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(54) Clay mineral-type color developer composition for pressure-sensitive recording sheets.

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Description

This invention relates to a color developer composition which demonstrates pronounced color development effects when used in making pressure-sensitive recording sheets which can produce copies by handwriting, printing or typing without the use of conventional carbon paper.

Pressure-sensitive recording sheets, except a few special cases, utilize a color development reaction ascribable to the transfer of electrons between a colorless organic dye compound having electron donating property and a color developer acting as an electron acceptor (U.S. Patent No. 2,5-48,366).

Generally, two kinds of dyes which assume different states of coloration are used together as the colorless dye compound. One of them is a dye, such as a triphenylmethane phthalide dye, which forms an intense color immediately upon contact with a solid acid, but the color fades easily (primary color-forming dye). The other is a dye which does not immediately form a color upon contact with a solid acid but completely develops its color several days thereafter with sufficient fastness to sunlight. An example is a leucomethylene blue dye (secondary color-forming dye).

Crystal violet lactone (CVL) is a typical primary color-forming dye. As the secondary color-forming dye, benzoyl leucomethylene blue (BLMB) is widely used.

In recent years, fluoran-type green or black dyes, Michler's hydrol derivatives such as Michler's hydryl-para-toluenesulfinate (PTSMH), diphenylcarbazolylmethane dyes and spirodibenzopyran dyes have also been used either singly or in combination with the aforesaid primary color-forming dye.

Solid acids are generally used as the color developer which is an electon acceptor. It is known that above all, dioctahedral montmorillonite clay minerals show excellent color-developing ability. Acid clay and sub-bentonite are especially preferred as the dioctahedral montmorillonite clay minerals.

It has been known that the specific surface area of montmorillonite clay minerals such as acid clay and sub-bentonite can be increased to 180 m^2/g or higher by treating them with acids, and the acid-treated clay minerals exhibit increased color-developing ability with respect to primary color-forming dyes such as triphenylmethane phthalide dyes. For instance, the acid-treated acid clay is generally referred to as activated acid clay, and known widely as a coloring developer for pressure-sensitive recording paper.

Both inorganic and organic acids can be used in the acid treatment, but inorganic acids, particularly sulfuric and hydrochloric acids, are preferred because of their reasonable cost and the ease of handling.

The acid-treating conditions are not critical. If a diluted acid is used, either the treating time becomes longer or the quantity of the required acid increases. On the other hand, if an acid of high concentration is used, either the treating time becomes shorter or the quantity of the acid required becomes smaller. If the treating temperature is high, the treating time can be shortened. Hence, the acid concentration can be freely selected within the range of 1 to 98%. It is known however that in practice, the acid treatment is preferably carried out at an acid concentration of about 15 to 80% and at a temperature of 50 to 300°C because of the ease of handling.

JP-A-55-103994 and JP-A-55-97982 describe the use of magnesium compounds, such as the hydroxide or carbonate, to improve the storage stability of acid-treated clays, including montmorillonite clay intended for use as color developers.

EP-A-44645 discloses a color developer composition for pressure-sensitive recording sheets, comprising a color developer (1) which is derived from a clay mineral having a layer structure composed of regular tetrahedrons of silica and which shows after intense acid treatment and subsequent reconstruction of said layer structure

(A) a diffraction pattern attricutable to the crystals of layer structure composed of regular tetrahedrons of silica when subjected to an electron diffraction analysis, but

(B) substantially no diffraction pattern attribuable to the crystals of said layer structure when subjected to an X-ray diffraction analysis, and which

(C) contains at least silicon and magnesium and/or aluminium in addition to oxygen.

The present invention provides a color developer composition for pressure-sensitive recording sheets, comprising

(1) a said color developer (1) which contains magnesium and/or aluminium, any said magnesium content not being soluble in aqueous ammonium chloride solution,

(2) optionally color developer having a silica content of not more that 80% on a dry weight basis and composed of a dioctahedral montmorillonite clay mineral treated with an acid or a mixture of it with a naturally occurring dioctahedral montmorillonite clay mineral, said colour developer (2)

(D) showing a diffraction pattern attributable to the crystals of said layer structure when subjected to an X-ray diffraction analysis,

(3) 0.2 to 2 millimoles, per gram of the components (1), (2) when present, and (3) combined, of at least one metal compound selected from the oxide and hydroxides of calcium and zinc.

The attached drawing is a graph showing the relation of the mole ratio between two metal compound used in accordance with this invention to the light resistances of a colored dye.

Figure 1 is a graph showing the relation of the mole ratio between calcium hydroxide and zinc oxide to the light resistance of a colored dye in Example 2 to 6. The total amount of the two metal compounds per gram of the color developer is 0.1 millimole for curve *a*, 0.2 millimole for curve *b*, 0.4 millimole for curve *c*, 0.6 millimole for curve *d*, 0.8 millimole for curve *e*, 1.0 millimole for curve *f*, and 2.0 millimoles for curve *g*.

The dotted lines in Figure 1 shows the levels of the light resistance of colored dyes in Comparative Examples 1a, 2 and 1b, respectively.

Color developer (1)

The color developer (1) and a method of its production are disclosed in detail in EP-A-44645.

The color developer (1) in accordance with this invention can be produced, for example, through the steps of acid-treating a clay mineral having a layered structure composed of regular tetrahedrons of silica until its SiO_2 content reaches 82-96.5% by weight, preferably 85-95% by weight on dry basis (drying at 105°C. for 3 hours) (referred to as the first step for convenience), and then contacting the resulting clay mineral, in an aqueous medium, with a magnesium and/or aluminum compound, neutralizing the treated product with an alkali or an acid to form a hydroxide when the magnesium and/or aluminum compound is not a hydroxide, thereby introducing a magnesium and/or an aluminum component into the acid-treated clay mineral, and if desired, drying the product (referred to as the second step for convenience).

The compositions of typical clay minerals having the layer structures composed of regular tetrahedrons of silica are as shown in Table A below, in which the contents (%) of SiO_2, Al_2O_3 and MgO as the main components are given.

Table A

	SiO_2	Al_2O_3	MgO
Dioctahedral montmorillonite (acid clay, bentonite, etc.)	50 - 70	15 - 22	1 - 5
Kaolin	40 - 50	32 - 40	0 - 1
Halloysite	35 - 45	32 - 40	0 - 1
Attapulgite	50 - 60	5 - 12	5 - 12

These clay minerals having a layer structures composed of regular tetrahedrons of silica show a unique diffraction pattern characteristic of the crystals of the layer structure, when subjected to an X-ray diffraction analysis. In particular, a diffraction pattern attributable to the crystal faces having Miller's indices of (020), (200) and (060) appears most distinctly.

According to the present invention, the clay mineral having a layer structure composed of regular tetrahedrons of silica is intensely acid-treated until its SiO_2 content reaches 82-96.5% by weight, preferably 85-95% by weight, on dry basis (drying at 105°C. for 3 hours).

The acid treatment should be performed until not only the X-ray diffraction analysis but also an electron diffraction analysis of the acid-treated clay mineral no longer substantially show the characteristic diffraction patterns attributable to the crystals of the layer structure composed of regular tetrahedrons of silica which the untreated clay mineral has.

The clay mineral which has been acid-treated as above is then contacted in an aqueous medium with a magnesium and/or an aluminum compound. If the magnesium and/or aluminum compound is not a hydroxide, the contacted product is neutralized with an alkali or acid so that a hydroxide of magnesium and/or aluminum is formed therein, thereby introducing a magnesium and/or aluminum component into the acid-treated clay mineral. The product is thereafter dried, if desired.

Preferably, the color developer (1) used in this invention contains at least silicon and magnesium in addition to oxygen in regard to the requirement (C).

Preferably, the color developer (1) used in this invention, which satisfies the conditions (A), (B) and (C), further meets the requirement that it contains silicon and magnesium and/or aluminium in such proportions that the atomic ratio of silicon to magnesium and/or aluminum is from 12:1.5 to 12:12, particularly from 12:3 to 12:10 [requirement D].

Typical examples of the clay mineral of a layer structure composed of regular tetrahedrons of silica which is used as a raw material for the production of the color developer (1) are given below.

1) Dioctahedral and trioctahedral montmorillonite clay minerals such as acid clay, bentonite, beidellite, nontronite and saponite;
2) kaolinite clay minerals such as kaolin, halloysite, dickite and nacrite;
3) sepiolite-palygorskite clay minerals such as sepiolite, attapulgite and palygorskite;
4) chlorite clay minerals such as leuchtenbergite, sheridanite, thuringite and chamosite; and
5) vermiculite clay minerals such as vermiculite, magnesium vermiculite and aluminum vermiculite.

Preferred among them are dioctahedral montmorillonite clay minerals such as acid clay, kaolinite clay minerals such as kaolin and halloysite, and chain clay minerals such as attapulgite.

