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METHOD OF PRODUCING PRESSURE-SENSITIVE RECORDING PAPERS

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ABSTRACT OF THE DISCLOSURE

A single-sheet pressure-sensitive recording material is produced by applying to a substrate an electron-acceptive adsorbent and microcapsules formed by coacervating a hydrophilic material around colorless electron donors. By incorporating 5–15 parts by weight, based on the weight of the materials used to form the wall of the microcapsules of a water-soluble alkyd resin, a water-dispersible metal soap, a water-dispersible paraffin or an aqueous emulsion of a paraffin wax and rosin into the composition used to coacervate the microcapsules prior to application onto the substrate an improved pressure sensitive recording material is obtained.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The present invention relates to a method of producing pressure-sensitive recording papers and more particularly it relates to a method of producing a pressure-sensitive recording paper by applying to the same surface thereof an adsorbable colorless organic material and an electron acceptive adsorbent.

(2) Description of the prior art

Usually so-called pressure-sensitive recording papers are composed of a capsule paper having a layer of microcapsules containing therein an electron-donor, adsorbable, and colorless organic material capable of causing color reaction or coupling reaction, such as Leucomethylene Blue, Crystal Violet Lactone, or the like and a clay paper having thereon a layer of an electron acceptive adsorbent, such as acid clay, kaolin, or the like. When the capsule paper is superposed on the clay paper and they are pressed partially by, e.g., handwriting or typewriting, the microcapsules at the pressed portions are ruptured to cause the color reaction or coupling reaction of the colorless organic material and the clay.

Recently, however, a single sheet type of pressure-sensitive recording paper utilizing the aforesaid coupling mechanism has been proposed for recording using only one recording sheet or, in the case of typewriting, for typewriting thereon without using a typewriting ribbon. That is, an electron-donor, adsorbable, and colorless organic material and an electron-acceptive adsorbent are applied to the surface of a sheet or paper in a layer or layers. When the surface of the layer thus formed is partially pressed by writing, the microcapsules containing the colorless organic material are ruptured to release therefrom the colorless organic material, which comes into contact with the adsorbent to cause coupling. However, such a type of pressure-sensitive recording paper prepared by conventional methods is colored spontaneously when it is not pressed, for example, by writing. Hence, a pressure-sensitive recording paper which can be preserved stably or without being accompanied by coloring for a long period of time is not obtained by conventional methods.

Thus, an object of this invention is to provide a method of producing a pressure-sensitive recording paper free from such spontaneous coloring.

SUMMARY OF THE INVENTION

According to the method of the present invention, the single sheet type pressure-sensitive recording paper is prepared by applying to the surface of a paper an electron-acceptive adsorbent and microcapsules containing therein an electron-donor type, adsorbable, and colorless organic material, wherein at least one of a water-soluble alkyd resin, water-dispersible metal soap, a water-dispersible paraffin and an aqueous emulsion of paraffin wax and rosin is incorporated in the capsule-containing coating composition.

DETAILED DESCRIPTION OF THE INVENTION

A coating composition of microcapsules containing an electron-donor type, adsorbable, and colorless organic material may be prepared, for example, by the coacervation method described in U.S. Pat. 2,800,457. In the method of this invention, in the coating composition prepared, for example, by the aforesaid coacervation method, there is dispersed at least one of aforesaid water-soluble alkyd resin, water-dispersible metal soap, water-dispersible paraffin, and an aqueous emulsion of paraffin wax and rosin. The dispersion thus prepared is applied to the surface of a paper or other substrate. Then a coating composition containing an electron-donor type adsorbent is applied to the capsule-containing layer thus formed. The adsorbent layer may be formed on the surface of the paper before the formation of the capsule-containing layer. Further, the capsules and the adorbent may be applied in a layer together with the additives.

As the additives used in the present invention, there may be illustrated DEF–922 (made by Nisshin Kagaku Kenkyu-Sho), P-Coat (Nisshin Kagaku Kenkyu-Sho), Amberlack 165 (made by Rohm and Haas Co.), Alwax (made by American Cyanamid Co.), Waxing Size (made by American Cyanamid Co.), and the like. The preferred proportion of the additive is from 5 to 15 parts by weight per 100 parts by weight of the components used for forming the microcapsules, such as, gelatin and gum arabic, although the proportion thereof in this invention is not limited to that value.

