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(54) **PRESSURE-SENSITIVE COPYING PAPER.**

(57) Pressure-sensitive copying paper comprising a support having coated thereon a layer containing microcapsules retaining a color former, or a colorless dye, capable of reacting with a color developer to form color, said layer further containing both fine cellulose powder and fatty acid amide. The cellulose powder and the amide are remarkably effective in preventing smudge of the copying paper.

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DESCRIPTION

PRESSURE-SENSITIVE COPYING PAPER

FIELD OF THE INVENTION

This invention relates to a pressure-sensitive copying paper, particularly, a pressure-sensitive copying paper free from smudge.

DESCRIPTION OF THE PRIOR ART

Pressure-sensitive copying papers consist basically of (a) an upper sheet obtained by coating one side of a substrate such as a paper with microcapsules containing an oil type solution containing an electron-donating, colorless dye as a color former and drying the coated substrate, (b) a lower sheet obtained by coating one side of a substrate with a coating fluid containing an electron-accepting, solid acid (a color developer) and an adhesive and drying the coated substrate, and optionally (c) an intermediate sheet obtained by coating one side of a substrate with said microcapsules and the other side of the substrate with said electron-accepting, solid acid and said adhesive and drying the coated substrate (such pressure sensitive copying papers being referred to as separating type pressure sensitive paper). There are also self-contained type pressure-sensitive copying papers wherein a substrate is coated at same one side with color former-containing

microcapsules and a color developer.

In pressure-sensitive copying papers consisting of an upper sheet, a lower sheet and optionally an intermediate sheet, the side of each sheet coated with color former-containing microcapsules and the side coated with a color developer contact with each other frequently during a step of sheet production, a printing step, a step of production of ledger, chit, etc. and so forth.

They contact with each other, for example, at the time of winding the intermediate sheet, during cutting or during collating. During their contact, color former-containing microcapsules receive a certain pressure or frictional force, whereby it may happen that the microcapsules are destroyed and abnormal color development or staining (this phenomenon is called smudging) appears on the surface of an electron-accepting, solid acid. To prevent the smudging, a substance having a particle diameter larger than that of the microcapsules is used together with the microcapsules as a capsule-protecting agent (hereinunder referred to as a "stilt"). As the stilt, there are generally used cellulose fine powders, starch grains, beads of various plastics, etc.

As described in Japanese Patent Publication No. 1178/1972, Japanese Patent Publication No. 33204/1973, etc., starch grains show a fairly good effect in smudge prevention. However, because starches have a specific gravity of 1.6 which is considerably larger than that

(about 1) of microcapsules and moreover there are used starches having particle diameters ordinarily of 20 to 30 μ, when a coating fluid containing one of these starches together with microcapsules is allowed to stand, starch grains cause precipitation, whereby the coating fluid causes compositional change during a continuous, long term coating operation and there occurs quality deterioration of sheets due to color development, smudging, etc. of microcapsules-coated sheet surfaces. Further, the particle diameters and hardnesses of starch grains reduce the color developability between a color former and a color developer at a low writing pressure, whereby color development becomes insufficient in copying of a large number of sheets.

On the other hand, cellulose fine powders are obtained by grinding a wood pulp mechanically or chemically, and their particle sizes are broad with a medium size being about 30 μ in width and about 100 μ in length and their specific gravities are about 1. When one of these powders is used in a coating fluid as a stilt, because its specific gravity is about same as the specific gravity of microcapsules, there is no anxiety for the cellose fine powders to precipitate. Therefore, there is no compositional change of the coating fluid even in long term coating and accordingly there occurs no quality deterioration of coated sheets and the color developability at a low writing pressure is good. However, there are some cases that prevention of staining

due to rubbing is insufficient probably due to the inherent shape of cellulose fine powder and an improvement for this drawback has been desired. In self-contained type pressure-sensitive copying papers, smudging is more striking than in separating type pressure-sensitive copying papers consisting of an upper sheet, a lower sheet and optionally an intermediate sheet, because both a color former and a color developer are coated on same one side of a substrate.

DISCLOSURE OF THE INVENTION

The present inventors made an extensive study on further improvement of the smudge preventability of a coating containing microcapsules and cellulose fine powder fluid free from precipitation and excellent in color developability at a low writing pressure. As a result, it was found that combined use of (a) a cellulose fine powder as a stilt and (b) a fatty acid amide as a lubricant in a coating fluid shows an outstanding smudge prevention effect without sacrifying the merits of an original coating fluid. Based on this finding, the present invention has been attained.

It was found that, when a fatty acid amide as a lubricant is added in a coating fluid containing microcapsules, the fatty acid amide gives little effect for improvement of smudge prevention. In addition, the fatty acid amide is used in a coating fluid containing microcapsules and starch grains or plastic beads as a

stilt, the fatty acid amide gives little effect for improvement of smudge prevention but, when the fatty acid amide is used in a coating fluid containing microcapsules and a cellulose fine powder as a stilt, the fatty acid amide does show an outstanding effect.