As already mentioned, it has been the long practice to use the color developer (2), i.e., montmorillonite clay minerals, particularly acid clay, which have been treated with mineral acids such as sulfuric, nitric and hydrochloric acids, most commonly sulfuric acid, as a color developer, for pressure-sensitive recording sheets.

When an acid clay is treated with such a mineral acid as mentioned above, the acid-soluble basic metal components in the developer, for example, such metal components as aluminum, magnesium, iron, calcium, sodium, potassium and manganese (which are present predominantly in the form of oxides or hydroxides) dissolve in the mineral acid, and consequently the SiO_2 content of the acid clay increases.

If the acid treatment is performed to a high degree (intensely) to dissolve and remove too much of the basic metal components, the resulting acid-treated acid clay (which also known as activated acid clay) decreased in its color-developing ability with respect to a secondary color development, and the light resistance of a developed color of a primary color development dye (e.g., CVL) in the main is markedly deteriorated.

Accordingly, the degree of acid treatment of acid clay is inherently limited, and under the conventionally adopted acid-treating conditions, the resulting acid-treated product (activated clay) has a SiO_2 content of 68-78% by weight. Even under considerably rigorous acid-treating conditions, the SiO_2 content is at most 80% by weight.

On the other hand, it has been known of old that the aforementioned montmorillonite clay minerals, kaolinite clay minerals, sepiolite-palygorskite clay minerals, chlorite clay minerals and vermiculite clay minerals have crystals of layer structure composed of regular tetrahedrons of silica, and hence, when examined by X-ray (or electron) diffraction analysis, they give unique diffraction patterns ascribable to the crystals of layer structure [Mineralogical Society (Clay Mineral Group), London, 1961, The X-Ray Identification and Crystal Structures of Clay Minerals, ed. by G. Brown].

When those clay minerals having the crystals of layer-structure composed of regular tetrahedrons of silica are acid-treated to such an advanced degree that their SiO_2 contents reach 82-96.5% by weight, particularly 85-95%: by weight, on dry basis (e.g., after a drying at 105°C. for 3 hours), their crystals of layer-structure composed of regular tetrahedrons of silica are gradually destroyed as the acid treatment progresses, until, when the SiO_2 content reaches 82% by weight or higher, particularly 85% by weight or higher, the treated clay minerals no longer show the diffraction pattern characteristic of the crystals of such layer-structure in X-ray (or electron) diffraction analysis.

Of course, the correlations among the degree of acid treatment, destruction of the crystals having the layer-structure and the ultimately occurring substantial disappearance of the characteristic diffraction patterns vary depending on the type and purity of clay minerals, pre-treating conditions which may be applied before the acid treatment (e.g., sintering and grinding conditions), etc. and are by no means definite. In all cases, however, as the acid treatment proceeds beyond a certain degree, the destruction of crystals having the layer-structure begins and progresses to result ultimately in the substantial disappearance of the diffraction patterns attributable to the aforesaid crystals.

In acid-treating, for example, montmorillonite clay minerals for making a color developer [color developer (2) used in the invention] for pressure-sensitive recording paper, it has been previously considered essential to select such acid-treating conditions as would not cause destruction of crystalline structure of the clay minerals, because otherwise the color-developing ability of the color developer would be seriously reduced [e.g., Journal of Industrial Chemistry (Kogyo Kagaku Zasshi), Vol. 67, no. 7 (1964) pp. 67-71].

As described above the color developer (1) can be produced by a method comprising the first and second steps referred to above.

It is important in the first step that

(A) the clay mineral should be so acid-treated that its SiO_2 content should reach 82-96.5% by weight, preferably 85-95%' by weight, on dry basis (drying at 105°C for 3 hours), and

(B)it should be so acid-treated as to have a SiO_2 content within the above-specified range, and furthermore until it shows substantially no diffraction pattern attributable to the crystals of layer-structure composed of regular tetraheorons of silica possessed by the starting clay mineral (before the acid treatment), when examined by X-ray diffraction and electron diffraction.

According to our studies, if the acid-treatment is performed too rigorously until the SiO_2 content of the acid-treated clay mineral exceeds 96.5% by weight (on dry basis), the layers themselves which are composed of regular tetrahedrons of silica are excessively destroyed, and it is impossible to reconstruct the layered crystalline structures composed of regular tetrahedrons of silica as will be later described, even by the treatment with a magnesium and/or an aluminum compound according to the second step. Hence the resulting clay mineral has markedly inferior color-developing ability to the color developer (1) in the present invention. It is essential, therefore, that the acid-treatment of the first step should be performed to such an extent that the SiO_2 content of the acid-treated clay mineral should not exceed 96.5% by weight.

When the acid treatment is continued until the SiO_2 content of the treated clay mineral exceeds 95% by weight (on dry basis), the treating conditions become rigorous, and many treating hours are required. In addition to such-economical disadvantages, the resulting product does not necessarily exhibit improved color-developing ability, and some types of clay minerals even show a reduced color-developing ability.

Accordingly, the acid-treatment is carried out preferably to such an extent that the SiO_2 content of the acid-treated clay mineral becomes 85 to 95% by weight, in order to secure economic advantages and to protect the layer composed of regular tetrahedrons of silica from excessive destruction.

The electron diffraction patterns in Figures 1 to 4 of U.S. Patent No. 4,405,371 (European Laid-Open Patent Publication No. 0044645A1) which describes the research work of the present inventors on the color developer (1) give the following information. For example, the dioctahedral montmorillonite clay mineral occurring in Arizona (U.S.A.) shows a characteristic diffraction pattern attributable to the layered crystalline structure (Fig. 1). When it is intensely acid-treated (SiO_2 content, about 94% by weight), the diffraction pattern attributable to the crystals substantially disappears in electron diffractometry (Fig. 2). When the acid-treated clay mineral is treated, for example, with an aqueous magnesium chloride or aluminum chloride solution according to the second step, neutralized with an aqueous caustic soda solution, washed with water and dried, the product again shows diffraction pattern characteristic of the layered crystalline structure when examined by electron diffractometry, as shown in Figs. 3 and 4. This fact is believed to show that although the crystals having the layer-structure composed of regular tetrahedrons of silica are destroyed by the acid-treatment of the first step, the layers themselves remain without complete destructions and that the remaining layers composed of regular tetrahedrons of silica are re-constructed into crystals by the magnesium and/or aluminum component.

An analysis of the electron diffraction pattern of the re-constructed crystals shows that the spacing of the crystals re-constructed by the magnesium component very closely resembles that of the starting montmorillonite clay mineral, but that of the crystals re-constructed by the aluminum component is narrower than that of the starting montmorillonite clay minerals.

These facts seem to suggest that the reconstructed crystals, particulrly those reconstructed by the aluminum component, differ from the crystals of the starting clay mineral. Nevertheless, the color developer (1) used in this invention which shows the diffraction pattern of the crystals reconstructed by a magnesium or an aluminum component in electron diffractometry (the product of the second step) exhibits an improved color-developing ability particularly with respect to a primary color-forming dye over the acid-treated product, and also shows an improved color-developing ability with respect to a secondary color-forming dye. Furthermore, the color developer (1) scarcely decreases in color-developing ability after storage in an atmosphere kept at a high humidity and a high temperature, and evidently, a marked improvement in color-developing ability is noted.

Further investigations of the present inventors showed that when a color formed by the color developer (1) is exposed to sunlight, particularly to ultraviolet light, the color tends to fade and/or discolor. In an attempt to improve the light resistance of the color developer (1), the present inventors made various investigations, and finally found that a color formed by the color developer (1) can be markedly protected from fading and discoloration by incorporating a small amount of at least one metal compound (3) selected from the oxides and hydroxides of calcium and zinc in the color developer composition.

The amount of the metal compound to be incorporated in the color developer (1) is 0.2 to 2 millimoles, preferably 0.4 to 1 millimole, per gram of the color developer (1), (2) when present, and the metal compound (3) combined.

The hydroxide of calcium and the oxide of zinc are preferred as the metal compound, and calcium hydroxide is especially preferred. These metal oxides or hydroxides can be used either singly or in combination with each other.

When two or more of these metal compound are used together, a combination of calcium hydroxide and zinc oxide is preferred. Advantageously, in these combinations, the mole ratio of calcium hydroxide to zinc oxide is adjusted to from 0.9:0.1 to 0.2:0.8. By using the metal compound in combination as described above, the light resistance of a color formed by the color developper (1) or a mixture of the color developer (1) and the color developer (2) can be further increased.

