March 1, 1960 W. H. VANDER WEEL 2,927,039

HEAT SENSITIVE COPYING SHEET

Filed March 7, 1957

FIG. 1

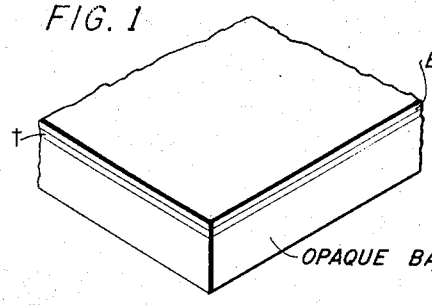


FIG. 4

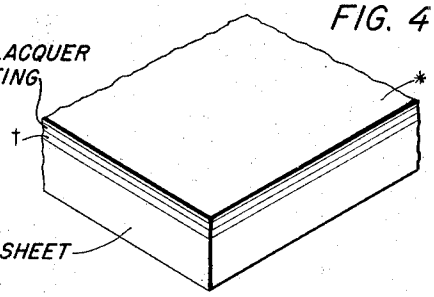


FIG. 2

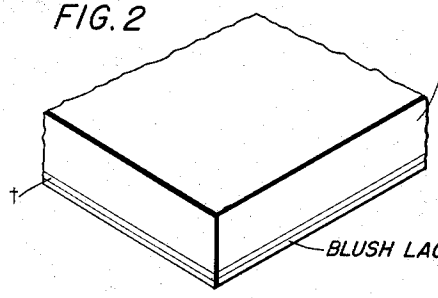


FIG. 5

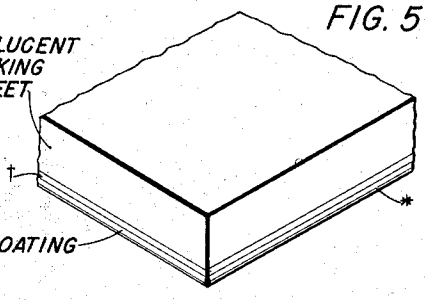


FIG. 3

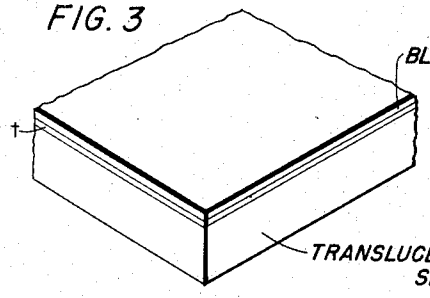
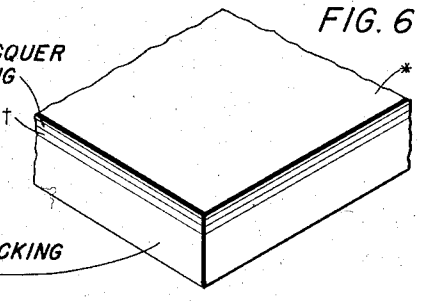


FIG. 6



* THIN FLEXIBLE HEAT RESISTANT ORGANIC POLYMERIC FILM

† COATING OF FUSIBLE MATERIAL

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HEAT SENSITIVE COPYING SHEET

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10 Claims. (Cl. 117—36)

This invention relates to copying sheets which may be utilized to make copies of original graphic material such as typewritten sheets, printed pages, photographs and the like by exposing to heat the original graphic material together with a copying sheet.

It has been proposed heretofore to provide copying sheets from which copies of such original material may be made by placing the copying sheet against the sheet or body of original material to be copied and exposing to radiant heat energy the two sheets thus placed in juxtaposition.

Furthermore a variety of compositions have been proposed for application to paper to provide such copying sheets and also to provide temperature-sensitive sheets of other types such as sheets for recording data in instruments of various sorts.

Such copying sheets to be of greatest value should meet a large number of requirements. They should have wide latitude, that is, at a given temperature the image in the copying sheet should be formed quickly and yet it is desirable that it be possible to cause the image to be formed in said copying sheet by exposure at any temperature within a fairly wide temperature range. It is desirable that they have a high speed. A sheet having a low speed must be exposed for a long time in order to cause image formation, and a sheet having a narrow latitude must be exposed at precisely the correct temperature in order to provide for the formation of an image consisting of a suitable copy of the material to be copied. If a sheet having such narrow latitude be exposed at a higher temperature it will change color throughout its entire area no matter how quickly nor how long exposed rather than forming a copy of the material to be copied whereas if exposed at a temperature below those at which a reaction is induced it will not form a copy at all.

