

[54] **PROCESS FOR MANUFACTURING AN ACTIVATED CLAY-COATED PAPER FOR USE AS A PRESSURE-SENSITIVE COPYING PAPER**

[75] Inventors: **Hiroharu Matsukawa; Takao Hayashi**, both of Shizuoka, Japan

[73] Assignee: **Fuji Photo Film Co., Ltd.**, Japan

[22] Filed: **Mar. 25, 1974**

[21] Appl. No.: **454,497**

Related U.S. Application Data

[63] Continuation of Ser. No. 209,462, Dec. 17, 1971, abandoned, which is a continuation of Ser. No. 858,525, Sept. 16, 1969, abandoned.

[30] **Foreign Application Priority Data**

Sept. 16, 1968 Japan..... 43-66818

[52] **U.S. Cl.** **428/323; 427/145; 427/150; 428/454**

[51] **Int. Cl.²** **B41C 1/06; B41M 5/16**

[58] **Field of Search**..... 117/362, 36.8, 156; 106/130

[56]

References Cited

UNITED STATES PATENTS

2,961,334	11/1960	Clancy et al.	117/156
3,356,517	12/1967	Nakajima	117/156 X
3,372,044	3/1968	Weber	106/130
3,372,050	3/1968	Weber	117/156
3,427,971	2/1969	Steber et al.	117/156 X
3,432,327	3/1969	Kan et al.	117/36.2
3,554,781	1/1971	Matsukawa	117/36.8
3,684,549	8/1972	Shank	117/36.2

Primary Examiner—Thomas J. Herbert, Jr.

Attorney, Agent, or Firm—Sughrue, Rothwell, Mion, Zinn & Macpeak

[57]

ABSTRACT

A process for the production of a pressure sensitive copying paper which comprises coating the paper with a water dispersion of a clay; the improvement which comprises adding a water-dispersible emulsion of a hydrophobic oily material, said oily material being a liquid at room temperature, to the water dispersion of the clay.

12 Claims, No Drawings

PROCESS FOR MANUFACTURING AN ACTIVATED CLAY-COATED PAPER FOR USE AS A PRESSURE-SENSITIVE COPYING PAPER

This application is a continuation application of Ser. No. 209,462, filed Dec. 17, 1971, in turn a continuation application of Ser. No. 858,525, filed Sept. 16, 1969, both of said applications 209,462 and 858,525 being abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for manufacturing an activated clay-coated paper for use as a pressure-sensitive copying paper. More particularly, it relates to a manufacturing process for making a clay-coated paper for use as a pressure-sensitive copying paper in which the coloring property is sharply improved by adding to and mixing with a clay dispersion, a water-dispersible emulsion of a hydrophobic oily material which is liquid at room temperature.

2. Description of the Prior Art

Pressure-sensitive copying papers on which a localized pressure creates a distinctive color is based on the formation of a color due to the action of an electron-donating colorless organic compound with an electron-accepting adsorbent material through the medium of non-polar oil solvent.

Pressure-sensitive copying papers are usually composed of (1) a transferring paper coated with a layer of microcapsules, containing an electron-donating colorless organic compound (hereinafter the colorless organic compound will be referred to as the "color-former") dissolved in an oil, and (2) a receiving paper (hereinafter the receiving paper will be referred to as the "clay-coated paper") coated with a layer (hereinafter this layer will be referred to as the "clay-coated layer") of an electron-accepting material and a suitable binder. When these papers are juxtaposed such that the electron-donating layer contacts the clay-coated layer and a localized pressure, e.g., by handwriting or typewriting, is applied, the microcapsules affected by the localized pressure are ruptured. The colorless color-former contained in the microcapsules is released and is adsorbed on the electron-accepting material to form a definite color. Pressure-sensitive copying papers consisting of a sheet on which microcapsules containing a color-former dissolved in an oil and an electron-accepting adsorbent material have been applied simultaneously are also known. Pressure-sensitive copying papers and microcapsules are described in U.S. Pat Nos. 2,712,507; 2,730,456; 2,730,457 and 2,800,457.