Preferably, the metal compound and the color developer (1) are mixed as uniformly as possible to obtain the composition of this invention. For this purpose, the metal compound preferably has such a particle size that when its particle size is measured by the Andreasen pipette, the proportion of particles having a particle diameter of not more than 10 μm is at least 70% by weight. It is particularly advantageous that the metal compound contains at least 90% by weight of particles which have a size 325 mesh under according to the Tyler's mesh.

The color developer (1) can be used as a mixture with an acid-treated dioctahedral montmorillonite clay mineral or a mixture of it with a naturally occurring dioctahedral montmorillonite clay mineral (to be referred to as the color developer (2)] which minerals have heretofore been known as color developers for pressure-sensitive recording sheets. As described in the specification of U.S. Patent No. 4,405,371 (European Laid-Open Patent Publication No. 0044645A1) cited above, a mixture of the color developer (1) and the color developer (2) with the proportion of the color developer (1) being at least 3% by weight based on the mixture, when formed into an aqueous composition for coating on a receiving sheet, has a much lower viscosity than that of an aqueous composition of the color developer (2) alone. Accordingly, the aqueous composition in a high concentration can be coated on the receiving sheet, and the coating operation and drying become easy. When a mixture of at least 10% by weight, especially at least 20% by weight, of the color developer (1), and the color developer (2) is used as a color developer for pressure-sensitive recording sheets, the presence of the color developer (1) increases the color-developing ability of the mixture and its aqueous composition decreases in viscosity. Hence, this color developer is very useful in practical applications. Even when such a color developer mixture is used, the inclusion of the aforesaid metal compound makes it possible to prevent effectively a color formed by the color developer mixture from fading or discoloration.

Accordingly, in the present invention, the metal compound specified above can be incorporated also in the mixture of the color developer (1) and the color developer (2) in the same way as described above with regard to the color developer (1).

The color developer (2) will be described below in detail.

Color developer (2)

The color developer (2) used in this invention may be any of conventional known color developers for pressure-sensitive recording sheets which are composed of acid-treated products of dioctahedral montmorillonite clay minerals such as acid clay and sub-bentonite, or mixtures thereof with naturally occurring dioctahedral montmorillonite clay minerals. The acid-treated products of the montmorillonite clay minerals especially an active clay obtained by acid-treatment of acid clay, are preferred. The acid treatment for production of these is carried out under such conditions that the treated product does not lose the diffraction pattern attributed to the crystals of a layer structure composed of regular tetrahedrons of silica, which the starting clay has.

The acid-treatment under the relatively mild conditions described above increases the specific surface area of the starting clay mineral. The color developer (2} used in this invention preferably has a specific surface area of at least 180 m^2/g.

A typical method for producing the color developer (2) is described in the specification of U.S. Patent No. 3,622,364. Preferably, when a secondary color is formed by the reaction of the color developer (2) with benzoyl leuco methylene blue described in the above-cited patent specification, the color developer (2) has a secondary color developing performance K_2, defined by the following equation, of at least 1.40.

$$K_2 = \frac{R_{430}}{R_{550}} + 2/1\ (1 - R_{550})$$

where R_{430} and R_{550} are the reflectances of light having a wavelength of 430 mμ and 550 mμ respectively.

The color developer composition of this invention comprises the color developer (1) or a mixture of the color developer (1) and the color developer (2) and 0.2 to 2 millimoles, preferably 0.4 to 1 millimole, of the aforesaid metal compound per gram of the color developer or developers and the metal compound combined. Preferably, the composition is prepared by blending in the dry state the metal compound with a dried product of the color developer (1) or a mixture of it with the color developer (2). When the color developer (2) is used together, it is possible to blend the color developer (2) with the metal compound and then adding the color developer (1) to the mixture. Alternatively, the metal compound is blended with, the color developer (1) and then a suitable amount of the color developer (2) is added to the mixture. Blending can be effected by any known method.

Preferably, the color developer composition of this invention comprising the color developer (1) and the metal compound, or the color developer (1), the color developer (2) and the metal compound has such a particle size that at least 99% by weight thereof consists of particles having a size 325 mesh under in accordance with the Tyler's mesh.

When the color developer composition of this invention is dipped in a 1M aqueous solution of ammonium chloride and maintained at ordinary temperature (for example, 25°C) for a suitable period of time (for example, 24 hours) preferably with occasional shaking, the metal compound blended with the color developer (1) or the mixture of the color developers (1) and (2) dissolves in the aqueous ammonium chloride solution. Hence, the amount of the metal compound in the color developer composition can be determined by this method (for details, see the testing method described hereinafter).

The color developer (1) used in this invention is obtained by intensely acid-treating a clay mineral of a layer structure composed of regular tetrahedrons of silica such that the treated product does not substantially show the diffraction pattern attributed to the crystals of layer structure composed of regular tetrahedrons of silica which the clay mineral before the acid-treatment has and contacting the treated product with at least partially soluble magnesium and/or aluminum compound to reconstruct the crystals of the layer structure so that they show a diffraction pattern attributed to the layer structure composed of regular tetrahedrons of silica in electron diffractometry. The magnesium and/or aluminum consumed in the reconstruction of these crystals is not dissolved out by the aforesaid treatment with the aqueous ammonium chloride solution, but is still retained in the color developer (1). But that portion of the magnesium compound used in the reconstruction which remains free in the color developer (1) in a very small amount dissolves in the aqueous ammonium chloride solution as does the metal compound blended in the color developer (1).

That portion of the magnesium compound used in the reconstruction which remains free in the color developer (1) and dissolves in the aqueous ammonium chloride solution is usually very small in amount, and insufficient to improve the light resistance of a color formed by the color developer (1). But when combined with the metal compound included in the color developer (1), it serves to increase the light resistance.

The clay minerals used as raw materials for the production of the color developers (1) and (2) contain calcium or magnesium, but calcium and magnesium are not dissolved out by treatment with the aqueous ammonium chloride solution.

In preparing an aqueous composition from the color developer composition for coating on a receiving sheet, the concentration of the color developer composition can be adjusted to about 20 to about 50% by weight. A suitable amount of a water-soluble or water-dispersible binder can be added to the aqueous coating composition.

Examples of the water-soluble binder are starch, carboxy methyl cellulose (CMC), polyvinyl alcohol (PVA), casein and gelatin. Starch and carboxymethyl cellulose are preferably used. Examples of the water-dispersible binder are a styrenebutadiene type latex, an acrylic latex, a vinyl acetate-type emulsion and vinyl chloride-type emulsion. The styrene-butadiene type latex is preferred. The combined use of the water-soluble binder and the water-dispersible binder is especially preferred. The amount of the binder used, as solids content, is 10 to 30% by weight, preferably 13 to 20% by weight, based on the solids content of the aqueous coating composition.

The aqueous coating composition may further contain at least one of pH adjusting agents, dispersing agents and viscosity adjusting agents.

The pH adjusting agents may include the hydroxides and carbonates of alkali metals or alkaline earth metals such as sodium hydroxide, lithium hydroxide, potassium hydroxide, calcium hydroxide, sodium carbonate and lithium carbonate; sodium silicate; and ammonia.

Examples of the dispersing agents include polyphosphates such as sodium hexametaphosphate and sodium pyrophosphate, and polycarboxylic acid salts such as sodium polycarboxylate and ammonium polycarboxylate.

As the viscosity adjusting agents, talc, mica and asbestos (Japanese Patent Publication No. 23177/ 1970), and kaolin, and calcium carbonate (Japanese Patent Publication No. 47992/1980) may be used.

As required, an extender or a color developer other than the color developers (1) and (2) may further be included in the aqueous coating composition in accordance with this invention.

The color developer compositions of this invention have a great color-developing ability with respect to primary color-forming dyes and secondary color-forming dyes, and their color-developing ability shows only a very low degree of reduction after storage at high temperatures and humidities.

The following Examples and Comparative Examples illustrate the present invention more specifically.

The various tests used in these examples are described below.

1. Mesurement of the particle diameter

(1) Content of particles having a particle diameter of not more than 10 microns (by the Andreason pipette method)

Six grams (after drying at 110°C) of a color developer sample was taken into a 1-liter narrow-mouthed bottle, and 600 ml of water was added. Then, 0.8 g of sodium pyrophosphate of first class reagent grade was added, and the bottle was sealed up. The bottle was shaken for 60 minutes by a shaking machine at 140 reciprocations per minute (amplitude 8 cm) to disperse the sample. The dispersion was then transferred to an Andreason pipette (JIS Z-8901, DIN 51033) and the pipette was manipulated in accordance with the pipette operating method. Immediately, a suspension as a blank was collected, and after drying at 110°C, its weight was measured (S g). Then, after a certain period of time, a suspension containing particles having a particle diameter of not more than 10 microns calculated by the Stokes equation was collected by the pipette. It was dried at 110°C, and its weight (W g) was precisely measured. The content (%) of particles having a particle diameter of not more than 10 microns is calculated from the following equation.

$$\text{Content of particles having a particle diameter of not not more than 10 microns (\%)} = \frac{W}{S} \times 100$$

(where S is the weight of the blank and W is the weight of particles having a particle diameter of not more than 10 microns)

(2) Content of particles having a size 325 mesh under

Fifty grams of a color developer sample (after drying at 110°C) was taken into a 500 ml beaker. Water was added and the sample was well dispersed by a glass rod. The dispersion was gently poured little by little onto a 325-mesh sieve, and passed therethrough fully together with flowing water.

