(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 006 599**
B1

(12) # EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **03.10.84**

(51) Int. Cl.³: **B 41 M 5/16**

(21) Application number: **79102082.9**

(22) Date of filing: **25.06.79**

(54) **A self-contained color forming pressure sensitive record paper of the single coating type.**

(30) Priority: **26.06.78 JP 77264/78**

(43) Date of publication of application:
09.01.80 Bulletin 80/01

(45) Publication of the grant of the patent:
03.10.84 Bulletin 84/40

(84) Designated Contracting States:
BE DE FR GB

(56) References cited:
DE-A-1 805 292
FR-A-2 004 897
FR-A-2 137 758
FR-A-2 151 990
FR-A-2 235 804
GB-A-2 006 851

The file contains technical information submitted after the application was filed and not included in this specification

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Description

This invention relates to an improvement in a self-contained color forming pressure sensitive record paper comprising a base sheet coated with a single record layer of a mixture of color former-containing microcapsules and color developer-containing microcapsules.

From DE—A—1 805 292 a pressure sensitive record paper is known which has been prepared by coating a base paper sheet with a uniform coating mixture of an aqueous suspension of microcapsules and wherein a powdered polyolefin is added in an amount of 1/4 to 1/3 with reference to the weight of the solid content of the microcapsules to obtain a pressure sensitive paper of higher quality and to avoid premature breakage of the microcapsules.

The quality of a self-contained color forming pressure sensitive record paper of the single coating type can be defined by the intensity of image color developed by the impression with typewriter (TI) and by the smudge caused by friction (FS). TI and FS are calculated from the following formula:

$$\frac{\text{Reflectance of typed area or of smudged area}}{\text{Reflectance of untouched area}} \times 100\ (\%)$$

A larger value of TI or FS indicates a lower intensity of image color or a lighter smudge. The color development by creasing is evaluated from the reflection density measured by means of a microdensitometer on the area where smudge has been developed by creasing. A smaller value indicates a lighter smudge.

In the self-contained color forming pressure sensitive record paper of the single coating type according to DE—A—1 805 292, by the addition of polyethylene in an amount of 1/4 to 1/3 with respect the solid content of the microcapsules, the addition of 30 to 35 parts per weight per 100 part per weight of total capsule resulted in an increase of the TI values from 38 to 40 and in the FS values from 64 to 66 and thus in an image contrast (FS − TI) of 26. Even an increase to 50 or 80 weight parts of polyethylene per 100 weight parts of total capsule would result only in an improved image contrast (FS − TI) of 30 and 39 respectively.

It was surprisingly found that by further increasing the amount of powder polyolefin added to 100 to 200 parts by weight per 100 parts by weight of total capsule a record paper is obtained having superior properties compared with the prior art. For results of tests carried out, please see the table submitted with the Applicants letter of 23.12.82 reflecting these superior properties.

The invention relates to a self-contained color forming pressure-sensitive record paper of the single coating type prepared by coating a base paper sheet with a uniform coating mixture of an aqueous suspension of microcapsules containing a color former and an aqueous suspension of microcapsules containing a color developer and then drying, characterized in that to said coating mixture a powdered polyolefin is added in an amount of 100 to 200 parts by weight per 100 parts by weight of total capsule.

It is generally required that a pressure sensitive copying paper has a TI value of below 60% and an FS value of 90% or more. The claimed range i.e. from 100 to 200 parts by weight of polyethylene enables one to give a pressure sensitive copying paper having the required TI value and FS value. In contrast, a smaller polyethylene amount cannot give the required FS value and a larger polyethylene amount cannot give the required TI value.

Although the Ti level within the range of 100 to 200 parts by weight of powdered polyolefin per 100 parts by weight of total capsules is higher than the TI values obtained with the lower polyethylene amounts, in accordance with the teaching of DE—A—1 805 292, the polyethylene amounts used in the present invention result in higher FS values as well as much lower color development due to creasing without the TI values being increased. Thus the claimed self-contained color forming pressure sensitive record paper of the single coating type has properties which, in combination, are not only novel but also superior to the properties of the known record sheets.

Another important feature of the present record paper is a marked reduction in the smudging due to unintentional folding of the record paper. A conventional self-contained color developing pressure sensitive paper, whether a multi-coating type or a single-coating type, is subject to smudging due to color development along the crease line, whereas the single-coating type record paper according to this invention is more resistant to such smudging and is of better practical use, compared with starch-containing ones. The reason for this cannot be explained, but the fact remains evident.

It is probable in the single coating-type self-contained record paper that since both of the color former (pressure sensitive dye) and the color developer (acidic substance) are enclosed in capsules, the total amount of capsules per unit area is approximately twice that of the multi-coating type; accordingly, not only the particle size but also the physical properties of the capsule-protective agent have a large effect on the resistance of capsules to rupture.

To meet the requirements for quality design, the powdered polyolefin can be used jointly with starch particles without much losing the advantage of the former.

