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Hayashi et al.

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[54] **METHOD FOR PRODUCING CLAY COATED PAPER FOR PRESSURE SENSITIVE COPYING PAPER**

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Related U.S. Application Data

[63] Continuation of Ser. No. 83,211, Oct. 22, 1970, abandoned.

[30] **Foreign Application Priority Data**

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[58] **Field of Search** 117/36.9, 36.2

[56] **References Cited**

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[57] **ABSTRACT**

A method for preparing a clay-coated paper for pressure-sensitive copying which comprises, applying to a paper support having a layer of microcapsules containing at least one color former, a slurry comprising an alkali dispersing agent an anionic high molecular weight electrolyte, an electron-acceptive adsorbent clay, and a binder, and product so obtained.

13 Claims, No Drawings

METHOD FOR PRODUCING CLAY COATED PAPER FOR PRESSURE SENSITIVE COPYING PAPER

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a Continuation application of our earlier copending application Ser. No. 83,211 filed Oct. 22, 1970, now abandoned, which claims priority from Oct. 22, 1969, based on Japanese Patent Application No. 84537/69.

BACKGROUND OF THE INVENTION

The present invention relates to a method for producing clay coated papers used for pressure-sensitive copying papers, and more particularly, to a method of improving properties and activity of a coated clay layer by adding an anionic high molecular weight electrolytic compound to the slurry of clay and binder (e.g., latex) in the production of clay-coated paper for pressure-sensitive copying.

The clay-coated paper normally employed for pressure-sensitive copying is generally produced by coating a clay, (e.g., attapulgite, bentonite Japanese acid clay, active clay, or zeolite), and a binder (e.g., styrene-butadiene latex, styrene-butadiene latex-casein or starch, acrylic ester copolymer latex, or acrylic ester copolymer latex-starch or casein) on the surface of a paper. When this clay-coated paper is piled on a capsule-coated paper produced by applying many micro capsules containing an oil solution of a color precursor or former (e.g., crystal violet lactone, or acylated benzoil leucomethylene blue) and locally pressurized with suitable pressure, such as handwriting or typewriting, the pressurized portion of the clay-coated paper is colored. These clay-coated papers contain excess amounts of binder in order that ∓picking" (stripping off of the clay-coated layer) during printing, may be prevented. In spite of this, commercial clay-coated papers for pressure-sensitive copying are still apt to cause picking during printing, as compared with art paper or coat paper. The reason for this is considered to be dependent upon the clay. This is also apparent from the fact that the dirt is found in the branket of the offset printing machine is not as pronounced after a printing of 6000 sheets of commercial coat paper. In addition, the printed figures remain clear. On the other hand, the dirt found in the branket is extremely noticeable after printing only 3000–4000 sheets of commercial clay-coated paper and the printed images remain unclear. Furthermore, the excess amounts of binder cover the active points of the clay (points to color the color precursor or former) and reduce its activity (color-forming capacity of clay-coated paper), which is the most important property of the clay-coated paper. In addition to this, the activity is extremely reduced in relatively short periods of time by exposing the clay-coated paper to air. This will be hereinafter designated as "activity reduction by time lapse".

SUMMARY OF THE INVENTION

Therefore, the primary object of this invention is to provide a method for producing clay-coated paper for the pressure-sensitive copying having high membrane strength, activity and time lapse activity.

Accordingly, the inventors have now discovered that the amount of binder necessary to obtain clay-coated paper having a high membrane strength can be considerably decreased by adding an anionic high molecular weight electrolyte to the clay slurry. This binder saving effect is especially effective when a metal oxide, such as zinc oxide, aluminum oxide, manganous oxide, or a metal salt, such as magnesium carbonate, magnesium hydroxide, zinc chloride, or aluminum hydroxide is added to the clay slurry or coating composition.