All the material left on the sieve was put in a 100 ml beaker using a washing bottle, and dried. The weight (M g) of the solid obtained (after drying at 110°C) was measured, and the content (%) of particles having a size 325 mesh under was calculated from the following equation.

$$\text{Content of particles having a size 325 mesh under} = \frac{(50-M)}{50} \times 100\ (\%)$$

2. Method of testing color-developing ability and method of measuring the viscosity of the coating composition

(1) Preparation of a coating composition

One gram of sodium hexametaphosphate was dissolved in 175 g of water, and 100 g (after drying at 110°C) of a color developer sample was added. A 20% aqueous solution of sodium hydroxide was added to adjust the pH of the solution to about 9.5 (when the pH of the solution before addition of sodium hydroxide exceeds 9.5, the addition of sodium hydroxide is unnecessary). Then, 15 g of a 20% aqueous solution of starch and 34 g of SBR latex (Dow 620, solids concentration 50%) were added, and the pH of the solution was again adjusted to 9.5 with a 20% aqueous solution of sodium hydroxide. Water was further added to adjust the total amount of the slurry to 400 g. It was fully agitated by an agitator to form a uniform dispersion.

(2) Color-developing ability test

Preparation of receiving sheets

The resulting coating slurry was coated on 8 sheets of paper (4 sheets coated at a high rate and 4 sheets coated at a low rate) by means of two coating rods (wire diameter: 0.10 mm and 0.05 mm. respectively). The coated papers were dried in the air and then dried at 110°C for 3 minutes. The amount of the coating solution applied was measured (determined from the dry weight difference between a sample of the uncoated paper and a sample of a uniformly coated portion of the coated paper, both samples having the same area). The coated sheets of paper were cut into halves to form two 4-sheet sets (having the same coating amount). The amounts of coating of the two types were slightly more and slightly less than 6 g/m^2.

Initial color-developing ability test

One of the two 4-sheet sets of receiving sheets was put in a desiccator (relative humidity 75%) containing a saturated aqueous solution of sodium chloride, and stored in the dark at 25°C. After the lapse of about 24 hours from the coating, it was taken out and exposed indoors (kept constantly at about 25°C and a relative humidity of about 60%) for 16 hours, and then subjected to color development. Color development was carried out by the following procedure. The receiving sheets were superposed on two different types of transfer sheets, either (1) a transfer sheet coated with microcapsules containing CVL (Crystal Violet Lactone) which is an instantaneously color-forming leuco dye (CVL dye sheet) or (2) a commercial transfer sheet coated with microcapsules containing a mixture of CVL, BLMB (Benzoyl Leuco Methylene Blue) and a fluoran-type dye (mixed dye sheet), with their coated surfaces facing each other, and together inserted between a pair of steel rolls, and revolving the rolls under pressure to rupture the microcapsules completely.

The color-developing ability of each of the receiving sheets was evaluated by measuring the density of the color one hour after color formation by means of a densitometer (Fuji Densitometer Model-P, made by Fuji Shashin Film K.K.), and averaging the measured values on four sheets. High densities show high color-developing ability.

The color-developing ability of a sample color developer (density [A]) is expressed by the density [A] on the receiving sheet coated with 6 g.m^2 of the color developer calculated from the density [A_1] of the thinly coated (a, g/m^2) receiving sheet and the density [A_2] of the thickly coated (a_2 g/m^2) receiving sheet.

In the calculation, because the density and coating amount are in substantially linear relationship (direct proportion) with the receiving sheets coated with an identical sample in the amounts around 6 g/m^2, the density [A] can be determined from the equation below.

Initial color-developing ability:

$$[A] = [A_1] + \frac{\{[A_2] - [A_1]\}\,(6-a_1)}{a_2 - a_1}$$

Light resistance test

The color-developed sheet used in the initial color-developing ability test was irradiated with an artificial light (carbon arc lamp) for two hours, as set in a weatherometer (Suga Shikenki K.K., Standard Sunshine Weatherometer, WE-SUN-HC mode!). The density of the developed color which faded upon the irradiation was measured. The density (B) of the developed color on the receiving sheet coated with 6 g/m^2 of sample color developer, after fading, was calculated from the similar densities of thinly coated and thickly coated receiving sheets ([B_1] and [B_2], respectively) as in the foregoing. The light resistance is expressed by the ratio of [B] to the initial color-developing density ([A]), i.e. ([B]/[A]).

$$[B] = [B_1] + \frac{\{[B_2] - [B_1]\}\,(6-a_1)}{a_2 - a_1}$$

Light resistance: [B]/[A]

(3) Measurement of the viscosity of the coating solution

Two hundred grams of the coating solution obtained in (1) above was transferred to a 300 ml beaker equipped with an agitator (having four perpendicularly crossing blades, 20 mm x 20 mm), and agitated at a speed of 500 rpm in a constant temperature water vessel at 25°C for 15 minutes. The viscosity of the solution, two minutes after starting of rotation at 60 rpm, was measured by a B-type rotary viscometer.

Comparative Example 1a

Montmorillonite clay occurring in Arizona, U.S.A. was crushed by agitating it together with water to form a 20% slurry. To 500 g of the slurry was added 150 g of 97% sulfuric acid, and further 50 g of water was added. The mixture was heated for 10 hours in a water bath at 95°C. During this time, the slurry was agitated every 30 minutes to promote the reaction. After the heating, the treated slurry was suction-filtered, and again water and 150 g of 97% sulfuric acid were added to adjust the total amount of the slurry to 700 g. It was then acid-treated at 95°C for 10 hours. The treated product was washed with water by filtration, and the cake was put in a pot mill. Water was added, and pulverized in the wet state together with Korean chart pebbles to obtain a 15% slurry. (First step).

429 g (SiO_2 content 60 g) of the resulting slurry (SiO_2 content of the dry solid: 93.30%) was heated to 80°C, and with stirring, 500 ml of a 1M aqueous solution of magnesium chloride was added dropwise over the course of about 30 minutes. The mixture was aged for 30 minutes. Then, a 10% aqueous solution of sodium hydroxide was added dropwise over the course of about 30 minutes to perform neutralization. The mixture was aged for 30 minutes to complete the reaction. The reaction mixture was washed with water by filtration, and the filtration cake was dried at 110°C. The dried product was pulverized by a small-sized impact pulverized and coarse particles were removed by a winnowing type classifying machine to obtain fine white particles (color developer 1a). (Second step).

The electron diffraction pattern and the X-ray diffraction pattern of the color developer (1a) are shown in Figures 3 and 7 (Example 1a) of a U.S. Patent No. 4,405,371 (European Laid-Open Patent Publication No. 0044645 A1).

Comparative Example 1b

Water (350 g) and 250 g of 97% sulfuric acid were added to 100 g of metakaolin produced by calcining a kaolin clay powder occurring in Georgia, U.S.A. at 700°C for 2 hours. The mixture was heated on a water bath at 95°C for 10 hours. During this time, the slurry was agitated every 30 minutes to promote the reaction. After the heating, the reaction mixture was suction-filtered, and water and 250 g of 97% sulfuric acid were again added to adjust the total amount of the mixture to 700 g. It was acid-treated at 95°C for 10 hours. The treated product was washed with water by filtration, and the filtration cake was put in a pot mill. Water was added, and the entire mixture was pulverized in the wet state together with Korean chart pebbles to obtain a 15% slurry. (First step).

455 g (SiO_2 content 60 g) of the resulting slurry (SiO_2 content of the dry solid: 87.91 %) was heated to 80°C, and with stirring, 500 ml of a 1M aqueous solution of aluminum chloride was added dropwise over the course of about 30 minutes. The mixture was aged for 30 minutes. Then, 600 g of a 10% aqueous solution of sodium hydroxide was added dropwise over about 45 mintues to perform neutralization. The product was aged for 30 minutes to terminate the reaction. The reaction mixture was washed with water by filtration, and the filtration cake was dried at 110°C. It was pulverized by a small-sized impact pulverizer, and coarse particles were removed by a winnowing-type classifier to obtain fine white particles as a color developer (1b). (Second step).

The electron diffraction pattern and X-ray diffraction pattern of the color developer (1b) are shown in Figures 5 and 7 (Example 2) of U.S. Patent No. 4,405,371 (European Laid-Open Patent Publication No. 0044645A1).

