Copied materials and emulsions


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The present invention relates to a novel process for producing novel pressure-sensitive record or copying material and to the material thereby produced. The invention further relates to novel hot-melt emulsions for producing the novel pressure-sensitive record material of the invention.

The pressure-sensitive record or copying material which is still predominantly used in commerce today is the transfer paper commonly referred to as "carbon paper." Such ordinary carbon paper usually consists of paper coated with a homogeneous mixture of waxes and pigments with a coloring material uniformly and homogeneously dispersed in the mixture. This homogeneous coating is generally applied to the surface of the sheets as a hot melt or molten mass. The resulting pressure-sensitive record material provides a mark under the pressure of writing, typing, etc., by transfer, at the areas of pressure, of a complete mass of the coating composition containing the color therein. In order to provide a reasonable degree of transfer when a copy is produced, the waxy composition which is transferred is, of necessity, relatively soft and of low tensile strength. The coating is, therefore, prone to smear or offset onto adjacent objects, including an adjacent sheet of clean paper. Furthermore, the mark or copy produced is prone to smudge on the receiving sheet and also to offset onto the hands and clothing of the user.

Because of the shortcomings of ordinary carbon paper, a great deal of research effort has gone into the search for a more suitable copying material. One of the attempts to solve the shortcomings of carbon paper has employed a colorless dye intermediate which reacts to form a color only when brought into contact, with sufficient pressure, with a suitably prepared receptive sheet containing a resistant which will react with the colorless dye intermediate to form a colored image or marking. It was hoped that the use of the colorless marking materials would help in eliminating the offset which normally occurs with ordinary carbon paper.

However, to produce a sufficiently rapid development of color on the clay surface of the receiving sheet of such a system, very rapid adsorption of the dye intermediate into the clay surface is required. For this purpose, rapid migration of the dye intermediate to the clay surface from the transferred mass must take place and this could only be achieved in part by incorporating an excess amount of solvent for the dye intermediate in the wax coating mixture. Consequently, the transfer mark or character was even more prone to smear than that produced with a good quality ordinary carbon paper. Since manifold systems employing sheets of transfer material require that the transfer surface be placed in contact with the receptive reactive surface over relatively long periods of time during storage, offset and unwanted production of color on the receptive sheet frequently occurred. In such a system, this difficulty could not easily be overcome. Consequently, in a manifold system, record sheets of this type, utilizing a colorless dye intermediate, possessed the advantage that the dye intermediate did not form color on the hands and clothing of the user.

Over the years, efforts have been directed to a further type of pressure-sensitive copying material which employs, on one side of a sheet, a continuous coating containing discrete inclusions of a marking fluid. This type of system employs as the coating, a continuous film containing microscopic droplets of an oily marking material and is the type of system described in British Patent No. 582,220, United States Patents Nos. 2,299,694 and 2,374,862. In this type of coating sheet, the marking fluid may be colored, or it may be colorless but capable of forming a color upon chemical reaction with the chemical deposited on the contacting surface of the adjacent sheet. Under the pressure of writing or typing, the coating ruptures and droplets of marking fluid exude onto the copy sheet to provide a mark by direct color transfer or due to the color-forming chemical reaction which takes place between the co-reacting chemicals.

While this latter type of pressure-sensitive copying material provided certain advantages, it did not overcome all of the disadvantages of ordinary carbon paper. Furthermore, it brought about new disadvantages such as time-consuming, costly production operations and handling problems, with resulting high prices to the users which, in turn, have caused its commercial use to lag.

By means of the present invention it is possible to overcome all of the difficulties of the prior systems mentioned hereinabove, and to provide pressure-sensitive copying materials which are superior both in their properties and performances, and which may be efficiently and inexpensively produced.

It is an object of the present invention to provide a superior pressure-sensitive copying material which eliminates the disadvantages of ordinary carbon papers as well as those of prior art copying materials, while retaining their better characteristics.

It is also an object of the present invention to provide a clean, non-smudging pressure-sensitive copying material which eliminates staining and offsetting of color on a contacting copy receiving sheet and which provides a copy which does not smear, stain or offset by virtue of the fact that the marking fluid which provides the copy is absorbed into the receiving surface of the copy sheet.

It is also an object of the present invention to provide a pressure-sensitive copying material having a continuous rupturable coating of a film-forming material melttable within the range of 130°—350° F. and containing dispersed therein discrete droplets of a non-viscous marking fluid which is capable of being exuded from the coating under writing pressure, to give a mark on an adjacent receiving surface, and which has superior copy write-off intensity for both multiple as well as one-time use.

It is an additional object of the present invention to provide a pressure-sensitive copying material in which the non-viscous marking fluid is dispersed as discrete droplets throughout a scuff-resistant, non-transferable coating which is insensitive to drying out or humidity conditions and not subject to cracking with premature release of the marking fluid.

It is another object of the invention to provide stable emulsions of a non-viscous marking fluid dispersed as microscopic discrete liquid particles in a continuous phase of non-aqueous molten fluid composition, said dispersion of microscopic discrete liquid particles of marking fluid not being subject to coalescence on storage of the composition or during repeated solidification and remelting cycles.

Another object of the invention is to provide a molten coating composition readily applied to a web such as paper by conventional coating and printing equipment and methods, and which does not require the removal and/or recovery of volatile solvents or water.

The above enumerated objects, as well as other objects, together with the advantages of the invention, will
be readily comprehended by persons skilled in the art upon reference to this description.

