Nov. 10, 1970 H. H. BAUM 3,539,375

THERMO-RESPONSIVE RECORD SHEET

Original Filed June 1, 1966 2 Sheets-Sheet 1

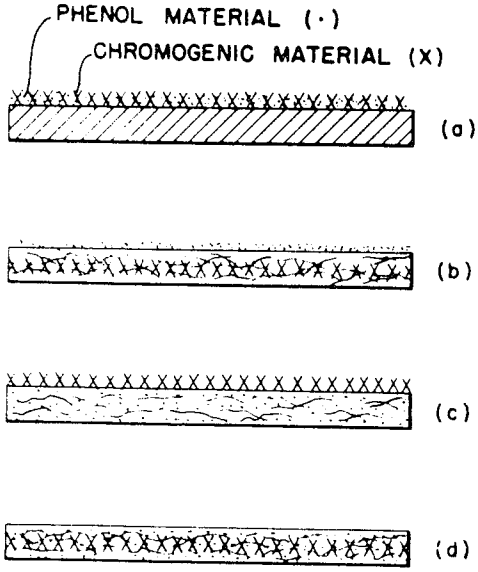
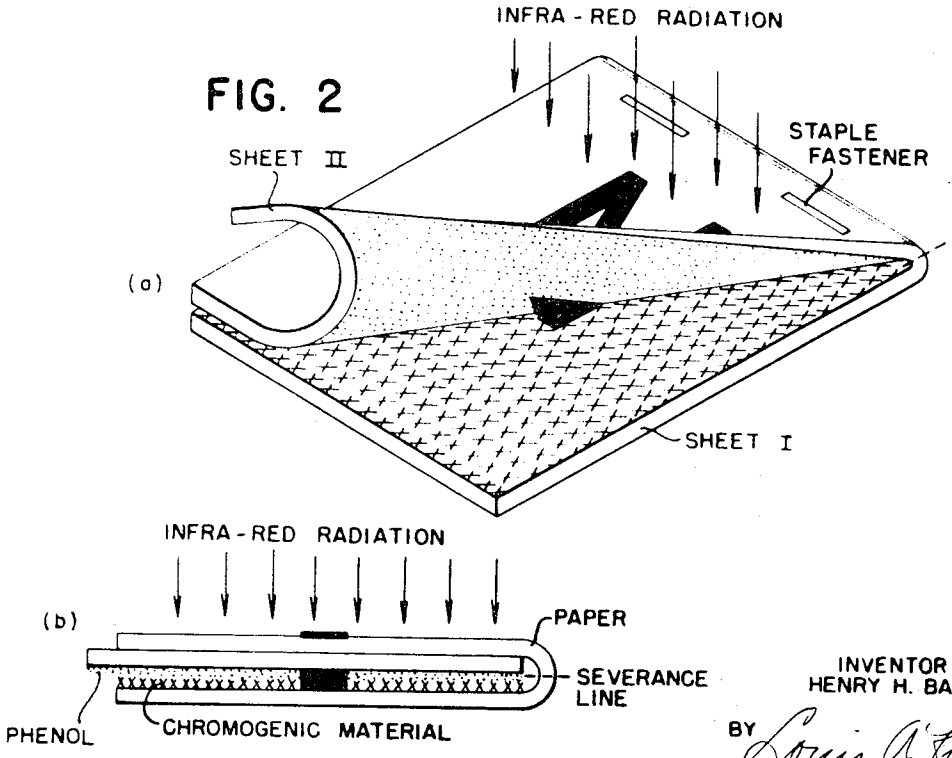


FIG. 1

FIG. 2



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THERMO-RESPONSIVE RECORD SHEET