Referential Example 1

Eight liters of 34% sulfuric acid was added to 4.5 kg of a pulverized product (water content 32%) of acid clay occurring in Nakajo-machi, Niigata-ken, Japan, and the mixture was heated on a water bath at 85°C to perform acid treatment (the same as acid treating conditions (B) for sample No. 11 given in Table 1 of U.S. Patent No. 3,622,364). By filtration, the treated product was washed with water, and the filtration cake was dried at 110°C, and pulverized. Coarse particles were removed by winnowing to obtain fine white particles as a color developer (2).

The color developer (2) is a known color developer for pressure-sensitive recording sheets. By the methods described in the specification of U.S. Patent No. 3,622,364, it was found to have a specific surface area of 295 m^2/g and a secondary color-developing performance, K_2, of 1.78.

Comparative Example 2

The color developer (1a) obtained in Comparative Example 1a and the known clay mineral-type color developer (2) obtained in Referential Example 1 were uniformly mixed in a ratio of 50:50 by weight in a fluidizing-type mixer (Supermixer) to obtain a white color developer powder (this is the same as sample E of Example 1 given in U.S. Patent No. 4,405,371 (European Laid-Open Patent Publication No. 0044645A1).

Example 1 (1a-1g)

A powder of calcium hydroxide from which coarse particles had been removed by winnowing was added to the color developer (1a) obtained in Comparative Example 1 a in an amount of 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and 2.0 millimoles respectively per gram of the entire dry mixture (upon drying at 110°C). They were uniformly mixed by a fluidizing-type mixer to form a white color developer powder.

Example 2 (2a-2g)

A powder of calcium hydroxide from which coarse particles had been removed by winnowing was added to the color developer powder obtained in Comparative example 2 in an amount of 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and 2.0 millimoles respectively per gram of the entire dry mixture (upon drying at 110°C, and they were uniformly mixed in a fluidizing-type mixer to obtain a white develop color developer powder.

Example 3 (3a-3g)

Calcium hydroxide powder and zinc oxide powder from which coarse particles had been removed by winnowing were uniformly mixed in a mole ratio of 0.75:0.25 (3:1). The resulting mixture was added to the color developer powder obtained in Comparative Example 2 in an amount of 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and 2.0 millimoles respectively per gram of the entire dry mixture (upon drying at 110°C), and they were uniformly mixed in a fluidizing-type mixer to form a white color developer powder.

Example 4 (4a-4g)

Example 3 was repeated except that the mixing mole ratio of calcium hydroxide to zinc oxide was changed to 0.5:0.5 (1:1).

Example 5 (5a-5g)

Example 3 was repeated except that the mixing mole ratio of calcium hydroxide to zinc oxide was changed to 0.25:0.75 (1:3).

Example 6 (6a-6g)

Example 2 was repeated except that zinc oxide was used instead of calcium hydroxide.

Example 7 (7a-7g)

A powder of zinc hydroxide from which coarse particles had been removed by winnowing was added to the color developer (1b) obtained in Comparative Example 1b in an amount of 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and 2.0 millimoles per gram of the entire dry mixture (upon drying at 110°C), and they were mixed uniformly in a fluidizing-type mixer to form a white color developer powder.

Example 8 (8a-8g)

A powder of calcium hydroxide from which coarse particles had been removed by winnowing was added to the powdery developer (1b) obtained in Comparative Example 1b in an amount of 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and 2.0 milliomoles, respectively, per gram of the entire dry mixture (upon drying at 110°C). They were uniformly mixed by a fluidized-type mixer to obtain a white color developer powder.

Example 9 (9a-9g)

Example 1 was repeated except that calcium oxide was used instead of calcium hydroxide.

Example 10 (10a-10g)

Example 1 was repeated except that zinc hydroxide was used instead of calcium hydroxide. The zinc hydroxide used a powder obtained by adding an aqueous solution of sodium hydroxide to an aqueous solution of zinc sulfate, washing the resulting white precipitate with water, drying it at less that 100°C, pulverizing it and removing coarse particle by winnowing.

Example 11 (11a-11g)

Example 1 was repeated except that zinc oxide was used instead of calcium hydroxide.

Example 12 (12a-12c)

A powder of calcium hydroxide with varying particle sizes obtained by winnowing was added to the color developer powder (1a) obtained in Comparative Example 1a in an amount of 0.6 millimole per gram of the entire dry mixture (upon drying at 110°C). They were mixed uniformly by a fluidized mixture to obtain a white color developer composition.

Table 9 shows the effect of the content of particles having a particle diameter of not more than 10 microns and the content of particles having a size 325 mesh under in the metal compound on the color-developing performance of each of the resulting color developer compositions.

Tables 1 to 7 summarize the result of the test of color developing ability of the color developer samples obtained by the above example. Table 8 shows the results of measuring the content of particles having a particle diameter of not more than 10 microns, the content of particles having a size 325 mesh under, and the viscosities of the coating slurries.

Table 1

Sample	Amount of $Ca(OH)_2$ added (mmoles/g)	Color development performance (testing method 2)					
		CVL color development			Mixed color development (CVL, BLMB and fluoran)		
		Initial color density [A] (x 10^{-2})	Density after light fading [B] (x 10^{-2})	Light resistance $\frac{[B]}{[A]}$	Initial color density [A] (x 10^{-2})	Density after light fading [B] (x 10^{-2})	Light resistance $\frac{[B]}{[A]}$
Referential Ex. 1	—	76	42	0.55	79	53	0.67
Comp. Ex. 1a	—	106	70	0.66	107	87	0.81
Ex. 1a	0.10	107	73	0.68	108	89	0.82
1b	0.20	107	75	0.70	108	90	0.83
1c	0.40	109	81	0.74	109	94	0.86
1d	0.60	110	84	0.76	109	95	0.87
1e	0.80	109	82	0.75	109	95	0.87
1f	1.00	107	78	0.73	108	92	0.85
1g	2.00	104	72	0.69	106	88	0.83

- to be continued -

Table 2

Sample	Amount of the metal compound added (mmoles/g)			Color development performance (testing method 2)					
				CVL color development			Mixed color development (CVL, BLMB and fluoran)		
	$Ca(OH)_2$	ZnO	Total amount	Initial color density [A] ($\times 10^{-2}$)	Density after light fading [B] ($\times 10^{-2}$)	Light resistance $\frac{[B]}{[A]}$	Initial color density [A] ($\times 10^{-2}$)	Density after light fading [B] ($\times 10^{-2}$)	Light resistance $\frac{[B]}{[A]}$
Referential Ex. 1	-	-	-	76	42	0.55	79	53	0.67
Comp. Ex. 2	-	-	-	101	68	0.67	103	82	0.80
Ex. 2a	0.10	-	0.10	103	71	0.69	104	84	0.81
2b	0.20	-	0.20	104	74	0.71	105	86	0.82
2c	0.40	-	0.40	108	81	0.75	107	91	0.85
2d	0.60	-	0.60	109	84	0.77	107	92	0.86
2e	0.80	-	0.80	109	83	0.76	107	91	0.85
2f	1.00	-	1.00	106	78	0.74	106	89	0.84
2g	2.00	-	2.00	100	69	0.69	103	83	0.81
Ex. 3a	0.075	0.025	0.10	104	73	0.70	105	86	0.82
3b	0.15	0.05	0.20	105	76	0.72	105	87	0.83
3c	0.30	0.10	0.40	108	82	0.76	107	91	0.85

- to be continued -

Table 2 (continued)

Sample	Amount of the metal compound added (mmoles/g)			Color development performance (testing method 2)					
				CVL color development			Mixed color development (CVL, BLMB and fluoran)		
	$Ca(OH)_2$	ZnO	Total amount	Initial color density [A] ($\times 10^{-2}$)	Density after light fading [B] ($\times 10^{-2}$)	Light resistance $\frac{[B]}{[A]}$	Initial color density [A] ($\times 10^{-2}$)	Density after light fading [B] ($\times 10^{-2}$)	Light resistance $\frac{[B]}{[A]}$
Ex. 3d	0.45	0.15	0.60	110	86	0.78	108	94	0.87
3e	0.60	0.20	0.80	110	86	0.78	108	94	0.87
3f	0.75	0.25	1.00	107	81	0.76	106	90	0.85
3g	1.50	0.50	2.00	103	74	0.72	104	86	0.83
Ex. 4a	0.05	0.05	0.10	103	71	0.69	104	84	0.81
4b	0.10	0.10	0.20	104	74	0.71	105	86	0.82
4c	0.20	0.20	0.40	108	80	0.74	107	90	0.84
4d	0.30	0.30	0.60	109	83	0.76	107	91	0.85
4e	0.40	0.40	0.80	111	87	0.78	108	94	0.87
4f	0.50	0.50	1.00	110	86	0.78	108	94	0.87
4g	1.00	1.00	2.00	108	80	0.74	106	89	0.84
Ex 5a	0.025	0.075	0.10	102	69	0.68	104	84	0.81
5	0.05	0.15	0.20	103	72	0.70	104	85	0.82
5c	0.10	0.30	0.40	105	76	0.72	105	87	0.83