The pressure-sensitive record material of the present invention consists of a web support, such as paper, having coatings on at least a portion of a surface thereof, a continuous film of a water-immiscible substance in the range of 130°-350° F. and containing dispersed therein, microscopic droplets of a non-viscous marking fluid such that, under pressure of pencil or machine writing, the film is ruptured and the marking fluid exudes to mark an adjacent receiving sheet. This pressure-sensitive coating is characterized by being applied to the paper as a stable dispersion of marking fluid droplets in the molten 100% solids continuous phase and chiled thereon.

Throughout the present application the term "emulsion" refers to a dispersion of marking fluid in the molten material of the continuous phase, regardless of whether or not the marking fluid has been encapsulated in a protective shell previous to dispersion in the continuous phase.

The marking fluid may be colored or colorless. If colorless, it will form a color upon color reaction with a co-reactant on an adjacent contacting sheet. The fluid of the marking fluid must be substantially insoluble in the film-forming material of the continuous phase.

Under pressure of writing and typing, the film of the coating is ruptured and the marking fluid, by virtue of its non-viscous nature, is exuded to give a mark on a receiving sheet. In the case of the marking fluid being colorless, the receiving sheet may be just an ordinary sheet of paper into which the color fluid is absorbed. In the case of the marking fluid containing a color-forming dye intermediate, the receiving surface contains, impregnated or coated thereon, the co-reactant necessary to produce color by reaction with the exuded marking fluid.

Under the writing pressure, the marking fluid only is transferred to the receiving sheet, the film of the coating being of a nature such that no transfer of the film to the receiving sheet takes place. The mark on the receiving sheet is produced by absorption of the marking fluid into the surface of the receiving sheet and thus presents no surface deposit which might be susceptible to smudging as in the common transferable wax type of carbon paper and the transferable wax sheets of the prior art. In the coated sheet of the present invention, the marking fluid droplets are occluded within the film of the coating and the actual fluid is protected from contact with hands and clothing and does not come into contact with the receiving sheet until such time as the film is ruptured during the process of producing a copy. The surface of the coated sheet is, therefore, clean and non-smudging. This cannot be said of the coatings utilizing homogenous wax compositions, as the surface material in these coatings constitutes part of the transferable marking medium and is very susceptible to smudging, staining and offsetting on contact with hands and the receiving sheet.

In previous copying materials coated from solvent solutions, there has been little control of droplet diameter, and inadequate occlusion of surface droplets by these methods has resulted in the occurrence of very marked bleeding of marking fluid from the surface of such coating. Because of the preferred emulsion system utilized in the present invention, droplet size is uniform, and occlusion of surface droplets is much more complete, and insures cleanliness and negligible bleeding characteristics.

Emulsion systems which are necessary to give clean, non-bleving characteristics in coatings, have heretofore been confined to hydrophilic colloidal materials because of their natural tendencies to stabilize aqueous emulsions. Unfortunately, coatings prepared from these materials tend to crack and give unsatisfactory results because of the premature release of the marking fluid through the cracks which form.

The advantages of using film-forming materials other than humidity-susceptible, water-soluble, hydrophile colloids in emulsion coatings are obvious, but the use of non-aqueous materials has previously been limited because of the difficulty of preparing suitable non-aqueous emulsions. The present invention provides stable non-aqueous emulsions having excellent coating properties.

The greater portion of the coating and record materials are manufactured by processes involving hot melt methods, and aqueous coatings are not readily adaptable to this equipment. Since the equipment required to process aqueous coatings is not generally utilized by manufacturers of, for example, manifolding business forms, the coated stock has generally been brought in from an outside source. This involves the disadvantages of extra shipping and handling and burdensome inventories. The excessive handling is particularly undesirable in pressure-sensitive systems wherein a colorless color-forming dye intermediate is coated on one side of a paper and the receptive coating necessary to produce color is applied to the opposite side of the paper. It has been found that such sensitive paper is difficult to supply in tight rolls and that the rolls require special handling to overcome premature offset. In addition, even with special precautions, waste of precoated materials during fabrication of such products as business forms, is excessive.

In order to minimize offsetting of the copying material, it is advantageous to the manufacturer of manifolding business forms to be able to apply the pressure-sensitive coating at the press at a location after the printing, punching, perforating, and slitting operations have taken place. Water-based coatings utilized in this manner are not feasible with the equipment presently available in the carbon coating and printing industry and to be of utility, it would be necessary either to install additional costly equipment or to obtain precoated materials from an outside source. In the latter place, the versatility and flexibility of manufacturing operations are considerably reduced but, in either case, costs are considerably higher.

One of the advantages of the copying material of the present invention is its direct utility on existing production equipment without additional limitations in manufacturing flexibility.

Other important contributing factors which made possible the advantages of the product of the invention is the nature of the continuous phase of the coating. The emulsions from which these coatings are produced will be described in greater detail hereinafter.

The continuous phase of the coating and the emulsion comprises a hydrophobic film-forming material, is in the solid state at ordinary temperatures at which the copying material is to be used and meltable without decomposition at elevated temperatures up to about 350° F., and preferably between about 130 and 320° F. This is one of the essential characteristics of the film-forming material. It is this characteristic which permits the application of the coating to paper employing a hot-melt technique.

