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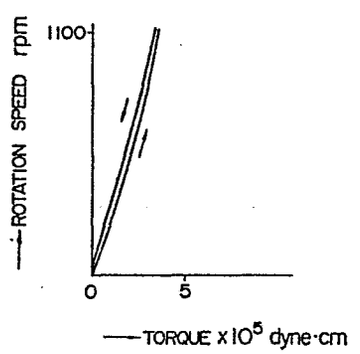
(54) **PROCESS FOR MANUFACTURING COLOR-DEVELOPING SHEET FOR IMAGE-RECORDING MATERIAL.**

(57) A process for manufacturing a color-developing sheet from a combination of an electron-donating colorless dye such as no-carbon pressure-sensitive recording material, heat-developable image-recording material using heat-sublimable colorless dye, heat-sensitive, color-transferring image-recording material, etc. and an electron-accepting color-developing agent which comprises preparing a coating solution containing at least an inorganic color-developing agent, calcium carbonate, and a bisphenol compound. This coating solution has a low viscosity and a good fluidity at high solids, concentration in spite of the use of inorganic color-developing agent which usually causes troubles such as gelation. Thus, it facilitates coating work and provides good color-developing power of the color-developing sheet, thus being excellent in printing properties.

FIG. 1



EP 0 160 106 A1

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SPECIFICATION

TECHNICAL FIELD

This invention relates to a proces for producing a color-developing sheet for image-recording materials. More particularly, the invention relates to a process for producing a color-developing sheet for image-recording materials, wherein, in production of a color-developing sheet for use in image-recording materials consisting of an electron-donating colorless dye and an electron-accepting color-developing agent, a preferable coating fluid is prepared to improve the production technique of said color-developing sheet for image-recording materials, said color-developing agent being particularly selected from inorganic color-developing agents such as an active clay (e.g. acid clay and activated clay) or a semi-synthetic solid acid produced by acid-treating a clay mineral having a layer structure consisting of regular tetrahedrons of silica so that the treated clay mineral has a SiO_2 content of 82 to 96.5% by weight on a dry basis (drying of 3 hr at 105°C), contacting the resulting clay mineral, in an aqueous medium, with a magnesium and/or aluminum compound at least partially soluble in said medium and, when the soluble compound is not a hydroxide, neutralizing the soluble compound with an alkali or acid so as to form a hydroxide,

to introduce a magnesium and/or aluminum component into the acid-treated clay mineral, and, if necessary, drying the resulting caly mineral.

BACKGROUND ART

As an image-recording material utilizing a color development reaction based on a combination use of an electron-donating colorless (leuco) dye and an electron-accepting color-developing agent, there are, as well known, non-carbon (or carbonless) pressure-sensitive recording materials as described in, for example, USP No. 2505470, USP No. 2550471, USP No. 2730456 and USP No. 3418250. These pressure-sensitive recording materials have an established history and have already developed into a large industry. There are other image-recording materials utilizing the same color development theory, such as, for example, thermally color-developing image-recording materials using a heat-sublimable colorless (leuco) dye [Japanese Patent Application Kokai (Laid-open) No. 149123/1977, Japanese Patent Application Kokai (Laid-open) No. 53538/1979, etc.], heat-sensitive, thermal transfer, image-recording materials and the like.

Non-carbon pressure-sensitive recording materials basically consist of a colorless (leuco) dye donor sheet (upper sheet) and a color-developing sheet (lower sheet). (Some of these materials include a middle sheet further or consist of a self-contained sheet.) The colorless (leuco) dye is, in many cases, dissolved in a high boiling solvent

and contained in microcapsules.

This encapsulation has been conducted by a coacervation method, an in-situ polymerization method, an interfacial polymerization method, etc. As the colorless (leuco) dye, there are used triarylmethanephthalides such as Crystal Violet Lactone, 3-3-bis(p-dimethylaminophenyl)-naphthalide and 3-(p-dimethylaminophenyl)-3-(2-methylindole-3-yl)-6-dimethylaminophthalide; acyrl (benzoyl, anisoyl, pivaloyl, etc.) derivatives of Methylene Blue; xanthene-phthalides such as 3-diethylamino-6-methyl-7-chlorofluoran, 3-diethylamino-7-dibenzylaminofluoran, 3-diethylamino-6-methylanilinofluoran, 3-methyl-cyclohexylamino-6-methyl-7-anilinofluoran and 3-ethyl-p-tolylamino-6-methyl-7-anilino-fluoran; and other leuco dyes.

As the high boiling solvent often used in non-carbon pressure-sensitive recording materials, there are aromatic hydrocarbons such as alkylnaphthalenes represented by diisopropylnaphthalene, diarylalkanes represented by 1-phenyl-1-xylylethane, alkylbiphenyls represented by isopropylbiphenyl, triaryldimethanes, alkylbenzenes, benzylnaphthalenes, diarylalkylenes, arylindanes and the like; carboxylic acid ester compounds such as dibutyl phthalate, dioctyl maleate and the like; phosphoric acid ester type compounds represented by tricresyl phosphate; natural animal and vegetable oils and fats such as castor oil, soy bean oil, cotton seed oil, whale oil and the like as well as their modified products; high boiling fractions (composed of aliphatic hydrocarbons) of natural products

such as mineral oils; and so forth.

