

1

3,090,697

HEAT SENSITIVE MARKING PAPERS AND METHODS FOR MAKING SAME

William R. Lawton and Harry A. Smith, Nashua, N.H., and James N. Copley, North Chelmsford, Mass., assignors to Nashua Corporation, Nashua, N.H., a corporation of Delaware

No Drawing. Filed Feb. 13, 1961, Ser. No. 88,661
2 Claims. (Cl. 117—36.7)

This invention relates to recording or graphic reproduction sheet materials and to compositions useful in the production of such materials. The invention is directed specifically toward the novel use of a class of materials generally known as molecular compounds, which materials, when incorporated in coating compositions for paper or similar web materials, result in an improvement in thermosensitive recording or copying sheets and method for preparing such sheets.

There are available today a number of papers which may be generally classified as thermosensitive marking sheets in that a coating or other type of potentially active surface will react under the influence of localized heating to produce a localized area of contrasting shade, color, or the like. Such contrasting areas are usually in the form of letters, numerals, or other types of intelligible characters, or continuous graphic representations.

One group of such thermosensitive papers may be characterized by the fact that the contrasting mark or inscription results directly from a heat-initiated loss of opacity of a masking coating with consequent revelation of an undercoating or carrier sheet of contrasting color, shade, or hue. Legibility of such recorded markings is usually dependent upon the contrast between surface coating and under coating or carrier sheet and high contrast is generally obtained with a combination of a light colored or white coating upon a dark base sheet.

The most widely used method of masking the dark background or base sheet is through the use of heterogeneous film coatings which by their light scattering effect achieve high opacity and whiteness. Such a light scattering film is represented by the "blushed" lacquer coating of James in U.S.P. 2,519,660 or the cellular coating of Rosenthal in U.S.P. 2,739,909.

The blushed coating is basically a dispersion characterized by the presence of particles of a thermoplastic resin dispersed in a continuous phase of the same or a similar resin, while the cellular coating is a "dispersion" of voids or air bubbles throughout a continuous phase of thermoplastic resin. In either of these constructions it will be found that the continuous phase of resin, when taken by itself as a film, displays a high degree of transparency. Disruption of the continuity of such films by the introduction of a multitude of interfaces such as at the surfaces of precipitated resin particles, as in James, or at the surfaces of dispersed air bubbles, as in Rosenthal, results in a heterogeneity which is responsible for the coating whiteness and opacity.

The proper formation of the masking coatings of the blushed or cellular types is extremely dependent upon careful control of ingredient proportions in the coating mix and the even more important control of drying conditions and drying rates. Minor variations of control and conditions in the preparation of such coatings will result in a substantial loss of disrupting media with accompanying loss of opacity, masking power, and subsequent marking contrast.

It will be noted that the means of thermally inscribing permanently legible markings on "blushed" type recording papers is by the fusion of the thermoplastic resin of the continuous phase and the dispersed particles of thermo-

2

plastic resin with subsequent combining of fused materials to locally form a continuous, transparent film. The dark background visible through these transparent areas provides the necessary legible contrast. Permanency of trace is dependent upon the compatibility of the fused particles and film, and in the case of blushed coatings such compatibility is usually guaranteed since the materials of the two phases are for the most part of identical composition. It is evident that incompatibility of the fused materials will shortly lead to recrystallization or resolidification with resulting heterogeneous opaque coating structure and consequent loss of legible contrast.

Application of heat to coatings of the cellular type results in legible markings by the same general manner as that involved with "blushed" coatings, with the exception that fusion of the continuous phase allows collapse of the cellular structure to a continuous transparent area and no requirement for compatibility exists.

Another method known to the art of providing a masking layer makes use of a dispersion of solid particles in a liquid vehicle, such as employed in paints, inks, and the like. Although the method is extremely simple and economical, it has not heretofore been useful in heat marking paper because the material properties required to provide an opaque coating of solid particles dispersed in a continuous film do not meet the requirements necessary to provide a permanent transparent trace when the coating is heated. For the latter, the dispersed particles and continuous film must exhibit sufficient compatibility for the components to combine into a homogeneous transparent film upon the application of localized heating. Materials of such compatibility are, however, generally soluble in the same solvents and it is not, therefore, a simple matter to disperse particles of one in a solution of the other while maintaining the phase distinction necessary to produce a coating of adequate opacity and whiteness.