DETAILED DESCRIPTION OF THE INVENTION

Among the anionic high molecular weight electrolytes applicable to the present invention are sodium polyacrylate, sodium alginate, carboxymethylcellulose, carboxyethylcellulose, gum arabic, the sodium salt of styrene-maleic anhydride copolymers, sodium polymethylacrylate, sodium polyglutamate, sodium polyasparaginate, sodium polymethacrylate, the sodium salt of butadiene-methacrylate copolymers, sodium salt of methylvinylether-maleic anhydride copolymers, the sodium salt of polyethylene-maleic anhydride copolymers, pectin, pectinic acid, carboxymethyl starch, starch sulfate, starch phosphate, potassium polyvinylbenzene sulfonate, carboxymethylether of hydroxyethyl-cellulose, sulfuric acid ester and the phosphoric acid ester of hydroxyethyl cellulose.

The above examples of anionic high molecular electrolytes are for the most part sodium salts, but they may be other alkali metal salts such as potassium salt or lithium salt, as well.

The effective amounts of these compounds to be added to the clay are at least 0.2% by weight based on the clay, and preferably, 0.5–5% by weight. The properties of the clay-coated paper for the pressure-sensitive copying obtained by this method are not influenced by the program or order of the addition of these compounds to the clay slurry.

The amount of binder latex necessary is 10–20% by weight based on the clay, and is remarkably reduced by the incorporation of anionic high molecular weight electrolyte.

The sodium alginate or sodium polyacrylate among the above-mentioned compounds have been used previously as the dispersing agents for the production of the art paper or coat paper, but have not been used in a similar manner for the production of the clay-coated paper. Caustic soda, caustic potash, or sodium hexamethaphosphate have been the primary dispersing agents employed.

The above-mentioned compounds are not used as the dispersing agent in the present invention but are employed as additives capable of eliciting the following effects.

1. The 'wet' between the clay and the binder is enhanced by adding at least 0.2 wt. % of said compounds to the clay, thus increasing the adhesion therebetween.

2. unfavorable influence of the free metallic ions on the latex is eliminated by protecting the metallic ions, thus increasing membrane strength.

Thus, the present invention increases the strength of the membrane coated on the surface of the clay-coated paper for pressure sensitive copying, increases the activity of the clay-coated paper by the reduction of the binder amounts, minimizes the reduction of the time lapse activity and prevents the yellow color change thereof.

A better understanding of the present invention will be attained from the following examples which are

merely illustrative and not limitative of the present invention. All parts are by weight unless otherwise stated.

EXAMPLE 1

250 parts of water and 10 parts of a 20% caustic soda solution as the dispersing agent for Japanese acid clay were mixed, and then 100 parts of Japanese acid clay was then added to the resulting liquid with stirring. To the resulting slurry, 0.8 parts of sodium alginate dissolved in 10 parts of water was added and then 15 parts of a styrene-butadiene latex, (as solid content), was added to prepare a coating composition. The resulting coating composition was coated on the surface of paper having a unit weight of 40 parts/m^2 in an amount of 8.5 parts/m^2, which is calculated based upon the amount of dry acid clay. After drying, the material was subjected to super-calendering, whereby a clay-coated paper for pressure-sensitive copying was obtained.

Comparative Example

In comparison with the method of the invention, a conventional method was conducted as follows.

250 parts of water and 10 parts of a 20% caustic soda solution as a dispersing agent were mixed and 100 parts of Japanese acid clay was then added with stirring. After stirring the mixture sufficiently, 18 parts, (as solid content), of a styrene-butadiene latex as a binder was added to prepare a coating composition. This composition was then coated on a paper having a unit weight of 40 parts/m^2 in an amount of 8.5 parts/m^2. The material was then dried and subjected to super-calendering, whereby a clay-coated paper for pressure-sensitive copying paper was obtained.

Though an amount of binder contained in the clay-coated layer of the invention was 15.8 parts to 100 parts of Japanese acid clay and was smaller than that of conventional clay-coated paper which contains 22 parts of binder, the strength of membrane was far superior. Moreover, since the amount of binder was decreased, the activity and the activity after the lapse of time thereof were excellent. The results are shown in the following table:

	Example 1	Comparative Example
Strength of Membrane *A	+++	+
Offset Printability *B	5000 sheets	3000 sheets
Activity (D_1) *C	0.98	0.85
Activity After the Lapse of Time *D ($D_2/D_1 \times 100$)	85%	75%

*A The strength of the membrane was tested by stripping the surface of membrane by means of a printability tester using various types of inks having mutually different tacks. The stripped conditions of the clay-coated paper were inspected with the naked eye and compared with each other. The stronger membrane was denoted by an increase in the "+" sign.