The hydrophobic film-forming material of the continuous phase may consist of one or more components selecting a wide variety of materials, satisfying the conditions of thermoplasticity mentioned above. Generally, materials which give low viscosity and low coating temperatures are most desirable from the point of view of application ease. However, the use of high melting, high viscosity polymers is not excluded from the scope of the invention since coatings having such materials as the main or sole constituent of the continuous phase can readily be coated on paper by extrusion methods, similar to the extrusion of sheet plastics.

Among the hydrophobic materials which can be used to produce the continuous phase, either singly or in com-
Combination, are the thermoplastic acrylic resins, such as polymethyl methacrylate and its copolymers; cellulose derivatives, such as cellulose acetate butyrate; coumarone-indene resins; petroleum hydrocarbon resin such as the "Piccopole" resins (thermoplastic hydrocarbon resins derived from high temperature cracking of petroleum consisting of a mixture of straight chain hydrocarbon resins in which considerable cyclic, but no aromatic structures are present); isolation resins, such as polyisobutylene; phenolic resins, such as Durez 219 (a terpene, phenolic, oil soluble thermoplastic resin having a melting point of about 270°F and an acid number of about 63); polyamide resins, such as alkyo substituted nylon; chemically modified rubbers, such as cyclized rubber; styrene resins, such as polystyrene; terpene resins, such as "Piccolyte" resins (a terpene polymer having a molecular weight of approximately 1200, a softening point of about 115°C, and a density of 15.5°C of 0.980), vinyl resins, such as vinylvinylacetate, and vinyl stearate and copolymers; natural and synthetic waxes such as the vegetable waxes, candleella (a hard vegetable wax composed of a high proportion of hydrocarbons and resins with a small amount of lactones, a melting point of 149-162°F, an acid number of 11-19, a saponification number of 46-56 and a specific gravity of 0.982 to 0.993 at 15°C), carnauba, and sugar cane wax or other similar waxes, such as beeswax, paraffin and microcrystalline waxes, mineral waxes such as montan and Utah wax (an amorphous mineral wax from Utah containing a melting point of 73°C, a cloud point of 76°C and an acid number of 0), synthetic waxes such as polyethylene and FT-200 wax (a synthetic mineral wax having a melting point of 210-219°F, a saponification value of less than 0.5 and an acid value of 0) prepared by the Fischer-Tropsch process, and also chemically modified natural waxes such as chlorinated paraffins and oxidized microcrystalline waxes. The above materials are hydrophobic in nature, but hydrophilic materials may also be used. For example, polyethylene glycols which are solids at temperatures of normal usage, but melttable at temperatures between about 130°F and 350°F, may be used. Thus, polyethylene glycol, molecular wt. 6000-7500, melting point 140-145°F, is suitable.

It is desirable that the high melting point and viscosity in the lower melting point materials such as the waxes, compositions have been obtained of excellent coating viscosity for carbon paper coating equipment yet possessing some of the properties of the higher melting constituent.

The addition of surface-active agent or protective colloid to the continuous phase composition generally enhances the stability of the emulsion or dispersion, excellent results have been obtained in accordance with the present invention, employing a wax such as candleella as the sole component of the continuous phase with no emulsifying agent. As will be apparent to those skilled in the art, other waxes possessing a melting point above about 130°F and less than about 350°F may be employed.

One valuable addition to the continuous phase is a cyclized rubber resin. This resin imparts toughness to the coating layer on the paper while also providing the important function of being an efficient emulsion stabilizer. As little as 3% of this resin in a coating having paraffin wax as the sole component of the continuous phase, produces an emulsion of excellent stability otherwise unobtainable. Examples of this resin are Alpek resin and Pelilite resin. The latter resin may be produced by reacting rubber in the presence of an ammonia or chloroformic acid and isolating the resulting cyclized resin. This resin is substantially a condensation derivative of rubber and its preparation is described in U.S. Patent No. 2,052,391.

One preferred continuous phase of the emulsion of the invention comprises one or more thermoplastic polymeric resins having a melting point of between about 130 and 350°F, constituting between about 25 and 80% by weight of the film-forming component, and between about 20 and 75% by weight of one or more hydrophobic waxes and between about 1 and 10% and preferably between about 2 and 5% by weight of a cyclized rubber resin.

The proportions of marking fluid containing the pigment, dye, or dye intermediate, relative to the amount of film-forming component may vary over a wide range, depending upon the materials used. Best results have been obtained employing the marking fluid in an amount of between about 20 and 60%, preferably between about 35 and 50%, by weight of the total emulsion or coating composition.

The microscopic discrete liquid particles of the nonviscous marking fluid in the coating are desirably solutions or suspensions of a dye, pigment, or colorless color-forming dye intermediate in a liquid which is inert to and substantially insoluble in the molten continuous phase.

The marking fluid may comprise any nonviscous liquid, whether organic or inorganic, of such polarity as to render it substantially insoluble in the hydrophobic film-forming composition, which will provide a suspending or dissolving medium for the pigment, or colored dye or colorless color-forming dye intermediates. The nonviscous liquid should not be too viscous since it is important that it be able to accommodate the pigment or dye without becoming so viscous as to lose its freeflowing characteristics. Desirably, the fluid medium (solvent or suspending liquid) shall have a low volatility, i.e., wherein less than about 10% of the liquid evaporates through the continuous film over a period of several years of normal storage. Liquids having vapor pressure of less than 0.01 mm. of mercury at 75°F are particularly satisfactory in this respect. Additionally, the fluid shall desirably have a low freezing point, i.e., a freezing point of less than 0°F, preferably as low as -30°F. Also, the fluid shall desirably have a high boiling point which will provide reduced volatility at temperatures of use. Fluids having boiling points in excess of 212°F are usually suitable in this respect. An additional important property of the fluid is that it have a flash point above the manufacturing temperatures. Fluids having a flash point above 212°F are generally satisfactory. As those skilled in the art will appreciate, the product will be more useful, permanent and safe with liquids having higher boiling point flash points and flash points and lower volatility and freezing points. Of course, as mentioned hereinabove, the fluid must not dissolve, or by encapsulation is prevented from dissolving, the film-former. Among the satisfactory fluids which may be employed are those listed below in Table 1:

