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54 Self-contained pressure sensitive recording paper.

57 A self-contained pressure sensitive recording material having reduced tendency of spontaneous background staining and capable of forming an impressed image of deep color, comprising a supporting material and coated thereon a layer composed of (1) a colorless dye as color former, (2) a phenolic resin or a salicyclic acid derivative or its metal salt as color developer, (3) starch particles, (4) a pigment and (5) a binder; either said color former and/or color developer being in the form of liquid composition and encapsulated in microcapsules of a melamine-formaldehyde resin as wall material. The color developer is a phenolic resin or a salicyclic acid or a metal salt thereof and the starch particles are present in an amount of at least 1.5 times the weight of the encapsulated material(s). It is preferable for both the former and developer to be microencapsulated and for microencapsulation of the developer to be carried out by in situ encapsulation.

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SELF-CONTAINED PRESSURE

SENSITIVE RECORDING PAPER

1 This invention relates to a self-contained pressure sensitive recording paper of novel construction.

The pressure sensitive recording paper system generally comprises a combination of a top sheet coated with microcapsules enwrapping a colorless dye as color former and an undersheet coated on one side with a color developer which is an acidic substance such as, for example, activated acid clay, a phenolic resin, or a salicylic acid derivative or its metal salt. When both sheets are placed so that the coated sides may confront with each other, and localized pressure is applied by means of a typewriter or a writing instrument, the intended duplicate record is obtained on the side of sheet coated with the color developer. Such a recording paper system has been publicly known and is widely in use.

15 There is also known a self-contained pressure sensitive recording paper comprising a supporting sheet and, coated on one side, two consecutive coatings of a color former-containing microcapsule layer and a color developer layer. This recording paper can be printed with letters by means of a typewriter without using an inked ribbon, or can provide a copy by writing or printing on a superposed ordinary paper sheet. Such specific uses recently give rise to increasing demand for the paper.

25 Japanese Patent Application Laid-open No. 6,207/72

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1 has disclosed an improved coater for applying two coating
layers in manufacturing the said self-contained pressure
sensitive recording paper.

Further, a self-contained pressure sensitive
5 recording paper of the single layer type applied with
a single coating composition containing the color
former and the color developer has been disclosed in
Japanese Patent Publication No. 16,096/72. Although
this type of recording paper is improved in regard to spontane-
10 ous background staining (self-staining), the present
inventors found that said recording paper has disadvantages
of marked yellowing and insufficient density of the
developed image color, because a hydrophilic film-
forming polymeric substance impregnated with a phenol-
15 aldehyde resin is used as the capsule wall material.
Japanese Patent Application Laid-open No. 6,413/75 has
proposed the addition of amines to alleviate the self-
staining. Although effective to some degree, the addition
of an amine in an amount required for the complete
20 prevention of self-staining brings about an interference
with the color-forming reaction and also a yellowing
tendency of the sheet surface.

A method is described in Japanese Patent
Publication No. 10,780/72, in which the coating composi-
25 tion is incorporated into the paper web during web
formation. In such a record paper, unlike the coated
paper, the color forming reaction takes place within
the paper sheet, resulting in insufficient density of

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1 the image color.

Further, as disclosed in Japanese Patent
Laid-open No. 37,710/74, attempts have been made to
prepare a self-contained pressure sensitive recording
5 paper improved with regard to self-staining by improving the
encapsulation method using the reaction of polyvalent
isocyanate, polyhydroxy compound and polyamine compound.
Although self-staining is improved by the use of a wall
material and an encapsulation procedure as disclosed in
10 said patent application, it is necessary for the complete
elimination of self-staining to increase the capsule
wall thickness, leading to deterioration of the color
forming performance of the coating layer. The disclosed
method, moreover, is not suitable for encapsulating
15 oil-soluble acidic color developers such as phenolic
resins, salicylic acid derivatives or metal salts
thereof, because active hydrogen atoms of these color
developers react with isocyanate compounds used in
forming the capsule membrane.

20 This invention provides a self-contained
pressure sensitive recording paper of the single coating
layer type which has novel construction, is resistant
to spontaneous background staining and has an excellent
color forming ability.

25 The coating layer of the present recording
paper is formed by the application of a mixture of the
following five components onto a substrate sheet: (1)
a colorless dye as color former, (2) a phenolic resin,

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1 a salicylic acid derivative or its metal salt as color
developer, (3) starch particles, (4) a pigment, and
2 (5) a binder; either or each of said color former (1)
and color developer (2) being encapsulated in liquid
3 form with the wall membrane material of a melamin-
formaldehyde resin to prevent self-staining and to
4 improve color-forming quality.