The reason is not well known. However, it is inferred that, when the fatty acid amide as a lubricant is used in a coating fluid containing microcapsules and a cellulose fine powder as a stilt, the fatty acid amide is located close to the surface of a coated layer due to the affinity of the amide with the coated layer when the coating fluid is coated at a high speed by a coater or the like and dried rapidly or due to the migration of the amide and thereby the fatty acid amide can function well as a lubricant.

BEST MODE FOR CARRYING OUT THE INVENTION

As the fatty acid amide used as a lubricant in the present invention, there can be mentioned fatty acid amides such as stearamide, ethylenebisstearamide and the like. In combination with these fatty acid amides there may be used other lubricants such as aliphatic hydrocarbons (a paraffin, a polyethylene and the like), higher fatty acids derived from tallow, coconut oil and the like, higher aliphatic alcohols, metal soaps (calcium stearate, zinc stearate and the like), and higher fatty acid esters.

With respect to the amounts of the cellulose

fine powder (stilt) and the fatty acid amide (lubricant) used in the present invention, 5 to 70 parts by weight (hereinunder referred to simply as parts) of the cellulose fine powder is preferable relative to 100 parts of microcapsules. When the fatty acid amide is used in an amount of 0.9 part or less, the effect is low. When it is used in an amount of 16 parts or more, color developability is badly affected. Therefore, 1 to 15 parts of the fatty acid amide is preferable. 15 to 60 parts of the cellulose fine powder and 2 to 10 parts of the fatty acid amide are more preferable.

In the present invention, the microcapsules can be produced, for example, by the following methods.

1. A method by phase separation from an aqueous solution (US Patent No. 2800457, the Patent No. 2800458, etc.)
2. An interfacial polymerization method (Japanese Patent Publication No. 19574/1963, Japanese Patent Publication No. 446/1967, Japanese Patent Publication No. 771/1967, etc.)
3. A method by monomer polymerization (Japanese Patent Publication No. 9168/1961, Japanese Laid-open Application No. 9079/1976, etc.)
4. A melting-dispersion-cooling method (UK Patent No. 952807, UK Patent No. 965074, etc.)
5. A spray-drying method (US Patent No. 3111407, UK Patent No. 930422, etc.)

Of course, microcapsules production is not restricted to these methods.

As the colorless dye which is a color former, there can be used known leuco dyes for pressure-sensitive recording, such as, for example, a triphenylmethane compound, a diphenylmethane compound, a xanthene compound, a thiazine compound and a spiropyran compound.

These color formers are dissolved or dispersed in an appropriate oily solvent, emulsified into minute droplets in water or in a hydrophilic solvent and then microencapsulated by one of the above mentioned encapsulation methods. As the oily solvent, there are used non-volatile solvents such as alkylnaphthalenes, diarylethanes, alkylbiphenyls, hydrogenated terphenyls and esters.

As the electron-accepting substance which is a color developer and forms a color by contacting with the above mentioned color former, there are known inorganic color developers (e.g. acid clay, active clay, attapulgite, zeolite), phenols, phenol-aldehyde polymers, phenol-acetylene polymers, maleic acid-modified rosin, aromatic carboxylic acids (e.g. salicylic acid or its derivatives) and their metal salts, etc.

A coating fluid is coated on a substrate at a high speed by the use of a coater having a coater head such as an air knife, a blade roll, a bar or the like.

The present invention will be described more specifically by means of Examples. As is easily appreciated by those skilled in the art, the pressure-sensitive copying paper of the present invention is not

restricted to a separating type mentioned in Examples but does also include a self-contained type.

EXAMPLE 1

100 Parts of an aqueous solution containing 10% of an ethylene-maleic anhydride copolymer, 10 parts of urea, 1 part of resorcin and 200 parts of water were mixed and made into a solution. The solution was adjusted to a pH of 3.5 by the use of a 20% aqueous sodium hydroxide solution. A dye solution obtained by dissolving 10 parts of Crystal Violet Lactone in 90 parts of diisopropylnaphthalene was dispersed in the above aqueous solution to prepare an oil-in-water type emulsion having oil droplets of 3 to 5 μ in diameter. Thereto was added 25 parts of a 37% aqueous formaldehyde solution. The system was kept at 55°C with stirring. In two hours, wall membranes of an urea-formaldehyde polymer were formed around the oil droplets. The system was adjusted to a pH of 9.5 by dropwise addition of a 20% sodium hydroxide solution, whereby encapsulation was completed and a dispersion of color former-containing microcapsules was obtained.

A coating fluid having a total solid content of 20% was prepared by mixing the following materials.

Solid of the above microcapsule dispersion	100 parts
KC Flock W-200 (a cellulose fine powder, manufactured by Sanyo-Kokusaku Pulp K.K.)	25 parts

Ethylenebisstearamide	5 parts
15% aqueous polyvinyl alcohol solution	100 parts

This fluid was coated on a plain paper of 40 g/m^2 by the use of an air knife coater at a speed of 100 m/min so that the coated amount became 5 g/m^2, and the coated paper was dried to obtain a color former sheet. As the color developer sheet, there was used a pressure-sensitive copying paper (Mitsubishi NCR paper CF) wherein a substrate was coated at one side with a solid acid as an electron-accepting substance (oil-soluble phenol resin of novolac type). These sheets were superimposed so that their coated sides faced with each other. Then, color development characteristic and smude-preventing characteristic were examined. The results are shown in Table 1.