<table>
<thead>
<tr>
<th>Compound</th>
<th>V.P.</th>
<th>Freezing Point, Degrees C.</th>
<th>Boiling Point, Degrees C.</th>
<th>Flash Point, Degrees C.</th>
<th>Approximate Viscosity Centipoise at 70°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>polyethylene glycol (mol. wt. 400)</td>
<td>4-8</td>
<td>435</td>
<td>370</td>
<td>350</td>
<td>100</td>
</tr>
<tr>
<td>dichloro ethylene glycol</td>
<td>0.01</td>
<td>-8.0</td>
<td>265.5</td>
<td>200</td>
<td>36</td>
</tr>
<tr>
<td>diethylene glycol</td>
<td>0.01</td>
<td>-10.0</td>
<td>282.0</td>
<td>300</td>
<td>49</td>
</tr>
<tr>
<td>toluene diethylene glycol</td>
<td>0.01</td>
<td>-16.7</td>
<td>265.8</td>
<td>295</td>
<td>14</td>
</tr>
<tr>
<td>methyl phthalic acid glycolate</td>
<td>0.01</td>
<td>-35</td>
<td>374</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>pyroxyline carbonate</td>
<td>0.01</td>
<td>-49.2</td>
<td>241.7</td>
<td>3</td>
<td>120</td>
</tr>
<tr>
<td>pyroxyline ethylene glycol (from liquid 1,1,1412)</td>
<td>0.01</td>
<td>-20</td>
<td>300</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>pyroxyline with (mol. wt. 400)</td>
<td>0.01</td>
<td>1.00</td>
<td>1,070</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is important that the marking fluid be of a nonviscous nature to permit it to exude readily from the coating of the copying material when subjected to writing pressures. Viscous or pasty fluid droplets, and par-
particularly if the fluid comprises a small part of the coating, will not exude from the coating when subjected to writing pressure. Under such circumstances, instead of exuding, the marking fluid is transferred to the copy sheet together as a unit of the entire coating thereby causing copy smudging as is typical with ordinary carbon papers. To permit the marking fluid to exude from the coating without any transfer of coating film itself, it is desirable that the marking fluid have a viscosity of less than about 30,000 centipoises at 70° F., preferably between about 30 and 30,000 centipoises at 70° F., and for best results between about 50 and 3,000 centipoises at 70° F.

Another important feature which provides excellent exudation of the marking fluid is to employ a coating emulsion containing substantial amounts of the marking fluid. It is generally advantageous to employ a coating emulsion containing at least about 20% up to about 60%, and preferably about 35 to 50%, by weight of marking fluid, based upon the total weight of coating emulsion.

The marking fluid may contain various amounts of solvent or suspending liquid depending upon the nature of and color of pigment or dye, the nature of the solvent or suspending liquid, and somewhat upon the nature of the film-forming or continuous phase of the coating emulsion.

The marking fluid may contain a colored pigment or dye or it may contain a colorless color-forming dye intermediate which will react to produce a color when brought into contact with a co-reactant. The line of demarcation between pigments and dyes is often difficult to delineate. As used herein, a pigment is considered to be a colored or colorless color-forming substance which is insoluble in the fluid of the marking fluid while a dye is herein considered to be a colored or colorless color-forming substance which is soluble in the fluid of the marking fluid.

Colored substances which may be employed include materials normally classified as pigments such as carbon blacks, iron blues, alkali blues, phthalocyanines, cadmium reds, ultramarine blues, phospho- and molybdenum acid laked colors; and materials normally classified as dyes such as d and tri-aryl methane dyes, e.g., malachite green and crystal violet, azo dyes, indigoid, thionigoid and anthraquinone dyes, acridine, azure, oxazine, and thiazine dyes.

Among the useful color-forming dye intermediates are: stabilized diazotized salts, the carbinoles, leuco and ether derivatives of the triaryl and diarylmethane dyes, and acid esters of leuco indigoid and thionigoid dyes. Examples of suitable intermediates of db- and triaryl-methane dyes which may be employed are the butyl ethers of methyl violet 2B, methyl violet 10B, magenta, malachite green A, auramine derivatives such as N-acetylated auramine and leucoauramines.

One type of colorless color-forming dye system which may be advantageously employed in the coating products of the invention is that described in British Patent No. 757,136. In accordance with that patent a colorless color-forming dye intermediate, such as an ether of a triphenylmethane dye-former is maintained in an alkaline condition, by neutralizing the dye former with an alkaline substance, in which form the dye former is colorless, and then producing a color by bringing the alkaline colorless dyeustuff into contact with an excess of an acid which converts the dye former into a colored product. In accordance with one embodiment of the present invention the marking fluid may contain the colorless color-forming dye intermediate along with a small amount of an alkaline substance, such as sodium carbonate, potassium hydroxide, organic alkali, etc.

