

1

3,746,675

HEAT SENSITIVE RECORD MATERIAL

James H. Blose, Appleton, Wis., and Shashikant G. Talvarkar, Dayton, Ohio, assignors to The National Cash Register Company, Dayton, Ohio

No Drawing. Original application July 15, 1970, Ser. No. 55,233, now Patent No. 3,674,535. Divided and this application Mar. 22, 1972, Ser. No. 236,979

Int. Cl. C08f 19/14

U.S. Cl. 260—23 EM

3 Claims

ABSTRACT OF THE DISCLOSURE

A heat sensitive record material which comprises (1) a base sheet such as paper, and (2) a coating of a colorless chromogenic material and a bis phenol distributed in a polyvinyl alcohol in combination with a filler such as clay, a lubricant such as zinc stearate and a nontacky wax. Conventional wetting agents and defoamers also are present in the record material. This material is resistant to pick-off of the record sheet surface and freeze-sticking of the record sheet to the printing heat when the record material is used in conjunction with a rapidly heated and cooled printing head.

This is a divisional application of U.S. patent application Ser. No. 55,233, filed July 15, 1970 now Pat. No. 3,674,535, issued July 4, 1972, on the application of James H. Blose et al.

Heat-sensitive record materials of the type shown in an application for Letters Patent of the United States, Ser. No. 808,379, Mar. 14, 1969, now U.S. Pat. No. 3,539,375, issued Nov. 10, 1970, on the application of Henry H. Baum, owe their heat-sensitive characteristics to a thermoplastic film coating which contains in it heat-responsive chemically reactive color-producing material in dispersed solid particulate form. The flowing together of these materials under conditions of the coating's being subjected to a printing contact with hot type causes coloration of the film coating at the typed points.

As long as the applied type is hot as it is withdrawn from contact with the record material and does not pick up the melted material, there is no pick-off problem to spoil the print or dirty the type face. However, there have been developed planographic surface printing plates or surfaces that have heatable matrices flush with the planosurface, which matrices are selectively operable by flash heating to print the selected symbol. These symbols, for example, can be made up of selected elements of a "Solomon's Seal" type of matrix, which elements are, individually for an instant, rendered very hot (250 degrees centigrade) and suddenly cooled by heat conduction into a heat sink to make them ready for printing another selected symbol, the record material being advanced or moved across the printing plate between symbol-printing operations or a single thermal head moved across the medium to form a contextual data message. The heating and sudden cooling of the type face can freeze the melted film to the printer plate, resulting in rupture of the film coating or its supporting substrate of paper or paper-like material and, in addition, fouling the printing head.

It has been discovered that the heat-sensitive reactants of the Baum patent, hereinabove identified and herein-after referred to, can be employed in the anti-pick record material of this invention. Generally, the color reactants are comprised of the pair 3,3-bis(4-dimethylaminophenyl) 6-dimethylaminophenyl phthalide, hereinafter referred to as crystal violet lactone or CVL, and a bis phenol such as 4,4'-isopropylidenediphenol.

These reactants can be dispersed as solid fine particles in a water solution of a suitable grade of polyvinyl alco-

2

hol. The dispersion can be applied to and subsequently dried on a prepared paper sheet to produce a heat-sensitive coating which responds by blue coloration to hot type pressed thereagainst. This coated sheet has the infirmity, however, of sticking to or picking-off onto a planographic type surface having rapidly heating and cooling configurations adjacent to constantly cool areas (room temperature) across which the sheet is passed step by step in another embodiment, the thermal head is moved across the medium and is cooled between the printing of two symbols. The damage to the record is more apparent with finer printing than with larger printing, as would be obvious. The printing head itself, by picking up the coating, is likewise subject to fouling and consequently is rendered incapable of giving a sharp print.

It has been found that by combining the thermal sensitive dye and bis phenol with a filler, lubricant and wax, the sticking, or picking-off, of the materials onto the planar printing element is prevented, and the sharp print property is preserved. The resulting thermal medium is extremely stable to wide ambient conditions, i.e., at temperatures ranging from 0 to 140° F. and relative humidities ranging from 0 to 100 percent.

As noted above, crystal violet lactone is the colorless chromogenic material. The phenols that can be employed in this invention have a low vapor pressure. Normally, the phenols liquefy or vaporize to a sufficient extent at the usual thermographic temperatures of 150 to 200° C. Examples of the phenols that can be employed in this invention are disclosed in the previously-identified Baum patent, and are incorporated herein by reference thereto.

The colorless chromogenic material and bis phenol are distributed in a polyvinyl alcohol film, which acts as a binder to hold the chemicals together on the support means. The polyvinyl alcohol preferred is a medium-viscosity grade of 99 percent hydrolysis. Various binders are Elvanols from Dupont, Vinols from Air Reduction and other non-reacting water soluble binders.

The fillers that can be employed in the invention are at least partially reactive with the colorless chromogenic material. Specific examples are Klondyke Clay and other filler materials such as titanium dioxide, zinc oxide, clays, silicates and carbonates which are insoluble in water.

Lubricants also are employed in this invention. Generally, the lubricants increase light fade resistance as well as lubricate. Specific examples are zinc stearates as well as other water insoluble stearates of calcium, iron, cobalt, nickel, aluminum, manganese, lead and the like.

The release agent is of high enough melting point so that it will not melt and react with the coating under normal storage conditions. A wide variety of waxes can be employed in this invention, preferably Acra Wax C is employed.