Color-formers which have been used are basic color-formers such as Crystal violet lactone, Malachite green lactone, Benzoil leuco methylene blue, Rhodamine β lactam, Michler's Hydrol, and the Leuco auramines. Known electron-accepting adsorbent materials are activated clay, Japanese acid clay, zeolite, attapulgite, bentonite, etc. and synthetic compounds containing silicon. Suitable binders of clay include styrene-butadiene latex, acrylic latex, starch, casein, polyvinyl alcohol, carboxymethylcellulose, gum arabic, and the like.

With the increased demand in recent years for pressure-sensitive copying papers, various new encapsulating methods and new color-formers have been developed and described in an effort to improve the performance of the pressure-sensitive copying papers. Little

work on methods of improving the clay-coated paper has resulted. One specific method of manufacturing a clay-coated layer, excellent in color density, is the clay-coated paper containing an oil-soluble phenol resin described in British patent specification No. 1,065,587.

DESCRIPTION OF THE INVENTION

An object of the present invention is to provide an entirely new method of activating the clay-coated paper for use in pressure-sensitive copying paper wherein the color-forming capacity of the clay-coated paper is improved in contacting the clay-coated paper with the color former.

It has been found that a clay-coated paper prepared by adding a water-dispersive emulsion of a hydrophobic oil material, liquid at room temperature, to a clay slurry results in color capacity which is superior to that of a clay-coated paper prepared using non-emulsion techniques. Using the process of this invention, an improvement in activation of the clay-coated paper is thus obtained.

DETAILED DESCRIPTION OF THE INVENTION

The hydrophobic oily material to be used in this invention can be any oily material so long as the coloring capacity of the clay-coated paper is not adversely affected.

Suitable hydrophobic oily materials to be used in the present invention are vegetable oils, animal oils, mineral oils, synthetic oils and the usual organic solvents. Suitable vegetable oils are olive oil, castor oil, cottonseed oil, lemon oil, corn oil and other rind oils. Suitable animal oils are fish oil, whale oil and the like. Appropriate mineral oils are fish oil, whale oil and the like. Appropriate mineral oils are those obtained primarily from petroleum, namely, various paraffin oils, kerosene, petroleum naphtha and the like. Suitable synthetic oils are chlorinated diphenyls, chlorinated paraffins, octyldipthalate, dimethylphthalate, diethylphthalate, dibutylphthalate, dioctylphthalate, butylbenzylphthalate, tricresylphosphate, trioctylphthalate, silicon oil, and fluorinated oils. Suitable organic solvents are aliphatic hydrocarbons such as octane, decane, dodecane or cetane, aromatic hydrocarbons such as benzene, toluene, xylene, amylbenzene, ethylbenzene, diethylbenzene or triethylbenzene, and halogenated hydrocarbons such as carbon tetrachloride, ethylene chloride, trichloroethane, trichloroethylene, dichlorobutane, chlorobenzene, trichlorobenzene and chlorotoluene.

The hydrophobic oily material useful in this invention preferably has a boiling point of 60° to 500°C., but this is not limiting. The amount of the hydrophobic oily material to the clay is preferably 1:50 to 1:2 parts by weight.

The hydrophobic oily material is applied as an oil-in-water emulsion to obtain the objects of this invention. Emulsification of the oily material in water, which is accomplished by the use of a dispersing agent, or emulsifier. Protective colloidal solutions can be used. Emulsification is by means of a stirrer having a high shearing force, such as a homomixer or an ultrasonic emulsifying apparatus. These oily emulsions are simply added to and dispersed in the clay slurry. The resulting dispersion is then coated on a paper.

Activation of the clay-coated paper increases the greater the amount of the oily emulsion used in the clay slurry.

While an important object of this invention is the improvement of the color activation of pressure-sensitive copying paper, an improvement in coloring properties is also achieved. The writing on current pressure-sensitive copying papers now on the market loses color density (fade) as time passes or discoloration and low-

the ratio of 8.0 g./m.² to prepare clay-coated pressure-sensitive papers. The clay-coated paper, thus prepared was coupled with a transferring paper and pressure applied to bring out the color. The color density at the maximum absorbing wavelength of 600 mμ was measured. The results are shown in the following table.