In encapsulating the color former (1) or
the color developer (2), it is used generally in the
5 form of dispersion or solution in an oily substance,
except for the case of a phenolic resin (color developer)
if it is liquid at ambient temperatures. The color
former used is a known electron donating leuco dye such
as typically crystal violet lactone or a fluorane
6 derivative. The color developer used is typically
7 a substituted phenol-formaldehyde resin described in
Japanese Patent Publication No. 20,144/67 and a poly-
valent metal salt of a salicylic acid derivative described
8 in Japanese Patent Publication No. 25,174/76. Examples
9 of desirable color developers include p-phenylphenol-
formaldehyde resin, 3,5-di-tert-butylsalicylic acid or
zinc salt thereof, and 3,5-di(dimethylbenzyl)salicylic
10 acid or zinc salt thereof.

The high-boiling oily substances for use in
11 combination with a color former or color developer
include "SAS" (a diarylethane type oil produced by
Nippon Petrochemical Co.) and "KMC" (a dialkylnaphthalene
12 type oil produced by Kureha Chemical Industry Co.),

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1 both of which have been used in customary carbonless
copy paper sheets. If necessary, these oils can be
admixed with known oils of the ester type or aliphatic
type.

5 The properties of capsule membrane are
important particularly when a self-contained pressure
sensitive recording paper is to be prepared with a
single coating composition. It is necessary to
encapsulate at least one of the color former and color
10 developer with a wall material comprising substantially
a melamine-formaldehyde resin. A satisfactory self-
contained pressure sensitive recording paper is not
obtained if encapsulation is performed by conventionally
used or proposed coacervation of gelatin or interfacial
15 polymerization of a polyamide, presumably because of
unsatisfactory properties of the capsule wall. Although
the reason why the melamine-formaldehyde resin alone
yields a satisfactory capsule membrane is yet to be
elucidated, it seems that owing to dense and water-
20 resistant capsule walls formed from said resin, the
capsules are able to retain the content firmly
throughout the coating operation. The encapsulation in
this case is best performed by the in situ process
disclosed, for example, in Japanese Patent Application
25 Laid-open No. 49,984/79. Above all, capsules excellent
in uniformity of the particle size and heat resistance
of the capsule wall are obtained, when a styrene-
maleic anhydride is used as the emulsifier.

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1 One of the features of this invention is the
amount of starch particles in the coating layer.

 According to this invention, the amount of
starch should be 1.5 times or more the weight of capsules
5 in terms of solids. Although the use of granular starch
in carbonless copy sheets has been known (Japanese Patent
Publication Nos. 1,178/72 and 33,204/73), it is used,
according to the description, in an amount of at most
50% of the weight of capsules in the capsule-containing
10 coatings of a top sheet and an intermediate sheet. In
the case of a self-contained copy sheet of this invention,
if starch is used in such an amount, the resulting copy
sheet is still susceptible to self-staining or causes
smudging on other paper sheets. A suitable size of
15 starch particles is in the range from about 10 to
about 30 μ .

 As for the pigments, use is made of those
well known to the art such as clays, kaolin, calcined
clays, calcium carbonate, titanium oxide, zinc oxide,
20 and plastic pigments. The pigment is used to improve
the brightness of paper, printability and color forming
performance. The amount to be used is preferably in
the range of from about 10 to about 100 parts for 100
parts of capsules, depending on the type of pigment
25 used.

 The binders used in this invention are the
same as those generally used in usual copying paper,
such as hydroxyethylcellulose, modified starches,

carboxymethylcellulose, acrylic latices, SBR latices, and polyvinyl alcohol.

As described before, most of the conventional self-contained pressure sensitive recording paper systems have been of the superposed coating layer type prepared by applying onto one side of a supporting sheet (paper, film or the like) two consecutive layers; a coating of color former-containing microcapsules and a coating of color developer. Quite recently, with technical progress in microencapsulation, it has become possible to obtain microcapsules less susceptible to leakage of the contained substance. Therefore, attempts have been made to prepare a self-contained pressure sensitive copying paper with single layer of a coating composition containing a mixture of color former and color developer, either or each of which is entrapped within microcapsules. According to the experimental results of the present inventors, a self-contained pressure sensitive recording paper which is practically white in background color, and which therefore is the most preferred embodiment of the invention, was obtained when the color former and the color developer were each microencapsulated and, in addition, microencapsulation of the color developer with wall material of melamine-formaldehyde resin was carried out by the above-mentioned in situ process.