EXAMPLE 2

2 Parts of Crystal Violet Lactone was dissolved in 100 parts of Hisol SAS-295 (diarylethane type solvent, manufactured by Nippon Petrochemicals Co., Ltd.). This solution was subjected to dispersion and emulsification. Encapsulation was conducted by a coacervation method using gelatin-gum arabic. The microcapsule dispersion had a microcapsule content of 20% and the microcapsules had an average particle diameter of 10 μ.

A coating fluid having a total solid content of

20% was prepared by mixing the following materials.

The above microcapsule dispersion	100 parts
KC-Flock W-200 (a cellulose fine powder, manufactured by Sanyo-Kokusaku Pulp K.K.)	25 parts
Ethylenebisstearamide	5 parts
15% Aqueous oxidized starch solution	60 parts

The results are shown in Table 1.

COMPARATIVE EXAMPLE 1

The same procedure as in Example 1 was conducted except that ethylenebisstearamide used in Example 1 was not added. The results are shown in Table 1.

COMPARATIVE EXAMPLE 2

The same procedure as in Example 1 was conducted except that KC Flock used in Example 1 was replaced by wheat starch. The results are shown in Table 1.

COMPARATIVE EXAMPLE 3

The same procedure as in Comparative Example 2 was conducted except that ethylenebisstearamide used in Comparative Example 2 was not added. The results are shown in Table 1.

Table 1

	Color development T.I. (%)	Smudging F.S. (%)	Prevention of precipitation in coating fluid	Stilt / lubricant
Example 1	57.0 ○	89.5 ○	○	C/used
Example 2	55.5 ○	87.0 ○	○	C/used
Comparative Example 1	54.5 ○	76.0 X	○	C/not used
Comparative Example 2	62.0 Δ	85.0 ○	X	S/used
Comparative Example 3	62.0 Δ	84.5 ○	X	S/used

Explanation:

○ Good viewed from practical application

Δ Insufficient viewed from practical application

X Unusable

C Cellulose fine powder

S Wheat starch

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In Table 1, color development (T.I.) is given as a concentration of a color developed by a typewriter and smudging (F.S.) is an index indicating the staining of a coating layer due to friction. They are given by the following formula.

$$\text{T.I. or F.S.} = \frac{\text{Reflectance of typed or stained part}}{\text{Reflectance of background part}} \times 100$$

A larger number indicates lower color development or less staining. ○, Δ and X are results by visual evaluation.

As is obvious from Table 1, combination of a cellulose fine powder as a stilt and a fatty acid amide as a lubricant is good in both color development characteristic and smudge-preventing characteristic and is free from precipitation in coating fluid.

WHAT IS CLAIMED IS:

1. A pressure-sensitive copying paper comprising a substrate having on one side a coating layer containing microcapsules containing a colorless dye as a color former which develops a color upon reaction with a color developer, characterized in that the coating layer further contains a cellulose fine powder and a fatty acid amide.

2. A pressure-sensitive copying paper according to Claim 1, wherein the fatty acid amide is ethylene-bisstearamide.

3. A pressure-sensitive copying paper according to Claim 1, wherein the amount of the cellulose fine powder is 5 to 70 parts by weight (hereinunder referred to simply as parts) relative to 100 parts of the microcapsules.

4. A pressure-sensitive copying paper according to Claim 3, wherein the amount of the cellulose fine powder is 15 to 60 parts.

5. A pressure-sensitive copying paper according to Claim 1, wherein the amount of the fatty acid amide is 1 to 15 parts relative to 100 parts of the microcapsules.

6. A pressure-sensitive copying paper according to Claim 5, wherein the amount of the fatty acid amide is 2 to 10 parts.

7. A pressure-sensitive copying paper according to Claim 1, which is a separating type pressure-sensitive copying paper comprising an upper sheet and a lower sheet.

8. A pressure-sensitive copying paper according

to Claim 7, which has at least one intermediate sheets between the upper sheet and the lower sheet.

9. A pressure-sensitive copying paper according to Claim 1 which is a self-contained type pressure-sensitive copying paper in which (a) microcapsules containing a colorless dye as a color former and (b) a color developer are coated on the same side of a substrate.

INTERNATIONAL SEARCH REPORT

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International Application No. PCT/JP84/00160

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int. Cl[3] B41M5/12

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
IPC	B41M5/12-5/22

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

Jitsuyo Shinan Koho 1960 - 1983
Kokai Jitsuyo Shinan Koho 1971 - 1983

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category*	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
Y	JP, A, 56-60289 (Mitsubishi Paper Mills, Ltd.), 25 May, 1981 (25. 05. 81)	1 - 9
Y	JP, A, 56-121790 (Mitsubishi Paper Mills, Ltd.), 24 September, 1981 (24. 09. 81)	1 - 9

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
June 25, 1984 (25.06.84)	July 2, 1984 (02.07.84)
International Searching Authority [1]	**Signature of Authorized Officer [20]**
Japanese Patent Office	