With respect to the electron-accepting color-developing agent, there have been proposed and are already in actual use, for example, inorganic color-developing agents such as natural clay minerals (e.g. acid clay, attapulgite clay) and activated clay produced by simply subjecting an acid clay which is a montmorillonite type clay mineral, to mild or medium degree treatment with an inorganic acid (mineral acid) such as hydrochloric acid, nitric acid, sulfuric acid or the like, as well as organic color-developing agents such as pehol compounds, novolak type phenol resins, and aromatic carboxylic acids and their polyvalent metal salts.

Of these color-developing agents, novolak type phenol resins as well as substituted salicyclic acids (aromatic carboxylic acids) and their salts, which are all organic color-developing agents, are excellent in that they can be coated on a substrate sheet in the form of a coating fluid of high concentration and the resulting color-developing sheet gives a high density of developed color; however, they are slow in color-developing speed and the developed color image vanishes in contact with plasticizers for plastics or with oils. Further, they are poor in printability such as ink setting and are expensive because they are a product of organic synthesis. Meanwhile, inorganic color-developing agents are excellent in printability such as ink setting and inexpensive and accordingly attractive as an industrial material; however,

they have a big drawback in production of color-developing sheets using them. That is, it is difficult to prepare a coating fluid containing an inorganic color-developing agent because, in most cases, the coating fluid becomes a gel and accordingly, coating of an inorganic color-developing agent at a high concentration on a substrate sheet becomes impossible.

Activated clay as an inorganic color-developing agent is produced, as described in Japanese Patent Publication No. 2373/1966, Japanese Patent Publication No. 7622/1966 and Japanese Patent Publication No. 8811/1967, by treating acid clay or other similar mineral clay with a mineral acid to dissolve and extract basic components soluble in the acid such as aluminum, iron and the like and to allow the treated clay to possess a surface area of 200 m^2/g or larger. Activated clay is amorphous when observed through X-rays and has a large specific surface area and thus its properties are greatly different from those of clays used for coating of ordinary papers. In actual dispersion of activated clay in water, a large amount of water is required because of the unique particle shape and surface activity of activated clay.

Kaolin which is a typical clay used for paper coating, when dispersed in water, can retain fluidity until the solid content in the dispersion increases to 70% or higher. In contrast, activated clay, when dispersed in water, loses fluidity because of high viscosity and causes gelation already when the solid content in the dispersion

reaches about 40%.

Coating of a coating fluid containing a color-developing agent at a concentration as high as possible is desired in view of productivity and energy saving. However, inorganic color-developing agents such as activated clay and the like, because preparation of a coating fluid containing such a color-developing agent at a high concentration is very difficult as mentioned above, is currently coated, in most cases, in the form of a low concentration fluid (for example, solid content: about 30%) by the use of an air knife coater.

As a method for producing a coating fluid containing an inorganic color-developing agent at a high concentration, there is described in Japanese Patent Application Kokai (Laid-open) No. 2608/1977, a method wherein calcium carbonate or kaolin is added to activated clay. According to the experiment by the present inventors, this method certainly provides a slightly high concentration fluid; however, the fluid tends to cause gelation, has insufficient fluidity and accordingly is not suited for practical application.

In Japanese Patent Application Kokai (Laid-open) No. 97782/1980, there is described a method wherein a magnesium compound is added to activated clay. This method is not sufficient due to the same reasons as mentioned above. Also, there is described a method wherein a latex type binder is added to activated clay before the activated clay is mixed with water. According to the experiment by

the present inventors, in order to obtain nearly complete dispersion of activated clay, a strong stirring force is required, which causes destruction of latex emulsion by a high viscosity and a temperature increase, reduction of surface strength of a coated sheet and deterioration of printability. Thus, this method can bot be put into practical application.

The object of the present invention is to develop a coating fluid for color-developing sheets using an inorganic color-developing agent which is low in viscosity, has good fluidity and enables high concentration coating, as well as to produce a color-developing sheet of excellent printability by using said coating fluid.

DISCLOSURE OF THE INVENTION

According to the present invention, in production of an image-recording material consisting of an electron-donating colorless dye and an electron-accepting color-developing agent capable of allowing said colorless dye to develop a color, a coating fluid is prepared which comprises at least an inorganic color-developing agent, calcium carbonate and a bisphenol compound. By adding the inorganic color-developing agent with calcium carbonate and the bisphenol compound in combination and each in a relatively small amount, there can be prepared a coating fluid having a sufficiently reduced viscosity, a high solid content and good fluidity. The color-developing sheet produced by coating the coating fluid on a substrate has sufficient color develop-

ability and is excellent in printability, etc.

