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Sugahara et al.

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[54] **PRESSURE SENSITIVE RECORDING PAPER**

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[63] Continuation-in-part of Ser. No. 775,126, Nov. 12, 1968, Pat. No. 3,622,364

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[51] **Int. Cl.**..... **B41m 5/22**

[58] **Field of Search**..... 117/36.2; 106/288 B

[56] **References Cited**

UNITED STATES PATENTS

3,622,364	11/1971	Sugahara et al.	106/288 B
3,330,722	7/1967	Amano	117/36.2
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[57] **ABSTRACT**

A pressure sensitive recording paper comprising a paper substrate and a coating thereon comprising a color former which comprises a member selected from the group consisting of acid-treated dioctahedral montmorillonite clay minerals and mixtures of such minerals with natural dioctahedral montmorillonite clay minerals, the minerals having a secondary color development property, K_2, of at least 1.40, the value of K_2 being represented by the formula

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

wherein R_{430} and R_{550} are reflectances of light having wavelengths 430 mμ and 550 mμ, respectively, when the minerals are developed by benzoyl leuco methylene blue.

4 Claims, No Drawings

PRESSURE SENSITIVE RECORDING PAPER

This application is a continuation-in-part of application Ser. No. 775,126, filed Nov. 12, 1968, now U.S. Pat. No. 3,622,364.

This invention relates to a pressure sensitive recording paper having as a coating, a color former which demonstrates pronounced color development effect, such pressure sensitive recording paper being capable of reproducing copies by hand writing, printing or typing without the necessity of the conventional carbon paper.

The pressure sensitive recording papers, with a few exceptions in the case of special papers, are in all cases those in which the color development reaction is attributable to the transfer of electrons between the colorless compound of organic coloring matter having electron donating properties and a color former, the electron acceptor. (U.S. Pat. No. 2,548,366).

Two classes of coloring matter, each of which exhibits different behaviours of coloration, have been used as the colorless compound of organic coloring matter. One of these is that which, as in the case, for example, of the triphenyl methane coloring matter, develops color intensely immediately upon contacting a solid acid, but which has a tendency to fade easily (primary color development coloring matter). The second coloring matter used is one which does not immediately develop color upon contacting a solid acid but develops its color completely after several days have elapsed and exhibits adequate fastness to sunlight. The acyl leuco methylene blues, for example, are used as such coloring matter (secondary color development coloring matter).

On the other hand, solid acids are generally used as the color former and the electron acceptor. In the past, materials such as kaolin, bentonite, attapulgite, aluminum sulfate, natural zeolite, silica gel, feldspar, pyrophyllite, halloysite, magnesium trisilicate, zinc sulfate, zinc sulfide, calcium fluoride, calcium citrate as well as the organic acids as tannic acid and benzoic acid have been used.

The pressure sensitive recording paper using these color development coloring matter and color formers is made up of two classes of papers: one, the transfer sheet (referred to as the coated back or CB), a paper which has been coated with the coloring matter in solution in oil and encapsulated by using such materials as gelatin, gum arabic or synthetic resin, the size of which capsules is several microns in diameter, and the other, the receiving sheet (referred to as the coated front or CF), a paper coated with the color former. When such two papers are superposed facing each other and pressure is applied with either a steel pen or a typewriter, the capsules of that portion to which the pressure has been applied rupture and the oil and the colorless coloring matter come into contact with the color former to develop color and thus impress that portion with a mark. When three or more copies are required, one or more intermediate sheets, which are generally referred to as a coated front and back sheet (or CFB), i.e., one which has the front coated with the color development coloring matter and the back coated with the color former, are used interleaved between the transfer sheet and the receiving sheet.

According to previous proposals, it can be seen that in all cases, research concerning the pressure sensitive recording paper has emphasized the process of synthesizing the organic coloring matter and encapsulation thereof and practically no studies have been made regarding the color former of the pressure sensitive recording paper. Accordingly, in the present state of the art, the practice is to use attapulgite, a kind of naturally obtained clay, in its as-obtained state.

However, the conventional color formers such as indicated above were either those in which, notwithstanding their good color development effect relative to the primary color development coloring matter, their color development effect relative to the secondary color development coloring matter was poor, or, notwithstanding their good color development effect relative to the secondary color development coloring matter, their color development effect relative to the primary color development coloring matter was poor. Thus, to date no color former which demonstrates excellent color development effects relative to the primary as well as secondary color development coloring matter has been found.

It is, therefore, a primary object of the present invention to provide pressure sensitive recording paper having a color former coated thereon which demonstrates excellent color development effects relative to the primary as well as secondary color development coloring matter.

Still another object of the present invention is to provide such pressure sensitive recording paper having a color former coated thereon which not only excels in its color development effects relative to the primary as well as secondary color development coloring matter but also causes fewer smudges. Smudge, as herein used, refers to a non-intended color development phenomenon (soiling) which occurs, for example, during preservation, carrying, handling, etc.

An additional object of the present invention is to provide such pressure sensitive recording paper wherein the color former has less exfolidation phenomenon after its application to the paper.

