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HEAT-SENSITIVE COPYING SHEETS

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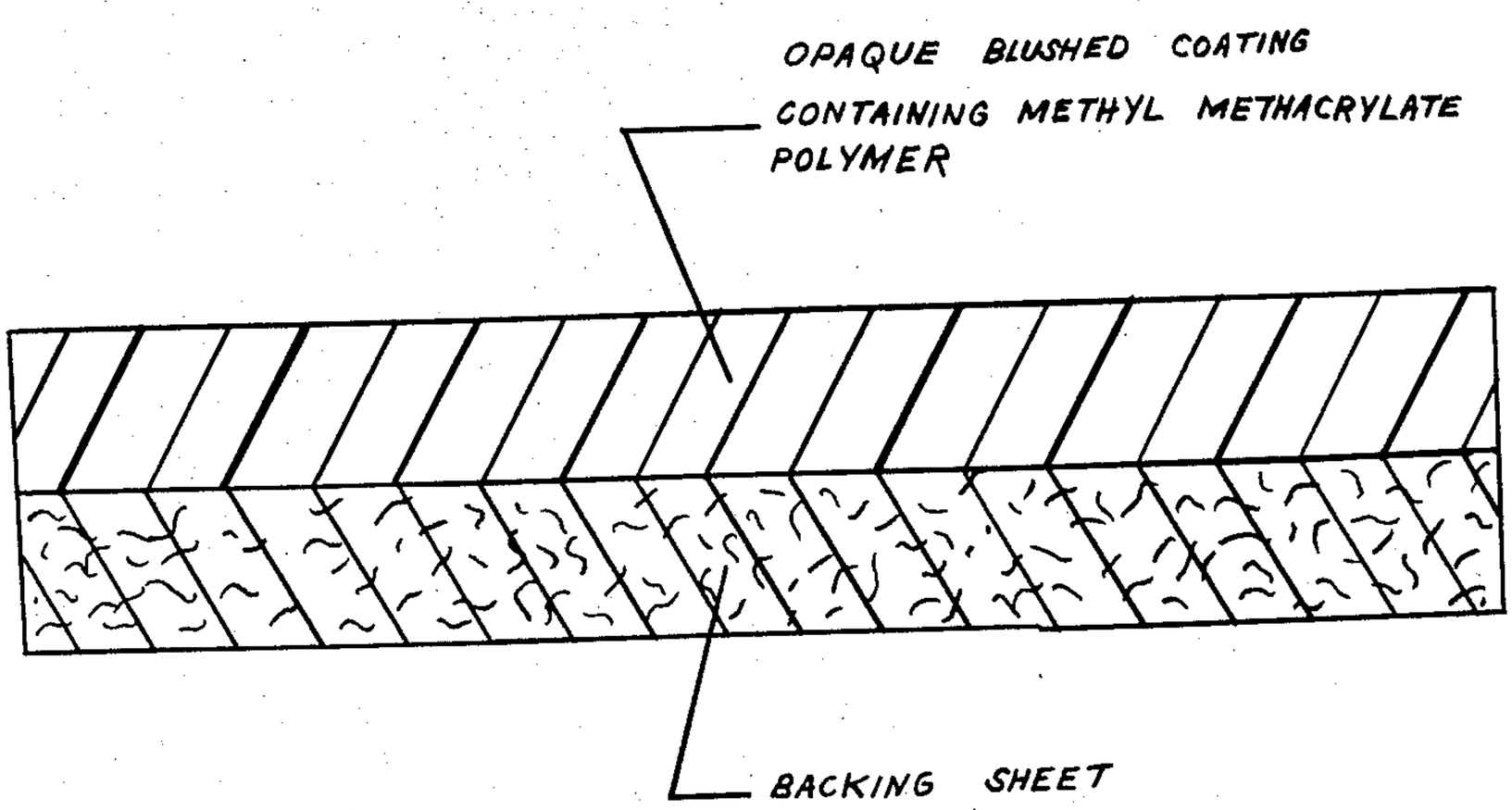

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HEAT-SENSITIVE COPYING SHEETS

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This application is a continuation-in-part of our application S.N. 841,673, filed September 23, 1959 (now abandoned). This invention relates to heat-sensitive copying paper useful in preparing copies of printed matter or other graphic originals.

Heat-sensitive copying papers are old in the art. In fact, there are at least two distinct types of such paper. One operates by means of a heat activated chemical change that occurs in the paper, or in the coating on the paper. Another type operates by means of a physical change that is produced by heat. The present invention relates specifically to the type of heat-sensitive copy paper wherein the image on the copy sheet is produced by a physical change in the coating.