BRIEF DESCRIPTION OF DRAWINGS

Fig. 1 is a rheological diagram of the coating fluid of Example of the present invention.

Fig. 2 is a rheological diagram of the coating fluid of Comparative Example 1.

Fig. 3 is a rheological diagram of the coating fluid of Comparative Example 2.

Fig. 4 is a rheological diagram of the coating fluid of Comparative Example 3.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention can be applied to all image-recording materials utilizing a color-developing reaction between an electron-donating colorless (leuco) dye and an electron-accepting color-developing agent, such as non-carbon pressure-sensitive recording materials, thermally color-developing image-recording materials using a heat-sublimable colorless (leuco) dye, heat-sensitive, thermal transfer, image-recording materials and the like. Accordingly, although the present specification described in detail mainly the effects on a production process of a color-developing sheet for non-carbon pressure-sensitive recording materials, the invention can of course be applied also to other image-recording materials. While the non-carbon pressure-sensitive recording materials consist basically of an upper sheet and a lower sheet, the present invention can be applied also to a middle sheet, a self-

contained sheet, etc.

Of inorganic color-developing agents usable in the present invention, particularly recommended is a semi-synthetic solid acid obtained by the production process proposed in Japanese Patent Application Kokai (Laid-open) No. 15996/1982.

This semi-synthetic solid acid is an inorganic color-developing agent of new type produced by acid-treating a clay mineral having a layer structure consisting of regular tetrahedrons of silica so that the treated clay mineral has a SiO_2 content of 82 to 96.5% by weight, preferably 85 to 95% by weight on a dry basis (drying of 3 hr at 105°C), contacting the resulting clay mineral, in an aqueous medium, with a magnesium and/or aluminum compound at least partially soluble in said medium and, when the soluble compound is not a hydroxide, neutralizing the soluble compound with an alkali or acid so as to form a hydroxide, to introduce a magnesium and/or aluminum component into the acid-treated clay mineral, and, if necessary, drying the resulting clay mineral.

This color-developing agent is called "semi-synthetic solid acid" in the present specification.

The semi-synthetic solid acid is produced by a novel process. The acid-treated clay mineral mentioned above, when measured by X-ray diffraction and electron rays diffraction, does not substantially show a diffraction pattern as given by a layer structure crystal consisting of regular tetrahedrons of silica, of the above mentioned

clay mineral before acid treatment. Meanwhile, the acid-treated clay mineral into which a magnesium and/or aluminum component has been introduced, when measured by electron rays diffraction, shows a diffraction pattern as given by said layer structure crystal consisting of regular tetrahedrons of silica, but, when measured by X-ray diffraction, shows no such diffraction pattern as given by said layer structure crystal.

The semi-synthetic solid acid is a new type of color-developing agent which can greatly improve the drawbacks of conventional color-developing agents of clay mineral type represented by acid clay and activated clay, namely, insufficient density of developed color and reduction of density of developed image under high humidity conditions.

The present inventors found that, when a coating fluid containing a low concentration of an inorganic color-developing agent, particularly, the new type of the color-developing agent, namely, the semi-synthetic solid acid produced as above is prepared and a color-developing sheet is produced with the coating fluid, the color-developing sheet gives a higher density of developed color and lessens reduction of density of developed image under high humidity conditions. The present inventors also found that, when there is prepared a coating fluid containing a high concentration of the semi-synthetic solid acid, the coating fluid, as often seen in coating fluids containing conventional type activated clay, has a high viscosity, causes gelation and possesses no fluidity leading to low productivity.

Hence, the present inventors conducted extensive research in order to look for a substance which can improve the fluidity of a coating fluid containing a high concentration of one of inorganic color developers, a semi-synthetic solid acid. As a result, it was found that, by adding to a semi-synthetic solid acid as a color-developing agent calcium carbonate and a bisphenol compound in combination, there can be obtained a coating fluid containing a high concentration of a semi-synthetic solid acid which has a low viscosity and accordingly fluidity, and that the color-developing sheet produced with the coating fluid causes neither reduction of density of developed image under high humidity conditions nor vanishing of developed image in contact with plasticizers or oils and moreover has excellent printability. This novel knowledge has led to the present invention.

The calcium carbonate used in the present invention has no particular restriction. It is a white pigment called HAKUENKA (TRADE MARK) in some cases, used for paper coating and can be selected from heavy calcium carbonate and light calcium carbonate. If boldly said, light calcium carbonate gives a better result.

Calcium carbonate is added preferably in an amount of 2.5 to 40 parts by weight and particularly preferably in an amount of 5 to 30 parts by weight based on 100 parts by weight of inorganic color-developing agent. When it is added in an amount smaller than 2.5 parts by weight, the addition is not effective for reduction in viscosity of

coating fluid. When it is added in an amount larger than 40 parts by weight, such addition reduces the density of developed color.