Although not limitative, the processes for producing microcapsules suitable for use in the method of this invention include:

(1) phase separation from aqueous solutions (for example, U.S. Patents 2,800,457 and

2,800,458),

(2) interfacial polymerization (for example, Japanese Patent Publications, 19,574/63, 446/67 and 771/67),

(3) polymerization of monomers (for example, Japanese Patent Publication 9,168/61; Japanese Patent Application Laid-open 9,079/76),

(4) cooling of melt dispersion (for example, British Patents 952,807 and 965,074), and

(5 spray drying (for example, U.S. Patent 3,111,407 and British Patent 930,422).

Suitable color formers are known leuco dyes for pressure sensitive recording such as, for example, triphenylmethane compounds, diphenylmethane compounds, xanthene compounds, thiazine compounds and spiropyrane compounds. These color formers are dissolved or dispersed in a suitable oily solvent, or emulsified to minute droplets in water or a lyophilic solvent and are then microencapsulated by a suitable method. Suitable oily solvents are selected from nonvolatile solvents such as alkylnaphalenes, diarylethanes, alkylbiphenyls, hydrogenated terphenyls, and esters.

Most suitable microcapsules containing color developers are those having capsule walls substantially made of a urea-formaldehyde resin, the internal phase being acidic organic substances dissolved in or swollen with an oily solvent. The methods of microencapsulation using a urea-formaldehyde resin as wall material have been described in Japanese Patent Application Laid-open 9,079/76; Japanese Patent Publications 30,282/71 and 23,165/72. Suitable oily solvents for dissolving or swelling the color developers are selected from toluene, xylene, alkylnaphthalenes, diarylethanes, alkylbiphenyls, and esters. Desirable color developers among acidic organic compounds are various oil-soluble phenolic resins and oil-soluble aromatic carboxylic acid compounds.

Suitable polyolefins include homopolymers of olefins such as, for example, ethylene, propylene and styrene, copolymers of two or more olefins, and blends of these polymers. An aqueous suspension of powdered polyolefins can be prepared by modifying a polyolefin resin with an unsaturated carboxylic acid such as, for example, maleic anhydride, melting the modified resin together with, if necesary, a surface active agent, and dispersing in hot water (Japanese Patent Application Laid-open 36,540/75) or by heating a mixture of a polyolefin, organic solvent, nonionic surface active agent and water at a temperature above the melting point of said polyolefin, then cooling the heated mixture to a temperature below the melting point of said polyolefin to obtain an emulsion which is then freed from the organic solvent (Japanese Patent Application Laid-open 138,735/76). However, the powdered polyolefins suitable for use are not necessarily prepared by the above methods.

According to the methods described above, it is easy to obtain powdered polyolefins having a particle diameter of 5 to 30 μm and in spherical form, which are suitable as a microcapsule-protective agent according to this invention. A desirable result is obtained by adding to the coating composition a powdered polyolefin in the form of an aqueous dispersion as such. The particle diameter of the powdered polyolefin is preferably 10 to 30 μm. The softening point should be higher than the maximum temperature of the paper material during application of the pressure sensitive record coating and is preferably 70°C or higher.

In actual practice, a single coating-type self-contained color-developing pressure sensitive record paper is prepared by mixing together an aqueous dispersion of a powdered polyolefin, microcapsules containing a color former, microcapsules containing a color developer, and, if necessary, a water-soluble amino resin such as a cation-modified urea resin or a cation-modified polyamide-epichlorohydrin resin; adding to the resulting mixture a binder such as polyvinyl alcohol, latex, hydroxyethylcellulose or oxidized starch, a clay such as kaolin clay, monomorillonite clay or talc, and other customary additives to obtain a coating composition; they applying to the base paper said coating composition by means of an air knife coater, blade coater, roll coater, bar coater or other coating machines.

As described in the foregoing, this invention is very useful for the manufacture of single coating-type self-contained color developing pressure sensitive record papers.

The invention is illustrated below in detail with reference to Examples, but the invention is not limited to Examples. In Examples all parts are by weight.

Example 1

Preparation of color former-containing microcapsules:

A solution was prepared by intermixing 100 parts of a 10% aqueous solution of ethylene-maleic anhydride copolymer, 10 parts of urea, 1 part of resorcinol and 200 parts of water. The resulting solution was adjusted to pH 3.5 with a 20% aqueous sodium hydroxide solution. A color former solution was prepared by dissolving 10 parts of crystal violet lactone in 90 parts of diisopropylnaphthalene. This solution was dispersed in the aqueous solution prepared above to obtain an emulsion of the oil-in-water type containing dispersed oil droplets, 3 to 5 μm in diameter. After addition of 25 parts of 37% formalin, the emulsion was kept at 55°C. After 2 hours, a wall membrane of the urea-formaldehyde condensate was formed around each droplet. The emulsion was then adjusted to pH 9.5 by the dropwise addition of a 20% aqueous sodium hydroxide solution to terminate the encapsulation and a dispersion of color former containing microcapsules was obtained.