Original Filed June 1, 1966 2 Sheets-Sheet 1

FIG. 3

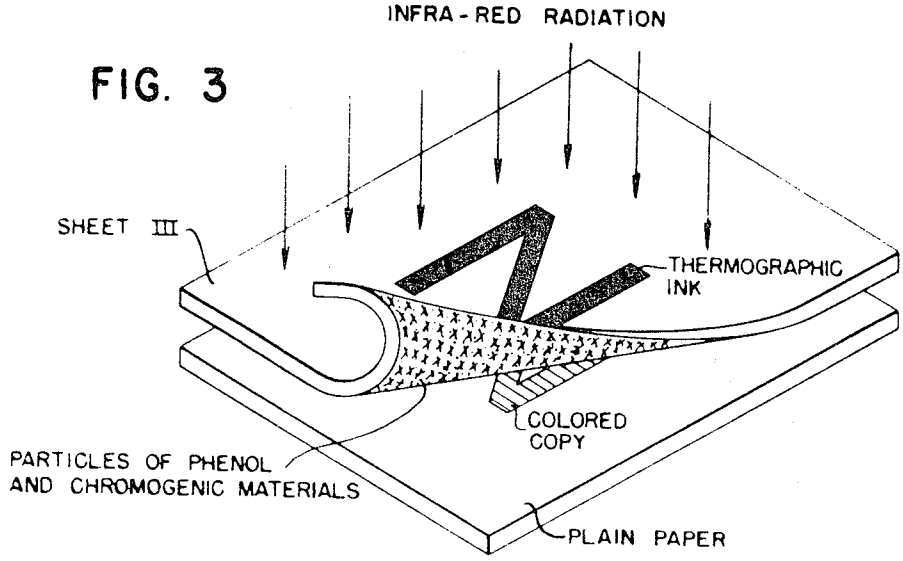
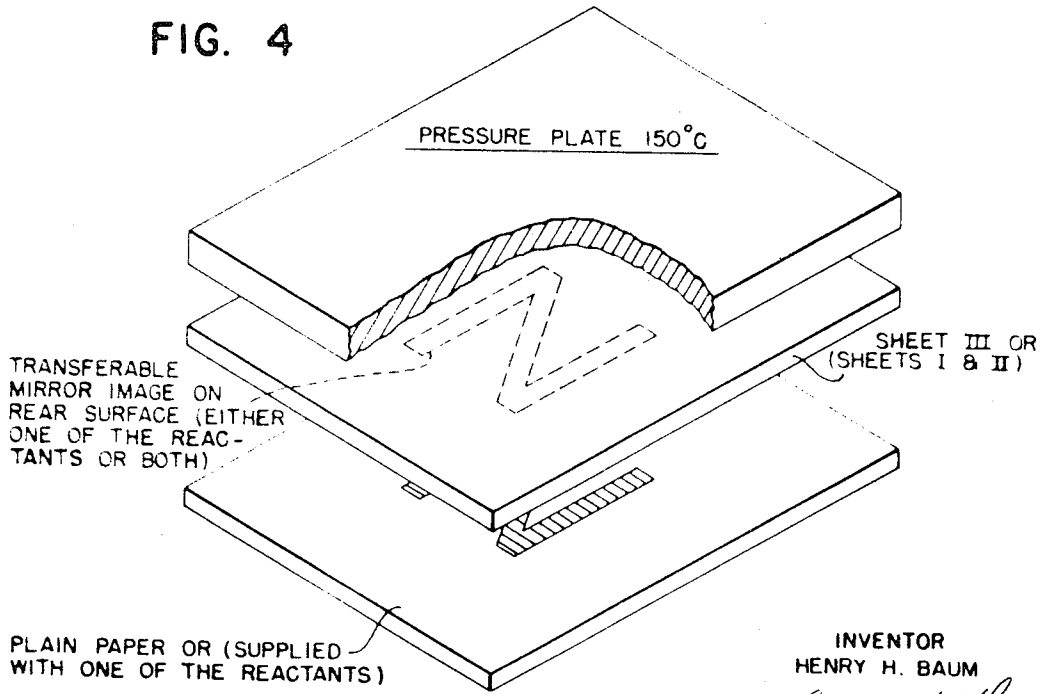