	1	2	Sample Number 3	4	5	6
Amount of Liquid Paraffin Emulsion Added (parts)	0	0.2	0.4	0.6	0.8	1.0
Color Density (Absorbency)	0.83	0.91	0.96	1.05	1.20	1.25

ering of the activity occurs when the paper is exposed to the air for hours. With the clay-coated paper prepared by the process of the present invention such loss of performance is minimal and any running of the ink is minimized by adsorption of the oil on the surface of the clay-coated paper.

The following examples exemplify the present invention, but this invention is not to be limited thereby. In

It can be seen from the above table that the color density increases as the amount of the liquid paraffin increases.

Next, the surface of the clay-coated paper was exposed to a 500 watt mercury lamp for 15 hours and the change in color of the clay-coated layer on the clay-coated paper was measured with Hunter color and gloss meter. The following values were obtained.

	1	2	Sample Number 3	4	5	6
Amount of Liquid Paraffin Emulsion Added (parts)	0	0.2	0.4	0.6	0.8	1.0
Whiteness (Hunter L Value)	69.8	70.1	70.6	72.0	73.5	74.1

the examples given hereinafter, the tests were carried on in the following manner. To determine the color density generated using the clay-coated paper, the transferring paper was prepared by applying 6.0 g./m.² of microcapsules containing 3.5 g./m.² of a 2% chlorinated diphenyl solution of Crystal Violet lactone as the color-former to a paper having a weight of 40 g./m.² The two papers were then placed together, a load of 100 kg./cm.² was applied to the papers and the color density of the mark thus formed was measured with a spectrophotometer. The degree of yellow fade was measured with a Hunter color and gloss meter. All parts are by weight unless indicated otherwise.

EXAMPLE I

An oil-in-water emulsion of liquid paraffin was prepared by emulsifying 50 parts of liquid paraffin having a specific gravity of 0.855 in a solution of 50 parts of water, 1 part of the sodium salt of casein, and 1 part of 20% potassium hydroxide using an ultrasonic emulsifier until the diameter of such particle was 0.1–0.5μ. Then, 350 parts of water, 8 parts of sodium hydroxide and 100 parts of activated Japanese acid clay were introduced into a glass container and dispersed by means of a propeller stirrer. To the dispersion, after 30 minutes of stirring, were added 30 parts of a styrene-butadiene latex (Dowlatex 631, Dow Chemical Co.) and 50 parts of a 10% aqueous solution of the sodium salt of casein as a binder to make coating composition. Ten parts of the above coating composition were introduced into each of five containers, and the oil-in-water emulsion of liquid paraffin prepared above was added to these containers in varying amounts, viz. 0.2, 0.4, 0.6, 0.8 and 1.0 part, respectively, to produce dispersions of five different densities. The dispersions were then applied to a paper, having a weight of 40 g./m.², at

It will be seen that the larger the rate of adding the liquid paraffin emulsion, the smaller the change of color on the clay-coated paper through ultra-violet rays.

EXAMPLE II

An oil-in-water emulsion was prepared as in Example I except that the liquid paraffin was replaced by fluorine oil (fluoroethylene chloride; Difloil No. 3, manufactured by Osaka Kinzoku Kogyo Kabushiki Kaisha). A clay-coated paper was prepared by adding 0.5 part or 1.0 part of this oil-in-water emulsion to 10 parts of the clay coating composition of Example I, in the same ratio of Example 1. The color density values of the clay-coated paper and its resistance to fading are summarized in the next table.

	Sample Number 1	2	3
Quantity of Fluorinated Hydrocarbon Emulsion Added	0	0.5	1.0
Color Density (Absorbency)	0.85	1.03	1.18
Whiteness	69.5	70.4	70.8

EXAMPLE III

An oil-in-water emulsion was prepared as in Example I, except that the liquid paraffin was replaced by Silicon oil KF 96 (made by Shin-etsu Kagaku Kogyo Kabushiki Kaisha), and the samples prepared as in Example II. The color densities and whiteness tests were run as in Example II, and the results obtained are as follows.