U.S. Patent No. 2,710,263 and Reissue Patent No. 24,554 described heat-sensitive coatings for making copying paper in which the image appearing on the copy sheet results from a physical change in the coating corresponding to the image copied. According to the teachings of these prior art patents a heat-sensitive copying paper can be prepared by coating a dark colored supporting base with a composition consisting of particles of a normally transparent stable organic fusible solid, melting within the range of 60–115° C., dispersed in a solution of a transparent film-forming binder in a volatile solvent, evaporating the solvent without fusing or dissolving the particles so as to provide a non-transparent, infrared transmitting, heat-sensitive layer. A protective layer of film forming material can be applied over the heat-sensitive layer if desired. Heating the sheet at temperatures corresponding to the melting point of the fusible solid melts the heat-sensitive coating and allows the dark colored base sheet to show through at the heated areas. In making copies of graphic originals the heated areas would correspond to the image on the original and would result from heat generated by exposing the original to high intensity infrared radiation. Preferably the copy is made by placing the copy sheet on the original with its uncoated side next to the original and then exposing the original through the heat-sensitive copy sheet. In an alternate technique the original would be exposed to infrared radiation directly with the coated side of the heat-sensitive paper immediately back of it. By this "back-printing" technique it is not necessary, of course, that the heat-sensitive paper be infrared transparent. Both the "back-printing" and the "front-printing" techniques are described in the prior art patents mentioned above and also in U.S. Patent No. 2,859,351.

The art also teaches how to make heat and pressure-sensitive sheet, or paper, e.g., to be used with recording instruments having heated styli. The coating on these papers, like that of the U.S. patents referred to above, are discontinuous films of the film forming materials which may or may not be plasticized with solvent type plasticizers. The heat-sensitive papers of this type that are known to the art are not heat-sensitive enough to have any practical use in the thermocopying process of U.S. Patent No. 2,859,351. For instance, when they are employed in the method of U.S. Patent No. 2,859,351 for making copies they give only faint copies or no copies at all.

Heat and pressure-sensitive papers that are designed for use with heated styli, and which comprise discontinuous film-forming resin coatings on a dark colored base sheet are prepared either by the "bushing lacquer" technique (U.S. Patent No. 2,519,660) or by coating with a water-in-lacquer emulsion (U.S. Patent No. 2,739,909) wherein the solvent of the lacquer is more volatile than water. The film-forming resin may be a cellulose ether or ester, polymethyl methacrylate, polystyrene, vinyl-chloride-vinyl acetate copolymers, and coumarone-indene resins. Addition of solvent type plasticizers to these coatings improves the heat-sensitivity but it also softens the coatings to the extent that they are not sufficiently abrasion resistant for ordinary handling in making copies and in filing, mailing, etc.

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It has now been discovered that very desirable heat-sensitive papers for use in the process of Patent No. 2,859,351 can be produced by the blushed lacquer technique provided certain specific limitations are met. The limitations are: (1) the film-forming material must be thermoplastic material which melts above about 125° C., and (2) the film must contain a minor amount of a liquid or low melting, substantially non-volatile non-solvent type plasticizer, or lubricant.

In accordance with the invention there is provided a heat-sensitive copying sheet composed of a non-metallic supporting base and a non-transparent, heat-sensitive, blushed lacquer coating thereon containing a major amount of a solid thermoplastic polymer and a minor amount of non-solvent, lubricant type plasticizer. The stability of the coating during storage is largely governed by the melting point of the thermoplastic film-forming polymer; for this reason a polymer having a high melting point is desirable. On the otherhand, the polymer, or at least the polymer plus the secondary plasticizer, must be heat-sensitive at a reasonable temperature, i.e., the coating must transparentize at a temperature that is readily obtainable and is not high enough to damage the base sheet.

Polymethyl methacrylate polymers having a melting point above 125° C. and a molecular weight above 300,000 (as determined by intrinsic viscosity measurements) have been found to be ideally suited as the major film-forming material of the blushed film. A typical polymer that is commercially available is Lucite 41 having a melting point of about 150° C. and a molecular weight of 334,000 as determined by intrinsic viscosity measurements.

For overall properties butyl stearate has been found to give the best product of any of the non-solvent type plasticizers tested. As the name indicates, the non-solvent plasticizer, or lubricant type plasticizer, is substantially incompatible with the polymer, at least at room temperature. The lower limit of non-solvent plasticizer content is not particularly critical and is governed largely by the temperature at which the heat-sensitive paper is to be used. Using commercially available equipment, such as the Thermo-Fax Copying Machine (from Minnesota Mining and Manufacturing Co.) a blushed film containing 20 parts butyl stearate to 80 parts Lucite 41 has been found to be very desirable. Lower ratios can, of course, be used, especially when the paper is to be used at higher development temperatures. Higher ratios of butyl stearate can be used but are less desirable especially when good abrasion resistance is needed. By experience it has been noted that ratios higher than about 45% non-solvent plasticizer are not sufficiently abrasion resistant to be of any practical use in the Thermo-Fax Copying Machine.