Such sheets should also have high temperature storage stability, that is, they should not deteriorate under conditions under which most paper and office materials are used and stored in business, industry and commerce. Storage rooms and offices often contain storage cabinets located above or adjacent to heating units such as radiators and the like and temperatures in such storage cabinets not unusually reach temperatures of from 140 to 160° F. Duration of storage in such places may be from only a few days to as much as one to two years or more. It is also of importance that the copying paper not have a surface which will stick or adhere or offset, i.e., transfer, in any fashion to the surface of the original material being copied. The surface also should be one which will prevent "blocking," i.e., partial adherence between sheets of copying paper stacked on top of one another. In order to avoid such adherence or offsetting or blocking it is necessary that the surface not be greasy or waxy or tacky. It should not be greasy in the manner exhibited by wax-impregnated paper normally referred to as "wax paper" and represented by wax coatings applied over paper stock or by "carbon paper" which comprises

a thin paper stock having a coating of wax thereon with carbon black or other pigment material dispersed in the wax. A tacky surface is represented in an outstanding instance in a particularly objectionable manner for this present purpose by the surface of pressure sensitive tapes wherein a rubber base adhesive is applied to a base sheet such as cellophane or paper.

It is also extremely desirable that suitable thermal-copying paper be insensitive to pressure from sharp instruments of the sort it is likely to undergo in handling; it should be insensitive to the pressure of styli, pencils, finger nails, corners of typewriters, staplers and other office equipment which may be sharply brought in contact with it.

Suitable copying sheets should also be relatively easily fileable, i.e., not too flimsy to be placed easily into file folders and should not have a tendency to curl since curling also makes handling and filing of the sheets more difficult. It is also necessary and desirable that the copying sheet be stable to light; or in other words, to radiation from the electro-magnetic spectrum in the visible range.

In accordance with my invention I provide a thermal-copying sheet having improved high temperature storability, higher speed and wider latitude and greater resistance to blocking and offsetting or adhesion to material to be copied than sheets heretofore proposed. In accordance with a preferred embodiment of my invention I provide a sheet of white paper, more or less opaque to light, about .015 inch thick with a first coating of a waxy or other fusible material melting between 165° F. and 210° F. and over this second coating I provide a non-waxy, non-tacky layer of non-stylus pressure sensitive blush coating which has a thermal-sensitivity above 215° F., i.e., which melts above 215° F. and is adapted to be transparentized or at least translucentized throughout suitable areas corresponding to material to be copied by causing areas of said first coating adjacent thereto to become a liquid; the second layer does not itself become melted or softened.

There have been heretofore proposed a number of formulations for coatings on paper to provide thermal-copying paper wherein sensitivity to thermal-radiation is obtained by providing in said formulation two reactants which are of light color or disposed in a light colored media and which react upon being exposed to a suitable temperature to provide a dark colored reaction product. Usually one of such reactants has been a metal salt, often a salt of a heavy metal, and in some cases both of said reactants have been salts of heavy metals. With such formulations it has been generally necessary that one of the reactants, or both of the reactants or one of the reactants and the media in which the reactants are dispersed, melt within a range to which the material is to be sensitive and such sheets have exhibited a narrower latitude and lower speed than desirable and have been particularly deficient in being storable for only very short periods at high temperatures. Thus one sample of a thermal-copying paper utilizing a metal salt in the sensitive layer thereof and believed to contain in said sensitive layer an iron salt such as ferric myristate or ferric stearate and a compound such as tannic acid or hexamethylenetetramine-gallic acid reaction product, turned cloudy gray when stored for six hours at 140° F. and were unusable. Likewise storage of such papers at 100° F. for four days or at 110° F. for 2 days caused them to be unusable.

Another disadvantage exhibited by previous heat-sensitive copying papers has been poor contrast due to the color of reactants and reaction products utilized which limits the colors which may be used to those provided by such reactants and products; for example, the

previously mentioned paper has a buff or salmon colored surface prior to being heated and changes to no more than a blue-grey or a dull blue-black upon being heated. A paper is desirable which will exhibit sharp contrast, having a chalk white or very light colored surface prior to being heated and exhibiting jet black or other very dark color in the areas after being heated.

In accordance with my invention I provide a paper which exhibits these colors and the desired color change in a preferred embodiment. Other embodiments can be provided to exhibit any desired color contrast, there being no limitation imposed by reason of being limited to certain combinations of reactive chemicals.

Certain patents have heretofore proposed providing a blush lacquer coating on paper backing sheets. United States Patent 2,591,660 provides a blush coating on a backing sheet which is described as sensitive to a temperature of 80° and Patent 2,299,991 also describes such a coating on a dark surfaced foundation, the coating of the latter patent however, being sensitive to pressure such as may be exerted by a cold stylus or other extraneous influences such as finger nails, paper clips and the like, a particularly objectionable feature for thermal-copying paper. In the latter patent the backing sheet is dark paper or paper which is darkened by coating with a hardened dark colored coating. In other words, each of these patents provides a dark foundation backing sheet covered with a single blush lacquer layer. The material described in Patent 2,299,991 is not suitable as a thermal-copying paper because of its pressure sensitiveness while the material described in Patent 2,591,660 has less than desirable latitude, contrast and speed and fails to have other desirable qualities as herein set forth to an extent sufficient to make it relatively ineffective as a suitable copying paper. Because the blush lacquer layer is directly receptive to indicia producing media in both of these sheets, there exists a tendency to offset or transfer material of the coating to adjacent surfaces. This is especially true, moreover, of sheets having a waxy layer of material present and providing one surface of a sheet, as for example in carbon paper, wherein copies are made by utilizing such offsetting or transferring tendency.