FIG. 4



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United States Patent Office

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3,539,375

THERMO-RESPONSIVE RECORD SHEET

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Continuation of application Ser. No. 554,565, June 1, 1966. This application Mar. 14, 1969, Ser. No. 808,379
Int. Cl. B41m 5/22
U.S. Cl. 117—36.2 8 Claims

ABSTRACT OF THE DISCLOSURE

In a temperature-responsive record material comprising a support sheet having crystal violet lactone and a phenolic arranged such that application of heat will produce a mark-forming reaction between the lactone and the phenolic, the improvement comprising disposing the lactone and phenolic in a matrix of polyvinyl alcohol.

This application is a continuation of application Ser. No. 554,565, filed June 1, 1966, now abandoned.

This invention is concerned with a temperature-responsive record material and more particularly an improved mark-forming system for use in a temperature-responsive record material.

In co-pending United States patent application Ser. No. 366,524, filed May 11, 1964, in the name of Henry H. Baum, and assigned to the assignee herein, a mark-forming temperature-responsive record material system is described which broadly involves the migration or transfer of a substantially colorless mark-forming component(s), particulate at room temperature but transferable and/or vaporizable at elevated temperature from its support sheet to the site of a second substantially colorless mark-forming component to thereby produce a mark according to an applied temperature pattern. For example, the colorless mark-forming components described above may be arranged in juxtaposition in a single support sheet, this arrangement being commonly referred to as a "self-contained" system. Application of heat to the sheet causes a migration of the liquefied or vaporized particulate material to a juxtapositioned mark-forming component to thereby produce a mark.

The mark-forming components generally comprise a basic chromogenic material in its colorless state and an acidic material, such as the diphenols, which react upon contact to produce a color.

An alternative form to the self-contained system is to dispose a component on one sheet and another component on a second support sheet, the components being placed in face-to-face relation, so that, upon application of heat, the liquefied and/or vaporized mark-forming component transfers to the loci of the other mark-forming component and thereat produces a mark. This latter system is generally referred to as a "transfer" system.

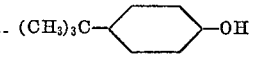
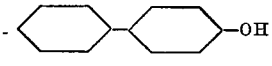
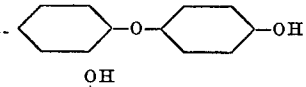
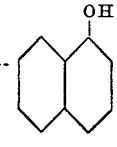
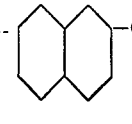
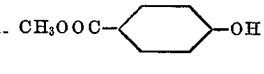
In the afore-described mark-forming systems, it has been found desirable to provide an overlay of polymer film on a sheet or sheets coated with one or both of the mark-forming components. For example, a protective coating comprising a polyvinyl alcohol-carboxymethylcellulose film has been found satisfactory.

