July 13, 1965

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3,194,677

PROCESS FOR FORMING NON-TRANSPARENT HEAT AND/OR PRESSURE TRANSPARENTIZABLE FILMS

Filed March 20, 1962

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This invention relates to a process for forming non-transparent thermoplasticizable films on various solid transparent materials; more particularly it relates to a process for forming non-transparent films on such materials which films are adapted upon application of localized heat and/or pressure to revert to transparent state.

While the present invention has particular utility in the graphic reproduction arts wherein the characteristics of films on copy sheets are changed in response to locally applied heat and/or pressure, it is to be understood that the method of the present invention is eminently suited to the production of non-transparent films on any of a variety of solid transparent thermoplastic materials.

The prior art includes many examples of copy sheets having opaque heat and/or pressure transparentizable films coated thereon. These prior art opaque film coats are produced in the main by dissolving organic transparent substances in solvent-non solvent mixtures or in selected combinations of solvents to produce the well known blushed surface. Similar methods are based on the fact that some organic materials in the form of emulsions or suspensions dry to an opaque film. In all of the prior art methods the solutions are coated on suitable background sheets and dried through evaporation of the solvents and non-solvents to produce films characterized by light diffusing properties and characterized by their ability to be rendered transparent in response to heat and/or pressure.

The methods employed to produce the prior art opaque transparentizable film coats generally require large amounts of solvents and other vehicles to keep the compounds sufficiently fluid. This requires close supervision as a judicious balance of the proportions of the ingredients must be maintained. Further, the prior art methods require special machinery such as solvent recovery devices, drying channels, humidity controls, etc.

In accordance with the present invention organic thermoplastic materials either with or without binders, coloring agents, substances to regulate the melting point range, heat transfer characteristics, and hardness, as well as other substances to advantageously change other physical properties and chemical characteristics, may be rendered fluent by the use of heat, thinners or solvents, and thereafter coated, sprayed or brushed on carrier members, or may be extruded and settled on a carrier member, depending on the manufacturing process. The coating on the carrier member, after it has solidified in the case of a hot melt coating, after it has dripped in the case of a solvent or spray coating, or after it has cured or settled in the case of an extruded coating process, is rendered non-transparent by subjecting it to a developer fluid which may be spread upon the coating by ink rollers, gravure cylinders, cut out rollers, or sprayed or brushed on the coating, or the coated carrier can be immersed in the developer by driving it through an ink pan containing the developer fluid whereby the developer fluid will act to etch or otherwise cause the coating to become light diffusing hence non-transparent.

In the specification by developer fluid it is meant a solution having a desired solvent power, or a solvent solution which may include color forming components, film formers and other substances as may hereinafter appear which serve, for example, to enhance the opacity and to control properties of the finished coating or film, such as flexibility, color and hardness.

While the coating may be applied by any of the hereinafore mentioned processes, the hot melt coating process lends itself most readily to the manufacturer of heat and/or pressure sensitive sheets in accordance with the invention, particularly with conventional carbon paper coating machines. Hence after a hot melt is coated on a carrier and solidifies, it may be run through an ink pan containing a developer fluid. The developing step may be speeded up by running the wet coated carrier over an equalizer, doctor or air knife, or by blowing air of predetermined humidity over the wet coated carrier.

In the above processes, with the developing step as the last manufacturing act, there results a simple, inexpensive method inasmuch as the complex balancings of components of the prior art coating processes are unnecessary. Hence the present process requires only minimum supervision to achieve a good product. Further as only small amounts of developer fluid are required, solvent recovery systems are unnecessary.

The choice of materials for the production of heat and/or pressure sensitive copy paper depends on the properties required in a copy sheet; properties such as resistance to scratching, hardness of the coating, opacity, sensitivity to lateral heat flow, etc. Where the hot melt coating process is employed the choice also depends on the hot melt coating machinery employed. In hot melt coating machines, such as conventional production carbon paper coating machinery which are designed for fast solidifying hot melt materials, the choice of materials is of necessity limited to those which have proper flow characteristics, low solvent retention characteristics and which solidify rapidly. Similarly the choice of developer is limited to those which evaporate rapidly and which preferably are non toxic and not flammable as well.