Preparation of color developer-containing microcapsules:

A solution was prepared by mixing together 200 parts of a 10% aqueous solution of ethylene-maleic anhydride copolymer, 20 parts of urea, 2 parts of resorcinol and 400 parts of water. The resulting solution was adjusted to pH 3.5 with a 20% aqueous sodium hydroxide solution. A color developer solution was prepared by dissolving with heating 100 parts of p-phenylphenol-formaldehyde resin in 100 parts of diisopropylnaphthalene. This solution was dispersed in the aqueous solution obtained above to form an emulsion of the oil-in-water type containing oil droplets, 3 to 5 μ in diameter. The emulsion was admixed with 50 parts of 37% formalin and kept at 55°C with stirring. After 2 hours, a wall membrane of urea-formaldehyde condensate was formed around each oil droplet. The emulsion as adjusted to pH 9.5 to terminate the encapsulation and a dispersion of color developer containing microcapsules was obtained.

Preparation of single coating-type self-contained color developing pressure sensitive record paper:

A uniform self-contained coating composition was prepared by intermixing those dispersions of color former-containing capsules contained in an amount of 20 parts by weight and color developer-containing capsules contained in an amount of 30 parts by weight, respectively, which were obtained above, 300 parts of a 5% aqueous polyvinyl solution, 30 parts of kaolin clay, 40 parts of a 5% aqueous solution of cation-modified polyamide-epichlorohydrin resin, and 200 parts (80 parts on dry basis) of a 40% dispersion of powdered polyethylene in water ("Chemi-Pearl" supplied by Mitsui Petrochemical Co.; softening point and particle diameter of dispersed polyethylene are 76°C and 19 μm, respectively). The above coating composition was applied to a base sheet, 50 g/m^2 in basis weight, at an application rate of 8—9 g/m^2 by means of an air knife coater to obtain a single coating-type self-contained color developing pressure sensitive record paper.

Example 2

Preparation of single coating type self-contained color developing pressure sensitive record paper:

A single coating type self-contained color developing pressure sensitive record paper was obtained by repeating the procedures of Example 1, except that the amount used of the 40% aqueous dispersion of powdered polyethylene was 150 parts (60 parts on dry basis) in place of 200 parts.

Example 3

Preparation of single coating type self-contained color developing pressure sensitive record paper:

A single coating type self-contained color developing pressure sensitive record paper was obtained by repeating the procedures of Example 1, except that 100 parts (40 parts on dry basis) of a 40% aqueous dispersion of powdered polyethylene, 75 parts of starch particles, and 25 parts of water were used in place of 200 parts of a 40% aqueous dispersion of powdered polyethylene.

Example 4

Preparation of a single coating type self-contained color developing pressure sensitive record paper:

A single coating type self-contained color developing pressure sensitive record paper was obtained by repeating the procedures of Example 1, except that powdered carboxyl-modified polyethylene having a softening point of 70°C and a particle diameter of 20 μ was used in place of polyethylene.

Claims

1. A self-contained color forming pressure sensitive record paper of the single coating type prepared by coating a base paper sheet with a uniform coating mixture of an aqueous suspension of microcapsules containing a color former and an aqueous suspension of microcapsules containing a color developer and then drying, characterized in that to said coating mixture is added a powdered polyolefin in an amount of 100 to 200 parts by weight per 100 parts by weight of total capsule.

2. A record paper according to Claim 1, wherein the powdered polyolefin contains a major amount of polyethylene, has an average particle diameter of 10 to 30 μm and is added in the form of aqueous dispersion.

Patentansprüche

1. Selbstaufzeichnendes, druckempfindliches Papier vom Einzelschichttyp, hergestellt, indem man ein Grundpapierblatt mit einer gleichmässigen Beschichtungsmischung aus winer wässrigen Suspension von Mikrokapseln, enthaltend eine Farbbildner, und einer wässrigen Suspension von Mikrokapseln, enthaltend einen Farbenwickler, beschichtet und dann trocknet, dadurch gekennzeichnet, dass zu der Beschichtungsmischung ein gepulvertes Polyolefin in einer Menge von 100 bis 200 Gew.-Teilen pro 100 Gew.-Teilen der Gesamptkapseln zugegeben wird.

2. Aufziechnungspapier gemäss Anspruch 1, worin das gepulverte Polyolefin eine Hauptmenge an Polyethylen mit einem durchschnittlichen Teilchendurchmesser von 10 bis 30 µm enthält und in Form einer wässrigen Dispersion zugegeben wird.

Revendications

1. Papier pour documents sensibles à la pression, formant de la couleur auto-contenue du type revêtement unique, préparé par revêtement d'une feuille de papier support avec un mélange pour revêtement uniforme d'une suspension aqueuse de microcapsules contenant un formateur de couleur et d'une suspension aqueuse de microcapsules contenant un révélateur de couleur et puis séchage, caractérisé en ce qu'on ajoute audit mélange pour revêtement une polyoléfine en poudre dans une proportion de 100 à 200 parties en poids par 100 parties en poids, de capsule totale.

2. Papier pour documents selon la revendication 1, dans lequel la polyoléfine en poudre contient une quantité majeure de polyéthylène, a un diamètre moyen de particules de 10 à 30 µm et est ajoutée sous la forme d'un dispersion aqueuse.