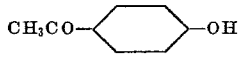
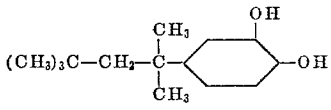
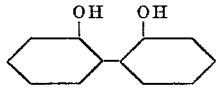
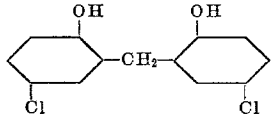
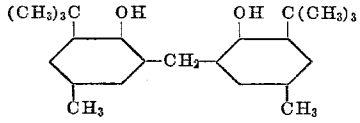
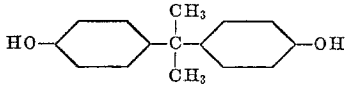
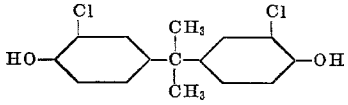
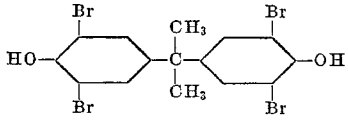
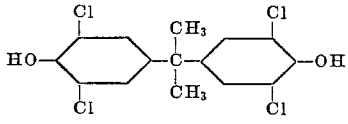
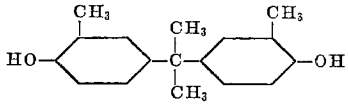
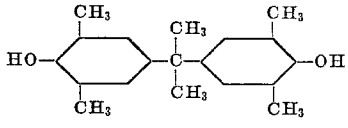
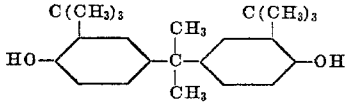
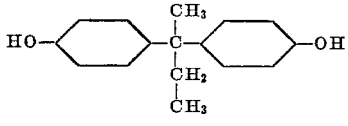
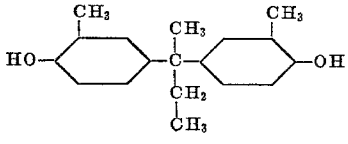
It has now been found that a mark-forming system comprising a certain chromogenic material—namely, 3,3-bis(4-dimethylaminophenyl)-6-dimethyl phthalide (crystal violet lactone)—and a diphenol, triphenol, or polymer thereof, capable of liquefying and/or vaporizing at the temperatures normally employed in thermographic processes, when distributed in a polyvinyl alcohol film, possesses unexpected properties which make it uniquely attractive as a temperature-responsive record material.

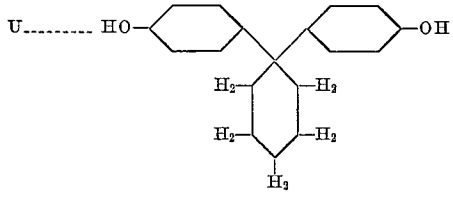
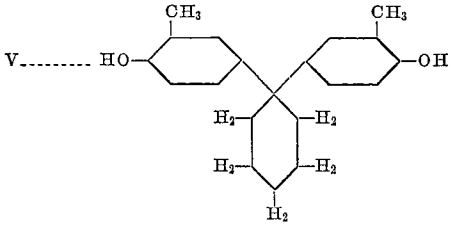
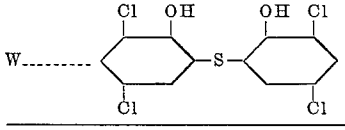
It is well known and not considered to be a part of this invention that basic chromogenic materials, such as crystal violet lactone, and acidic materials, such as attapulgite clay, inorganic and organic acids, and monomeric phenols, such as, for example, phenol, and cresols react to produce a color, as reported, for instance, by O. Fischer and F. Romer, Berichte der deutschen chemischen Gesellschaft, volume 42, pages 2934 and 2935 (1909). Moreover, single-sheet (self-contained) and manifold (transfer) sheet temperature-responsive systems which depend on the reaction of a basic chromogenic material and acidic particulate material are not novel, being disclosed in U.S. Pats. Nos. 2,172,507, issued July 5, 1955, on the application of Barrett K. Green, and 2,730,457, issued Jan. 10, 1956, on the application of Barrett K. Green and Lowell Schleicher, for example.

As noted above, crystal violet lactone is the colorless chromogenic material. The diphenols, triphenols, or polymers thereof useful in this invention should have a low vapor pressure below 60 degrees centigrade to prevent loss by evaporation during storage prior to use in the mark-forming reaction but should liquefy and/or vaporize to a sufficient extent at the usual thermographic temperatures of 150 to 200 degrees centigrade.