As the bisphenol compound used in the present invention, there are, for example, 4,4'-isopropylidenediphenol, 4,4'-cyclohexylidenediphenol, bis(4-hydroxyphenyl) sulfone, thiobis(3-methyl-6-t-butylphenol), 4,4'-butylidenebis(3-methyl-6-t-butylphenol), 2,2'-methylenebis(4-methyl-6-t-butylphenol), etc. Particularly preferable is bis(4-hydroxyphenyl)sulfone.

The bisphenol compound is added preferably in an amount of 2.5 to 40 parts by weight and particularly preferably in an amount of 10 to 30 parts by weight based on 100 parts by weight of inorganic color-developing agent.

When the bisphenol compound is added in an amount smaller than 2.5 parts by weight, the addition is not effective for reduction in viscosity of coating fluid. When it is added in an amount larger than 40 parts by weight, the addition hinders color development and reduces the density of developed color.

The bisphenol compound is added to an inorganic color-developing agent after the compound has been ground and dispersed in a small amount of a dispersing agent by the use of a wet grinder such as a ball mill, an attritor, a sand grinder or the like.

The present invention is characterized in that a coating fluid is prepared by adding to an inorganic color-developing agent at least calcium carbonate and a bisphenol

compound in combination. Addition of calcium carbonate or a bisphenol compound alone reduces the viscosity of the coating fluid slightly but insufficiently. In order to sufficiently reduce the viscosity of a coating fluid by addition of calcium carbonate or a bisphenol compound alone, the addition amount becomes very large, which induces the low content of an inorganic color-developing agent in the color-developing layer of the color-developing sheet produced with the coating fluid and this reduces the color developability of the sheet and impairs the printability; thus, such a coating fluid can not be used practically.

In contrast, when calcium carbonate and a bisphenol compound are added in combination, although the reason is not clarified yet, their addition each in a relatively small amount gives a coating fluid of sufficiently low viscosity, of good fluidity and yet of high solid content (for example, 40% or above). Further, the color-developing sheet produced with the coating fluid has sufficient color developability and is excellent in printability, etc.

According to the present invention, to an inorganic color-developing agent are added calcium carbonate and a bisphenol compound in combination; thereto are further added an inorganic dispersing agent (e.g. sodium tripolyphosphate, sodium hexametaphosphate, sodium pyrophosphate, sodium silicate), an organic dispersing agent (e.g. a carboxylic acid type such as acrylic acid salt, a maleic acid type such as styrene maleic anhydride salt, a sulfonic

acid type such as naphthalenesulfonic acid salt), a water-soluble binder (e.g. starch, a polyvinyl alcohol), an emulsion binder (e.g. a styrene-butadiene rubber latex, an acrylic type latex) and additives (a dusting-preventing agent, a defoamant) to obtain a high concentration coating fluid containing 40% or more of solid; and this coating fluid is coated on a substrate sheet such as a paper industrially desirably by the use of a blade coated and then dried to obtain a color-developing sheet for image-recording materials.

In the present invention, as necessary, there may further be added to the coating fluid a pigment such as clay, kaolin, magnesium carbonate, satin white, titanium oxide, zinc oxide, an urea resin pigment, a plastic pigment, talc, alumina, aluminum hydroxide and the like.

According to the present invention, the dispersibility and fluidity of an inorganic color-developing agent in water has been greatly improved, whereby preparation of a coating fluid of low viscosity as well as coating of an inorganic color-developing agent on a substrate sheet at a high concentration have become possible and accordingly coating operation, energy consumption and productivity have been improved. Moreover, the color-developing sheet produced with such a coating fluid possesses improved printability as represented by improved surface quality, good surface smoothness, lower smudge (lower staining by color development due to rubbing) and improved surface strength.

Incidentally, the addition order of chemical substances in preparation of a coating fluid is not restricted. Any coating fluid comprising at least an inorganic color-developing agent, calcium carbonate and a bisphenol compound is included in the coating fluids used in the present invention.

As mentioned previously, an inorganic color developing agent particularly recommended in the present invention is a semi-synthetic solid acid described in Japanese Patent Application Kokai (Laid-open) No. 15996/1982. Not only this agent but also other inorganic color-developing agents adsorb a colorless (leuco) dye on their surfaces and thereby develop a color. Accordingly, a large surface area per unit weight gives a higher efficiency of color development. In other words, the smaller the particle diameters of a color-developing agent, the better the color development. However, as the surface area gets larger (the particle diameters get smaller), the coating fluid has a higher viscosity and preparation of a coating fluid containing an inorganic color-developing agent at a high concentration becomes difficult.

The present invention exhibits the best effects when an inorganic color-developing agent having particle diameters as small as possible is used for improvement of color development efficiency and there is prepared a high concentration coating fluid having fluidity and causing no gelation for energy saving and productivity improvement. As the coater used at this time, a blade coater is best.