In a manifesting set of record forms, the emulsion containing the marking fluid is coated on the back surface of the sheets so that the coating can come in contact with the front surface of the sheets which follow the first sheet in the set. On the front surface of the sheets is placed a co-reactant for the dye intermediate, in order to produce a color.

Among the co-reactants which may be used in the coating composition for the front surface of the sheets are acids such as: tannic, gallic, citric, boric, tartaric, oxalic, and phospho-tungous acids. Also one may employ other co-reactants such as: colloidal silicas, calcium silicate, attapulgite clay, and the like.

As will be apparent to those skilled in the art, from the teachings of this disclosure it is possible to incorporate the co-reactant into the marking fluid of the emulsion on the back surface of the sheets and to place the colorless color-forming dye intermediate on the front surface of the sheets. In either instance when pressure is exerted through two or more sheets in the manifesting set, rupture of the continuous film will produce intermixing of the reactive chemicals to produce a color or copy at the sites where pressure is applied.

Coatings weighing 1 to 12 lbs per 500 sheets of 20 inch x 30 inch paper in which 20 to 60 percent of the weight of the coating consists of marking fluid have been found to be satisfactory. For one time use coatings, a desirable weight range from 1 to 6 lbs., preferably 2 to 4 lbs., and for multiple use coatings, a desirable weight range is from 6 to 12 lbs., preferably 8 to 10 lbs. In addition to single-face coatings, double face coatings are desirable colorants.

The discrete microscopic particles of marking fluid contained in the coating and emulsion are desirable of from between about 0.1 and 70 microns in diameter. More desirably, the diameter of the liquid particles is from about 0.5 to 20 microns. For preferred results, it has been found that droplets thinner than 1 and 5 microns is most satisfactory. When the particle size exceeds 20 microns in diameter, a coating containing the droplets on a paper surface may become slightly dirty to the touch because the diameter of the droplets is about the same as the thickness of the coating which is therefore easily broken. Below a diameter of one micron, the coating is less sensitive to rupture when subjected to the pressure employed to produce copying. Since it is desired to employ the coating of the invention in pressure-sensitive copying systems which do not require the use of excessive pressure, it is desirable to provide droplets having a diameter of from about 1 to 5 microns.

As will be appreciated by those skilled in the art, the sensitivity to rupture under pressure is dependent upon the size of the droplet as well as the nature of the film, with the large size droplets having greater tendency to rupture when subjected to pressure than the smaller size droplets. The discontinuous phase of the emulsion shall constitute the marking fluid which comprises the pigment, colored dye or colorless color-forming dye intermediate suspended or dissolved in a non-volatile liquid. Emulsions are produced by placing the two mutually insoluble liquids in a blender or emulsifier and by agitation producing a stable emulsion with droplets of marking fluid of the desired particle size, desirably less than about 10 microns, and preferably 1 to 5 microns in diameter. The resulting emulsion can then be applied to paper by the hand spread or printing methods such as: letter press, direct or offset gravure, direct or reverse roll, knife, flexographic, etc.

Among the important advantages of the emulsion coatings of the invention is the extreme flexibility and versatility in the manner in which they may be applied to the web distri-bution along with an amount of an alkaline substance, such as sodium carbonate, potassium hydroxide, organic alkali, etc.

In order more clearly to disclose the nature of the
present invention, specific examples illustrating the practice of the invention will hereafter be described. It should be understood, however, that this is done solely by way of example and is intended neither to delineate the scope of the invention nor limit the ambit of the appended claims. The amounts of components are given in terms of parts by weight, unless otherwise specified.

**Example 1**

This example describes the preparation of a preferred copying sheet according to the invention coated with a film comprising a continuous phase of a blend of cyclized rubber resin, polyterpene resin and a paraffin wax mixture. Which film has disposed therein microscopic discrete liquid particles of a marking fluid containing a colored dye.

A molten mixture having a temperature of 240°F. was prepared by mixing together and heating 180 parts of Schenectady resin ST-5115 (a polyterpene resin made from pine pitch having a melting point of about 225°F.), 70 parts of "FT-200" paraffin wax (a synthetic high molecular weight aliphatic hydrocarbon wax having a melting point of 210-214°F. and having a molecular weight of about 750 corresponding to a long hydrocarbon chain containing about 50-55 carbon atoms per molecule, produced by the Fischer-Tropsch process), 50 parts of microcrystalline paraffin wax ("Warco 180," a hard,brittle, while microcrystalline petroleum wax having a melting point of 180-185°F., an acid number of 0, a saponification number of 0), 65 parts of paraffin wax having a melting point of 135°F., and 20 parts of cyclized rubber resin (Alpex resin). The resulting mixture, having its temperature maintained at 240°F., was passed through a homogenizing mill and was then mixed with the solution of 28 parts of crystal violet dye dissolved in 257 parts of polyethylene glycol having a molecular weight of 400.

The solution of the dye in polyethylene glycol had a viscosity of 156 centipoises at 70°F. when measured with a Brookfield viscometer using the No. 2 spindle at a speed of 60 r.p.m. Homogenization by passing the hot mixture through the homogenizing mill was then continued for 3 minutes thereby providing an excellent stable emulsion of liquid dye-containing particles of 1-10 microns in diameter uniformly dispersed in the wax and resin base. The resulting emulsion was stable over a period of 72 hours while maintained in the molten condition at 240°F. Upon solidification and remelting at 240°F., with stirring, no separation of the emulsion could be observed. The molten emulsion (at a temperature of 240°F.) was coated on paper, the excess being removed by means of a doctor bar to provide a coating weight of 3 pounds per 500 sheet ream of paper of 20 inches by 30 inches size. The discrete fluid particles of marking liquid were retained in the coating upon cooling. The resulting coated sheets provided excellent copying paper when used in the manner that ordinary carbon paper is used. The copying paper possessed excellent cleanliness and non-smear characteristics, with little offset. Copies made with this paper were characterized by a strong color, good definition and legibility and excellent resistance to smudging.