Examples of suitable phenolic material are:

	Structure	Formula	M.P., ° C.
A		4-tertiary butylphenol	94-99
B		4-phenylphenol	166-167
C		4-hydroxydiphenyloxyde	85
D		α-Naphthol	95-96
E		β-Naphthol	119-122
F		Methyl-4-hydroxybenzoate	126-128

	Structure	Formula	M.P., ° C.
G		4'-hydroxyacetophenone	108–110
H		4-tertiary-octylcatechol	109
I		2,2'-dihydroxydiphenyl	103–109
J		2,2'-methylene bis (4-chlorophenol).	164
K		2,2'-methylene bis (4-methyl-6 tertiary butylphenol).	125–130
L		4,4'-isopropylidenediphenol	156
M		4,4'-isopropylidene bis (2-chlorophenol).	90–91
N		4,4'-isopropylene bis (2,6-dibromophenol).	172–174
O		4,4'-isopropylidene bis (2,6-dichlorophenol).	
P		4,4'-isopropylidene bis (2-methylphenol).	136
Q		4,4'-isopropylidene bis (2,6-dimethylphenol).	168
R		4,4'-isopropylidene bis (2-tertiary butylphenol).	109–114
S		4,4'-sec. butylidenediphenol	118–121
T		4,4'-sec. butylidene bis (2-methylphenol).	

Structure	Formula	M.P., ° C.
U..... 	4,4'-cyclohexylidenediphenol..	180
V..... 	4,4'-cyclohexylidene bis (2-methylphenol).	184
W..... 	2,2'-thio bis (4,6-dichlorophenol).	

Particularly useful, and the preferred phenolic material for use with crystal violet lactone, is 4,4'-isopropylidenediphenol (Compound L).

The polyvinyl alcohol useful in this invention may be completely or partly hydrolyzed, it having been found that polyvinyl alcohol acetate is useful.

The preferred support sheet is paper because of its response to thermographic practices in terms of heat and light conductivity and its known properties as a record material. However, sheets or bands of film-like polymeric material, woven material, or laminated materials may be used. Such a sheet or band may be impregnated or coated with the mark-forming components, such coating or impregnation fitting the proposed use as to depth of penetration of the components if penetration is involved, or with respect to the total or restricted location of the components as to the broad surface areas of the sheet, or with respect to amounts and kinds of components.

For the purposes of this disclosure, unless otherwise specified, it is to be considered that the support means is a thin, relatively opaque white paper sheet, and that any written or printed data to be used in conjunction therewith for control of recording be of a marking material that is raised in temperature relative to the supporting member when it is irradiated by infra-red radiation.

The particles of phenolic material should be as small in size as is consistent for the necessary resolution and coating properties—such as, say, around three microns in average largest particle dimension—and the particles of chromogenic material should be of similar dimensions, although the size is not critical if the optical effect is sufficiently good with respect to resolution. In respect to resolution, the particles preferably should be supplied in such quantity in an area to be served as to give no perception of individual existence. All of the named materials either are colorless (apparently white in powdered form) or have such small coloration in the unreacted state as to be considered colorless.

The relative amounts of crystal violet lactone, phenolic material, and polyvinyl alcohol may vary, suitable ranges of crystal violet lactone being 1% to 15% by weight, of phenolic material 45% to 94% by weight, and of polyvinyl alcohol 5% to 40% by weight. All weights are on a dry basis.

Where both mark-forming components are contained in the same sheet, they may be interspersed or arranged in layers, be one or both on a surface, partly within the sheet, or entirely within the sheet.

The structural combination of elements in a number of forms illustrative of the invention is shown in the drawings which form part of this specification but which are not to be deemed to limit the claimed subject matter.

Of the drawings:

FIG. 1 is a schematic diagram of several constructions in cross-section of a sheet supplied with the mark-forming components, (a) showing a sheet of paper having the mark-forming components coated on a surface in interspersion, (b) showing the chromogenic components distributed throughout a sheet of paper and the phenolic component on a surface, (c) showing the reverse of (b), and (d) showing both mark-forming components interspersed throughout the paper sheet.