Its use also allows high speed coating, safety and hygiene of working environments and good surface condition of coated sheet.

Conventional inorganic color-developing agents have ordinarily used particle diameters of 5 to 6 μ cut (particles which pass through a mesh of 5 to 6 μ). While, in the present invention, there can be used an inorganic color-developing agent having particle diameters of 4 μ cut and, even with an inorganic color-developing agent having particle diameters of 3.5 μ, preparation of a coating fluid as well as its coating by a blade coater is possible.

Next, there is described a process for producing a color-developing (agent) sheet [colorless (leuco) dye donor sheet] for blue color development which is used in the example of the present invention. All parts shown below are parts by weight.

Process for producing a color-developing (agent) shet for blue color development.

3.5 parts of Crystal Violet Lactone which is a colorless (leuco) dye and 1 part of Malachite Green Lactone were dissolved in 100 parts of a diarylethane type organic solvent which is a high boiling solvent. The resulting solution was added to 160 parts of an aqueous solution containing 10% of an acid-treated gelatin (isoelectric point: 7.8) and the mixture was made an emulsion.

This emulsion was added to a solution produced by dissolving 20 parts of gum arabic in 1,500 parts of water. The mixture was adjusted to a pH of 8.5 with sodium

hydroxide, kept at 50°C, adjusted to a pH of 4.4 with acetic acid, and cooled to 10°C. Thereto was added 20 parts of an aqueous solution containing 37% formalin, and the mixture was stirred for 24 hr. Then, the mixture was adjusted to a pH of 10 with sodium hydroxide to obtain microcapsules.

To 100 parts (as solid) of the microcapsules were added 50 parts of an aqueous solution containing 10% of a polyvinyl alcohol and 30 parts of wheat starch. The mixture was coated on a plain paper of 40 g/m^2 by the use of an air knife coater so that the coated amount became 5 g/m^2 (as solid). The coated paper was dried to obtain a color-developing (agent) sheet for blue color development.

The preferable embodiment and excellent effects of the present invention will specifically be explained below by way of the most representative example.

Example

A 40% bisphenol compound dispersion was prepared by subjecting 100 parts of bis(4-hydroxyphenyl)sulfone, 5 parts of sodium polymethacrylate and 145 parts of water (250 parts in total) to grinding by a ball mill for 2 days.

To 55 parts of water were added 2 parts of an aqueous solution containing 30% of sodium silicate and 100 parts of an aqueous solution containing 10% of an oxidized starch, and they were stirred. Thereto was added 10 parts of light calcium carbonate and it was dispersed therein. Then, 37.5 parts of the above prepared 40% bis(4-hydroxyphenyl)sulfone dispersion was added and the mixture was

stirred. Thereafter, 100 parts of a semi-synthetic solid acid was slowly added and dispersed with stirring, after which 20 parts of a 50% styrene-butadiene rubber latex was added and the resulting mixture was stirred to obtain a coating fluid. This coating fluid had a solid content of 45% and good fluidity as stated later. When the coating fluid was coated on a plain paper of 40 g/m^2 by the use of a blade coater so that the coated amount became 5 g/m^2 (as solid) and dried, the coating and drying operations were smooth and a good color-developing sheet was obtaied.

Comparative Example 1

To 45 parts of water were added 2 parts of an aqueous solution containing 30% of sodium silicate and 100 parts of an aqueous solution containing 10% of an oxidized starch, and they were stirred. Thereto was slowly added 100 parts of a semi-synthetic solid acid with stirring and it was dispersed. Then, 20 parts of a 50% styrene-butadiene rubber latex was added and the resulting mixture was stirred to obtain a coating fluid. This coating fluid was coated on a plain paper of 40 g/m^2 by the use of a blade coater so that the coated amount became 5 g/m^2 (as solid) and then dried to obtain a color-developing sheet. The coating fluid was very viscous and poor in fluidity; therefore, its coating was difficult.

Comparative Example 2

To 77 parts of water were added 2 parts of an

aqueous solution containing 30% sodium silicate and 100 parts of an aqueous solution containing 10% of an oxidized starch. Thereto was added 25 parts of light calcium carbonate and it was dispersed. Further, 100 parts of a semi-syntehtic solid acid was slowly added with stirring and dispersed. Thereafter, 20 parts of a 50% styrene-butadiene rubber latex was added and the resulting mixture was stirred to obtain a coating fluid. This coating fluid was coated on a plain paper of 40 g/m^2 by the use of a blade coater so that the coater amount became 5 g/m^2 (as solid) and then dried to obtain a color-developing sheet. The coating fluid had a high viscosity and poor fluidity; therefore, its coating was difficult.

