tackifying temperature for a period of time at least long enough to permit transfer of tackified material to a receiving surface at a selected transfer temperature substantially below said original tackifying temperature, and

said material further having the property of recrystallizing at temperatures in the range from 15 to 35° C. from said amorphous state to a state having a tackifying temperature higher than said selected transfer temperature, said process comprising the steps of:

A. preferentially heating selected image areas on the matrix to a temperature above said original tackifying temperature to activate heat-sensitive material in those areas; and

B. during the period after said preferential heating step while the tackifying temperature of the activated material is below said selected transfer temperature, pressing the heat-sensitive layer of the matrix in contact with a receiving surface at said selected transfer temperature with sufficient pressure to transfer tackified material from the matrix to the receiving surface; and

C. after activated material on the matrix has recrystallized at room temperature to a state having a tackifying temperature above said selected transfer temperature, repeating the steps A and B using the same matrix.

2. The method of claim **1** wherein the period of time required for recrystallization at room temperature of activated material from the amorphous state to a state having a tackifying temperature above said selected transfer temperature is in the range from about 2 seconds to about one hour.

3. The method of claim **2** wherein said period of time is in the range from 30 seconds to 10 minutes.

4. The method of claim **1** wherein said matrix is substantially infrared transparent and said preferential heating of image areas in the matrix is accomplished by placing one side of the matrix in contact with the printed face of a document having image areas that are infrared absorbent and background areas that are relatively non-absorbent of infrared radiation, and while the matrix and document are in contact, exposing the document to infrared radiation, thereby raising the temperature only in areas of the matrix opposite image areas of the document above the original tackifying temperature of the heat-sensitive material on the matrix.

5. The method of claim **1** wherein said heat-sensitive layer consists essentially of poly(cyclohexanedimethylene adipate) having inherent viscosity of 0.25 to 0.6 and from about 3 to about 20 parts by weight per 100 parts polymer of a compatible colorant.

References Cited by the Examiner

UNITED STATES PATENTS

2,653,880	9/1953	Hendricks et al.	117—122
2,769,391	11/1956	Roshkind	250—65 X
3,060,023	10/1962	Burg	96—28

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