	Sample Number		
	1	2	3
Quantity of Silicone Oil Emulsion Added	0	0.5	1.0
Color Density (Absorbency)	0.86	1.12	1.15
Whiteness	69.3	72.2	74.5

EXAMPLE IV

An oil-in-water emulsion was prepared as in Example I except that the liquid paraffin was replaced by chlorinated diphenyl KC-1000 (by Kanegafuchi Kagaku Kogyo Co., Ltd.), and the samples prepared as in Example II. The results of the color densities measured and the whiteness values obtained are shown below.

	Sample Number		
	1	2	3
Quantity of Chlorinated Diphenyl Emulsion Added	0	0.25	0.5
Color Density (Absorbency)	0.86	1.00	1.12
Whiteness	69.5	56.2	54.5

EXAMPLE V

An oil-in-water emulsion was prepared as in Example I except that the liquid paraffin of Example I was replaced by benzene. The samples were prepared as in Example II. The results of the color densities measured and the whiteness values obtained are shown below.

	Sample Number		
	1	2	3
Quantity of Benzene Emulsion Added	0	0.5	1.0
Color Density (Absorbency)	0.88	1.05	1.11
Whiteness	68.5	68.6	68.8

What is claimed is:

1. In a process for producing color on a support having coated thereon a layer of an electron accepting clay material capable of forming a distinct color when contacted with a colorless, electron donating color former wherein a layer of electron accepting clay material is applied to said support and thereafter said electron accepting clay is contacted with a colorless, electron donating color former, the improvement which comprises adding a hydrophobic oily material as an oil in water emulsion to a water dispersion of said clay and then coating the obtained water dispersible emulsion

and said clay onto the support and drying the clay coated support, the amount of said hydrophobic oily material to the clay ranging from 1:50 to 1:2 parts by weight.

2. The process of claim 1, wherein said hydrophobic oily material has a boiling point ranging from 60° to 500°C.

3. The process of claim 1, wherein said water dispersion of clay contains a binder.

4. The process of claim 1, wherein said hydrophobic oily material is a member selected from the group consisting of a vegetable oil, an animal oil, a mineral oil, a synthetic oil, and an organic solvent.

5. The process of claim 4, wherein the oily material is a synthetic oil and is selected from the group consisting of chlorinated diphenyl, chlorinated paraffin, octyldipthalate, dimethylphthalate, diethylphthalate, dibutylphthalate, dioctylphthalate, butylbenzylphthalate, tricresylphosphate, trioctylphthalate, silicone oil, and fluorinated oil.

6. The process of claim 4, wherein said oily material is an organic solvent and is a member selected from the group consisting of an aliphatic hydrocarbon, an aromatic hydrocarbon, and a halogenated hydrocarbon.

7. The process of claim 6, wherein said aliphatic hydrocarbon is a member selected from the group consisting of octane, decane, dodecane, and cetane.

8. The process of claim 6, wherein said aromatic hydrocarbon is a member selected from the group consisting of benzene, toluene, xylene, amyl benzene, ethylbenzene, diethylbenzene, and triethylbenzene.

9. The process of claim 6, wherein said halogenated hydrocarbon is a member selected from the group consisting of carbon tetrachloride, ethylene chloride, trichloroethane, trichloroethylene, dichlorobutane, chlorobenzene, trichlorobenzene, and chlorotoluene.

10. A pressure-sensitive copying paper comprising a layer of microcapsules containing a color former and a layer of an electron-accepting clay material capable of forming a distinct color when contacted with the color former, said layers coated on the same or different support, and said layer of electron-accepting clay material containing a binder and a hydrophobic oily material, the amount of said hydrophobic oily material to the clay ranging from 1:50 to 1:2 parts by weight.

11. The pressure-sensitive copying paper of claim 10, wherein said hydrophobic oily material is a member selected from the group consisting of a vegetable oil, an animal oil, a mineral oil, a synthetic oil, and an organic solvent.

12. The pressure-sensitive copying paper of claim 10, wherein said hydrophobic oily material has a boiling point ranging from 60° to 500°C.

* * * * *