As the adsorbable colorless organic material used in this invention, there may be employed Crystal Violet Lactone, Benzoyl Leucomethylene Blue, Rhodamine B Lactam, and the like, and as the adsorbent, there may be employed acid clay, montmorillonite, bentonite, attapulgite and the like.

Furthermore, more effective results can be obtained by applying, besides the method of this invention, the invention discovered previously by the same inventor and others. That is, by incorporating in the adsorbent-containing coating composition polyvinyl alcohol and then a water-dispersible type acrylic synthetic resin latex of a copolymer of polyacrylic ester or a copolymer of acrylic ester and styrene prior to applying, the formation of spontaneous coloring can be more effectively prevented.

The pressure-sensitive recording paper obtained by the method of this invention is completely colorless or white and is more beautiful than conventional pressure-sensitive papers of this type. When the recording paper is partially pressed by writing, the contrast between the colored portion and the blank portion of the paper is high and the colored portion becomes sharp, which makes legible the characters thus formed. Thus, the recording paper of this invention may be used not only for general office work but also for meter recordings in communications, scientific researches, medicines, and the like.

The invention will further be explained in detail in the following examples:

EXAMPLE 1

Dissolved into 400 parts by weight of water at 40° C. were 10 parts by weight of gelatin treated with acid and 10 parts by weight of gum arabic and in the resulting solution there was dispersed by emulsifying 40 parts by weight of a coupler oil while using 0.2 part by weight of Turkey red oil as an emulsifying agent. The coupler oil used above was one prepared by dissolving 2% by weight of Crystal Violet Lactone, 1.5% by weight of Benzoyl Leucomethylene Blue, and 4% by weight of Tinuvin-P (an ultraviolet absorber made by Geigy A.-G.) in an oil consisting of 4 parts by weight of chlorinated diphenyl and one part by weight of kerosene.

The emulsification was stopped when the size of the oil drops in the system reached 5 microns. Water was added to the system at 40° C., until the whole weight of the system reached 900 parts by weight and the system was stirred while maintaining the temperature of the system at about 40° C. Thereafter, the pH of the system was adjusted to 4.0–4.2 by the addition of 10% acetic acid to cause coacervation. Then, after continuing stirring for 20 minutes, the system was cooled by ice-cooled water to gel the coacervated films deposited on the surfaces of the oil drops.

When the temperature of the system reached 20° C., 7 parts by weight of 37% formaldehyde was added thereto and further, when the temperature of the system reached 10° C., the pH of it was adjusted to 9 by adding an aqueous solution of 15% sodium hydroxide carefully. Thereafter, the system was heated for 20 minutes to raise the temperature to 50° C. with stirring.

The capsule-containing coating composition thus prepared was allowed to stand for 24 hours in a tank and the supernatant liquid thus formed was removed. Then, just before coating, 10 parts by weight of cellulose powders, KD-Flock (made by Kokusaku Pulp K.K.) was added to the capsule-containing coating composition for increasing the abrasion resistance and compressive strength of the microcapsules. Then one part by weight of a water-soluble alkyd resin, Amberlack 165 (made by Rohm and Haas Co.), was added thereto for preventing spontaneous coloring of the couplers with the adsorbent described below. The resulting dispersion is designated Composition A.

Then, 100 parts by weight of acid clay which had been activated by treating with sulfuric acid was dispersed in 350 parts by weight of water and then the pH thereof was adjusted to 8–9 by adding an aqueous 20% NaOH solution as a dispersing agent. The resulting dispersion is designated Composition B. Composition B was applied to a paper in a thickness of 5–10 g./sq. m. Composition A was then applied on the layer thus formed in a thickness of 4–6 g./sq. m. The pressure-sensitive recording paper was white and was not colored when stored for a long period of time except when it was pressed partially by writing.