The present inventors found that the microcapsules with the wall phase of a melamine-formaldehyde resin are most suitable not only for entrapping the color developer for use in the above-said self-contained pressure sensitive recording paper of the single coating

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1 type having each of the color-forming reactants
encapsulated, but also for entrapping either of the
color former or the color developer, preferably the
latter, in preparing a self-contained pressure sensitive
5 recording paper of the single coating type having either
one of the reactants encapsulated. These findings
have led to the accomplishment of the present invention.

It may be easily understood that a self-
contained pressure sensitive recording paper of the
10 single coating type having one of the reactants
encapsulated is most preferable in view of not only
production cost but also product quality, particularly
the initial speed of image color formation. However,
commercialization of such a type of recording paper
15 has been hindered by lack of proper microencapsulation
techniques. For instance, if microcapsules having the
wall phase of gelatin as major component produced by
complex coacervation are used, coloration of the recording
paper will occur all over the coated side. When
20 microcapsules having the wall phase of urea-formaldehyde
resin, as described in Japanese Patent Application
Laid-open No. 9,079/76, is used, colored specks will
appear on the paper surface which is white in ground
color, and so makes the recording paper commercially
25 of no value. The microencapsulation using a prepolymer
of polyisocyanate compounds is unsuitable for the core
substances having such functional groups as -OH, >NH
and -COOH, because the wall material will react with

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1 the active hydrogen atoms in these functional groups.
Fortunately, the present inventors have found that when
a melamine-formaldehyde resin is used as capsule wall
material, it is possible to prepare a self-contained
5 pressure sensitive recording paper of the single coating
layer type, in which one of the reactants is satisfactorily
encapsulated without causing aforementioned difficulties.
This novel and important finding will be described
more particularly in the Examples presented hereunder.

10 In preparing the present recording paper,
it is possible to use, as usual, other known additives
such as, for example, ultraviolet absorbers, antioxidants,
dispersants, water-proofing agents, lubricants, defoamers,
etc. The coating composition is applied by known methods
15 such as air-knife coating, roll coating, blade coating,
etc.

The invention is illustrated below with
reference to Examples, in which "parts" are by weight.

Example 1

20 Encapsulation of color developer.

In 60 parts of "Hisol SAS" N-296 (an oil
produced by Nippon Petrochemical Co.), was dissolved
with heating 40 parts of p-phenylphenol (PR 26142
produced by Sumitomo Durez Co.; m.p. 85°C) to prepare
25 100 parts of an internal phase oil. This internal
phase oil was emulsified in 200 parts of a 5-% aqueous
styrene-maleic anhydride copolymer solution adjusted to

- 1 pH 5.3. A melamine-formaldehyde early-stage condensate was prepared by heating at 80°C a mixture of 20 parts of melamine and 45 parts of 37-% formalin, said mixture having been adjusted to pH 8.5 with sodium hydroxide.
- 5 The early-stage condensate was added to the above emulsion and the resulting mixture was allowed to react by heating at 70°C for one hour to obtain microencapsulated color developer having an average particle size of 5.2 μ .

10 Example 2

Encapsulation of color developer.

- Microencapsulation of a color developer was carried out in a manner similar to that in Example 1 using an internal phase oil comprising 20 parts of zinc
- 15 3,5-di-tert-butylsalicylate, 40 parts of KMC-113 (an oil produced by Kureha Chemical Industry Co.) and 40 parts of a high-boiling aliphatic hydrocarbon oil (No. 3 ink solvent). The resulting microcapsules had an average particle size of 3.5 μ .

20 Example 3

Encapsulation of a color former.

- Microencapsulation of a color former was carried out in a manner similar to that in Example 1 using an internal phase oil comprising 5 parts of crystal
- 25 violet lactone (CVL) and 95 parts of KMC-113 to obtain microencapsulated color former having an average particle

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1 size of 4 μ .