From the foregoing it is to be understood that the process is not limited to any particular coating materials, to any particular coating process, or to any particular developer except that the coating materials have as a major ingredient a transparent thermoplastic compound and the developer fluid must have suitable solvent properties for the particular thermoplastic material employed.

The compositions of the coating materials which when deposited by a hot melt coating process on a carrier member solidify into transparent or translucent solids may include binders, if the thermoplastic materials therein do not exhibit film properties, and also plasticizers, coloring agents, fillers, and materials which serve to regulate characteristics of the hot melt such as viscosity, and characteristics of the solidified hot melt such as heat transfer, melting point, hardness, resistance to offsetting and blocking, and degree of transparency as well as other characteristics of the finished product. When used as heat transparentizable copy sheets, the developed coating material must respond to temperatures generated in a particular thermocopy machine, and yield to the pressures developed by a marking instrument whereby employed as a pressure sensitive copy sheet material.

As will be understood the change in optical characteristics of a non-transparent coating in accordance with the process of the invention is caused by the thermal or pressure compacting of the coating whereby it is rendered transparent; and the clearer and more compacted areas, the greater is the contrast between compacted and non-compacted areas with the result that better visual copies are obtained. Hence where the
coating material includes non-fusible or non-transparent materials the thermoplastic ingredient should possess surfactant properties and wet the non-fusible and non-transparent ingredients so that they exhibit substantially the same refractive index as the solidified transparent thermoplastic material.

In most of the examples, thermoplastic materials are the major constituents of the final coating. Consequently they should be permeable to infra red radiation, they should be compatible with all of the constituents of the coating composition in solid, melted or fluid state, and they should be adapted for processing with machine equipment on hand. Many organic compounds satisfy the requirements for a thermoplastic material in accordance with the invention and a number of these compounds also have good binding properties, especially those suited for hot melt coating materials. Thus in the example formulations given infra a constituent may serve as a thermoplastic material or as a binder or both. Generally a binder serves to improve the adhesion of the coating to a carrier member, to enhance the flexibility, hardness and smoothness of the coating, and to control the melting point range.

Coloring materials in the coating such as dyes, dye intermediates and pigments, as well as fillers must exhibit with permeability to infra red radiation, low heat conductivity and low solvent retention and predetermined oil absorption. Moreover these ingredients must easily be wetted by and then yield approximately the same refractive index as the thermoplastic ingredients of the hot melt. The particles sizes of the coloring materials and fillers must be small on the order of 300 mesh and of soft texture. The color ingredients and fillers generally serve to influence the hardness, offsetting and opacity of the finished product. Some suitable pigments and fillers are talc, feldspars, pyrophyllites and magnesia silicates, calcium carbonate, aluminum hydrate, starches and their derivatives, bentonites, fine mica powders, titanium oxides and ultramarines.

The choice of plasticizers depends upon the thermoplastic and binder ingredients employed. The use of solid plasticizers is preferred as they are especially desirable in hot melt coatings. Plasticizers are added to the compounding for generally recognized reasons. Those selected however should possess proper heat conductivity as well as good wetting power. Solid plasticizers like some of the unsaturated polyhydroxyxylene may serve as plasticizer, binder, solvent or thermoplastic ingredient.

An object of the invention is to provide a process for producing copy sheets having a single homogeneous film coating.

Another object of the invention is in the provision of a process for producing thermographic copy sheets which exhibit long shelf life and are relatively immune to handling, cracking and ambient heat.

Still another object of the invention is in the provision of a novel process for producing blushed films on transparent materials.

Still another object of the invention is in the provision of a process for producing transparentizable blushed coatings which does not require close supervision and special machinery with concomitant costs.

A further object of the invention is in the provision of a process for enhancing the opacity of a non-transparent film.

A still further object of the invention is in the provision of a process for rendering a non-ink absorbent film, which has little affinity for ink, receptive to marking inks. Other objects and many of the attendant advantages of the invention will be readily appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings wherein the single figure is a diagrammatic illustration of the process of the invention.