*B The actual printing test was conducted by means of a Heidelberg offset printer (ROR type). Both dirt on the branket and the result of the printed sheets, in each of the methods employed, were compared with each other. Of the various sheets indicated in the table, each shows the dirtiness of the branket and the unclearness of sheets.

*C The activity was measured by contacting the clay-coated paper with a paper having coated thereon, a layer of microcapsules containing a color former dissolved in an oil, and by applying about 600 Kg/cm^2 of pressure to them in order to form a distinct color on the clay-coated paper. Subsequently, the density of the color dye at an absorption maximum of 600 mμ wave length was measured. (The measured value was indicated as D_1).

*D The activity after the lapse of time was measured by contacting the papers. One of these papers was a clay-coated paper which was allowed to stand in the atmosphere for 10 days and the other was a capsule-coated paper. 600 Kg/cm^2 of pressure was applied to the contacted papers to form a distinct color on the clay-coated paper. Then the density of the color dye at an absorption maximum of 600 mμ wave length was measured. The measured value was indicated as D_2 and the activity after the lapse of time was calculated from a formula of $D_2/D_1 \times 100$.

EXAMPLE 2

250 parts of water and 10 parts of a 20% aqueous solution caustic soda as dispersing agent for the Japanese acid clay were mixed. Then, 100 parts of Japanese acid clay was added thereto with stirring to prepare a slurry.

To the slurry, 0.8 parts of the sodium salt of a styrene-maleic anhydride copolymer dissolved in 10 parts of water was added. After stirring the mixture, 15 parts (as solid content) of a styrene butadiene latex was further added to obtain a coating composition. The coating composition was coated on paper in the same manner as in Example 1 to prepare a clay-coated paper.

In comparison with the present invention, a conventional method was conducted as follows.

250 parts of water and 10 parts of a 20% aqueous caustic soda solution as a dispersing agent for Japanese acid clay were mixed together. 100 parts of Japanese acid clay was then added to the mixture with stirring. After agitating the mixture fully, 40 parts of a 10% aqueous oxidized starch solution and 20 parts, (as solid content), of a styrene-butadiene rubber latex, as the binder, were further added to the mixture to obtain the coating composition. This composition was then coated on the surface of a paper having a unit weight of 40 parts/m^2 in an amount of 8.5 parts/m^2 (calculated on the amounts of dried acid clay).

The resulting clay-coated paper was subjected to super-calendering to form a clay-coated paper for pressure-sensitive copying paper.

The amount of binder in the clay coated layer produced by the present invention was 15.8 parts to 100 parts of the acid clay, whereas that in the clay-coated layer produced by the comparative method was 24 parts to 100 parts of the Japanese acid clay. In spite of these small amounts of binder, the clay-coated paper of the present invention had a stronger membrane strength, favorable activity, and time-prolonged activity, as shown in the following table. [The sodium salt of styrene-maleic anhydride copolymer was also regarded as the binder component because of binding property thereof].

	Example 2	Comparative Example 2
Strength of Membrane	+++	+
Offset Printability	6000 sheets	2500 sheets
Activity (D_1)	0.01	0.83
Activity After the Lapse of Time ($D_2/D_1 \times 100$)	88%	72%

EXAMPLE 3

To 250 parts of water and 10 parts of a 20% aqueous caustic soda solution were added 5 parts of zinc oxide with stirring. 100 parts of Japanese acid clay was then further added to prepare a slurry. To the slurry, 1 part, (as solid content), of sodium polyacrylate was added and, after stirring, 17 parts, (as solid content), of a methyl methacrylate-butadiene copolymer latex was added to the slurry.