The blushed film may contain small amounts of certain flatting agents to decrease the gloss of coating. We have found, for instance, that small amounts of metal soaps and ethyl hydroxyethyl cellulose will substantially reduce gloss. Such additives generally increase the heat and pressure sensitivity of the coating.

The blushed films are formed on the paper by coating with a blushing lacquer containing the thermoplastic polymer and butyl stearate, or equivalent non-solvent plasticizer, dissolved in a mixture of at least two volatile organic liquids, the more volatile of which is a solvent for the thermoplastic polymer and the other is a non-solvent for the polymer. When applied to the paper the two solvents are present in such a ratio that the polymer is in solution; however, as the more volatile solvent evaporates from the film faster than the non-solvent, the polymer tends to precipitate to form the blushed film that is required. As indicated hereinabove such technique for forming blushed lacquer films is known.

With polymethyl methacrylate as the thermoplastic film-forming polymer, a low boiling ketone, such as methyl ethyl ketone is a preferred volatile solvent for the polymer and a hydrocarbon fraction rich in aliphatics is the preferred non-solvent. Preferably the non-solvent should require at least five times as long to evaporate as the ketone solvent.

The preferred method of using the heat-sensitive copying paper of the present invention is by the "front-printing" method, i.e., the heat-sensitive paper is placed on top of the original to be copied and the original is exposed by passing infrared energy through the copy sheet. It follows therefore that in this preferred embodiment the copy sheet must be infrared transparent while at the same time it is substantially opaque to visible light.

Heat-sensitive papers made in accordance with the present invention have many advantages over commercially available heat-sensitive copying paper, the copies are more permanent when exposed to sunlight, the paper is not brittle and therefore has no tendency to crack or rupture when the paper is folded, the paper has no tendency to curl, the paper has no tendency to stick to the original during development of the color.

The following examples in which parts are by weight will further illustrate the invention:

The drawing shows a cross section of the copying sheet.

Example 1

A blushing lacquer consisting of 66.7 parts methyl ethyl ketone, 10.2 parts Lucite 41, 20.5 parts Mineral Spirits (Varnolene, boiling range 310–385° F.; KB 37.5), 2.6 parts butyl stearate was uniformly coated on a black carbonizing tissue that is infrared transparent at the rate of about 1.0 lb. of solids per 1000 sq. ft. The coating can be applied by conventional means, e.g., using a Mayer Rod coater. The opaque blushed film is developed by allowing the solvents to evaporate. The heat-sensitive papers produced can be used to produce copies by the front or back printing technique using the middle exposure range of the Thermo-Fax copying machine. If the butyl stearate concentration in the blushed film is increased less exposure is required to obtain copies which would indicate that the melting point of the composition is decreased. However, capillary tube melting points run on the finely divided coating indicate that as butyl stearate increases so does the temperature at which the coating becomes translucent. This indicates that factors other than the melting of the coating contribute to the successful application of the coated paper as a heat-sensitive copying paper. We have further noted that in actual performance in the Thermo-Fax machine, a coating which melts at 122° C. containing 67% Lucite 41 develops copies at a shorter exposure time than a coatinging that melts at 115° C. and containing 80% Lucite 41 and 20% butyl stearate. This again suggests that development of copies is not to be solely attributed to the melting point characteristics of the coating.

Other non-solvent plasticizers that have been substituted with some success for butyl stearate in the above example include oleic acid, paraffin oil, propylene glycol monoricinoleate and castor oil.

Example 2

A blushing lacquer consisting of 9.3 parts Lucite 41, 69.8 parts acetone, 18.6 parts mineral spirits (boiling range 247–290° F.; KB 33.8) and 2.3 parts butyl stearate was coated on black carbonizing tissue as in Example 1 to obtain an opaque white coated heat-sensitive paper that can be used to produce copies by the front or back printing technique described hereinabove.

The blushing lacquers of either Example 1 or 2 can be coated on both sides of the sheet. The double coated heat-sensitive sheets obtained in this manner are useful in the back-printing technique to produce copies on both sides of the sheet. The heat-sensitive coatings on the two sides of the sheet can be the same color or of different color as desired.

Advantageously in the practice of the present invention we can use a base paper stock that has been coated on the back side with a non-heat-sensitive resinous coating or pigmented resinous coating. Where the paper is to be used by the front printing technique it is of course necessary that the back coating on the paper be infrared transparent. Back coating of the paper provides a means of obtaining any desirable color on the back. A suitable infrared transparent back coating consists of:

	Parts
Styrene-acrylonitrile copolymer resin (e.g., Dow's Styril 767)	10
Methyl ethyl ketone	90

The coating is applied in conventional manner with a Mayer Coater using a #0 rod to insure the laying down of a minimum quantity of coating.