**Example 2**

This example describes the preparation of a copying system according to the invention in which the backs of sheets of paper are coated with a film comprising a continuous phase of a blend of cyclized rubber resin, polyterpene resin and a hydrophobic paraffin wax containing microscopic discrete liquid particles of a marking fluid containing a colorless color-forming dye intermediate capable of forming color upon reaction with an acidic material.

About 65 parts of Schenectady resin ST-5115, 45 parts of "FT-200" paraffin wax and 5 parts of cyclized rubber resin (Alpex resin) were mixed and melted together by heating them to a temperature of 240°F. A solution of 5 parts of p-phenylene shadowed in 60 parts of polya-kylyene glycol (Ucon LB-1145, a polyalkylene glycol having a viscosity index of 137, a pour point of -20°F., a flash point of 430°F. and a density at 60°F. of 1.003) containing 2 to 3 drops of ethanolamine was heated to 240°F. and added with rapid agitation to the mixture of resins and wax which had also been maintained at a temperature of 240°F. until a fine translucent stable emulsion was formed. This emulsion was spot printed onto the backs of sheets of paper by a flexographic process to provide sheets of paper having certain areas coated with the colorless, color-forming coating. When these sheets were in register with an adjacent receptive surface of paper coated with an acidic material, such as tannic acid, or other co-reactants, such as calcium silicate, and the writing pressure applied to the copying sheet, the liquid discrete particles of colorless color-forming marking material exuded from the emulsion coating onto the adjacent receptive surface to provide a blue mark. Copies made with this paper were characterized by strong color, good definition and legibility and excellent resistance to smudging or offset.

**Example 3**

This example describes the preparation of a preferred copying sheet according to the invention in which the discrete liquid particles of marking fluid contain a colored pigment.

About 25 parts of iron blue pigment were dispersed in 90 parts of polyethylene glycol having a molecular weight of about 400. This dispersion had a viscosity of 456 centipoises at 70°F. when measured on the Brookfield viscometer using a No. 2 spindle at 60 r.p.m. A molten mixture was prepared by mixing and heating together at a temperature of 240°F., 65 parts of Schenectady resin ST-5115, 45 parts of "FT-200" paraffin wax and 5 parts of cyclized rubber resin (Alpex resin). Into the molten mixture of resins and wax, was emulsified by violent agitation, 115 parts of polyethylene glycol (mol wt. 400) marking fluid containing the iron pigment. The resulting molten emulsion, maintained at a temperature of 240°F. was applied to the backs of sheets of paper. The resulting copying paper provided excellent copying when used in the manner that ordinary carbon paper is used. It was characterized by excellent cleanliness and resistance to smearing and produced very little offset. Copies made with this paper possessed a strong color, excellent definition and legibility, and resistance to smudging.

**Example 4**

This example describes the preparation of a copying sheet in accordance with the invention coated with a film comprising a continuous phase of a polyterpene resin which film has disposed therein microscopic discrete liquid particles of a marking fluid containing a colored dye.

A melt having a temperature of 240°F. was prepared by heating 365 parts of Schenectady resin ST-5115, 20 parts Alpex resin and 100 parts 100 second Sulfon mineral oil. This melt at a temperature of 240°F. was then mixed with a solution of 15 parts of crystal violet dye dissolved in 135 parts of polyethylene glycol having a molecular weight of 400. The dye solution had a viscosity of 156 centipoises at 70°F. when measured on the Brookfield viscometer using a No. 2 spindle at a speed of 60 r.p.m. Homogenization by passing the hot mixture through the homogenizing mill was then continued for 3 minutes thereby providing an emulsion of liquid dye-containing particles of 1-10 microns in diameter dispersed in the resin base.

The molten emulsion (at a temperature of 240°F.) was coated on paper, the excess being removed by means
of a doctor bar to provide a coating weight of 3 pounds per 500 sheet ream of paper of 20 inches by 30 inches size. The discrete fluid particles of marking liquid were retained in the coating upon cooling. The resulting coated sheets provided excellent copying paper when used in the manner that ordinary carbon paper is used.

**Example 5**

This example describes the preparation of copying sheets in accordance with the invention coated with a film comprising a continuous phase of cyclized rubber resin and paraffin wax, which film has disposed therein microscopic discrete liquid particles of marking fluid containing a colored dye.

About 3.0 parts of cyclized rubber resin (Alpex resin) was dissolved at 200°F in 54.3 parts of a close-cut paraffin wax having a melting point of 155°F (5512 wax, a close cut paraffin wax having a melting point of 153°F, a penetration value of 10 at 77°F, and a specific gravity at 60°F of 0.928). A solution of 4.2 parts crystal violet dye in 38.5 parts of polyethylene glycol (molecular wt. 400) at 200°F was homogenized into the resin solution and the resulting emulsion coated at 180°F on 50 lb. coating tissue to give a coating weight of ¾ lbs., 20" x 30", 500 sheet ream. The resulting coated sheets provided excellent copy and manifold qualities when used as a copying paper.

