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(54) **Mark-recording systems.**

(57) The invention relates to mark-recording systems, for example carbonless copying paper, in which a colourless chromogen is brought into contact with a chromogen-sensitizing agent in the presence of a liquid solvent for the chromogen, thereby producing a visible mark. In a system of the invention, the chromogen is a derivative of diphenylmethanol or diphenylmethylaniline, the sensitizing agent is an acid clay, and the solvent comprises an aliphatic benzyl phthalate.

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MARK-RECORDING SYSTEMS

This invention relates to pressure-sensitive mark-recording systems. The most familiar form of pressure-sensitive mark-recording system is the so-called carbonless copying paper which comprises a two-sheet system in which the under surface of the top sheet has a coating of microcapsules of a solution of a colourless chromogen, while the upper surface of the lower (receiver) sheet has an absorbent coating including a sensitizing agent for the chromogen. When a marking instrument is applied to the top sheet, the microcapsules are locally ruptured, thereby releasing the chromogen solution from the affected microcapsules to react with the underlying sensitizing agent and form coloured marks on the receiver sheet corresponding to the marks applied to the top sheet.

15 A successful carbonless copying paper system needs to meet a number of criteria. For example the marks on the receiver sheet should develop rapidly to a legible intensity of colour and a legible mark should persist for as long as the

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sheet is required to be kept. Whether the various criteria are met depends on a number of factors including the nature of the chromogen, the solvent and the sensitizing agent, and many different materials of each category have been proposed. Chromogens which have been proposed include phthalide derivatives, for example crystal violet lactone, and Malachite green lactone, indole-substituted pyromellitides, leucauramines, and diphenylmethane derivatives such as Michler's hydrol.

5 Solvents which have been proposed include hydrocarbons, for instance petroleum fractions or synthetic hydrocarbons such as hydrogenated terphenyls, halogenated hydrocarbons, for instance chlorinated biphenyls, and esters, for instance alkyl adipates and alkyl phthalates.

10 The sensitizing agent is usually an acid clay, for example an attapulgite or bentonite clay, or an acidic organic polymer, for example a phenol-aldehyde polymer or a partially or wholly hydrolysed styrene-maleic anhydride or ethylene-maleic anhydride polymer.

15 The chromogens which are probably most frequently referred to in the art are the phthalide derivatives, especially crystal violet lactone. These chromogens are usually used in solution in a hydrocarbon type solvent. One reason for this choice of solvent is

20 that although the phthalide colour-formers are soluble in esters, for example, it is found that esters and certain other solvents having similar polarity to the esters, show too great a tendency to compete with the chromogen in affinity for the sensitizing agent, so

25 that in some cases, no colour development occurs. This is especially so with certain acid clay sensitizing agents.

Certain chromogens that are diphenyl methane derivatives are less subject to this limitation and .

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can be used in conjunction with solvents such as esters, advantages of the latter over hydrocarbons being that the chromogens dissolve more readily and have higher solubilities. The use of diphenyl methane derivatives, 5 for instance Michler's hydrol, as chromogens in pressure sensitive mark-recording systems is described in, for example, British Patent Specification 1,381,928 and U.S. Patent Specification 4,000,087.

The present invention concerns an improvement relating 10 to the use in pressure-sensitive mark-recording systems, of chromogens that are diphenyl methane derivatives.

A pressure-sensitive mark-recording system of the invention comprises (a) sheet material, (b) mark-forming components supported by the sheet material and 15 arranged in juxtaposition but in unreactive condition, the said components comprising a chromogen which is a derivative of diphenylmethanol or of diphenylmethanamine and an acid clay sensitizer for the chromogen which produces a colour from the chromogen when brought into 20 contact with the chromogen in the presence of a liquid solvent for the chromogen comprising an aliphatic benzyl phthalate and (c) the said liquid solvent supported by the sheet material but separated from the sensitizing agent by a physical barrier which is rupturable on the 25 application of a marking instrument to the sheet material.

Compared with the solvents, for example xylene or dibutyl phthalates, hitherto proposed for use in conjunction with chromogens that are diphenylmethane derivatives, 30 use of solvents in accordance with the

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present invention results in an improvement in the resistance to fading of the marks on the receiver sheet during storage, particularly if storage occurs under conditions where fading is due to the action of oxygen.