- to be continued -

Table 2 (continued)

Sample	Amount of the metal compound added (mmoles/g)			Color development performance (testing method 2)					
				CVL color development			Mixed color development (CVL, BLMB and fluoran)		
	$Ca(OH_2)$	ZnO	Total amount	Initial color density [A] ($\times 10^{-2}$)	Density after light fading [B] ($\times 10^{-2}$)	Light resistance $\frac{[B]}{[A]}$	Initial color density [A] ($\times 10^{-2}$)	Density after light fading [B] ($\times 10^{-2}$)	Light resistance $\frac{[B]}{[A]}$
Ex. 5d	0.15	0.45	0.60	107	79	0.74	106	89	0.84
5e	0.20	0.60	0.80	108	81	0.75	107	91	0.85
5f	0.25	0.75	1.00	109	83	0.76	107	91	0.85
5g	0.50	1.50	2.00	106	80	0.75	106	90	0.85
Ex. 6a	-	0.10	0.10	102	69	0.68	104	84	0.81
6b	-	0.20	0.20	103	71	0.69	104	84	0.81
6c	-	0.40	0.40	104	73	0.70	105	86	0.82
6d	-	0.60	0.60	104	74	0.71	105	86	0.82
6e	-	0.80	0.80	105	75	0.71	105	86	0.82
6f	-	1.00	1.00	103	73	0.71	104	85	0.82
6g	-	2.00	2.00	102	71	0.70	104	85	0.82

Table 3

Sample	Amount of Zno added (mmoles/g)	Color development performance (testing method 2)					
		CVL color development			Mixed color development (CVL, BLMB and fluoran)		
	ZnO	Initial color density [A] ($\times 10^{-2}$)	Density after light fading [B] ($\times 10^{-2}$)	Light resistance $\frac{[B]}{[A]}$	Initial color density [A] ($\times 10^{-2}$)	Density after light fading [B] ($\times 10^{-2}$)	Light resistance $\frac{[B]}{[A]}$
Ex. 7a	0.10	103	66	0.64	104	79	0.76
7b	0.20	105	68	0.65	105	80	0.76
7c	0.40	106	70	0.66	105	81	0.77
7d	0.60	106	71	0.67	106	82	0.77
7e	0.80	107	72	0.67	106	82	0.77
7f	1.00	106	71	0.67	105	81	0.77
7g	2.00	105	69	0.66	105	81	0.77

Table 4

Sample	Amount of $Ca(OH)_2$ added (mmoles/g)	Color development performance (testing method 2)					
		CVL color development			Mixed color development (CVL, BLMB and fluoran)		
		Initial color density [A] ($\times 10^{-2}$)	Density after light fading [B] ($\times 10^{-2}$)	Light resistance $\frac{[B]}{[A]}$	Initial color density [A] ($\times 10^{-2}$)	Density after light fading [B] ($\times 10^{-2}$)	Light resistance $\frac{[B]}{[A]}$
Comp. Ex. 1b	—	102	64	0.63	103	77	0.75
Ex. 8a	0.10	105	69	0.66	104	80	0.77
8b	0.20	107	72	0.67	105	83	0.79
8c	0.40	109	77	0.71	107	86	0.80
8d	0.60	109	80	0.73	109	88	0.81
8e	0.80	110	79	0.72	107	87	0.81
8f	1.00	107	76	0.71	106	84	0.79
8g	2.00	105	70	0.67	104	81	0.78

- to be continued -

Table 5

Sample	Amount of the metal compound added (mmoles/g)	Color development performance (testing method 2)					
		CVL color development			Mixed color development (CVL, BLMB and fluoran)		
	CaO	Initial color density [A] ($\times 10^{-2}$)	Density after light fading [B] ($\times 10^{-2}$)	Light resistance $\frac{[B]}{[A]}$	Initial color density [A] ($\times 10^{-2}$)	Density after light fading [B] ($\times 10^{-2}$)	Light resistance $\frac{[B]}{[A]}$
Comp. Ex. 1a	-	106	70	0.66	107	87	0.81
Ex. 9a	0.10	107	72	0.67	107	88	0.82
9b	0.20	107	74	0.69	108	90	0.83
9c	0.40	108	79	0.73	108	92	0.85
9d	0.60	109	81	0.74	109	95	0.87
9e	0.80	109	80	0.74	108	93	0.86
9f	1.00	106	76	0.72	107	90	0.84
9g	2.00	104	73	0.70	106	88	0.83

Table 6

Sample	Amount of the metal compound added (mmoles/g)	Color development performance (testing method 2)					
		CVL color development			Mixed color development (CVL, BLMB and fluoran)		
	Zn(OH)$_2$	Initial color density [A] (x10^{-2})	Density after light fading [B] (x10^{-2})	Light resistance $\frac{[B]}{[A]}$	Initial color density [A] (x10^{-2})	Density after light fading [B] (x10^{-2})	Light resistance $\frac{[B]}{[A]}$
Comp. Ex. 1a	-	106	70	0.66	107	87	0.81
Ex. 10a	0.10	107	73	0.68	108	89	0.82
10b	0.20	108	74	0.69	109	90	0.83
10c	0.40	109	75	0.69	110	91	0.83
10d	0.60	109	77	0.71	111	95	0.86
10e	0.80	109	76	0.70	110	93	0.85
10f	1.00	108	75	0.69	109	90	0.83
10g	2.00	107	74	0.69	108	89	0.82

Table 7

Sample	Amount of the metal compound added (mmoles/g)	Color development performance (testing method 2)					
		CVL color development			Mixed color development (CVL, BLMB and fluoran)		
	ZnO	Initial color density [A] (x10^{-2})	Density after light fading [B] (x10^{-2})	Light resistance $\frac{[B]}{[A]}$	Initial color density [A] (x10^{-2})	Density after light fading [B] (x10^{-2})	Light resistance $\frac{[B]}{[A]}$
Comp. Ex. 1a	-	106	70	0.66	107	87	0.81
Ex. 11a	0.10	107	72	0.67	108	88	0.81
11b	0.20	107	73	0.68	108	89	0.82
11c	0.40	108	74	0.69	109	90	0.83
11d	0.60	108	76	0.70	110	91	0.83
11e	0.80	107	75	0.70	109	90	0.83
11f	1.00	107	74	0.69	108	89	0.82
11g	2.00	106	72	0.68	107	88	0.82

Table 8

Sample	Content of particles having a diameter of not more than 10μ (%) [method 1, (1)]	Content of particles having a size 325 mesh under (%) [method 1, (2)]	Viscosity of the 30% coating solution (cps) [method 2, (3)]
Ref. Ex. 1	95.5	99.9	65
Comp. Ex. 1a	95.0	99.9	10
Ex. 1d	94.1	99.9	43
Comp. Ex. 2	93.2	99.9	14
Ex. 2d	92.4	99.9	45
Ex. 4d	93.0	99.9	33
Ex. 6d	93.5	99.9	25
Comp. Ex. 1b	94.2	99.9	15

Table 9

Sample	Amount of $Ca(OH)_2$ added	Content of particles having a diameter of not more than 10μ(%) [method 1,(1)]		Content of particles having a size 325 mesh under (%) [method 1,(2)]		Color development performance (testing method 2)					
						CVL color development			Mixed color development (CVL, BLMB and fluoran)		
		$Ca(OH)_2$	Color developes composition	$Ca(OH)_2$	Color developes composition	Initial color density [A] $(\times 10^{-2})$	Density after light fading [B] $(\times 10^{-2})$	Light resistance $\frac{[B]}{[A]}$	Initial color density [A] $(\times 10^{-2})$	Density after light fading [B] $(\times 10^{-2})$	Light resistance $\frac{[B]}{[A]}$
Example 12a (=Ex. 1d)	0.6	74.5	94.1	98.8	99.9	110	84	0.76	109	95	0.87
Example 12b	0.6	70.5	93.9	90.2	99.5	109	80	0.73	109	93	0.85
Example 12c	0.6	61.6	93.5	75.0	98.8	107	72	0.67	108	88	0.81

Claims

1. A color developer composition for pressure-sensitive recording sheets comprising a color developer (1) which is derived from a clay mineral having a layer structure composed a regular tetrahedrons of silica and which after intence acid treatment and subsequent reconstruction of said layer structure

(A) shows a diffraction pattern attricutable to the crystals of a layer structure composed of regular tetrahedrons of silica when subjected to an electron diffraction analysis, but

(B)shows substantially no diffraction pattern attributable to the crystals of said layer structure when subjected to an X-ray diffraction analysis, and

(C) contains as constituent elements besides oxygen, at least silicon and magnesium and/or aluminium, characterised in that the composition comprises

(1) a said color developer (1) which contain megnasium and/or aluminium, any said magnesium content not being soluble in aqueous ammonium chloride solution, (2) optionally a color developer having a silica content of not more than 80% on a dry weight basis and composed of a dioctahedral montmorillonite clay mineral treated with an acid or a mixture of it with a naturally occurring dioctahedral montmorillonite clay mineral, said colour developer (2),

(D) showing a diffraction pattern attributable to the crystals of said layer structure when subjected to an X-ray diffraction analysis, and

(3) 0.2 to 2 millimoles, per gram of the components (1), (2) when present, and (3) combined, of at least one metal compound selected from the oxides and hydroxides of calcium and zinc.