"Acra Wax C" is a reaction product of hydrogenated castor oil and ethanolamine, is insoluble in boiling water, and has a melting point of 140 to 143 degrees centigrade, a flash point of 285 degrees centigrade (open cup), and a specific gravity of 0.97 at 25 degrees centigrade. It can be purchased as a fine powder under the quoted brand name from Glyco Chemicals, Inc., 417 Fifth Ave., New York, N.Y., United States of America. Although "Acra Wax C" has been specified as preferred, any similar anti-blocking wax or nontacky wax in powdered form can be used and will be specified in the claims as "nontacky wax."

Small amounts of conventional materials such as wetting agents and defoamers can be employed in the record material of this invention.

Under processing conditions, separate dispersions of the colorless chromogenic material and bis phenol are made to reduce excessive discoloration of the wet color.

Generally, the dye dispersion comprises crystal violet lactone and polyvinyl alcohol with small amounts of wetting agent and defoamer. The bis phenol dispersion comprises bis phenol, polyvinyl alcohol, clay, nontacky wax and a lubricant with small amounts of a wetting agent and defoamer.

Each dispersion can be comprised of 15 to 40 percent solids in water, preferably 20 to 30 percent. For example, for every 100 grams of dispersion there is 20 grams of dry solids and 80 grams of water. Generally, a period of time ranging from 8 to 24 hours is allowed to pass before the two dispersions are contacted with each other in order to reduce excessive discoloration of the wet color.

The amounts of material in the final formulation generally are as follows. Crystal Violet Lactone ranges from 3 to 9 percent by weight, bis phenol ranges from 39 to 41 percent by weight and polyvinyl alcohol ranges from 20 to 30 percent by weight. The final formulation also comprises about 20 weight percent filler, about 2 weight percent lubricant and about 2 weight percent release agent. Small amounts of a wetting and a defoamer also are present, generally less than 1 weight percent.

The particle size of the final formulation generally is in the range of 3 to 6 microns.

The support sheets that can be employed in this invention are those disclosed in the above-referred to Baum patent.

The following example further illustrates the invention.

EXAMPLE

In this embodiment, the substrate is bond paper of 13 pounds weight per ream of 500 sheet 17 by 22 inches having a medium calendered surface.

The dye dispersion is as follows:

	Percent solids (dry)
CVL	69.8
Vinol 325 ¹	30.0
Surfynol 104 ²	0.1
Nopco NDW ³	0.1

¹ Vinol 325 is a polyvinyl alcohol produced by Air Reduction Chemical Co.

² Surfynol 104 is a surface active agent of dl-tertiary acetylenic glycol produced by Air Reduction Chemical Co.

³ Nopco NDW is a defoaming agent produced by Nopco Chemical Company.

The bis phenol dispersion is as follows:

	Percent solids (dry)
4,4-isopropylidene diphenol (Bisphenol A)	43.55
Vinol 325	30.00
Klondyke Clay ¹	21.89
Acra Wax C	2.18
Zinc stearate	2.18
Surfynol 104	0.10
Nopco NDW	0.10

¹ Klondyke Clay is a conventional coating clay comprising mainly silicates, produced by Englehard Mineral & Chemical Company.

The dispersions were made using conventional grinding equipment at about 20 percent solids and mixed in the

above proportions. After 16 hours, the two dispersions were admixed in a ratio of 1 part dye dispersion per 10.67 parts reactive dispersion, resulting in the following formulation.

	Dry weight percent
Crystal Violet Lactone	6.0
Bisphenol A	39.8
Klondyke Clay	20.0
Vinol 325	30.0
Zinc stearate	2.0
Acra Wax C	2.0
Surfynol 104	0.1
Nopco NDW	0.1

The final formulation can be used in any record material coating meant to be melted to cause the bringing together of the color reactants and otherwise having a composition tending to be picked-off by hot type members as they are cooled. Further, the thermally sensitive reactants in combination with the filler, lubricant, binder and wax make it possible to produce a non-sticking thermally sensitive paper that is extremely stable to wide ambient conditions of temperature and humidity.

What is claimed.

1. A dispersion comprising 15 to 40 percent solids and 60 to 85 percent water wherein said solids contain finely divided solid crystal violet lactone, a finely divided bis phenol, a water insoluble filler at least partly reactive with the crystal violet lactone and selected from the group consisting of titanium dioxide, zinc oxide, clays, water insoluble silicates and water insoluble carbonates, a lubricant of a water insoluble stearate and a nontacky wax which will not melt and react with said crystal violet lactone and said bis phenol under normal storage conditions distributed in a binder of polyvinyl alcohol and wherein said solids contain 3 to 9 dry weight percent of said crystal violet lactone, 39 to 41 dry weight percent of said bis phenol, 20 to 30 dry weight percent of said polyvinyl alcohol, 20 dry weight percent of said filler, 2 dry weight percent of said lubricant and 2 dry weight percent of said wax.

2. The dispersion of claim 1 wherein said dispersion is 20 to 30 percent solids and 70 to 80 percent water.

3. The dispersion of claim 1 wherein said bis phenol is 4,4'-isopropylidene-diphenol, said filler is a clay and said lubricant is zinc stearate.

References Cited

UNITED STATES PATENTS

2,379,268	6/1945	Zimmer	260—23 ZM
3,539,375	11/1970	Baum	117—36.2

DONALD E. CZAJA, Primary Examiner

W. E. PARKER, Assistant Examiner

U.S. Cl. X.R.

260—41 C; 117—36.2, 36.8, 155