We have found, however, that it is possible and practical to employ the more economical and versatile dispersion system in the preparation of thermosensitive recording or copy papers through the use of a class of solid materials known as "molecular compounds." Such compounds are not new in themselves, but rather are generally described by P. Pfeiffer, *Organische Molekularverbindungen* (Ferdinand Euke, Stuttgart, 1927), and by F. Cramer, *Einschlussverbindungen* (Springer-Verlag, Berlin, 1954). Molecular compounds have the unique property of being dissociable under the influence of heat to yield the original materials of which such molecular compounds were composed. We find that most molecular compounds exhibit physical and chemical properties unlike those of the original components and accordingly may select compounds which are not soluble in the solvent used to dissolve the binder but of which one or more of the solid components is compatible with the binder resin.

Our invention will become apparent in the following typical examples. As previously noted, one may prepare a masking coating by dispersing finely divided particles of one material in a continuous phase of a second material of effectively different index of refraction. Such effective difference may result from included interfacial layers of substances, such as air, as well as from actual index difference. The resulting heterogeneous coating will be opaque due to the light scattering effect of the dispersed particles. For the purposes of use in a thermosensitive recording paper the continuous phase or binder portion of the coating may be selected from any of a large number of well known thermoplastic resins such as ethyl cellulose, polyvinyl acetate, polyvinyl butyrate, cellulose acetate, or the like. The most practical and generally employed method of forming such heterogeneous films is by dispersing the finely divided material in a lacquer or solu-

tion in a proper solvent, of the thermoplastic resin intended as the continuous phase, coating the resulting dispersion, and drying to remove the solvent. In order to maintain the discreteness of particles it is necessary that such particles be inert with respect to the solvency of the lacquer or lacquer solvent.

Example 1

One hundred and eighty-three (183) grams of carrier component tetrachlorobisphenol A was dissolved in three hundred and sixty-four (364) grams of toluol at a temperature of about one hundred and fifty degrees (150° F.) and fifty-three (53) grams of a co-reactant diethanolamine was added and stirred for thirty (30) minutes. The mixture was chilled for about fourteen (14) hours (overnight) at about minus thirty degrees (−30° F.), during which time a precipitate forms. The precipitate was filtered, washed thoroughly with n-hexane at room temperature seventy degrees (70° F.), and dried. The resulting product was the molecular compound tetrachlorobisphenol A/diethanolamine (M.P. 151–153° C.). Forty (40) grams of the molecular compound was added to one hundred and eighty (180) grams of a 2.5% solution of Ethocel N100 in trichloroethylene. This slurry was ground overnight in a ball mill at forty degrees (40° F.). The dispersion thus formed was coated on a black surfaced paper to effect a drying coating weight of eight (8) pounds per ream (24 x 36—500). The resulting coating exhibited a surface brightness of about thirty-six percent (36%) of a magnesium carbonate standard and produced a permanently legible trace under the heated stylus of a Sanborn Company Viso-Cardiette recording machine at trace velocities of one hundred to three hundred inches (100–300") per second.

As a counter-example we described:

Example 2

Forty (40) grams of tetrachlorobisphenol A was added to one hundred and eighty (180) grams of a two and five-tenths percent (2.5%) solution of Ethocel N100 in trichloroethylene. The slurry was ground overnight in a ball mill at forty degrees (40° F.). The resulting mixture was coated on a black surfaced paper to effect a dry coating weight of eight (8) pounds per ream (24 x 36—500). The dry coating thus formed exhibited a surface brightness of about three percent (3%) of a magnesium carbonate standard. Such low contrast is not sufficient to produce discernible markings even when the coating is subjected to temperatures well in excess of the melting point of any of the coating components. The coating of this example may be described as translucent and is of no value as a masking coating.

A comparison of Examples 1 and 2 will indicate the principle of our invention. The carrier compound, tetrachlorobisphenol A, is compatible with the Ethocel binder both in the fused state and in the lacquer solution. When added singularly as the particulate phase of the dispersion, as in Example 2, the TCBA dissolves with the Ethocel and forms, when coated, a substantially homogeneous translucent film. The solid complex or molecular compound formed as in Example 1 by the combination of tetrachlorobisphenol A and diethanolamine is, however, insoluble in the lacquer solution and may be combined with such solution in any proportion without loss of particulate identity. Size reduction of the dispersed particles, as by ball milling or the like, may even be accomplished without disrupting the inert qualities of the molecular compound with respect to insolubility in the lacquer.

Upon activation of the coating by the application of heat, the dissociation of the molecular compound occurs and the components of such compound regain their physical and chemical identities. In Example 1 the compatibility of the TCBA, after dissociation, with Ethocel results in the permanent fusion into a transparent, continuous film which, as previously shown, will appear in darker contrast to the unactivated areas.