The obtained coating composition was then coated on a paper by the same procedure as in Example 1 to prepare a clay-coated paper for pressure-sensitive copying. In comparison with the present invention, a conventional method was conducted as follows.

250 parts of water and 10 parts of a 20% aqueous caustic soda solution as a dispersing agent were mixed. 5 parts of zinc oxide was subsequently added with further stirring and then 40 parts of a 10% aqueous casein solution and 22 parts, (as solid content), of methyl methacrylate-butadiene copolymer latex were added to prepare a coating composition. The composition so obtained was coated on a paper by the same procedure as in Example 1, to obtain clay-coated paper for pressure-sensitive copying.

Though an amount of binder in the clay-coated paper produced by the present invention was 17.8 parts to 100 parts of acid clay (sodium acrylate was regarded as the binder because of the binding property) and was smaller than that of the comparative clay-coated paper which contains 25 parts of binder to 100 parts of acid clay, the membrane strength was stronger. Moreover, since the amount of binder was reduced, the activity and the activity after the lapse of time were excellent. The results are shown in the following table:

	Example 3	Comparative Example 3
Strength of Membrane	+++	+
Offset Printability	5000 sheets	3000 sheets
Activity (D_1)	0.93	0.82
Activity After the Lapse of Time ($D_2/D_1 \times 100$)	82%	73%

EXAMPLE 4

250 parts of water and 10 parts of a 20% caustic soda solution as a dispersing agent were mixed, and 8 parts of calcium carbonate was then added thereto with stirring. After stirring the resulting mixture, 100 parts of Japanese acid clay was added to prepare a slurry. To this slurry, 1 part of gum arabic dissolved in 10 parts of water and then 15 parts (as solid content) of a styrene-butadiene latex was added to obtain a coating composition. This composition was coated on a paper by the same procedure as in Example 1 to prepare a clay-coated paper for pressure-sensitive copying.

In comparison with the above clay-coated paper of the present invention, the following clay-coated paper was prepared by the same procedure as the above preparation, except that 40 parts of a 10% aqueous starch solution was employed instead of one part of gum arabic dissolved in 10 parts of water. 20 parts of a styrene-butadiene latex was also employed.

Similar results as with Examples 1–3 were obtained and are shown in the following table:

	Example 4	Comparative Example 4
Strength of Membrane	++	+
Offset Printability	5000 sheets	2500 sheets
Activity (D_1)	0.96	0.82
Activity After Lapse of Time ($D_2/D_1 \times 100$)	86%	74%

EXAMPLE 5

250 parts of water and 10 parts of a 20% aqueous caustic soda solution as a dispersing agent were mixed. After stirring the resulting mixture, 100 parts of Japanese acid clay was added to prepare a slurry. To this slurry, 15 parts (as solid content) of a styrene-butadiene latex was added with stirring, followed by the addition of 1 part of sulfate starch dissolved in 10 parts of water. The coating composition obtained, was coated on a paper by the same procedure as in Example 1, to prepare a clay-coated paper for pressure-sensitive copying.

In comparison with the above clay-coated paper of the present invention, the following clay-coated paper was prepared by the same procedure as the above preparation, except that 40 parts of 10% aqueous casein solution was employed instead of one part of sulfate starch dissolved in 10 parts of water. 18 parts (as solid content) of styrene-butadiene latex was also used.

Similar results as with Examples 1-4 were obtained and are shown in the following table.

	Example 5	Comparative Example 5
Strength of Membrane	++	+
Offset Printability	5000 sheets	3000 sheets
Activity (D_1)	0.95	0.85
Activity After the Lapse of Time ($D_2/D_1 \times 100$)	86%	74%

Although the present invention has been adequately described in the foregoing specification and examples included therein, it is readily apparent that various changes and modifications may be made without departing from the scope thereof.