Comparative Example 3

To 40 parts of water were added 2 parts of an aqueous solution containing 30% of sodium silicate and 100 parts of an aqueous solution containing 10% of an oxidized starch, and they were stirred. Thereto was added 50 parts of the 40% bis(4-hydroxyphenyl)sulfone dispersion prepared in Example and they were stirred. Then, 100 parts of a semi-synthetic solid acid was slowly added with stirring and dispersed. Further, 20 parts of a 50% styrene-butadiene rubber latex was added, and the resulting mixture was stirred to obtain a coating fluid. This coating fluid was coated on a plain paper of 40 g/m^2 by the use of a blade coater so that the coated amount became 5 g/m^2 (as solid) and then dried to obtain a color-developing sheet. The

coating fluid had a high viscosity and poor fluidity and its coating was difficult.

Test method

The coating fluids and color-developing sheets thus obtained were subjected to measurements according to the following methods.

Coating fluid

o Viscosity

A viscometer of B type manufactured by Tokyo Keiki was used. A value right after 1 min of rotating at 60 rpm by the use of a No. 4 rotor was measured. Figs. 1, 2, 3 and 4 show viscosity curves obtained using a Hercules II type high shear viscometer manufactured by Nihon Rigaku Kogyo.

o Solid content

Drying was conducted for 16 hr at 105°C to measure the solid content of a coating fluid

Color-developing sheet

o Density of developed color

A color-developing sheet was superimposed on the previously mentioned color-forming (agent) sheet and they were passed through a calender to develop a color. Using a color difference meter, the density of the color as defined by the following formula was measured. When a density of developed color has a smaller value, the density

is higher.

Density of developed color (%)

$$= \frac{\text{Reflectance of color-developed portions}}{\text{Reflectance of background portion}} \times 100$$

o Smoothness

Measurement was made using a Beck smoothness tester. A larger value (expressed in seconds) means better smoothness.

o Smudge (Staining by developed color due to rubbing)

A color-developing sheet was superimposed on the previously mentioned color-forming sheet, and they were rubbed against each other with a weight placed on them. The staining of the color-developing sheet was measured as a reflectance (%) using a color difference meter. Accordingly, a high smudge value means lower staining.

o Surface strength (Printability test)

Measurement was made using an IGT tester. The strength obtained was expressed by o, Δ, or x (o is good and x is poor).

Test results

o Charactersitics of coating fluids

Table 1

	Viscosity, cps	Solid content, %	Fluidity
Example	510	45.1	Very good
Comparative Example 1	10,000 or above	45.0	No fluidity due to gelation
Comparative Example 2	2,880	45.2	Gelation
Comparative Example 3	2,350	45.1	Gelation

As a obvious from Table 1, the coating fluid of the Example of the present invention, as compared with the coating fluids of Comparative Examples 1, 2 and 3, has about the same solid content (%) but a far smaller viscosity.

As is also obvious from Figs. 1, 2, 3 and 4, the coating fluid of Comparative Examples 1, 2 and 3, as compared with the coating fluid of Example, have higher viscosities at high rotation speeds and even at low rotation speeds, have higher viscosities and are in a gel state.

Coating of the coating fluids of Comparative Examples 1, 2 and 3 by a blade coater was very difficult due to high viscosity and gelation.

o Characteristics of color-developing sheets

Table 2

	Density of developed color (%)	Smoothness (sec)	Smudge (%)	Surface strength
Example	23.8	97	95.0	o
Comparative Example 1	24.0	33	83.3	x
Comparative Example 2	25.4	41	90.7	Δ
Comparative Example 3	24.7	42	91.0	Δ

As is obvious from Tables 1 and 2 and Figs. 1, 2, 3 and 4, in production of a color-developing sheet using a semi-synthetic solid acid, use of calcium carbonate and a bisphenol compound in combination in a coating fluid containing said solid acid is very effective for the viscosity and fluidity of said coating fluid as well as for the smoothness, smudge and surface strength of a color-developing sheet produced with said coating fluid.

INDUSTRIAL APPLICABILITY

As stated above, the process for producing a color-developing sheet for image-recording materials according to the present invention can be used for production of a color-developing sheet for use in image-recording materials consisting of an electron-donating colorless dye

and an electron-acception color-developing agent, particularly, an inorganic color-developing agent excellent in printability and advantageous in cost such as an active clay, namely, a so-called semi-synthetic solid acid (e.g. acid clay and activated clay). This color-developing sheet can effectively be used in non-carbon pressure-sensitive recording materials, thermally color-developing image-recording materials using a heat-sublimable colorless dyes, heat-sensitive, thermal transfer, image-recording materials, etc.

WHAT IS CLAIMED IS:

1. A process for producing a color-developing sheet for image-recording materials consisting of an electron-donating colorless dye and an electron-accepting color-developing agent capable of allowing said colorless dye to develop a color, the process being characterized by preparing a coating fluid comprising at least an inorganic color-developing agent, calcium carbonate and a bisphenol compound, coating the coating fluid on a substrate sheet and drying the coated sheet.