With the copying sheet according to my invention, there is no offsetting or transfer of any of the material of the copying sheet onto the sheet of material being copied because no waxy surface is present at an outside surface of the copying sheet, the waxy or other fusible material being entirely covered by the blush coat and the blush coat itself being neither waxy nor greasy and not having been melted or softened as a result of the application of the heat. In the copying sheet of my invention the heat which produces the image in the copying sheet causes melting only of the layer of fusible material and this layer does not cause melting of the material of the blush or top coat.

It is thus an object of my invention to provide an improved heat-sensitive copying sheet which is not sensitive to stylus pressure, which is non-sticky and non-blocking, i.e., has a non-tacky surface devoid of greasiness and waxiness and which has improved latitude, speed and contrast by reason of comprising a backing sheet provided with a first coating which is waxy, i.e., fusible in nature and a second coating which consists essentially of a blush lacquer.

Further objects will become apparent from the drawings and the following detailed description in which it is my intention to illustrate the applicability of the invention without limiting its scope to less than that of all those equivalents which will be apparent to one skilled in the art. In the figures like reference numerals refer to like parts and:

Figure 1 is a magnified perspective view of a portion of a copying sheet adapted for printing by transmission of infrared rays passing through the sheet of material to be copied onto the coatings of the copying sheet;

Figure 2 is a magnified perspective view of a portion of a copying sheet adapted for reflex printing by passage of infrared rays downward through the translucent or transparent backing sheet, thence against the surface of material to be copied and thence by re-radiation or conduction into the coatings on the copying sheet;

Figure 3 is a magnified perspective view of a portion of a copying sheet adapted for reflex printing by passage of infrared rays downward through the coatings at the top of the copying sheet, thence through the translucent or transparent backing sheet into contact with the material to be copied and thence back therefrom upwardly by reflection, re-radiation or conduction through the translucent backing sheet into contact with the coatings thereon;

Figure 4 is a magnified perspective view of a portion of a modified form of the sheet of Figure 1;

Figure 5 is a magnified perspective view of a portion of a modified form of the sheet of Figure 2; and

Figure 6 is a magnified perspective view of a portion of a modified form of the sheet of Figure 3.

As shown in the figures, a backing sheet which may be opaque, as shown in Figures 1 and 4, or translucent or transparent, as shown in Figures 2, 3, 5 and 6, is provided with a first coating of fusible material and on top of the first coating of fusible material, with a second coating consisting essentially of a blush lacquer. Copying sheets made with translucent backing sheets may be utilized for reflex copying whereas if the backing sheet is opaque, copying is by the transmission method.

As shown in Figures 4, 5 and 6 the sheets of Figures 1, 2 and 3 may be modified by applying over said second coating a layer of thin flexible heat resistant organic polymeric film. The film may be formed apart from the sheet and applied by laminating or may be formed in situ by coating or dipping. The base material is preferably one which has sufficient rigidity to provide for suitable fileability; that is, it should provide a copying sheet which will not curl or be flimsy and which therefore can be easily placed in files and the like.

Materials heretofore proposed have generally been flimsy and have generally curled badly so that filing of them has been difficult. A preferred base material is an opaque material which is reasonably transparent to heat, has a rough surface to provide good adhesion to coatings and has excellent uniformity of fiber structure and is devoid of fiber and filler irregularities which tend to cause graininess in an image. Suitable papers include a .019", 13 lb. (per 500 sheets of 20 x 30 inch size) milo paper produced by S. D. Warren Company, Portland, Maine; a .020", 15 lb. (per 500 sheets of 20 x 30 inch size) white milo paper produced by the same company; and a .015", 25 lb. (500 sheets of 24 inch x 36 inch size) white grease-proof paper made by the Riegel Paper Company. Observations of these and other papers were made with an Ansco-Macbeth densitometer to determine transparency to infrared rays and these were found highly satisfactory for this purpose. Other opaque and transparent papers may be used and there may also be used plastic sheet materials such as cellulose acetate, cellophane, Mylar, cellulose acetate butyrate, or sheets of thermo-setting resin reinforced with glass fibers as set forth in U.S. Patent 2,718,476. For certain purposes, such as utilization in the aircraft industry for outlining templates to be cut from sheets of metal, the coatings as hereinafter described may be provided on a base sheet consisting of steel or aluminum or other metal and for utilization for copies having high dimensional stability in connection with various applications in the cartographic and graphic arts industries, the coatings may be applied on a base material comprising tracing paper which normally consists of a cotton or linen woven fabric impregnated with calendered starch or other thermoplastic material.

The color of said backing material is preferably light

to provide improved contrast but under circumstances as hereinafter described wherein the first fusible coating placed thereon is made relatively transparent, an opaque paper may be provided in a color sufficiently dark to contrast with the light color of the second layer hereinafter described.

Generally speaking a backing sheet paper which provides a particularly satisfactory copying sheet in accordance with the invention is from .012" to .030" thick.