2. composition according to claim 1 wherein the clay mineral from which the color developer (1) is derived is at least one montmorillonite clay minerals, kaolinite clay minerals, sepiolite-palygorskite clay minerals, chlorite clay minerals and vermiculate clay minerals.

3. A composition according to claim 1 or 2 wherein the color developer (1) cantains silicon and magnesium and/or aluminum in an atomic ratio, silicon/(magnesium and/or aluminum), of from 12:1.5 to 12:12.

4. A composition according to claim 1, 2 or 3 wherein any color developer (2) has a specific surface area of at least 180 m^2/g.

5. A composition according to any one of the preceding claims wherein any color developer (2) is an acid-treated acid clay (active clay) or a mixture of it with naturally occurring acid clay.

6. A composition according to any one of claims 1 to 4 wherein the color developer (2) is an acid-treated dioctahedral montmorillonite clay mineral or a mixture of it with a naturally occurring dioctahedral montmorillonite clay mineral, and when it is subjected to secondary color development with benzoyl leuco methylene blue, it has a secondary color development performance, K_2 defined by the following equation, of at least 1.40,

$$K_2 = \frac{R_{430}}{R_{550}} + 2/1\,(1-R_{550})$$

wherein R_{430} and R_{550} represent the reflectances of light having a wavelength of 430 mμ and 550 mμ respectively.

7. A composition according to any one of the preceding claims wherein the color developer (1) is obtained by treating a clay mineral having a layer structure composed of regular tetrahedrons of silica with an acid so that upon drying at 105°C for 3 hours it has a SiO_2 content of 82 to 96.5% by weight, contacting the treated clay mineral in an aqueous medium with a magnesium and/or an aluminum compound, neutralizing the product with an alkali or an acid to form a hydroxide when the magnesium and/or aluminum compound is not a hydroxide thereby to introduce magnesium and/or aluminum into the acid-treated clay mineral and, if desired, drying the product.

8. A composition according to claim 7 wherein the acid-treatment is carried out until upon X-ray analysis the acid-treated clay mineral does not substantially show the diffraction pattern attributable to the crystals of the layer structure composed of regular tetrahedrons of silica possessed by the clay mineral before the acid treatment.

9. A composition according to any one of the preceding claims wherein the amount of the metal compound is 0.4 to 1 millimoles per gram of the components (1), (2) when present, and (3) combined.

10. A composition according to any one of the preceding claims wherein the metal compound (3) is calcium hydroxide.

11. A composition according to any one of the preceding claims wherein the metal compound (3) has such a particle size that at least 70% thereof consists of particles having a particle diameter of not more than 10 μm when measured by the Andreasen pipette method.

12. A composition according to any one of the preceding claims wherein the metal compound (3) contains at least 90% by weight of particles which pass through a size 325 mesh Tyler Standard screen.

13. A composition according to any one of the preceding claims which contains at least 99% by weight of particles which pass through a size 325 mesh Tyler Standard screen.

14. Pressure sensitive recording sheets comprising a coating of a color developer composition as claimed in any one of the preceding claims.

Patentansprüche

1. Farbentwicklermasse für druckempfindliche Aufzeichnungsblätter, enthaltend einen Farbentwickler (1) auf der Basis eines Tonminerals mit einer Schichtstruktur aus regulären SiO_2-Tetraedern, welcher nach intensiver Säurebehandlung und anschließender Rekonstruktion der Schichtstruktur

(A) ein Beugungsmuster zeigt, das den Kristallen einer Schichtstruktur aus regulären SiO_2-Tetraedern zukommt, wenn einer Elektronenbeugungsanalyse unterworfen, jedoch

(B) im wesentlichen kein Beugungsmuster zeigt, das den Kristallen dieser Schichtstruktur zukommt, wenn einer Röntgenbeugungsanalyse unterworfen, und

(C) als Bauelement neben Sauerstoff, zumindest Silicium und Magnesium und/oder Aluminium enthält, dadurch **gekennzeichnet**, daß die Masse zumindest umfaßt

(1) den Farbentwickler (1), enthaltend Magnesium und/oder Aluminium, wobei der Magnesiumgehalt in wässriger Ammoniumchloridlösung nicht löslich ist,

(2) gegebenenfalls einen Farbentwickler mit einem SiO_2-Gehalt von nicht mehr als 80 % auf Trockengewichtbasis aus mit einer Säure behandeltem doppeltoktaedrischem Montmorillonit-Tonmineral oder einem Gemisch davon mit natürlich vorkommendem doppeltoktaedrischem Montmorillonit-Tonmineral, wobei der Farbentwickler (2)

(D) ein Beugungsmuster aufweist, das den Kristallen dieser Schichtstruktur zukommt, wenn der Röntgenbeugungsanalyse unterworfen, und

(3) 0,2 bis 2 mmol/g der Komponenten (1), (2) und (3) zusammen zumindest einer Metallverbindung in Form der Oxide und/oder Hydroxide von Calcium und Zink.

2. Masse nach Anspruch 1, worin das Tonmineral, aus dem sich der Farbentwickler (1) ableitet, wenigstens eines aus der Reihe der Montmorillonit-, Kaolinit-, Sepiolit- Palygorskit-, Chlorit- und Vermiculit-Tonmineralien ist.

3. Masse nach Anspruch 1 oder 2, worin der Farbentwickler (1) Silicium und Magnesium und/oder Aluminium in einem Atomverhältnis Silicium/(Magnesium und/oder Aluminium) von 12 : 1,5 bis 12 : 12 enthält.

4. Masse nach Anspruch 1, 2 oder 3, wobei der Farbentwickler (2) eine spezifische Oberfläche von zumindest 180 m^2/g besitzt.

5. Masse nach einem der vorstehenden Ansprüche, worin der Farbentwickler (2) ein säurebehandelter saurer (aktiver) Ton oder seine Mischung mit natürlich vorkommendem sauren Ton ist.

6. Masse nach Anspruch 1 bis 4, worin der Farbenwickler (2) ein säurebehandeltes doppeltoktaedrisches Montmorillonit-Tonmineral oder seine Mischung mit natürlich vorkommendem doppeltoktaedrischem Montmorillonit-Tonmineral ist und er, wenn einer zweiten Farbentwicklung mit Benzoylleukomethylenblau unterworfen, ein sekundäres Farbentwicklungsvermögen K_2 gemäß nachstehender Gleichung von zumindest 1,4 besitzt, wobei

$$K_2 = \frac{R_{430}}{R_{550}} + 2/1\ (1—R_{550})$$

worin R_{430} und R_{550} die Lichtreflexionen bei Wellenlängen von 430 µm bzw. 550 µm bedeuten.

7. Masse nach einem der vorstehenden Ansprüche, worin der Farbentwickler (1) erhalten wird durch Behandeln eines Tonminerals mit einer Schichtstruktur aus regulären SiO_2-Tetraedern mit einer Säure, so daß nach dem Trocknen bei 105°C während 3 Stunden der SiO_2-Gehalt 82 bis 96,5 Gew.-% beträgt, Inberührungbringen des behandelten Tons in einem wässrigen Medium mit einer Magnesium- und/oder Aluminiumverbindung, Neutralisieren des erhaltenen Produkts mit Alkali oder Säure unter Bildung eines Hydroxids, wenn die Magnesium- und/oder Aluminiumverbindung kein Hydroxid ist, um dadurch in das säurebehandelte Tonminerial Magnesium und/oder Aluminium einzuführen und - falls erwünscht - Trocknen des Produkts.

8. Masse nach Anspruch 7, worin die Säurebehandlung so lange vorgenommen wird, bis das säurebehandelte Tonmineral in der Röntgenanalyse im wesentlichen kein Beugungsmuster mehr zeigt, das Kristallen der aus regulären SiO_2-Tetraedern zusammengesetzten Schichtstruktur des Tonminerals vor der Säurebehandlung zuzuschreiben ist.