Example 4

A uniform fluid composition was prepared by thorough mixing of the following components:

	Parts, solids	(Parts, water, inclusive)
Encapsulated color developer of Example 1	100	
20% CVL (color former) dispersion	4	(20)
Wheat starch particles	200	
Calcium carbonate	30	
10% Aqueous PVA solution	20	(200)

5 The above composition was applied by means of a metering bar onto a paper sheet to prepare a self-contained pressure sensitive sheet of single coating layer type having one of the color-forming reactants microencapsulated. The application rate was 6 g/m².

10 The above 20-% CVL dispersion was an aqueous dispersion of finely ground CVL crystals, said CVL being in solid state and not encapsulated. There was obtained a self-contained recording sheet of excellent brightness and exhibiting no self-staining tendency. Upon impression
15 by means of a typewriter, a colored sharp image was obtained.

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1 Example 5

A coating composition of the following formulation was prepared.

	Parts, solids	(Parts, water, inclusive)
Encapsulated color developer of Example 1	50	
Encapsulated color former of Example 3	50	
Wheat starch particles	250	
Kaolin clay	30	
25% Aqueous solution of oxidized starch	50	(200)

The above coating composition was applied by means of an air-knife coater onto a sheet of fine paper at an application rate of 7.5 g/m^2 in terms of solids to prepare a self-contained recording sheet of the single coating layer type having color-forming reactants each encapsulated. This white self-contained pressure sensitive recording sheet showed no self-staining tendency. Upon impression by means of a typewriter, there was instantly formed a sharp image, bright deep blue in color.

The experimental results described in the above Examples demonstrate the novel fact that by the encapsulation with a melamine-formaldehyde resin as wall material, it is possible to prepare a self-contained pressure sensitive recording paper of the single coating

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layer type having either or each of the color-forming reactants encapsulated.

Claims:

1. A self-contained pressure sensitive recording paper of the single coating layer type comprising a supporting paper sheet and coated thereon a single layer of a mixture including a color former, a color developer, and starch particles, characterized in that (1) the color developer is a phenolic resin or a salicylic acid or its metal salt, and (2) at least one of said color former and said color developer is a liquid encapsulated by a wall membrane of a melamine-formaldehyde resin, and (3) the amount of starch particles used is 1.5 times or more the weight of the encapsulated material(s).
2. A self-contained pressure sensitive recording paper according to Claim 1, wherein color developer is a liquid and is encapsulated by the wall membrane of the melamine-formaldehyde resin as wall material.
3. A self-contained pressure sensitive recording paper according to Claim 1, wherein each of the color former and the color developer is encapsulated by the melamine-formaldehyde resin.
4. A self-contained pressure sensitive recording paper according to claim 2 or claim 3 wherein, at least the developer is encapsulated by an in situ microencapsulation process.
5. A self-contained pressure sensitive recording paper according to claim 4 wherein, a styren maleic anhydride is used as emulsifier.

6. A self-contained pressure sensitive recording paper according to any one of the preceding claims wherein, the starch particles are present in an amount of 150% by weight or more of the microcapsules as solids.



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	
	<p><u>DE - A - 2 820 462 (MITSUBISHI)</u></p> <p>* Claims; page 6, lines 13-22; page 8, line 26 - page 9, line 10; page 8, lines 7-13; example *</p> <p style="text-align: center;">--</p> <p>RESEARCH DISCLOSURE, february 1978 Industrial Opportunities Ltd, no.16645, pages 37-38 Hamont, Hampshire GB</p> <p>* Page 38, left-hand column, lines 32-37 *</p> <p style="text-align: center;">--</p> <p><u>GB - A - 1 507 739 (WIGGINS TEAPE)</u></p> <p>* Claims *</p> <p style="text-align: center;">--</p> <p>PE <u>GB - A - 2 021 512 (3M)</u></p> <p>* Claims *</p> <p>& FR - A - 2 425 889 & DE - A - 2 919 838</p> <p style="text-align: center;">--</p> <p>PE <u>GB - A - 2 015 611 (MITSUBISHI)</u></p> <p>* Claims *</p> <p style="text-align: center;">-----</p>	<p>1-6</p> <p>1-3</p> <p>1-3</p> <p>1-3</p>	<p>B 41 M 5/12 B 01 J 13/02</p> <p>TECHNICAL FIELDS SEARCHED (Int.Cl. 3)</p> <p>B 41 M 5/00 5/12 B 01 J 13/02</p> <p>CATEGORY OF CITED DOCUMENTS</p> <p>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</p> <p>&: member of the same patent family, corresponding document</p>
<p><input checked="" type="checkbox"/> The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
The Hague	17-07-1980	AMAND	