2. A process for producing a color-developing sheet for image-recording materials according to Claim 1, wherein the inorganic color-developing agent is a semi-synthetic solid acid produced by acid-treating a clay mineral having a layer structure consisting of regular tetrahedrons of silica so that the treated clay mineral has a SiO_2 content of 82 to 96.5% by weight on a dry basis (drying of 3 hr at 105°C), contacting the resulting clay mineral, in an aqueous medium, with a magnesium and/or aluminum compound at least partially soluble in said medium and, when the soluble compound is not a hydroxide, neutralizing the soluble compound with an alkali or acid so as to form a hydroxide, to introduce a magnesium and/or aluminum component into the acid-treated clay mineral, and, if necessary, drying the resulting clay mineral.

3. A process for producing a color-developing sheet for image-recording materials according to Claim 1, wherein the bisphenol compound is bis(4-hydroxyphenyl)sulfone.

4. A process for producing a color-developing sheet for image-recording materials according to Claim 1, wherein coating is conducted by a method using a blade coater.

5. A process for producing a color-developing sheet for image-recording materials according to Claim 1, wherein the inorganic color-developing agent is a powder having particle diameters substantially of 4 μ or less.

6. A process for producing a color-developing sheet for image-recording materials according to Claim 1, wherein the coating fluid comprising at least an inorganic color-developing agent, calcium carbonate and a bisphenol compound has a solid content of 40% by weight or more.