With reference to the single figure in the drawings there is shown a colored carrier member supply roll from which a carrier member 10 is drawn over a roller 12, 13 which picks up a hot melt of film forming thermoplastic material 15 and deposits it on the carrier member. The coated carrier member then passes over a chilled roller 13 whereby the thermoplastic material is solidified into a substantially transparent coating 14. After solidification the coated carrier is passed over a roller 15 which picks up a developer fluid 16. This fluid which evaporates on the order of seconds acts to render the thermoplastic coating opaque.

The Examples I-VIII hereinafter described provide specific heat and/or pressure sensitive copying papers employing hot melts and developers therefore, suited for production with conventional carbon paper coating machinery such as is diagrammatically illustrated in the drawings, but it is to be understood that the process of the invention is not to be limited to the specific examples since various equivalent compositions suitable for production by said machinery or other types of coating machinery may be employed to produce non-transparent films in accordance with the process of the invention.

In the examples colored carriers such as rag paper tissue, cellophane (solidified viscose), Mylar and others which varied in thickness from 0.005" to 0.002" were coated with hot melt coats which varied in thickness from 0.006" to 0.006". The constituents of the hot melts are hereinafter given in parts by weight.

**Example I**

<table>
<thead>
<tr>
<th>Octadecanamide</th>
<th>55-70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guttapercha compound</td>
<td>5-20</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>1-2</td>
</tr>
<tr>
<td>Dry Flow</td>
<td>4-16</td>
</tr>
</tbody>
</table>

In this formula octadecanamide serves as the thermoplastic material, guttapercha as a binder and plasticizer, and titanium dioxide and Dry Flow dispersed in the hot melt serve as whiting agents to give greater opacity to the final product. Dry Flow is a starch derivative marketed by the National Starch and Adhesive Co. The hot melt was coated on a selected carrier by conventional production carbon paper coating machinery. After cooling and solidification of the hot melt to a transparent film, which occurs on the order of seconds, the film coat was developed with methylene chloride, which evaporates on the order of seconds, leaving a non-transparent yellow-white temperature sensitive copying paper.

Another suitable developer for this hot melt material consisted of from 50-70 parts of methylene chloride and 5-15 parts of ethylene dichloride, in combination with 2-5 parts of heptane and 5-10 parts of methanol, the latter two substances being diluents for the former two substances. The resulting sheet was an off color white transparentizable in response to localized heat and pressure.

**Example II**

| Carnauba wax | 80 |
| Bhenic acid | 20 |

In this formula the wax and the acid serve as the thermoplastic material having good binding properties. The wax regulates the developing speed while the bhenic acid is responsible for the whiteness or opacity of the hot melt when it is developed.

**Example III**

| Octadecanamide | 33 |
| Zinc dibutyl dithiocarbamate | 17 |
| Ethyl cellulose, N-type | 63 |
| Polyethylene to the following | 22 |
| Dry Flow | 23 |
| Talcum | 1 |
In this formulation the first four ingredients, after development comprise the non-transparent thermoplastic material with good binding properties. The amide controls the developing properties and heat transfer characteristics, the zinc salt and the ethyl cellulose the heat conductivity, melting point and hardness of the composition, and the phenylisocynate the melting range and the viscosity of the hot melt.

**Example IV**

Carnauba wax .......................... 21
Diphenyl carbonate .................... 11
Oleic acid ................................ 22
Azelaic acid ............................ 42
Titanium dioxide ....................... 02
Aluminum hydride ...................... 02

In this formulation carnauba wax, diphenyl carbonate, and azelaic acid possess thermoplastic as well as binding properties, the azelaic acid being responsible for the non-transparency of the developed coating. The oleic acid is included for its plasticizing property and to control heat conductivity, and the titanium dioxide and aluminum hydride serve as whitening and viscosity control agents.

**Example V**

Wax #W (Hoescht AG) .................. 60
Acrawax C (Glyco Chem. Co) .......... 8
Phenylisocynate ....................... 4
Dry Flow ................................ 20
Etyl cellulose .......................... 4
Polyethylene ........................... 4

In this formula the waxes, phenylisocynate, and ethyl cellulose are the thermoplastic binder ingredients. The Acrawax also controls sensitivity to the developer fluid, the Dry Flow serves as a whitening, hardness, and viscosity control agent and the polyethylene serves to control the sensitivity to developer fluid.