FIG. 2 is a schematic showing in (a) two facing record sheet surfaces, each of the facing surfaces being coated with one of the mark-forming components, and showing how infra-red radiation is used in conjunction with a "thermographic" ink print to make a mark, view (a) showing two sheets stapled as a unit, and view (b) showing a folded sheet with a severance formation served with an interleaf sheet carrying one of the reactants. In FIG. 2, it is assumed that the chromogenic material is not rendered mobile by the temperatures used, but that the phenolic material is transferred.

FIG. 3 shows both mark-forming components on the rear surface of a sheet (Sheet III) bearing thermographically-responsive data on the front surface, so that heat engendered by infra-red radiation striking the data heats it, which heat turns the materials on the rear surface to a pattern of mobile fluid which may be transferred to a plain sheet of paper placed in contact therewith.

FIG. 4 shows an overlying sheet of paper having a mirror-image of data recorded in a pattern of one or both of the mark-forming components on the rear surface of a sheet, so that it may be passed to a plain sheet in a mobile fluid phase by a heat press; the plain sheet also may be supplied with one of the necessary reactants if it is missing, by intention, from the overlying sheet.

The following examples further illustrate the invention.

EXAMPLE I

This example describes the preparation of a composition containing the mark-forming components and its coating onto a paper support sheet for use as a thermocopy sheet.

Preparation of crystal violet lactone dispersion—Component A

An attritor was charged with 35 parts by weight of crystal violet lactone, 150 parts by weight of a 10%, by weight, aqueous solution of polyvinyl alcohol, and 65 parts by weight water, and ground for one hour. The polyvinyl alcohol used was approximately 98% hydrolyzed, and a 4%, by weight, aqueous solution which had a viscosity of 23 to 28 centipoises as determined at 20 degrees centigrade by the Hoeppler falling ball method was used. (ASTM–D–1343–56.) The particle size of the crystal violet lactone was approximately one to three microns after attrition.

Preparation of phenol dispersion—Component B

An attritor was charged with 35 parts by weight of 4,4′-isopropylidine diphenol (Bisphenol A), 150 parts by weight of the polyvinyl alcohol solution described used to form Component A, and 65 parts by weight of water, and the system was ground for one hour. The particle size of the phenol after attrition was approximately one to three microns.

Coating composition

Three parts by weight of Component A and 67 parts by weight of Component B were combined and coated on the paper at a weight of three to four pounds per ream (500 sheets 25 inches by 38 inches). The composition of the dried paper coating was:

	Percent by weight
Crystal violet lactone	3
Bisphenol A	67
Polyvinyl alcohol	30

EXAMPLE II

This example describes the preparation of a mark-forming composition and its coating on a paper support sheet for use as a thermal print sheet; that is, direct hot type on the paper coating.

Components A and B were prepared as in Example I.

Preparation of talc dispersion—Component C

A colloid mill was charged with 35 parts by weight of talc having an average particle size before milling of approximately 10 microns, 150 parts by weight of a polyvinyl alcohol solution (as described in Component A of Example I), and 65 parts by weight of water.

Coating composition

Three parts by weight of Component A, 27 parts by weight of Component B, and 40 parts by weight of Component C were combined and coated on paper at the weight of four to five pounds (dry) per ream (500 sheets 25 inches by 38 inches). The composition of the dried paper coating was:

	Percent by weight
Crystal violet lactone	3
Bisphenol A	27
Polyvinyl alcohol	30
Talc	40

The function of the talc is to prevent sticking of the coating to the printing head.

If desired, compatible defoaming or wetting agents may be added to the aqueous dispersion. When talc is employed in the coating composition, it is desirable to have a coating weight of at least four pounds per ream; also, where the system is a "transfer" type, the heavier coating weight is used to advantage.

The use of the sheet of Examples I and II

The sheet of Examples I and II may be used alone as a copy-receiving sheet by being served with a pattern of heat from front or back, as by a thermographically-heated original document, by trace of a hot stylus, by hot type, or by any other means giving a differential heat pattern by conduction.