There is applied to the backing material, as hereinbefore described, a first coating of fusible material which may comprise, for example, a mixture of a hard wax having a high melting point with a softer wax having a somewhat lower melting point and coloring matter such as one or more dyes to provide the desirable dark color therein. Carnauba wax, which melts at 170° F. to 200° F. is particularly suitable as a wax of the first type and montan or ceresin or paraffin wax may be suitably utilized as said second wax. The layer of fusible material may be clear, i.e., transparent or translucent, or it may be colored by addition of coloring material or use of colored waxy materials or both. As a coloring agent or coloring material to be included with the waxes there may be used a pigment or a dye; a pigment, however, tends to absorb infrared radiation with resultant heating and therefore reduces contrast and dyes are generally preferred since they tend to transmit infrared rays rather than absorbing and converting such rays into sensible heat. Suitable dyes which may be utilized include, for example, for a green color, a mixture of 10% Iosol Yellow (National Aniline Company) plus 90% of Victoria Blue, BOC, as sold by Du Pont, or Victoria Blue base, as sold by Du Pont. There may also be used Crystal Violet, as sold by Dye Specialties, Jersey City, or Methyl Violet, as sold by National Aniline Company. To provide a dark red color there may be suitably used Rhodamine B-base as sold by Du Pont.

Preferred colors are dark green and dark blue but it is preferred to provide for a plurality of colors so that various colors may be used for various purposes by ultimate users to indicate, for example, the types of material which have been copied or locations in which such copies should be filed or other information.

A suitable green color can be obtained by utilizing as a component in a wax formulation for the fusible layer, a ceresin wax which is yellow. There may be used, for example, ceresin #C–500 sold by Strahl & Pitsch, or any other suitable ceresin. Ceresin wax generally melts in the range 130 to 175° F.

As mentioned above, it is preferred to utilize both a hard high melting point wax and a soft low melting point wax in the formulation and it is generally preferred to use ratios of these two waxes of from about 2 to 1 to 9 to 1. With concentrations of soft wax higher than represented by a proportion of 2 to 1, the dye or dyes which tend to be soluble primarily in the harder waxes tend to be precipitated out and high temperature storage stability is reduced; with a proportion of over about 9 to 1 of hard wax to soft wax the layer is too brittle and tends to flake and break away from the base material and the top coating. The preferred range is from 5 to 1 to 3 to 1.

As mentioned hereinbefore, either carnauba, for example, triple refined No. 3 North Country wax or montan wax may be used. As a soft wax there may be used any one of a wide number of paraffins in place of ceresin as previously described.

There may also be provided in a formulation of waxes for the layer of fusible material a small quantity of oil for the purpose of reducing or eliminating any tendency to flake and in order to make the layer darker for higher contrast and to aid in assuring complete solution of the dye in the layer. With less than about .5% no useful results are obtained and generally about 1% is the minimum with which suitable improvement can be obtained by adding oil; the preferred amount of oil is about two percent and if more than four or five percent be used, the oil tends to bleed or exude from the layer into the top or second layer of blush coating with deleterious results. In the event that too much oil is used, this tends to happen particularly at higher temperatures and reduces storage stability at such temperatures. Suitable oils include castor oil, stearic acid or any long chain fatty acid, red oil and petrolatum.

The formulation for the wax is heated to from about 200° F. to about 230° F. and coated on a suitable backing sheet by any suitable means; for example, in the case of materials for templates wherein the coating is to be applied to aluminum or steel sheets, it may be applied with a brush or by spraying or dipping. Preferably it is applied by means of a suitable coating technique for obtaining a thin coating of relatively uniform thickness using standard coating equipment such as a knife coater, reverse roll coater, or the like. It is particularly suitable to coat with a transfer roll which operates with one side of the roll dipping into a pan of the material to be coated and the other side of the roll running against a web of paper or other sheet material. After passing over the roll the web is then passed over a Mayer equalizer rod consisting of a rod of about one quarter inch diameter wound with wire in the form of a tight coil or helix, the wire being preferably No. 6 wire. It is preferred to coat from about 3 to 7½ pounds of waxy or other fusible material per ream of 500 sheets of paper each sheet being 20 inches by 30 inches in size, which is equivalent to a coating of 3 to 7½ pounds per 283 square feet or 31½ square yards and optimum results are generally obtained with about 5 pounds per ream, although suitable results may be obtained with a coating as thin as .0005" or as thick as .010".

In place of the wax formulations as hereinbefore described there may be utilized a synthetic resin or synthetic resins of suitable melting point and adhesive characteristics; for example, modified rosin esters such as Staybelites made by Hercules Chemical Company or polyterpenes such as Piccolites made by Pennsylvania Industrial Chemical Company may be used or polyethylene glycols such as the Carbowaxes made by Carbide and Carbon Chemical Company or polyethylenes such as made by U.S. Industrial Chemicals Company or made by Allied Chemical and Dye Corporation or others may be used.