We have found that any number of various coating compositions for use in thermosensitive recording papers may be prepared according to the procedure generally outlined above. The examples below will indicate the versatility of our invention with respect to the variety of combinations which might be employed in the preparation of such coatings. It will be noted that various ranges of melting points may be tailored into the coatings by simple selection of molecular compound components. Variations in melting point of coatings might find practical use in the preparation of a series of temperature indicating papers or in the predetermination of the functional temperature ranges of recording or copying papers.

It will be evident when considering the end use intended for papers or sheets bearing our novel coatings that molecular compounds will primarily be selected with respect to their stability under conditions of temperature and humidity expected to be encountered by the coatings in manufacture, handling, shipment and storage. Exposed to reasonably anticipated conditions, such as are referred to herein and in the appended claims as "normal" conditions, the properly selected molecular compound will maintain its integrity and particularity, and will proceed to dissociation only when exposed to temperatures substantially above such normal conditions. Since the dissociation temperatures of the molecular compounds, hence the activation temperatures of the copy sheets, will vary according to the manufacturers' specific desires, such activation temperatures are generally referred to herein and in the appended claims as "elevated" temperatures.

We have found that molecular compounds most useful in the practice of our invention may be prepared with carrier components selected from any of the group of halogenated aromatic hydroxy compounds. Co-reacting components may be selected from the group of materials comprising primary, secondary, and tertiary amines, heterocyclic amines, and alcohol amines. The selection of specific molecular compounds is entirely dependent upon the preference of the person preparing the coating as to the range of coating activity and compatibility desired. Such specific selections are within the skills of the ordinary coatings technologist and are not considered as constituting per se a part of the invention.

The following examples are further representative of our invention and set forth the identities and proportions of ingredients involved in the preparation of various of our thermosensitive coatings for recording or copying papers. In each of these examples the carrier component was dissolved in the solvent and the co-reactant was added under constant agitation. The mixture was continually agitated for thirty (30) minutes and then chilled for about fourteen (14) hours at approximately minus thirty degrees (−30° F.), during which time the molecular compound precipitated. This molecular compound precipitate was thoroughly washed in n-hexane and was dispersed in the desired lacquer solution and reduced to fine particle size by ball milling at forty degrees (40° F.). The dispersions thus formed were coated to about eight (8) dry pounds per ream (24 x 36—500) on a dark surfaced paper (basis weight twenty-eight pounds (28 lbs.) per ream—24 x 36—500). Each coating exhibited good marking qualities and produced a permanent legible trace on the Sanborn Viso-Cardiette in the range of one hundred to three hundred (100–300) inches per second trace velocity.

Example 3

(a)

Molecular compound:

	Parts
Carrier: Tetrachlorobisphenol A (TCBA)-----	91
Co-reactant: Diethanolamine (DEA)-----	26.2
Solvent: Toluol -----	182
Molecular compound: TCBA / DEA—M.P. 151–153° C.	

5

(b)

Coating composition:

Lacquer: 5% Parapol S-50 in trichloroethylene 160
 Dispersed solid: TCBA/DEA----- 40
 Coating brightness: 36% of magnesium carbonate standard.

Example 4

(a)

Molecular compound: TCBA/DEA from Example 3.

(b)

Coating composition:

Lacquer: 5% of 1/2 sec. Butyrate in trichloroethylene ----- 160
 Dispersed solid: TCBA/DEA----- 40
 Coating brightness: 34% of standard.

Example 5

(a)

Molecular compound: TCBA/DEA from Example 3.

(b)

Coating composition:

Lacquer: 2.5% Butvar B76 in trichloroethylene 180
 Dispersed solid: TCBA/DEA----- 22.5
 Coating brightness: 36% of standard.

Example 6

(a)

Molecular compound: TCBA/DEA from Example 3.

(b)

Coating composition:

Lacquer: 5% Gelva V100 in trichloroethylene_ 160
 Dispersed solid: TCBA/DEA----- 40
 Coating brightness: 36% of standard.

Example 7

(a)

Molecular compound: TCBA/DEA from Example 3.

(b)

Coating composition:

Lacquer: 2.5% Polyox WSR35 in trichloroethylene ----- 180
 Dispersed solid: TCBA/DEA----- 22.5
 Coating brightness: 29% of standard.

Example 8

(a)

Molecular compound:

Carrier: Tetrachlorobisphenol A (TCBA)----- 91
 Co-reactant: Triisopropanolamine (TIPA)----- 48
 Solvent: Toluol ----- 182
 Molecular compound: TCBA / TIPA—M.P. 118–120° C.