**Example 6**

This example describes a hot melt emulsion system in accordance with the present invention employing a colored dye in the marking fluid.

A melt was prepared at 200°F of 35.7 parts Sun Wax 5512, 9.7 parts oxidized microcrystalline wax having a melting point of 195–200°F. (Cardol one emulsifiable oxidized petroleum wax having a melting point of 195–200°F, a penetration value of 1 to 2, an acid number of 12 to 16, and a saponification number of 55 to 65), 3.0 parts Alpex resin and 9.0 parts natural hydrocarbon resin (Parco #200 resin, a natural fossil hydrocarbon resin having an average molecular weight of about 732, a softening point of 160–170°C, an acid number of 6–8, an iodine value of 140–150 and a specific gravity of 1.03 to 1.06). A solution of 4.2 parts of crystal violet dye in 38.4 parts of polyethylene glycol (molecular weight 400) (the solution having a Brookfield viscosity of 136 centipoises at 70°F) was slowly added to the wax mixture at 200°F with rapid agitation in a Kady Mill. An excellent hot-melt emulsion was produced of very uniform size distribution between 1 and 10 microns diameter. When coated on paper, an excellent copying paper resulted.

**Example 7**

This example describes a copying system of the invention employing coating having a continuous phase of a polyethylene and wax blend.

About 3.0 parts Alpex resin, 12.6 parts polyethylene resin (grade 629, a low molecular weight emulsion grade of polyethylene having a melting point of 208–212°F, an acid value of 1.5–17 and a saponification No. of 14–17) and 4.5 parts sugar cane wax and 37.5 parts Sun Wax 5512 were melted together at 205°F. To this mixture was added at 205°F a solution of 4.2 parts crystal violet dye in 38.4 parts polyethylene glycol 400 (the solution having a Brookfield viscosity of 156 centipoises at 70°F) and the emulsion so formed agitated thoroughly. An excellent stable low viscosity emulsion was obtained which coated well at 205°F on 9 lb. carbonizing tissue by a scrape bar method. An excellent copying paper resulted giving an intense mark on a copy paper.

**Example 8**

This example describes the preparation of a preferred copying material according to the invention coated with a film comprising a continuous phase of a blend of cyclized rubber resin, a resin and a hydrophobic paraffin wax, which film has disposed therein microscopic discrete liquid particles of a colorless marking fluid containing a color-forming dye intermediate.

About 7 parts of colorless methyl violet carboline was dissolved in a mixture of 50 parts of ethoxytriglycerol, 50 parts of polyethylene glycol having a molecular weight of 400, and 2 parts of sodium hydroxide. The resulting solution had a viscosity of 47 centipoises at 70°F, when measured on the Brookfield viscometer employing a No. 2 spindle at a speed of 60 r.p.m. The resulting solution was emulsified by rapid agitation into a molten mixture prepared by mixing and heating together at 240°F, 360 parts of "FT-200" paraffin wax, 21 parts of commarone-indene resin having a melting point of 185°F ("Piscocap 85") and 70 parts of cyclized rubber resin ("Pliolite NR"). The resulting molten emulsion was coated onto the backs of sheets of paper and upon cooling provided a copy material having colorless fluid inclusions of marking fluid microscopically dispersed throughout the continuous coating of the mixture of resins and wax. The same sheets of paper were treated on the front surfaces with tannic acid coated sheets were collated in manifold form, with the tannic acid treated surfaces in contact with the colorless coating, and writing pressure applied to the front of the top sheet, a copy was produced on the fronts of all the sheets in the manifold. Copies made with this paper were characterized by strong color, substantially no offset, good definition and legibility and excellent resistance to smudging.

**Example 9**

This example describes the preparation of a copy material employing Candelilla wax as the film-former of the paper coating.

About 8 parts of crystal violet dye were dissolved in 92 parts of thiodiethylenglycol. The resulting solution had a viscosity of 75 centipoises at 70°F when measured on the Brookfield viscometer employing a No. 2 spindle at a speed of 60 r.p.m. 25 parts of the resulting solution was heated to 175°F and mixed with 100 parts of Candelilla wax molten at a temperature of 175°F with rapid agitation in a Kady mill for 10 minutes. The resulting emulsion contained microscopic discrete liquid inclusions of the crystal violet dye solution dispersed throughout the continuous phase of Candelilla wax. The resultant molten emulsion was coated onto one side of the sheets of paper and the excess removed with a doctor blade after which the coating was set by passing the coated paper over cold rollers. The copying material thus prepared provided excellent write-off properties and was much freer of offset and smudging than ordinary carbon paper.

**Example 10**

This example describes the preparation of copying sheets according to the invention in which both the continuous phase and the dispersed phase are water insoluble.

A dye solution was prepared by dissolving 28 grams of crystal violet dye into 257 grams polypropylene glycol of molecular weight 450 (Polyglycol 166–450). A melt was prepared at 200°F of 300 grams paraffin wax (5512 wax), 65 grams Cardol one wax, and 25 grams Alpex resin. The dye solution at 200°F was added to this melt at 200°F, with vigorous agitation in a Waring Blender. After homogenizing for 3 minutes at high speed, the resulting emulsion was coated at 200°F. By a gravity method onto 9 lb. Chaminol carbonizing tissue to give a coating weight of 3 lbs. for a 500 sheet ream of sheets 20 inches by 30 inches.