However, a preferred synthetic resin for the waxy or fusible layer is a latex or latex-like composition, i.e. an emulsion comprising an elastomeric or other polymeric synthetic resin which is thermoplastic in nature. Such a polymeric resin may be polyvinyl chloride, polyvinyl alcohol, polyethylene, polyvinyl acetate, copolymer of vinyl acetate and vinyl chloride, halogenated polyethylene, natural rubber i.e. polyisoprene, polychloroprene, polybutadiene, copolymer of any one of the last three with styrene and/or acrylonitrile, or other monomer adapted to undergo polymerization through ethylenic unsaturation. A suitable plasticizer may be included. A particularly suitable such polymeric composition has been found to be a rubber latex adhesive such as those sold commercially by Industrial Latex Corporation as RX 70 and RX 69. In order to make certain that a fusible layer comprising such composition does not exhibit pressure-sensitiveness which is objectionable as hereinbefore mentioned it is necessary that the thickness of such coating be maintained within the limits hereinbefore mentioned.

Rather than merely a layer of such polymeric resin I may suitably utilize a layer of material of relatively high melting point having dispersed therethrough a very large number of very small discrete fusible particles, crystalline or amorphous, rough and irregular or spheroidal, immiscible in the carrier. Thus I may provide a layer of cellulose acetate having dispersed therethrough small

particles of one or more substances such as stearic acid, potassium stearate, triphenylphosphate, N-ethyl o- and p-toluenesulfonamide, N-ethyl p-toluenesulfonamide, o- and p-toluene ethylsulfonamide, and N-cyclohexyl p-toluenesulfonamide (sold commercially by Monsanto Chemical Company as "Santicizer" 9, 3, 8, and 1–H, respectively), camphor and solid animal fat. Other suitable carrier materials include cellulose nitrate, cellulose propionate, ethyl cellulose, ethyl acrylate, and the like.

Particular advantages of the copying sheet according to my invention are that by reason of providing the first coat of fusible material and the second coat of blush coating material, the fusible material stays completely unchanged during storage resulting in high temperature storability for long periods. When a portion of the material is heated, for example, by being exposed to infrared rays while the copying sheet is in contact with the sheet of material to be copied so that portions of it are adjacent to black letters or symbols or other graphic material on the sheet to be copied, infrared rays are absorbed by such black indicia with the result that adjacent portions of the copying sheet are heated more than those portions of the copying sheet which are adjacent white portions of the sheet of material to be copied. The fusible material becomes melted adjacent to the black or dark indicia on the sheet of material to be copied and in such areas the fusible material transparentizes or translucentizes the blush coating by (it is believed) flowing into the pores thereof, i.e., the second coating is made transmissive to light to the extent of transmitting at least 50% of incident light rays in the visual range. In any event, upon removal of the heat source the fusible material sets again and stays set permanently. A copy of the original material to be copied is thus produced in the copying sheet by reason of the contrast between the translucentized or transparentized areas of the blush coat through which there is observable the dark colored fusible layer and those areas of the blush coat which have not been made transmissive and therefore remain opaque and light in color.

As hereinbefore mentioned, the layer of fusible material may be clear, i.e., all dye or other coloring matter may be omitted therefrom and the underlying base material may be made black or dark in color whereby when a portion of the sheet is heated after being coated with both the first and second coatings, the first coat translucentizes or transparentizes the second coat in the heated area thus causing the color of the backing material to be observable in contrast to the unchanged portion of the top or blush coat.

As a suitable formulation for the top or blush coating there may be utilized a lacquer made by dissolving scrap cellulose acetate in acetone and then adding acetone and water as blushing agents, in the proportions of about 10 parts of cellulose acetate dissolved in a solvent mixture comprised of about 90 parts of acetone and 10 parts of water or there may be suitably utilized pyroxylin dissolved in a solvent mixture which comprises water as set forth in Patent 1,449,157. Formulations utilizing ethyl cellulose or cellulose acetate dissolved in mixtures comprising acetone and water as set forth in Patent 2,519,660 may also be utilized.

If desired, a pigment or dye or other coloring matter may be incorporated as a tinting agent in the blush coat.

In order to improve the adhesion of the second coat for the first coat there may be added to the formulation for either of the coats from 1% to 3% of a relatively tacky material such as Flexowax or a modified rosin ester or rosin, the material preferably being added to the formulation for the first or fusible layer in order to avoid the presence of such material at the surface of the blush coating with possibility of resultant transfer or offsetting.

There may also be included in either the formulation for the first coating or the formulation for the second coating a so called matting agent for promoting adhesion. If added to the formulation for the top or blush coating such a matting agent may have the additional advantage of providing a more writable surface, i.e., a surface more receptive to pen and pencil. Such matting agents, include finely divided mineral products such as celite, bentonite, talc, diatomaceous earths and the like.

Another manner by which improved adhesion between the two layers may be obtained is to heat the top surface of the layer of fusible material just prior to applying the formulation of the blush coating so that at the time the blush coating is applied thereto the surface of the wax or other fusible material is soft or somewhat liquid.

It is generally desirable that the outer surface of the copying sheet according to the invention be receptive to pencil lead, ballpoint ink and fluid ink in order that corrections, interlineations or the like may be easily made thereon.