Other objects and advantages of the present invention will become apparent from the following description.

The foregoing objects and advantages are achieved according to the present invention by a pressure sensitive recording paper to which has been applied a color former which comprises a dioctahedral montmorillonite clay mineral and/or the acid-treated products thereof, the specific surface area of which is at least 180 m^2/g. Of the total mineral particles at least 75 percent by weight have a particle diameter 10 microns or less, and not more than 45 percent by weight are those of a diameter of one micron or less. Also, mineral and/or its acid-treated products have a secondary color development property, K_2, of at least 1.40, preferably at least 1.60, the value of K_2 being represented by the formula

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

wherein R_{430} and R_{550} are reflectances of light having wavelengths 430 m μ and 550 m μ, respectively, when the mineral and/or its acid treated products are developed by benzoyl leuco methylene blue.

It has been found that in accordance with the present invention that the color development effects of the color former in the secondary color development coloring matter, e.g., acyl leuco methylene blue, is con-

trolled to a great extent by the inherent properties of the natural solid acid, and that although the color development property of the natural solid acid relative to the secondary color development coloring matter can be improved somewhat by such chemical treatments as, for example, acid, alkali, oxidation and reducing treatments, a substantial improvement of the color development property cannot be attained. The solid acids, which are the color former, which have been known, are the natural clay minerals, such as kaolin, bentonite, attapulgite and natural zeolite; however, attapulgite has been principally used.

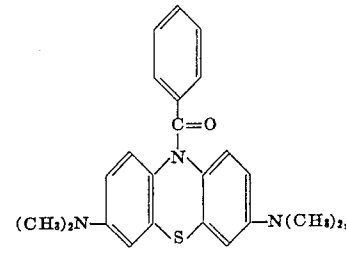
However, it was found in accordance with the present invention that the secondary color development property of these natural clay minerals was very irregular, there being a marked difference in the color development property even among those of the same class depending upon such factors as their locale of production or their position of burial within the same deposit.

Accordingly, when natural clay minerals, generally referred to as, for example, attapulgite or bentonite, are used nonselectively, little, if any, color development property is noted in some instances or the extent of the color dvelopment is not adequate in some instances, and, thus, a uniform secondary color development effect is not demonstrated. In addition, these natural clay minerals have the shortcoming that their primary color development effect is on the whole uniformly poor.

It has been discovered in accordance with the present invention that, of the natural clay minerals, dioctahedral montmorillonite clay mineral has a unique property in that a certain class of the montmorillonite clay mineral has, as its inherent property, an excellent color development property relative to the secondary color development coloring matter (secondary color development property). It has also been discovered that this characteristic differs from the other clay minerals in that the color development property relative to the primary color development coloring matter (primary color development property) can be enhanced remarkably by an acid treatment. Further, it was confirmed that a practically proportional relationship exists between the primary color development property of the hereinbefore indicated clay minerals and their specific surface area; and that the specific surface area of dioctahedral montmorillonite clay minerals adopted by the present invention is generally increased by its acid treatment though there is a difference in degree depending upon its class and that an enhancement of the primary color development property takes place in concomitance with this increase in specific surface area.

It has been found that a color former for pressure sensitive recording paper, which excels both in its primary and secondary color development property, can be obtained by first choosing from among the dioctahedral montmorillonite clay minerals those which excel in secondary color development property and, thereafter, subjecting these chosen montmorillonite clay minerals to an acid treatment until the desired specific surface area is obtained.

Further, it has been found that the color development property of the aforesaid montmorillonite clay minerals can be readily determined by measuring, in accordance with the measurement method given below, the reflectances R_{430} and R_{550} of light having wavelengths 430 m μ and 550 m μ when the minerals are developed by benzoyl leuco methylene blue of the formula



and comparing the value of K_2 calculated as follows:

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

Method of Measuring the Secondary Color Development Property

1. Preparation of the specimen.

The color former is prepared by winnowing it and comminuting it well in a mortar or pot mill so that of the total particles those of a diameter of 10 microns or less in diameter make up at least 75 percent by weight while those of a diameter of one micron or less make up no more than 45 percent by weight thereof. Five grams of this powder is then placed in a weighing bottle and is dried in a 110°C. constant temperature dryer for one hour followed by allowing it to cool in a desiccator.

The particle diameter of the color former is measured by means of the Andreasen sedimentation pipet. For particulars, reference is made to the Encyclopedia of Chemical Technology (R.E. Kirk, D. Othmer), Vol. 12, p. 490 (1954). The particle diameters used herein have all been made by this method of measurement.

2. Preparation of the color development coloring matter solution.

Five grams of benzoyl leuco methylene blue are dissolved in 95 grams of g.p. benzene.