EXAMPLE 2

To Composition B in Example 1 was added a further 45 parts by weight of an aqueous 10% solution of a low-viscous polyvinyl alcohol (PVA 205 made by Kurashiki Rayon Co.), and thereafter 30 parts by weight of an acrylic latex prepared by using a non-ionic emulsifying agent (Tocryl S–20 made by Toyo Ink Co.) was added to the solution followed by dispersing for one hour. Then, 0.5 part by weight of Quilon C (made by E. I. du Pont de Nemours & Co.) was added to the dispersion as a waterproofing agent for polyvinyl alcohol. The resulting dispersion is designated Composition B. Composition C was applied to a paper in a thickness of 5–10 g./sq. m. and then Composition A, from Example 1, was applied to the layer thus formed in a thickness of 4–6 g./sq. m. The pressure-sensitive recording paper thus obtained was more white and more stable than those obtained in Example 1.

EXAMPLE 3

In Example 2, coating Composition A was applied to the surface of a paper prior to applying Composition B. The pressure-sensitive recording paper thus obtained had sufficient stability and recording ability although the coloring density after pressing by writing was lower than that of the pressure-sensitive recording paper prepared in Example 2.

EXAMPLE 4

A mixture of 20 parts by weight of Composition B and 80 parts by weight of Composition A in Example 2 was applied to the surface of a paper in a thickness of 8–10 g./sq. m. The pressure-sensitive recording paper thus obtained could be sufficiently used in practice although it was colored when preserved for a long period of time.

EXAMPLE 5

The same procedure as in Example 1 was repeated while using DEF 922 (made by Nisshin Kagaku Kenkyu-Sho) instead of Amberlack 165. A stable and white sensitive pressure-sensitive recording paper was obtained.

What is claimed is:

1. In a method of producing a pressure-sensitive recording material by applying in a layer or layers a coating composition comprising an electron-acceptive adsorbent and a coating composition comprising a plurality of distinct hydrophilic microcapsules formed by coacervation and containing an electron-donor, adsorbable and colorless organic material to the same surface of a substrate, the improvement which comprises incorporating, prior to application to said substrate, in the coating composition which contains said microcapsules formed by coacervation from about 5 to 15 parts by weight per 100 parts by weight of the components used for forming the hydrophilic microcapsule walls of a material selected from the group consisting of a water-soluble alkyd resin, a water-dispersible metal soap, a water-dispersible paraffin, and an aqueous emulsion of paraffin wax and rosin, whereby the microcapsules are coated with a member from said group.

2. The method of producing a pressure-sensitive recording material according to claim **1** wherein said compositions are applied to a substrate in double layers and the coating composition comprising the adsorbent is first applied to the substrate prior to the application of the capsule-containing coating composition.

3. The method of producing a pressure-sensitive recording material according to claim **1** wherein said compositions are applied to the substrate in double layers and the capsule-containing coating composition is first applied to the substrate prior to the application of the adsorbent-containing composition.

4. A pressure-sensitive recording material prepared by the method claimed in claim **1**.

5. The process of claim **1** wherein said material is the water-soluble alkyd resin.

6. The process of claim **1** wherein said material is the water-dispersible metal soap.

7. The process of claim **1** wherein said material is the water-dispersible paraffin.

8. The process of claim **1** wherein said material is an aqueous emulsion of paraffin wax and rosin.

9. The process of claim **4** wherein said microcapsules are formed by coacervating a shell comprising gelatin and gum arabic around a coupler oil comprising said colorless organic material and an oily material.

10. The process of claim **9** wherein said colorless organic material is selected from the group consisting of Crystal Violet Lactone, Benzoyl Leucomethylene Blue and Rhodamine B Lactam.

11. The process of claim **9** wherein said microcapsules are coacervated from a liquid and, after coacervation, are mixed with said material from said group and subsequently applied to said substrate as a dispersion.

12. The process of claim 11 wherein said material from said group is added to said microcapsules while they are in at least a portion of the liquid from which the microcapsules are coacervated.

13. The process of claim 12 wherein said portion is the portion of said liquid which remains after the microcapsules are allowed to settle from said liquid thereby yielding a supernatant liquid layer, and said supernatant layer is removed from said microcapsules and said portion.

14. The process of claim 4 wherein said microcapsules are formed by coacervating a shell comprising a natural polymer around a coupler oil comprising said colorless organic material and an oily material.

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