The formulations enumerated in Examples II-V were melted and coated on colored carriers with conventional carbon paper coating machinery and after cooling and solidifying, the hot melt coat was developed with methyl chloride leaving non-transparent white coatings which were pressure as well as thermosensitive.

On non-porous slightly calendared rag paper 4–12 lbs./2000 square feet, a hot melt coating of from 140–175 mil was applied. The hot melt coating consisted of

**Example VI**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octodecanamide</td>
<td>22 20-30</td>
</tr>
<tr>
<td>Polyvinyl copolymer #VAGH (Union Carbide)</td>
<td>6  7-35</td>
</tr>
<tr>
<td>Butylcarbamate</td>
<td>52 60-85</td>
</tr>
<tr>
<td>Dry Flow</td>
<td>14 0-15</td>
</tr>
<tr>
<td>Tag</td>
<td>4  0-6</td>
</tr>
</tbody>
</table>

In this formula the octodecanamide, polyvinyl copolymer and butylcarbamate serve as thermoplastic binder material. The butylcarbamate, a co-solvent for the vinyl polymer, adjusts the viscosity and heat transfer characteristics. The Dry Flow and talcum serve as whitening agents which give greater opacity to the developed film.

The above solidified hot melt was developed with methyl chloride and produced a silver-gray-silver-white non-transparent thermosensitive coating. Alternatively the developer acetone was used to produce a grey-white coating, and a developer solution of acetone 95–99 parts and water 2–5 parts produced an opaque-white coating. Sheets of this formulation exhibited good thermosensitive properties and where the percentage of VAGH was low the film exhibited pressure sensitive characteristics as well.

On sulfite or rag paper of similar specifications as in the preceding example a hot melt consisting of

**Example VII**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinyl acetate (AYAA) Union Carbide</td>
<td>26 20-25</td>
</tr>
<tr>
<td>α,α'-Xylosidol</td>
<td>48 30-50</td>
</tr>
<tr>
<td>Dry Flow</td>
<td>18 10-20</td>
</tr>
<tr>
<td>Tag</td>
<td>4  0-6</td>
</tr>
</tbody>
</table>

In the above formulation the α,α'-xylosidol and amide when melted serve as a solvent and plasticizer for the polyvinyl acetate, the combination comprising the thermoplastic material of this formulation having good binding properties. The Dry Flow and talc also serve as whitening control agents.

The above solidified hot melt was developed with a solution of metylethyl chloride 70–95 parts and trichlorofluoromethane 5–30 parts, the latter serving as a diluent for the former. The resulting film was a non-transparent silver gray with good thermosensitivity.

Another developer found suitable for the above solidified hot melt was a solution of ethanol 10–50 parts, acetone 10–45 parts and water 1–5 parts. Again, a silver gray coating resulting having good thermographic characteristics.

A preferred hot melt material suitable for the production of heat and pressure transparentizable copying papers on conventional carbon paper machinery consisted of

**Example VIII**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyvinyl butyral (Butvar #6 Shafterglen Chem. Co.)</td>
<td>9.5 5-15</td>
</tr>
<tr>
<td>Polyvinyl butyral (Butvar #7 Shafterglen Chem. Co.)</td>
<td>4.5 0-5</td>
</tr>
<tr>
<td>Fatty Acid amide (Arclid #8 Armour Chem. Co.)</td>
<td>18.5 0-38</td>
</tr>
<tr>
<td>Sodium sodium (Santizer #8 Monsanto Chem. Co.)</td>
<td>28.3 48-75</td>
</tr>
<tr>
<td>Talc #825 mesh</td>
<td>11.1 0-16</td>
</tr>
</tbody>
</table>

With the exception of the talc all of the ingredients in the above formulation serve as the thermoplastic material having good binding properties. Arclid #18 also serves to render the coat less sensitive to lateral heat transfer or lateral bleeding, to reduce its sensitivity to the developer fluid and to reduce the viscosity of the hot melt. The Santicizer also serves as a solvent for the butyral, and the talc as a whitening control agent. The above solidified hot melt was developed with metylethyl chloride to produce an opaque white film which was heat and/or pressure transparentizable, relatively immune to handling and marproof.