For this purpose I may add a matting agent as mentioned above or may add instead or additionally a finely divided solid which is insoluble in the blush coating carriers, i.e., insoluble in the solvent system utilized for dissolving the resin of the blush coating formulation. Such a finely divided solid may be colored to provide a colored or tinted blush coat as hereinbefore mentioned but is generally preferably light colored or white and may improve adhesion of the blush coat to the underlying surface of the first coating. Utilization of such a finely divided solid has been found to provide an improved white or light color in the blush coat and has been found to increase the temperature resistance of the blush coat thereby increasing the high temperature storability and reducing the tendency of the blush coat to be melted or transparentized by application of heat thereto or to be translucentized or transparentized other than by melting of the underlying layer of fusible material. A preferred solid for this purpose is raw starch, for example rice starch, but there may be used other siliceous powder particles, ground earths, and the like it being necessary primarily that such material be finely divided and be absorbent with respect to the solvent and resinous components in the blush coating lacquer but be insoluble in the carriers for the blush coating, i.e., the solvent or the resinous components thereof and be light in color.

The second or blush coat may be applied by any suitable coating method; for example, it may be applied to stainless steel or aluminum sheets by spraying or brushing or dipping or to paper or plastic sheets in the same manner but it is preferred generally to apply it by means of standard coating techniques and standard coating equipment, i.e., by knife coating, reverse roller coating and the like. A preferred coating is obtained if the formulation is applied to a continuously advancing web of paper by means of a transfer roll and a Mayer equalizer rod in such quantity and at such a rate as to provide a coating having a thickness of .0002" to .008" and optimum results have been achieved with a coating .0005" to .006" thick. The blush coatings as thus described are non-pressure sensitive, that is are not sensitive to stylus pressure and do not mark or exhibit any indicia when scratched with a fingernail or with a sharp point as with a toothpick or stylus and they have non-greasy and non-waxy surfaces which are devoid of tackiness both during storage and during the time when heat is applied thereto to cause the underlying layer of fusible material to be melted in order to make the blush coat transmissive to visible radiation.

The invention is further illustrated by the following examples which illustrate certain embodiments but are not to be taken as limiting the invention only to those particular embodiments illustrated, it being understood

that other embodiments and equivalents will be apparent to those skilled in the art.

Example 1

A coating having the following formula:

24 pounds carnauba wax
12 pounds ceresin wax
1 pound dry blue base

was mixed and coated on a web of 16 pound white milo paper as hereinbefore described to provide a coating of six pounds per ream of fusible waxy material, green in color and about .003" thick. A second formulation was prepared as follows, in accordance with Example 1 of U.S. Patent 2,519,660:

	Pounds
Ethyle cellulose N–100	5
Acetone	45
Di-2-ethyl hexyl phthalate	.75
50% solution of acetone in water	100

Five pounds of raw rice starch were added and mixed with the other ingredients and the resulting material was coated on top of the green waxy layer of the web at room temperature using a Mayer equalizer rod to provide a second or top coating layer having a thickness of about .004". Copying sheets were cut from the resulting web, laid against printed sheets and exposed for about 20 seconds at 180° F. by utilizing a machine for exposing the sheets to infrared radiation as hereinafter described. Excellent copies of the printed material were obtained. The blush coating is described by James in said patent as softening sufficiently to provide marking with a stylus at 115° C. The presence of the starch tends to raise its melting point so that the value of 115° C. is low. It will be noted that this is well above the temperature at which I desire to print the sheets or at which the sheets were printed by exposing at 180° F. The top coating is translucentized and transparentized by reason of the melting of the first coating, i.e., the underlying layer of waxy material while the top blush coating itself remains unmelted. Copying sheets were stored for one week at 150° F. and no deterioration was observed. Both surfaces of the copying sheets prepared were free of tackiness and were neither waxy nor greasy and did not off-set against the printed sheet of the material being copied during printing.

Example 2

A sheet of cellulose acetate .015" thick is coated with two coatings in accordance with Example 1 to provide copying sheets with visually transparent backing material which exhibit the same desirable properties with respect to printing and storage as observed in the case of the sheets in Example 1.

Example 3

The following formulation:

24 pounds carnauba wax
6 pounds paraffin
1 pound dry blue base

was mixed and coated with a transfer roll and a Mayer equalizer rod on a web of 25 pound white grease-proof paper as hereinbefore described.

There is then applied a coating of the following formulation:

10 grams pyroxylin
100 cc. solvent mixture comprising 25% by volume of ethyl acetate and 100% by volume of a mixture of 90% ethyl alcohol and 10% water

The coating is applied to the web over the first coating with a Mayer equalizer rod and corresponds to the blush coating described in Patent 1,449,157 with the exception that the plasticizer is omitted in order to provide a blush coating which is non-stylus pressure sensitive and which has a melting point substantially above the melting point of the underlying fusible waxy layer. Copying sheets were cut from the resulting web and printed at 185° F. and tested for storage as described in Example 1 and were found to have the desired properties heretofore described.

Example 4

The web of Example 3 was provided with an overlying sheet of regenerated cellulose, i.e., cellophane in contact with the top or blush coating in order to increase the rigidity of the copying sheet and to reduce therein any tendency to curl under varying conditions of humidity or temperature.