9. Masse nach einem der vorstehenden Ansprüche, worin der Anteil der Metallverbindung 0,4 bis 1 mmol/g der Komponenten (1), wenn vorhanden (2) und (3) zusammen ist.

10. Masse nach einem der vorstehenden Ansprüche, worin die Metallverbindung (3) Calciumhydroxid ist.

11. Masse nach einem der vorstehenden Ansprüche, worin die Metallverbindung (3) eine solche Korngröße hat, daß wenigstens 70 % davon aus Teilchen mit einem Teilchendurchmesser von nicht mehr als 10 μm bestehen, bestimmt mit der Andreasen-Pipette.

12. Masse nach einem der vorstehenden Ansprüche, worin die Metallverbindung (3) zu wenigstens 90 Gew.-% aus Teilchen besteht, die durch ein 325 mesh Tyler-Standard-Sieb fallen.

13. Masse nach einem der vorstehenden Ansprüche, welche wenigstens 99 Gew.-% Teilchen enthält, die durch ein 325 mesh Tyler-Standard-Sieb fallen.

14. Druckempfindliche Aufzeichnungsblätter mit einer Beschichtung aus einer Farbentwicklermasse, wie in einem der vorstehenden Ansprüche beansprucht.

Revendications

1. Composition révélatrice de couleur pour feuilles d'enregistrement sensibles à la pression, comprenant un révélateur de couleur (1) qui est dérivé d'un minéral argileux ayant une structure en couches, composée de tétraèdres réguliers de silice et qui, après traitement intense par un acide et reconstruction ultérieure de ladite structure en couches,

(A) présente un spectre de diffraction qu'on peut attribuer aux cristaux d'une structure en couches, composée de tétraèdres réguliers de silice, quand on le soumet à une analyse par diffraction d'électrons, mais

(B) ne présente pratiquement aucun spectre de diffraction qu'on puisse attribuer aux cristaux de ladite structure en couches, quand on le soumet à une analyse par diffraction de rayons X et

(C) contient comme élément constituant, outre l'oxygène, au moins le silicium et le magnésium et/ou l'aluminium, **caractérisée** en ce que la composition comprend :

(1) un révélateur de couleur (1) qui contient du magnésium et/ou de l'aluminium, tout magnésium contenu n'étant pas soluble dans une solution aqueuse de chlorure d'ammonium,

(2) facultativement un révélateur de couleur ayant une teneur en silice qui ne dépasse pas 80 % en poids sec et composé d'une argile montmorillonite dioctaèdrique traitée par un acide, ou d'un mélange de celle-ci avec une argile montmorillonite dioctaèdrique naturelle, ledit révélateur de couleur (2)

(D) présentant un spectre de diffraction qu'on peut attribuer aux cristaux de ladite structure en couches quand on le soumet à une analyse par diffraction de rayons X, et

(3) 0,2 à 2 millimoles, par gramme des composants (1), (2) quand il est présent et (3) en combinaison, d'au moins un composé métallique choisi parmi les oxydes et hydroxydes de calcium et zinc.

2. Composition selon la revendication 1, dans laquelle le minéral argileux dont dérive le révélateur de couleur (1) est au moins l'une des argiles montmorillonites, des argiles kaolinites, des argiles sépiolites-palygorskites, des argiles chlorites et des argiles vermiculites.

3. Composition selon la revendication 1 ou 2, dans laquelle le révélateur de couleur (1) contient du silicium et du magnésium et/ou aluminium dans un rapport silicium/ magnésium et/ou aluminium) compris entre 12:1,5 et 12:12, en atomes.

4. Composition selon la revendication 1, 2 ou 3, dans laquelle tout révélateur de couleur (2) présente une aire spécifique d'au moins 180 m^2/g.

5. Composition selon l'une quelconque des revendications précédentes, dans laquelle tout révélateur de couleur (2) est une argile acide traitée à l'acide (argile active), ou un mélange de celle-ci avec une argile acide naturelle.

6. Composition selon l'une quelconque des revendications 1 à 4, dans laquelle le révélateur de couleur (2) est une argile montmorillonite dioctaèdrique traitée par un acide, ou un mélange de celle-ci avec une argile montmorillonite dioctaèdrique naturelle et, quand on le soumet à un développement de couleur secondaire avec le leucobenzoylique du bleu de méthylène, il présente un rendement de développement de couleur secondaire K_2, défini par l'équation suivante, d'au moins 1,40 :

$$K_2 = \frac{R_{430}}{R_{550}} + 2/1\,(1—R_{550})$$

dans laquelle R_{430} et R_{550} représentent les réflectances de lumières de longueurs d'onde respectives de 430 mμ et 550 mμ.

7. Composition selon l'une quelconque des revendications précédentes, dans laquelle on obtient le révélateur de couleur (1) en traitant une argile ayant une structure en couches, composée de tétraèdres réguliers

de silice, avec un acide de sorte que, après séchage à 105°C pendant 3 heures, sa teneur en SiO_2 soit de 82 à 96,5 % en poids, en mettant en contact l'argile traitée, en milieu aqueux, avec un composé de magnésium et/ou d'aluminium, en neutralisant le produit avec un alcali ou un acide pour former un hydroxyde quand le composé de magnésium et/ou d'aluminium n'est pas un hydroxyde, pour ainsi introduire du magnésium et/ou de l'aluminium dans l'argile traitée à l'acide et, éventuellement, en séchant le produit.

8. Composition selon la revendication 7, dans laquelle on effectue le traitement à l'acide jusqu'à ce que l'analyse aux rayons X de l'argile traitée à l'acide ne fasse pratiquement plus apparaître de spectre de diffraction qu'on puisse attribuer aux cristaux de la structure en couches composée de tétraèdres réguliers de silice, et que possédait l'argile avant le traitement à l'acide.

9. Composition selon l'une quelconque des revendications précédentes, dans laquelle la quantité de composé métallique est de 0,4 à 1 millimole par gramme des composants (1), (2) quand il est présent, et (3), en combinaison.

10. Composition selon l'une quelconque des revendications précédentes, dans laquelle le composé métallique (3) est l'hydroxyde de calcium.

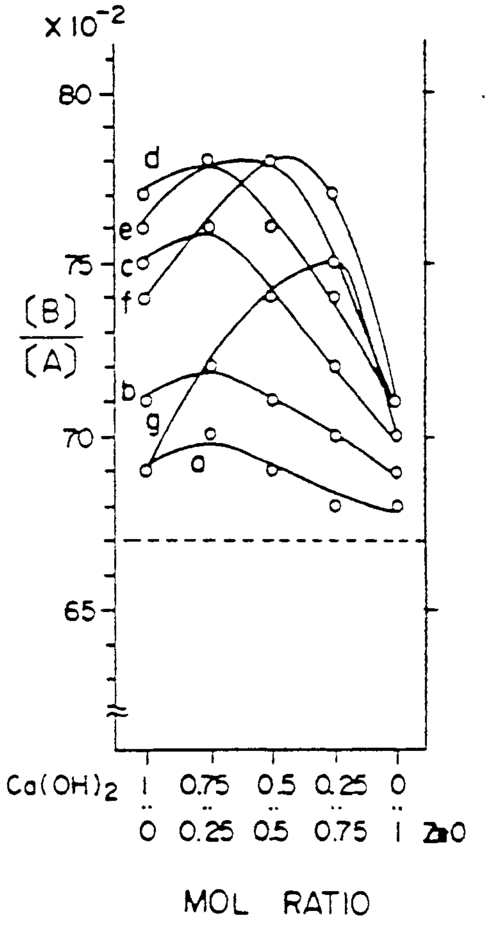
11. Composition selon l'une quelconque des revendications précédentes, dans laquelle le composé métallique (3) présente une taille de particules telle qu'au moins 70 % de ces particules sont des particules ayant un diamètre non supérieur à 10 μm, quand on le mesure par le procédé à la pipette d'Andreasen.

12. Composition selon l'une quelconque des revendications précédentes, dans laquelle le composé métallique (3) contient au moins 90 % en poids de particules qui passent à travers un tamis normalisé Tyler de 325 mesh.

13. Composition selon l'une quelconque des revendications précédentes, qui contient au moins 99 % en poids de particules qui passent à travers un tamis normalisé Tyler de 325 mesh.

14. Feuilles d'enregistrement sensibles à la pression comprenant un revêtement d'une composition révélatrice de couleur selon l'une quelconque des revendications précédentes.

FIG. 1


x 10⁻²
80
75
70
65
[B]/[A]
d
e
c
f
b
g
a
Ca(OH)₂ 1 : 0
0.75 : 0.25
0.5 : 0.5
0.25 : 0.75
0 : 1 ZnO
MOL RATIO