On colored paper, films of regenerated cellulose, cellulose esters, polyvinyl derivatives, polyesters and polypropylenes stained with dyeustuffs, a hot melt coating of the following was applied:

**Example IX**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clear polyvinyl plastisol</td>
<td>2.5 30-36</td>
</tr>
<tr>
<td>Hexadecanamide</td>
<td>15-35</td>
</tr>
<tr>
<td>Dry Flow</td>
<td>5-20</td>
</tr>
</tbody>
</table>

In this formula the plastisol and amide serve as the thermoplastic material with good binding properties, the amide serves also to reduce the sensitivity of the solidified hot melt composition to the developer fluid, and the Dry Flow serves as a whitening control and marproofing agent.

The above solidified film was developed with a solution of methylethyl chloride 60–90 parts, diluted with methanol 10–35 parts, and heptane 2–30 parts to which 2–8 parts of poly styrene was added. The poly styrene served to deposit a film on the developed hot melt film.

Further in accordance with the process of the invention color reactant ingredients such as phenolphthalein and propyl gallate may be included in the thermoplastic
coating. The fast evaporating fluids for such a coating will include insoluble color reactants such as ferric or ferrous salts which would deposit on the solidified thermoplastic coating. Upon application of localized heat or pressure the acids and salts will combine to produce a distinct color.

In the above examples of hot melt materials, the developer methylene chloride was the predominant choice only for the reason that it is nontoxic, nonflammable and has a high vapor pressure. However any similar developer fluids with the proper solvent power and sufficient vapor pressure as determined by experiment for a particular hot melt coating could be successfully employed.

It is to be here understood however that developers suitable for other types of thermoplastic materials and for other coating processes would require other solvents and non-solvents with specific properties all of which are known to the art and described in literature for ink, lacquer and paint manufacturing.

As stated hereinbefore bodies of solid thermoplastic materials can be treated with suitable developer fluids to produce non-transparent surface films which are heat transparencible. For example, an opaque heat transparencible film is formed on a clear body of polystyrene copolymer when the body is dipped in ethylene dichloride; or when dipped in methylene chloride, 99.8 parts, and urea hydrochloride, 2 parts, a yellow opaque heat transparencible film is formed.

Also an opaque heat transparencible film can be produced on a clear body of methacrylate polymer (Lucite) by brushing it with a developer consisting of pyridine, 50-80 parts, acetone, 10-30 parts, propyleneoxide 10-40 parts, and water 0-5 parts.

Further an opaque transparencible film can be produced on a clear body of cellulose acetate by dipping it in a developer consisting of acetone 50-85 parts.

Methyl ethyl ketone .................................. 5-20
1,4-dioxiane ........................................... 2-10
Ethanol ................................................... 5-40
Cellulose acetate butyrate .............................. 1-3
Water ..................................................... 2-8

The invention claimed is:

1. A process for forming non-transparent heat transparencible film coats on a colored background material, said process consisting of the steps of coating said background material with a transparent film forming thermoplastic material, and applying to said coating a solvent therefore which evaporates on the order of seconds and which acts upon evaporation to render said coating opaque.

2. A process for forming non-transparent heat transparencible film coats on background material of contrasting color, said process consisting of the steps of coating said background material with a fast drying hot melt of thermoplastic material, and applying to the solidified and transparent hot melt coating a solvent therefor which upon evaporation leaves the solidified hot melt coating non-transparent.

3. A process for forming non-transparent heat transparencible films on a colored sheet, said process comprising the steps of coating said sheets with a hot melt of thermoplastic material consisting of from 6-15 parts by weight of polyvinyl butyral, up to 24 parts by weight of fatty acid amide, 48-75 parts by weight of o,p-toluidin sulfonamide and 10-16 parts by weight of talcum, and applying a solvent for the solidified hot melt coating on the surface thereof, said solvent being characterized by its ability to evaporate on the order of seconds.

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