5 In an aliphatic benzyl phthalate useful in the present invention, one of the phthalate carboxyl groups is esterified by an aliphatic group and the other by a benzyl group. The aliphatic group can, for example, contain up to 24 carbon atoms, and may have a straight or a branched chain. 10 It can, for example, be an alkyl group, for example an ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-hexyl, isohexyl, n-octyl, 2-ethylhexyl, decyl, tetradecyl or octadecyl group. Preferred alkyl groups contain from 2 to 12 carbon atoms. Alternatively, the aliphatic group 15 may be an alkoxyalkyl or a group derived from an alkyl group by the replacement of more than one $-CH_2-$ group by the same number of oxygen atoms, and it may thus be, for instance, an ethoxyethyl or a 3,6,9-trioxaundecyl group. A third possibility is that the aliphatic group is one 20 derived from an alkyl ester of a hydroxy-carboxylic acid, for example a C_{1-18} alkyl ester of glycolic acid, beta-hydroxypropionic acid or gamma-hydroxybutyric acid; or from a hydroxyalkyl ester of an aliphatic carboxylic acid, where the hydroxyalkyl radical and the aliphatic 25 carboxylic acid may each contain up to 12 carbon atoms. Examples of such aliphatic groups are butoxycarbonylmethyl, (2-ethylhexyloxy)carbonylmethyl, 2(ethylcarbonyloxy)ethyl and 7(2,6,6,8-tetramethyl-4-oxa-3-oxononyl).

As used herein, the term "benzyl" is intended to cover 30 both unsubstituted benzyl $C_6H_5CH_2-$ and substituted benzyl, especially alkyl-substituted benzyl. For example, the nucleus of the benzyl group may contain up to three alkyl substituents, each, for example, being an alkyl group having up to four carbon atoms, for instance methyl or ethyl; or 35 one or both methylene hydrogen atoms of the benzyl group may be replaced by a similar alkyl group.

Specific examples of aliphatic benzyl phthalates useful in the present invention are butyl unsubstituted-benzyl phthalates, for instance n-butyl benzyl phthalate and isobutyl benzyl phthalate, octyl unsubstituted-benzyl phthalates, for instance n-octyl benzyl 5 phthalate and 2-ethylhexyl benzyl phthalate, and 7(2,6,6,8-tetramethyl-4-^{oxa-3-}oxononyl) unsubstituted-benzyl phthalate.

The solvents used in the present invention can contain more than one aliphatic benzyl phthalate, for example mixtures of alkyl benzyl phthalates having a range of alkyl group sizes, for 10 instance a C₅-C₇, a C₇-C₉ or a C₈-C₁₂ range. The solvents may optionally contain other components, for instance dialkyl phthalates such as dibutyl phthalate and dioctyl phthalates, and various hydrocarbons, for example C₆₋₁₂ alkylbenzenes, kerosene or other petroleum fractions which are useful as 15 diluents in certain circumstances to reduce the viscosity of the solvent. Preferably the solvent contains at least 50% by weight of an aliphatic benzyl phthalate or of a mixture of aliphatic benzyl phthalates. The proportions by weight of the aliphatic benzyl phthalate and the diluent in mixtures may, for example, 20 range from 50:50 to 90:10, for example 60:40, 70:30, 75:25 or 80:20. For rapid development of print intensity, the solvent is preferably one having a viscosity in the range 5 to 15 centistokes at 38°C.

The concentration of the chromogen in a solution of the 25 invention is generally of the same order as that in known solutions of chromogens which are diphenylmethanol or diphenylmethylamine derivatives, for example from 0.25 to 5%, more particularly from 0.4 to 4.0% by weight of the solution.

Chromogens which are especially suitable for use in the 30 present invention include Michler's hydrol, i.e. bis(p-dimethylaminophenyl)methanol, its ethers, for example the methyl ether of Michler's hydrol and the benzyl ether of Michler's hydrol, aromatic sulfonic and sulfinic esters of Michler's hydrol, for example the p-toluenesulfinate of 35 Michler's hydrol, and derivatives of bis(p-dimethylaminophenyl)methylamine, for example N/Bis(p-dimethylaminophenyl)methylmorpholine.

Several encapsulation systems have been proposed for the encapsulation of the chromogen solution for use

in carbonless copying paper, and the capsule walls in such systems generally may be formed from either natural or synthetic polymeric material. In the present invention, the capsule wall or shell is preferably made from a synthetic polymer, for example a polyurethane resin, a urea-formaldehyde resin, a melamine-formaldehyde resin or a polyamide resin. The use of such resins as shell-forming material in encapsulation is described in, for example, U.S. Patent 3,016,308, British Patent 939,264 and U.S. Patent 3,429,827. Shells of this kind can be made significantly less permeable to the aliphatic benzyl phthalates used in the present invention than shells made of natural polymeric material such as gelatin.