What is claimed is:

1. A method for preparing a clay-coated paper for pressure-sensitive copying which comprises applying to a paper support a slurry comprising an alkali dispersing agent, an anionic high molecular weight electrolyte, an electron-acceptive adsorbent clay, and a binder, said clay being reactive with a color-former to form a distinct color, the concentration of said electrolyte being in the range of from 0.2 to 5.0% by weight, based on the clay, and, said anionic high molecular weight electrolyte being selected from the group consisting of an alkali metal salt of polyacrylate, alginate, a styrene-maleicanhydride copolymer, polyglutamate, polyasparaginate, polymethacrylate, methylvinylether-maleic anhydride copolymers, a butadiene-methacrylate copolymer, a polyethylene-maleic anhydride copolymer, a polyvinylbenzene sulfonate, carboxymethyl cellulose, carboxyethyl cellulose, gum arabic, pectin, pectinic acid, carboxymethyl starch, starch sulfate, starch phosphate, the carboxymethyl-ether of hydroxyethyl cellulose, and the sulfate ester or phosphate ester of a hydroxyethyl cellulose.

2. The method of claim **1** wherein said electrolyte is a sodium or potassium salt.

3. The method of claim **1** wherein the concentration of said electrolyte ranges from 0.5 to 5.0% by weight, based on the clay.

4. The method of claim **1** wherein the concentration of said binder is 10.0–20.0% by weight, based upon the clay.

5. A pressure-sensitive copying paper comprising a support paper having coated thereon a layer comprising an alkali dispersing agent, a clay, a binder, and an anionic high molecular weight electrolyte, said clay being reactive with a color-former to form a distinct color, said electrolyte being present in a range of from 0.2 to 5.0% by weight, based on the clay, and said ani-

onic high molecular weight electrolyte being selected from the group consisting of an alkali metal salt of polyacrylate, alginate, a styrene-maleicanhydride copolymer, polyglutamate, polyasparaginate, polymethacrylate, methylvinylether-maleicanhydride copolymers, a butadiene-methacrylate copolymer, a polyethylene-maleic anhydride copolymer, a polyvinyl-benzene sulfonate, carboxymethyl cellulose, carboxyethyl cellulose, gum arabic, pectin, pectinic acid, carboxymethyl starch, starch sulfate, starch phosphate, the carboxymethyl-ether of hydroxyethyl cellulose, and the sulfate ester or phosphate ester of a hydroxyethyl cellulose.

6. The pressure-sensitive copying paper of claim **5** wherein said electrolyte is a sodium or potassium salt.

7. The pressure-sensitive copying paper of claim **5** wherein the concentration of said electrolyte ranges from 0.5 to 5.0% by weight, based on the clay.

8. The pressure-sensitive copying paper of claim **5** wherein the amount of binder employed is 10.0–20.0% by weight.

9. The pressure-sensitive copying paper of claim **5** wherein a layer of microcapsules containing a color-former is present on the clay-coated paper.

10. The pressure-sensitive copying paper assembly wherein said paper comprises a capsule coated paper containing at least one color-former and a clay-coated paper containing a binder and an anionic high molecular weight electrolyte, said clay contacted with said color former to form a distinct color, wherein said electrolyte is a member selected from the group consisting of a sodium or potassium salt of polyacrylate, alginate, carboxymethyl cellulose, carboxyethyl cellulose, gum arabic, a styrene-maleicanhydride copolymer, polyglutamate, polyasparaginate, polymethacrylate, methylvinylether-maleicanhydride copolymers, a butadiene-methacrylate copolymer, a polyethylene-maleic anhydride copolymer, pectin, pectinic acid, carboxymethyl starch, starch sulfate, starch phosphate, polyvinyl-benzene sulfonate, the carboxymethyl-ether of hydroxyethyl cellulose, and the sulfate ester or phosphate ester of a hydroxyethyl cellulose.

11. The pressure-sensitive copying paper assembly of claim **10** wherein the concentration of said electrolyte ranges from 0.2 to 5.0%, by weight, of the clay.

12. The pressure-sensitive copying paper assembly of claim **10** wherein the concentration of said electrolyte ranges from 0.5 to 5.0%, by weight, of the clay.

13. The pressure-sensitive copying paper assembly of claim **10** wherein the concentration of binder employed is 10.0–20.0% by weight, based upon the clay.

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