If the heavier coating is used, the sheet may be used reversely for a transfer sheet to produce multiple copies on unsensitized surfaces of any sort, such as bond paper, newsprint, cloth, film, and the like, as long as the pattern of heat is present to control the transfer.

EXAMPLE III

The sheet of Examples I and II, having a coating of four to six pounds per ream, was prepared as specified, and the data to be recorded was printed on the uncoated side. The coated side was placed against plain paper to form a record "pair," which was then subjected to a light source of infra-red wave length, so that the radiation directly struck the printing. A copy of the recorded data appeared on the plain paper. This could be repeated until the coating was exhausted. Moreover, the coated sheet could be used as an intermediate master sheet wherein the heavier coated sheet is written on with thermographic ink directly on the coated side. A piece of plain paper is placed in contact with the coated side of the sheet to form a pair, and the pair is subjected to infra-red radiation. This puts a colored mirror-image of the recorded data on the plain paper. This plain sheet then may be used over and over again against successive sheets of plain paper, and each pair is subjected to a hot press to transfer the colored image in direct reading form.

EXAMPLE IV

To form a transfer-type thermally-responsive record material, a sheet was coated with, for example, Component A of Example I to a weight of ½ pound to 1½ pounds per ream, and a second sheet was coated with Component B of Example I to a weight of 4 to 5 pounds per ream; the sheets being placed in face-to-face relation, hereafter called Sheet I and Sheet II, respectively.

Use of Sheets I and II together

In this instance of use, Sheets I and II (Fig. 2a) are placed in face-to-face relation, and the phenolic material only may be transferred to the sheet containing the crystal violet lactone if the right amount of heat is used. For instance, the original data is pre-recorded on the uncoated side of the Sheet II to provide thermographic-responsive representation of the data. On heating of the data with infra-red radiation, while the coated sides are in contact, the copy appears on the coated surface of Sheet I. Of course, Sheet I, particularly when heavily coated, may act as a master sheet, as described above. It has been found that the mark-forming system of the invention (that is, crystal violet lactone, the described phenolic material, and polyvinyl alcohol) as compared with other systems, including merely the substitution of a film-forming polymer for polyvinyl alcohol, has considerably improved wet stability and print stability. Wet stability is the resistance to coloration during preparation and drying of the applied mark-forming components.

What is claimed is:

1. In a mark-forming unit for use as a temperature-responsive record material comprising a supporting sheet material having finely divided solid crystal violet lactone and a finely divided phenolic material solid at room temperature but capable of liquefying and/or vaporizing at normal thermographic temperatures, said lactone and phenolic material being further capable of producing a mark-forming reaction upon reactive contact, the improvement which comprises having the lactone and the phenolic material distributed in a binder matrix of polyvinyl alcohol.

2. The unit of claim 1 wherein the phenolic material is 4,4'-isopropylidenediphenol.

3. The unit of claim 1 wherein the polyvinyl alcohol matrix of lactone and the phenolic material is disposed on a single support sheet.

4. The unit of claim 3 wherein the matrix of lactone and phenolic material is a coating on the support sheet.

5. The unit of claim 4 wherein the phenolic material is 4,4'- isopropylidenediphenol.

6. The unit of claim 1 wherein the lactone is disposed on the surface of a support sheet within a matrix of polyvinyl alcohol and the phenolic material is disposed on the surface of a second sheet within a matrix of polyvinyl alcohol.

7. The unit of claim 6 wherein the phenolic material is 4,4'-isopropylidenediphenol.

8. The unit of claim 1 wherein the relative amount of polyvinyl alcohol to crystal violet lactone and phenolic material is 5% to 40%, by weight.

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3,322,557	5/1967	Schwab	117—36.2

MURRAY KATZ, Primary Examiner

U.S. Cl. X.R.

117—36.8, 36.9, 155; 250—65