(b)

Molecular compound:

Lacquer: 2.5% Ethocel N100 in trichloroethylene ----- 180
 Dispersed solid: TCBA/TIPA----- 22.5
 Coating brightness: 33% of standard.

6

Example 9

(a)

Molecular compound:

Carrier: Tetrachlorobisphenol A (TCBA)----- 91
 Co-reactant: Beta isopropylaminopropionitrile (IPAPN) ----- 31.2
 Solvent: Toluol ----- 182
 Molecular compound: TCBA/IPAPN—M.P. 103–105° C.

(b)

Coating composition:

2.5% Ethocel N100 in trichloroethylene----- 180
 Dispersed solid: TCBA/IPAPN----- 22.5
 Coating brightness: 46% of standard.

Example 10

(a)

Molecular compound:

Carrier: Hexachlorophene (G11)----- 102
 Co-reactant: Ethylenediamine (EDA)----- 15
 Solvent: Toluol ----- 408
 Molecular compound: G11/EDA—M.P. 187–192° C.

(b)

Coating composition:

Lacquer: 2.5% Ethocel N100 in trichloroethylene ----- 180
 Dispersed solid: G11/EDA----- 20
 Coating brightness: 36% of standard.

Example 11

(a)

Molecular compound:

Carrier: Hexachlorophene (G11)----- 102
 Co-reactant: Dimethylformamide (DMF)--- 18.7
 Solvent: Toluol----- 408
 Molecular compound: G11/DMF—M.P. 100–102° C.

(b)

45

Coating composition:

Lacquer: 2.5% Ethocel in trichloroethylene_ 180
 Dispersed solid: G11/DMF----- 22.5
 Coating brightness: 48% of standard.

Example 12

(a)

Molecular compound:

Carrier: Pentachlorophenol (PENTA)----- 66.5
 Co-reactant: Triethanolamine (TEA)----- 74.4
 Solvent: Toluol----- 266
 Molecular compound: PENTA/TEA—M.P. 133–137°.

(b)

60

Coating composition:

Lacquer: 2.5% Ethocel N100 in trichloroethylene ----- 140
 Dispersed solid: PENTA/TEA----- 10.5
 Coating brightness: 22% of standard.

Example 13

(a)

70

Molecular compound:

Carrier: Pentachlorophenol (PENTA)----- 66.5
 Co-reactant: Propylenediamine (PDA)----- 36
 Solvent: Toluol----- 540
 Molecular compound: PENTA/PDA—M.P. 168–172° C.

7
(b)

Coating composition:

Lacquer: 2.5% Ethocel N100 in trichloroethylene	140
Dispersed solid: PENTA/PDA	10.5
Coating brightness: 29% of standard.	

Example 14

(a)

Molecular compound:	Parts	10
Carrier: Actamer (ACT)	89	
Co-reactant: Diethanolamine (DEA)	26.2	
Solvent: Toluol	540	
Molecular compound ACT/DEA—M.P. 143–147° C.		15

(b)

Coating composition:

Lacquer: 2.5% Ethocel N100 in trichloroethylene	180
Dispersed solid: ACT/DEA	22.5
Coating brightness: 48% of standard.	

Example 15

(a)

Molecular compound:	Parts	25
Carrier: Tetrabromobisphenol A (TBBA)	136	
Co-reactant: 2-amino, 2-ethyl 1,3 propanediol (AEP)	29.8	
Solvent: Toluol	544	
Molecular compound: TBBA/AEP—M.P. 139–140° C.		30

(b)

Coating composition:

Lacquer: 2.5% Ethocel N100 in trichloroethylene	180
Dispersed solid: TBBA/AEP	22.5
Coating brightness: 39% of standard.	

Example 16

(a)

Molecular compound:	Parts	
Carrier: Tetrabromobisphenol A (TBBA)	136	
Co-reactant: Methyldiethanolamine (MDEA)	60	
Solvent: Toluol	544	
Molecular compound: TBBA/MDEA—M.P. 100–115° C.		45

(b)

Coating composition:

Lacquer: 2.5% Ethocel N100 in trichloroethylene	180
Dispersed solid: TBBA/MDEA	22.5
Coating brightness: 57% of standard.	