Example 5

The following formulation:

24 pounds carnauba wax
6 pounds ceresin wax
2 pounds dry blue base dissolved in 2 pounds of castor oil

is applied to sheets of 25 pound mimeograph bond which is relatively transparent to infrared radiation by spreading the formulation, mixed and heated to 210° F., over the sheet with a rod to provide a coating having the thickness of from .0005" to .006". Over said first coating there then was applied at room temperature with a rod a second coating .001" to .004" thick of the following formulation:

15 pounds cellulose acetate
60 pounds acetone having added thereto a mixture of 25 pounds acetone and 30 pounds water

Sheets thus prepared were printed as in Example 1 and found to have the good properties therein described. The top coating formulation thus applied is described in Patent 2,519,660 as "marking at 170° C." In any event, it was found that the composition remained solid and provided the desirable surface properties of non-tackiness and being neither waxy nor greasy during printing, not off-setting on the copy sheet or other copying sheets during storage or on the material being copied during printing, the top coating remaining unmelted during printing, storing and being translucentized and transparentized entirely as a result of melting of the underlying waxy layer.

Example 6

Using the procedure of Example 3, an emulsion of rubber in water sold commercially by the industrial Latex Corporation as RX 70 was applied with transfer roll and Mayer equalizer in place of the wax formulation therein set forth and copying sheets were obtained having the same desirable properties.

Example 7

95 parts—
1500 grams polyvinyl acetate beads (sold commercially by Colton Chemical Corporation as Vinac B–75)
3500 mil. acetone
5 parts triphenyl phosphate

The above materials were thoroughly mixed to provide a viscous fluid which was then coated on a .003" white opaque specialty paper with a coating rod and dried to evaporate the solvent, to thereby provide a coating .0005" to .002" thick. A coating of the blush lacquer formulation of Example 1 was then applied thereupon and dried. Sheets thus prepared exhibit good high-temperature storability and suitability for thermal printing.

Any one of the several sheets prepared in accordance with the foregoing examples may be provided over the

aforedescribed top or blush coating with a layer of a transparent thin flexible heat resistant organic polymeric resin which may comprise, for example polymethyl methacrylate or may comprise cellulose acetate or regenerated cellulose or the like, generally a thermoplastic organic synthetic polymeric resin being preferred in a thickness of from .0002" to .002", to provide greater rigidity in the sheet, to reduce tendency to curl, to improve storageability and to provide a sheet having a glossy appearance. Said overlying layer may be a film and may be applied by laminating or may be applied by coating thereon a lacquer formulation comprising the desired resinous component or components. Such lacquer formulation may comprise the desired resinous component such as polymethyl methacrylate, polyethyl methacrylate, cellulose acetate, cellulose acetate butyrate, or the like dissolved in suitable solvents, the material being applied by any standard coating technique for this purpose such as spraying, dipping or brushing or preferably coating with a roller, knife, or Mayer equalizer rod or the like. It is desirable that the outer surface of such layer be receptive to pen and pencil and such receptivity to be provided by abrading with said paper or sand blast or the like, or by etching with a solvent or mixture of solvents or by calendering with a suitably embossed roll.

A particularly desirable attribute of copying sheets produced in accordance with my invention is that a copying sheet according to the invention which has been printed from original material, i.e., on which there has been printed an image by exposing the sheet to infrared radiation while in contact with material to be copied, may thereafter be used as an original from which another copy can be made on another copying sheet according to the invention. This has not been possible with thermal copying sheets hereinbefore. The sensitivity and the latitude, etc. of the sheets of my invention is such that the background in the copying sheet may not be blackened by infrared rediation when exposed for a short time together with another such copying sheet upon which an image has already been made and at the same time those portions of the second copying sheet in contact with previously exposed and printed portions of the first copying sheet print to form an image corresponding to the image on the first copying sheet.

Printing may be accomplished in any suitable manner; a preferred manner is to utilize a machine or any suitable device for exposing to a heat source the copying sheet while in contact with a sheet of original material to be copied such as a printed page or a sheet of paper having typewritten indicia thereon to a heat source. Suitable means is described in such patents as U.S. Patents 2,663,655 and 2,740,895 for reflecting infrared radiations from a highly heated rod or filament against a portion of both the copying sheet and the sheet of material to be copied while the sheets are passed over the rod or filament, being held in place between a belt of heat resistant synthetic resin, such as, for example polychlorotrifluoroethylene, and suitable holding means.

The copying sheets of the invention may not only be utilized for copying such conventional graphic material as printed or typewritten sheets but may be used to copy other graphic material such as photographic prints and negatives and hand-written or drawn sheets and non-graphic materials such as apertured and non-apertured masks or stencils carrying visually unobservable indicia or apertured indicia.