The acid clay used as sensitizing agent for the chromogen in the present invention can be any of those conventionally used for this purpose, including bentonite and attapulgite. The naturally occurring clay may be subjected to various treatments such as acid extraction or calcination before use as the sensitizing agent.

The mark-recording system of the present invention can be prepared according to well known conventional procedures. Descriptions of methods for preparing both the dye-carrying paper and clay-coated receiving paper are to be found in the literature.

Although a preferred embodiment of this invention comprises a two-sheet system wherein the acid clay is carried by one sheet and a marking fluid comprising a chromogen and solvent is carried by a second sheet, the invention is not limited to such systems alone. The only essential requirement is that the chromogen and the acid clay be maintained in a separate or unreactive condition until pressure is applied to the system and that upon the application of pressure the chromogen and

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acid clay are brought into reactive contact. Thus it is possible to have the chromogen and acid clay present in a dry and unreactive state on a common carrier and to have the solvent alone carried on a separate sheet whereupon the application of pressure would release the solvent into the chromogen-acidic material mixture and promote localized reaction and colour development. Obviously, many other arrangements, configurations and relationships of the solvent and the mark forming materials with respect to their encapsulation and location on the supporting sheet or webs can be envisaged, and such arrangements are within the scope of the present invention. For example, it is possible to coat a single paper or support member with all the components of this system to form a single self-contained unit which can be marked by the movement of a stylus or other pressure-imparting means upon the surface of the paper. Such papers are particularly useful for use in inkless recording instruments.

Solutions of the invention were evaluated by the following technique :

A 0.5% by weight solution of Michler's hydrol p-toluene-sulfinate in the solvent was prepared. To estimate print intensity, a plate engraved with a pattern of dots was coated with sufficient of the solution to give a coating 18 microns in thickness, using a doctor blade. A carriage-supported roller having a paper sheet coated with an acid clay sensitizing agent wrapped round the roller was then moved slowly across the solution-coated plate under constant pressure. Colour developed on the paper. The paper was removed from the roller, and the intensity of colour was measured using a Macbeth RD 514 reflectometer calibrated against a "perfect white" of 0.07 units of optical density and a "perfect black" of 1.78 units

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of optical density, using standard "perfect white" and "perfect black" plates supplied by the manufacturer. After the initial reading, the paper was transferred to a cabinet at 75°C. and 40% relative humidity. It
5 was removed at intervals for further colour intensity measurements.

To obtain the results shown in the tables below, the colour intensity was measured each time at 25 different points on the paper surface and the values
10 were averaged.

The following abbreviations are used :

DBP - dibutyl phthalate
DOP - dioctyl phthalate
BBP - butyl benzyl phthalate
15 OBP - octyl benzyl phthalate
TBP - 2,6,6,8-tetramethyl-4-oxa-3-oxonon-7-yl
benzyl phthalate
ALB - (C₈-alkyl)benzene

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Table 1 shows the results obtained using one manufacturer's clay-coated receiver sheets, the solvent in each case being a blend of the phthalate with either ALB in the proportions by weight 7:3 or with kerosene in the proportions by weight 8:2.

TABLE I

Solvent	Time (Hours)					
	0	3	6	7	22.5	25.5
1 DBP/ALB 7:3	0.616		0.532		0.492	
2 OBP(Sample 1)/ ALB 7:3	0.628		0.648		0.577	
3 OBP(Sample 2)/ ALB 7:3	0.606		0.624		0.544	
4 OBP(Sample 3)/ ALB 7:3	0.600		0.635		0.566	
5 TBP/ALB 7:3	0.579		0.602		0.553	
6 OBP(Sample 1)/ Kerosene 8:2	0.621	0.585		0.577		0.571
7 DBP/Kerosene 8:2	0.601	0.568		0.519		0.472

Comparison of Solvent 1 with Solvents 2-5, or of Solvent 6 with Solvent 7 shows that the print intensity fades significantly more slowly when the phthalate is an aliphatic benzyl phthalate than when the phthalate is dibutyl phthalate.

Table 2 shows the results obtained using a second manufacturer's clay-coated receiver sheets.