Example 3

A blushing lacquer consisting of 67.7 parts methyl ethyl ketone, 9.4 parts Lucite 41, 19.9 parts Mineral Spirits (boiling range 310–340° F.; Kauri-Butanol Value 34), 2.5 parts butyl stearate and 0.5 part zinc stearate was applied at the rate of 2 to 2.5 mg. per square inch to 8# Black Fenmore paper (Schweitzer Paper Co.) in conventional manner using a Mayer Coater. The heat-sensitive coated paper obtained can be used in the "front or back-printing" technique with the Thermo-Fax Copying Machine. The paper is less glossy than the heat-sensitive coated papers of Examples 1 and 2.

It is to be understood that the colored base sheet may consist of a layer or coating of a selected color coated upon a supporting base. Where such a base is used, the colored layer will be intermediate the supporting base and the heat-sensitive coating and consequently will show through at the heated areas. Such coated base sheets may be used both in the "front-printing" and "back-printing" processes. Of course in sheets used in the "front-printing" process, it is necessary that the colored layer as well as the supporting base be infrared transparent.

It has been found that a very desirable base sheet may be prepared by coating a supporting base with a composition comprising a Dianisidine Blue pigment Color Index (Second Edition) No. 21185 in a vehicle comprising a polymeric binder, a volatile organic solvent for said binder and a plasticizer.

Example 4

A coating having the following composition:

	Parts
Pigment consisting of 75% Dianisidine Blue C.I. No. 21185, 12% Medium Chrome Yellow and 12% Red Lake "C"	4.2
Cellulose acetate binder having a 39.8% acetyl content	8.5
Acetone	82.0
Sucrose acetate isobutyrate	5.3

was coated upon a white tissue in the conventional manner with a Mayer Coater using a #0 rod so that a coating

of less than 2 mg. per sq. inch was applied. The coating was then dried at 120° F. for about 1 minute to evaporate the acetone solvent. The resulting coating was opaque and dark. A blushing lacquer coating was then applied to the colored surface in accordance with the procedure set forth in Example 1. It should be understood that other polymeric binders, for example, methyl methacrylate may be used. The organic solvent selected is suitably a solvent for the binder. Other plasticizers, e.g., tricresyl phosphate may be used.

While the present invention has been primarily described as using opaque base sheets, particularly dark coated base sheets, it should be understood that the invention is not limited to such base sheets. In accordance with another aspect of this invention, the base sheet upon which the blushed lacquer films are coated may be transparent. When this copying sheet is used in the making of copies in the commercially available Thermo-Fax Copying Machine, the image or graphic representations of the original will appear as transparent areas against a visibly opaque background. In other words what results is a negative image not unlike that of a photographic negative. Copies of this type may be projected upon a surface such as a screen using a suitable projection device, e.g., overhead projection.

The transparent base sheet is preferably of a material which is highly transparent. Best results have been achieved using sheets of transparent polyethylene terephthalate, although transparent sheets of other materials such as cellophane, cellulose acetate, polyethylene, polypropylene and Celluloid may be used.

A highly desirable coated sheet having a transparent base may be obtained by coating the blushing lacquer composition set forth in Example 1 on a base made of a transparent sheet, 2 mils in thickness of polyethylene terephthalate resin marketed by E. I. du Pont de Nemours & Co., Inc. under the trademark "Mylar."

Although the invention has been described with particular reference to white, visibly opaque coatings on black paper, it is obvious that other contrasting color combinations can be employed.

We claim:

1. A heat-sensitive copying sheet comprising an infrared transmitting non-metallic supporting base and a visibly opaque, infrared transparent blushed coating thereon of contrasting color which transparentises when heated, said coating comprising a major amount of a solid thermoplastic polymer of methyl methacrylate having a melting point above 125° C. and a minor amount of butyl stearate.

2. A heat-sensitive copying sheet according to claim 1 wherein said supporting base is transparent.

3. A heat-sensitive copying sheet comprising an infrared-transmitting cellulosic sheet backing and infrared transmitting heat-sensitive blushed coating of contrasting color thereon, said coating comprising a major amount of a solid thermoplastic polymer of methyl methacrylate having a melting point above 125° C. and a minor amount of butyl stearate.

4. A heat-sensitive copying sheet comprising a supporting base comprising a non-metallic sheet having coated thereon a coating having a selected color and a visibly opaque, heat-sensitive blushed coating on said colored coating of contrasting color to said colored coating, said heat-sensitive coating comprising a major amount of a solid thermoplastic polymer of methyl methacrylate and a minor amount of butyl stearate.

5. A heat-sensitive copying sheet according to claim 4 wherein said colored coating is pigmented by Dianisidine Blue pigment.

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