FIG. 1

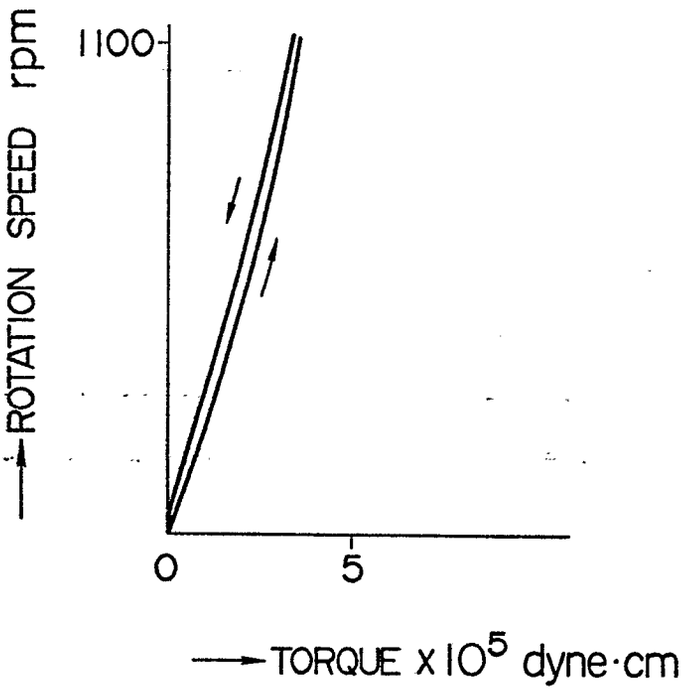

1100
ROTATION SPEED rpm
0
5
TORQUE x 10^5 dyne·cm

FIG. 2

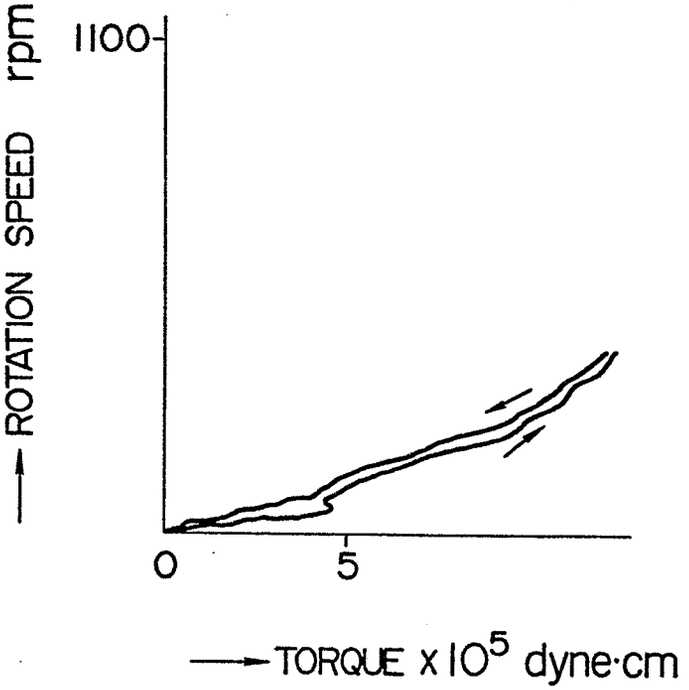

1100
ROTATION SPEED rpm
0
5
TORQUE x 10^5 dyne·cm

FIG. 3

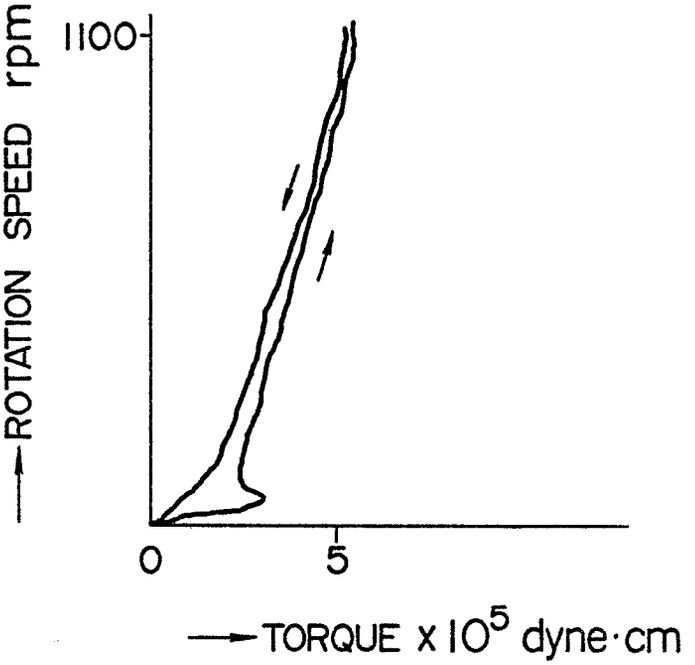
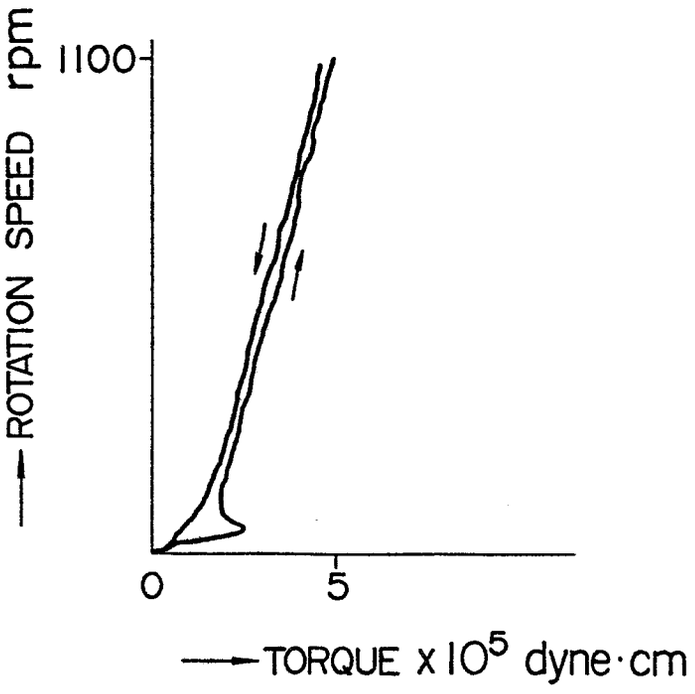

1100
ROTATION SPEED rpm
0
5
TORQUE x 10^5 dyne·cm

FIG. 4


1100
ROTATION SPEED rpm
0
5
TORQUE x 10^5 dyne·cm

INTERNATIONAL SEARCH REPORT

International Application No. PCT/JP84/00518 0160106

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[4] B41M 5/12

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
IPC	B41M 5/12 - 5/22

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

Jitsuyo Shinan Koho 1926 - 1983
Kokai Jitsuyo Shinan Koho 1971 - 1983

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category*	Citation of Document, [15] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	JP, B1, 48-33210 (Fuji Photo Film Co., Ltd.) 12 October 1973 (12. 10. 73) & GB, A, 1309512 & US, A, 3856553	1, 4
A	JP, A, 52-2608 (Moore Business Forms, Inc.) 10 January 1977 (10. 01. 77) & BE, A, 843016 & NL, A, 7606737 & DE, A, 2623802 & FR, A, 2314834 & US, A, 4042412 & AU, A, 1330076 & GB, A, 1524900 & CH, A, 623876	1 - 6
X	JP, A, 56-127486 (Fuji Photo Film Co., Ltd.) 6 October 1981 (06. 10. 81) (Family nashi)	1, 3, 4, 6
A	JP, A, 57-15996 (Mizusawa Kagaku Kogyo Kabushiki Kaisha) 27 January 1982 (27. 01. 82) & EP, A, 44645 & US, A, 4405371	2

* Special categories of cited documents: [16]

"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]
January 16, 1985 (16. 01. 85)	January 28, 1985 (28. 01. 85)
International Searching Authority [1]	Signature of Authorized Officer [20]
Japanese Patent Office	

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

A	JP, A, 56-113493 (Mitsubishi Paper Mills, Ltd.) 7 September 1981 (07. 09. 81) (Family nashi)	1 - 6

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers....., because they relate to subject matter [13] not required to be searched by this Authority, namely:

2. ☐ Claim numbers....., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [12], specifically:

VI. ☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.