As will be apparent to those skilled in the art other marking fluids, dyes, pigments and film-formers may be employed within the concept of the present invention.

The terms and expressions which we have employed are used as terms of description and not of limitation, and
we have no intention, in the use of such terms and expressions, of excluding any equivalents of the features shown and described or portions thereof, but we recognize that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. A pressure-sensitive copying material comprising a web having on at least a portion of a side thereof a coating having a melting point of between about 130 and 350° F., and consisting of a hydrophilic thermoplastic film-forming material, said film-forming material, having uniformly dispersed therein microscopic discrete non-viscous liquid droplets of a marking liquid which is substantially insoluble in said hydrophilic thermoplastic film-forming material, said coating when subjected to writing pressure, being rupturable thereby permitting the microscopic discrete liquid droplets to exude and produce a mark on an adjacent sheet.

2. A pressure-sensitive copying material as defined by claim 1 in which the marking liquid has a viscosity of less than about 50,000 centipoises at 70° F.

3. A pressure-sensitive copying material as defined by claim 1 in which the marking liquid has a viscosity of between about 30 and 30,000 centipoises at 70° F.

4. A pressure-sensitive copying material as defined by claim 1 in which the marking liquid comprises between about 20% and 60% of the weight of the coating.

5. A pressure-sensitive copying material comprising a web having on at least a portion of a side thereof a coating having a melting point of between about 130 and 350° F., said coating having a continuous phase of a hydrophilic thermoplastic film-forming material, said film-forming material which comprises between about 40% and 80% of the coating, and having a discontinuous phase comprising microscopic discrete non-viscous liquid droplets of a marking fluid substantially uniformly dispersed throughout the continuous phase.

6. A pressure-sensitive copying material comprising a web having on at least a portion of a side thereof a coating having a melting point of between about 130 and 350° F., and comprising a continuous phase of a rupturable hydrophilic thermoplastic film-forming material consisting of a polymer selected from the class consisting of natural hydrocarbon and coumarone-indene resins, a compatible waxy material and a hydrocarbon-soluble protective colloid and a discontinuous phase comprising microscopic discrete liquid droplets of a non-viscous marking fluid substantially uniformly dispersed throughout the continuous phase.

7. A pressure-sensitive copying material as defined by claim 6 wherein the polymer material comprises between about 23 and 80% by weight of the continuous phase, the compatible waxy material between about 10 and 75% by weight of the continuous phase, and the protective colloid between about 1 and 10% by weight of the continuous phase.

8. A stable hot-melt emulsion comprising a continuous phase of a hydrophilic thermoplastic film-forming composition being substantially a rigid solid at room temperature and having a melting point of between about 130 and 350° F., having dispersed therein microscopic discrete liquid droplets of a non-viscous marking fluid.

9. A stable hot-melt emulsion as defined by claim 8 in which the marking fluid has a viscosity of less than about 50,000 centipoises at 70° F.

10. A stable hot-melt emulsion as defined by claim 8 in which the marking fluid has a viscosity of between about 30 and 30,000 centipoises at 70° F.

11. A stable hot-melt emulsion as defined by claim 8 in which the liquid component of the marking fluid comprises between about 20 and 60% by weight of the total emulsion.

12. A stable hot-melt emulsion as defined by claim 8 in which the continuous phase contains at least one waxy material.

13. A stable hot-melt emulsion as defined by claim 8 in which the continuous phase comprises a polymeric resin selected from the class consisting of natural hydrocarbon and coumarone-indene resins having a melting point at a temperature of between about 130 and 350° F.

14. A stable hot-melt emulsion as defined by claim 12 in which the continuous phase comprises at least one waxy and at least one thermoplastic polymeric material.

15. A stable hot-melt emulsion as defined by claim 8 in which the continuous phase contains a protective colloid.

16. A stable hot-melt emulsion comprising a continuous phase having a melting point of between about 130 and 350° F., comprising about 25 to 80% of a polymeric hydrophilic thermoplastic film-forming material selected from the class consisting of natural hydrocarbon and coumarone-indene resins, about 10 to 75% of a compatible waxy material and from 1 to 10% of a cyclized rubber resin and a discontinuous phase comprising microscopic discrete liquid droplets of a non-viscous marking fluid substantially uniformly dispersed throughout the continuous phase.

17. A process for producing a pressure-sensitive copying material comprising a web having on at least a portion of a side thereof a coating having a melting point of between about 130 and 350° F., comprising a continuous phase of a hydrophilic thermoplastic film-forming material having dispersed therein microscopic discrete non-viscous liquid droplets of a marking fluid substantially uniformly dispersed throughout, said coating, when subjected to writing pressure being rupturable, thereby permitting the microscopic discrete liquid droplets to exude and produce a mark on an adjacent sheet, which process comprises applying the molten coating to a sheet and permitting it to cool.

18. A process for producing a pressure-sensitive copying sheet as defined by claim 17 in which the marking fluid has a viscosity of less than about 50,000 centipoises at 70° F.

19. A process for producing a pressure-sensitive copying sheet as defined by claim 17 in which the marking fluid has a viscosity of between about 30 and 30,000 centipoises at 70° F.

20. A process for producing a pressure-sensitive copying sheet as defined by claim 17 in which the continuous phase contains a waxy material.

21. A process for producing a pressure-sensitive copying sheet as defined by claim 17 in which the continuous phase contains a hydrocarbon-soluble protective colloid.

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