In the foregoing examples Tetrachlorobisphenol A and Tetrabromobisphenol A are commercial products sold by Monsanto Chemical Company. The carrier, Actamer, in Example 16, is sold by Monsanto Chemical Company under the commercial name of Bithionol. The carrier compounds, Hexachlorophene and Pentachlorophenol are commercial products sold by Sindar Corporation and Dow Chemical Company respectively. The co-reactant compounds in the foregoing examples were technical grade. The resin components in the examples were as follows:

Parapol S50—Co-polymer of styrene and polyisobutylene—Enjay Company
 ½ sec. Butyrate—polyvinyl butyrate—Tennessee Eastman Company
 Butvar B76—polyvinyl butyral—Shawinigan Resins Corp.
 Ethicol N100—ethylcellulose—Dow Chemical Company
 Gelva V100—polyvinyl acetate—Shawinigan Resins Corp.
 Polyox WSR35—polyethylene glycol ether—Union Carbide Chemical Company

8

It will be noted from the above description that the formation of legible characters on thermosensitive marking papers is a direct result of the heating of the masking coating thereof. In the examples above we have indicated the operability of our coatings by subjecting such coatings to direct contact with the heated stylus of a commercial electrocardiograph recorder. The activation of our coatings is not restricted to such conduction heating, but may also be accomplished by the use of converted radiant heat, internal resistance heating resulting from the passage of electrical current, or by various other heating means. We do not intend to imply that a specific heating means constitutes per se any part of our invention.

We have outlined the preparation of our novel coating compositions in terms of a practical method which we generally employed in the examples shown above, that is, by dispersing a prepared selected molecular compound in the selected lacquer solution. Other methods of introducing the coating components into the coatable composition may be equally well suited to the preparation of the compositions as, for example, the addition of the respective carrier component and co-reactant component directly to the thermoplastic resin solution with subsequent formation of molecular compound and size reduction as in the following example.

Example 17

The following components were charged to a porcelain ball mill and ground for six hours at room temperature to form a dispersion of coatable consistency:

	Parts
Tetrachlorobisphenol A	68.25
Triisopropanolamine	36
Ethocel N100	10
Toluol	280

The dispersion thus formed was coated to about eight (8) dry pounds per ream (24 x 36—500) as previously described. The resultant coating was equivalent to that prepared of the composition of Example 8.

The method of discrete particle size reduction used by us in the preparation of our above listed illustrative examples, i.e., ball milling of total suspension, is not intended to be restrictive of the method by which fine particle dispersions of our invention may be made. The selection of this method was predicated upon laboratory expedience and it is in no way to be implied that any known and accepted method of size reduction, such as, for example, dry or wet grinding of particles prior to dispersion, may not be equally well applied to the preparation of our coating mixes.

It is further recognized that any of the known methods of coating accepted by the art may be employed in the preparation of our novel coatings.

We claim as our invention:

1. A heat sensitive recording paper comprising a base sheet and a coating adherent thereto and obscuring a surface thereof, said coating comprising a continuous phase of a thermoplastic resin, which resin when taken by itself as a film is essentially transparent, and a dispersed phase of finely divided particles of a molecular compound distributed throughout said film and rendering the same opaque, said molecular compound consisting of an amine in combination with a halogenated aromatic hydroxy compound which is compatible with said resin, and being stable at normal conditions of temperature and humidity but dissociable at an elevated temperature to yield said amine and halogenated aromatic hydroxy compound, whereby upon heating said paper, said halogenated aromatic hydroxy compound and said resin coalesce and render said film transparent where heated.

2. In the manufacture of heat sensitive recording papers which comprise a base sheet and a substantially opaque contrasting obscuring coating therefor, said coat-

ing comprising a continuous phase of thermoplastic resins with discrete solid particles of thermally fusible material dispersed therein, in an amount sufficient to render said coating opaque: the method which comprises dissolving a thermoplastic resin in a suitable volatile solvent, dispersing in the solution finely divided particles of a solid molecular compound in an amount sufficient to render a film of said resin opaque, said molecular compound consisting of an amine in combination with a halogenated aromatic hydroxy compound which is compatible with said resin, and being stable at normal conditions of temperature and humidity but dissociable at an elevated temperature to yield said amine and halogenated

aromatic hydroxy compound, coating the resulting dispersion onto a base sheet, and drying said coating to form an opaque film on said base sheet.

References Cited in the file of this patent

UNITED STATES PATENTS

Re. 24,554	Clark et al.	Oct. 21, 1958
2,899,334	Crevling et al.	Aug. 11, 1959
2,900,388	Tien	Aug. 18, 1959
2,910,377	Owen	Oct. 27, 1959
2,967,785	Allen et al.	Jan. 10, 1961