In addition to the base material provided with a first layer of fusible material and a second or blush coat layer and, in some instances, a third layer of transparent organic synthetic resin, there may be provided on the opposite side of the base material from the aforesaid coatings, a coating of either waxy or other fusible material or lacquer such as a coating of raw or bleached montan wax or cellulose acetate or pyroxylin or the like in order to improve the properties of the sheet by making it more rigid and less likely to curl when exposed to excessively low or excessively high temperatures or humidities, etc. Such coating may in some instances have a somewhat deleterious effect on other desirable properties of the sheet but a coating is generally preferred which will not thus affect other properties of the copying sheet such as latitude, contrast, speed and resistance to blocking, off-setting and the like.

In some instances it is desirable to provide indicia on the copying sheet while in web form prior to cutting it into smaller sheets or on the smaller sheets after they are cut from the web for any one of a multitude of purposes: for example, advertising material, trademarks, indication of type or grade, product identification and the like may be desirably provided on the sheet. Such indicia may be provided by rolling a heated wheel or otherwise passing a marking tool along one or more edges of the web or small sheets cut from the web or coated individually, the wheel being provided with upraised or indented portions corresponding to the indicia to which it is desired to provide on the sheet to thereby heat these portions of the sheet contacted by the marking tool and cause indicia to appear thereat. Such indicia alternatively or additionally, if desired, may be provided by printing thereupon using standard printing inks and technique.

In some instances, it may be desired to provide copying sheets adapted for certain highly specialized uses wherein it is desired to make copies of not all but only a portion of the indicia appearing upon an original sheet. For example, it is a well known procedure in many businesses to prepare shipping lists or packing lists by making a copy of that portion of the indicia appearing upon the original invoice which relates only to packing or shipping. Normally the indicia which appear on the invoice and which it is desired to omit on the packing list are the prices and pricing information. For utilization in this manner, copying sheets can be prepared according to my invention wherein the first and second coating and, if desired, the third layer, are provided only in those areas of the coating sheet in which it is desired to make a copy of the indicia which appear upon certain original sheets.

It may be seen from the examples and description given herein that my invention is broad in scope and is to be limited only by the claims.

Having thus disclosed my invention, I claim:

1. A heat sensitive dry non-light sensitive copying sheet devoid of sensitivity to stylus-pressure and having surfaces devoid of tackiness and waxiness for making visible legible copies in contrasting tones directly from material to be copied by exposure to infrared rays comprising a sheet of backing material having thereon a first coating .0005" to .010" thick consisting essentially of a heat-sensitive fusible material which is solid and non-tacky below about 165° F. and melts to a viscous liquid at from 165° F. to 210° F. the combination of said backing sheet and said first coating being dark colored to contrast with a light colored second coating and having on said first coating a second coating of a non-stylus-pressure-sensitive blushed light-colored lacquer film devoid of tackiness which is normally opaque below a temperature of about 215° F. but which is adapted to be made at least translucent by melting of said first coating and to remain at least translucent upon subsequent solidification of said first coating and which has a non-greasy and non-waxy surface before, during and after being made translucent.

2. The copying sheet of claim 1 wherein said backing material is light colored substantially opaque paper .012" to .030" thick and relatively transparent to infrared rays and said first layer is of a color sufficiently dark to contrast with the light color of said second layer.

3. The copying sheet of claim 1 wherein said backing material is substantially opaque paper of a color suffi-

ciently dark to contrast with the light color of said second layer, .012" to .030" thick and relatively transparent to infrared rays and said first layer is substantially transparent.

4. The copying sheet of claim 1 wherein said backing material is substantially transparent organic polymeric material.

5. A copying sheet in accordance with claim 1 having on said second layer a thin flexible heat resistant organic polymeric film.

6. A heat sensitive dry non-light sensitive copying sheet devoid of sensitivity to stylus-pressure and having surfaces devoid of tackiness and waxiness for making visible legible copies in contrasting tones directly from material to be copied by exposure to infrared rays comprising a sheet of backing material having thereon a first coating .0005" to .010" thick consisting essentially of a heat-sensitive fusible material which is solid and non-tacky below about 165° F. and which melts to a viscous liquid at from 165° F. to 210° F. the combination of said backing sheet and said first coating being dark colored to contrast with a light colored second coating and having on said first coating a second coating .0002" to .008" thick of a non-stylus-pressure-sensitive blushed light-colored lacquer film devoid of tackiness which is normally opaque below a temperature of about 215° F. but which is adapted to be made to transmit 50% of incident light rays in the visual range by melting of said first coating and to remain thus transmissive to light upon subsequent solidification of said first coating and which

has a non-greasy and non-waxy surface before, during and after being made thus transmissive.

7. The copying sheet of claim 6 wherein said backing material is light colored substantially opaque paper .012" to .030" thick and relatively transparent to infrared rays and said first layer is of a color sufficiently dark to contrast with the light color of said second layer.

8. The copying sheet of claim 6 wherein said backing material is substantially opaque paper of a color sufficiently dark to contrast with the light color of said second layer, .012" to .030" thick and relatively transparent to infrared rays and said first layer is substantially transparent.

9. The copying sheet of claim 6 wherein said backing material is substantially transparent organic polymeric material.

10. A copying sheet in accordance with claim 6 having on said second layer a thin flexible heat resistant organic polymeric film.

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