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TABLE 2

Solvent	Time (Hours)							
	0	3	5.5	7	22	25.5	29.5	31.5
8 DBP	0.720		0.545		0.436		0.388	
9 BBP	0.671		0.621		0.565		0.489	
10 DBP/Kerosene 8:2	0.612	0.456		0.426		0.271		0.195
11 OBP/Kerosene 8:2	0.652	0.565		0.532		0.466		0.391

The superiority of the alkyl benzyl phthalates over dibutyl phthalate is shown by a comparison of Solvent 9 with Solvent 8 and of Solvent 11 with Solvent 10.

Table 3 shows the results obtained using the second manufacturer's clay coated receiver sheets, the solvent being in each case a blend of the phthalate with ALB in the proportions by weight 7:3.

TABLE 3

Phthalate	Time (Hours)			
	0	6.5	23	30
DBP	0.776	0.582	0.360	0.313
DOP	0.630		0.380	0.350
OBP (Sample 1)	0.689	0.628	0.417	0.401
OBP (Sample 2)	0.656	0.626	0.507	0.468
OBP (Sample 3)	0.658	0.611	0.473	0.416
TBP	0.713	0.629	0.434	0.384

Colour intensities are again shown to fade more slowly when the solvent comprises an aliphatic benzyl phthalate than when the solvent comprises a dialkyl phthalate.

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CLAIMS

1. A pressure-sensitive mark-recording system comprising (a) sheet material, (b) mark-forming components supported by the sheet material and arranged in juxtaposition but in unreactive condition, the said components comprising a chromogen which is a derivative of diphenylmethanol or of diphenylmethylaniline and an acid clay sensitizer for the chromogen which produces a colour from the chromogen when brought into contact with the chromogen in the presence of a liquid solvent for the chromogen and (c) the said liquid solvent supported by the sheet material but separated from the sensitizing agent by a physical barrier which is rupturable on the application of a marking instrument to the sheet material, characterised in that the liquid solvent comprises an aliphatic benzyl phthalate.
2. A system according to Claim 1 in which the aliphatic group of the aliphatic benzyl phthalate is an alkyl group containing up to 24 carbon atoms.
3. A system according to Claim 2 in which the aliphatic benzyl phthalate is a butyl unsubstituted-benzyl phthalate or an octyl unsubstituted-benzyl phthalate.
4. A system according to Claim 1 in which the aliphatic group of the aliphatic benzyl phthalate is derived from an alkyl ester of a hydroxy-carboxylic acid or from a hydroxy (C₁₋₁₂ alkyl) ester of an aliphatic C₁₋₁₂-carboxylic acid.
5. A solution according to Claim 4 in which the aliphatic benzyl phthalate is 7(2,6,6,8-tetramethyl-4-oxa-3-oxononyl) unsubstituted-benzyl phthalate.
6. A system according to Claim 1 in which the aliphatic group of the aliphatic benzyl phthalate is an alkyl group containing from 2 to 12 carbon atoms.
7. A system according to any of Claims 1 to 6 in which the solvent is a mixture of at least one aliphatic benzyl phthalate and a hydrocarbon diluent containing at least 50% by weight of the aliphatic benzyl phthalate or phthalates.



European Patent
Office

EUROPEAN SEARCH REPORT

0005921
Application number

EP 79 30 0801

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	CHEMICAL ABSTRACTS, vol. 81, no. 12, 23 September 1974 page 540, abstract no. 71124B COLUMBUS OHIO (US) & JA - A - 73 31 414 20-03-1974 SUDA HIDEAKI et al. "Solvents for color forming agents of pressure-sensitive copying papers" * the abstract * -- FR - A - 2 235 804 (BASF) * the claims * --	1-7 1	B 41 M 5/00 C 07 C 69/88
P	FR - A - 2 375 054 (MONSANTO) * the claims; page 10, table I * & BE - A - 862 257; DE - A - 2 757 865 GB - A - 1 542 360 --	1	TECHNICAL FIELDS SEARCHED (Int.Cl.³) B 41 M 5/00
A	US - A - 3 684 549 (J.L. SHANK) * column 5, lines 21-29 * --	1	
A	US - A - 3 016 308 (N. MACAULAY) * column 6, table I * -----	1	
			CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
 The present search report has been drawn up for all claims			&: member of the same patent family, corresponding document
Place of search		Date of completion of the search	Examiner
The Hague		23-08-1979	RASSCHAERT