3. Color development conditions.

Two grams of the foregoing dried specimen are weighed onto a watch glass 8 cm in diameter and spread out thinly. Four cc. of the benzoyl leuco methylene blue solution are then dropped in such a manner as to completely wet the whole specimen, after which stirring is carried out with a spatula to ensure that the system becomes homogeneous. If complete wetting of the speciman cannot be accomplished by 4 ml. of the solution owing to the greatness of the oil absorption value of the specimen, the foregoing operation is carried out after first adding benzene to the coloring matter solution in a necessary amount. This is followed by allowing the specimen to stand for 24 hours in a room of a temperature 15° – 20°C. into which the direct rays of sunlight do not shine. During this time the specimen is mixed two or three times with a spatula to ensure that the entire specimen becomes homogeneous. The specimen obtained is used for measuring the degree of color development.

4. Method of measuring the degree of color development.

The degree of color development of the specimen whose color has been developed in the foregoing manner is measured with a spectrophotometer. The specimen is packed in a powder cell of quartz and its reflectances of lights having wavelengths of 430 μ and 550 m μ are measured. The reflectance is expressed in per-

cent using as the basis 100 percent for the reflectance of an alpha-alumina shaped product.

5. Method of indicating the secondary color development property.

When the reflectances of the lights of 430 m μ and 550 m μ are designated respectively R_{430} and R_{550}, the secondary color development property is defined by the following equation

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

Thus, the greater the value of K_2, the better the secondary color development property. For the method of accurately indicating color, the methods of indication of the Commission on Illumination are used. The determinations of color development by means of the value of K_2, as defined hereinabove, and the results of determinations by means of the naked eye have been found to be in very good agreement.

Next, to clarify the fact that the specific surface area, primary color development property, secondary color development property and decolorizing property of the natural clay minerals differ greatly depending upon such conditions as their class, locale of production and position of production in the same locale and that there is a change over a broad range in these properties after the acid treatment of the minerals, these properties of the various classes of natural clay minerals are shown in Table I, below.

TABLE I-(i)

Class of the clay mineral	Name of the clay mineral	Locale of in which clay produced	Specimen No.	Property of untreated specimen: Specific surface area (m^2/g.)	Primary color development (K_1)	Secondary color development (K_2)	Decolorizing ability (percent)	Acid treatment: Specific surface area (m^2/g.)	Primary color development (K_1)
Attapulgite	Attapulgite	Florida (USA)	1	96	2.69	1.68	34.4	160	2.65
Kaolin mineral	Kaolinite	Georgia (USA)	2	24	2.06	1.17	39.5	40	2.38
	Halloysite	Niigata	3	72	2.20	1.35	29.3	160	2.28
Mica clay mineral	Sericite	Niigata	4	24	2.71	1.20	39.5	24	3.03
Talc mineral	Talc	Okayama	5	10	2.02	1.18	0	10	2.08
Dioctahedral montmorillonite.	Bentonite (I)	Okayama	6	15	1.74	1.19	0	25	1.78
	Bentonite (II)	Tsugawa (Niigata)	7	60	2.40	1.70	6.8	136	2.50
	Bentonite (III)	Gunma	8	72	2.63	1.84	6.8	100	2.22
	Sub-bentonite (I)	Mississippi (USA)	9	104	2.40	1.80	5.7	280	3.04
	Sub-bentonite (II)	Utah (USA)	10	72	2.48	1.30	1.1	232	2.96
	Japanese acid clay (I)	Nakajo (Niigata)	11	104	2.45	2.15	9.1	200	3.15
	Japanese acid clay (II)	do	12	96	2.48	1.63	18.2	240	2.70
	Japanese acid clay (III)	Shibata (Niigata)	13	128	3.10	1.29	42.1	160	3.43
	Japanese acid clay (IV)	Tsuruoka (Yamagata)	14	104	2.42	2.15	33.0	350	3.21
	Japanese acid clay (V)	do	15	136	2.19	1.39	18.2	144	2.35

TABLE I-(ii)

Speciman No.	Property of acid-treated specimen (A): Secondary color development (K_2)	Decolorizing ability (percent)	Acid treatment time	Property of acid-treated specimen (B): Specific surface acid (m^2/g.)	Primary color development (K_1)	Secondary color development (K_2)	Decolorizing ability (percent)	Acid treatment time	Suitability for use as color former for pressure sensitive recording paper
1	1.65	52.1	1	160	2.65	1.65	47.0	2	Satisfactory (primary color development effect inferior).
2	1.21	47.8	3	72	2.38	1.22	54.2	6	Poor.
3	1.33	74.4	3	190	2.33	1.32	79.7	6	Poor (decolorizing property very good).
4	1.20	39.6	1	32	3.11	1.20	42.5	5	Poor.
5	1.16	0	1	10	2.19	1.14	2.0	4	Do.
6	1.18	0	1	30	1.90	1.15	0	2	Do.
7	1.80	72.0	1	185	3.10	1.82	73.2	3	Excellent.
8	1.82	66.2	1	120	2.23	1.71	70.2	3	Poor.
9	2.22	87.1	5	350	3.41	2.26	75.7	9	Excellent (grade become acceptable as a result of acid treatment).
10	1.30	73.3	2	328	3.03	1.25	80.3	4	Poor (decolorizing property very good).
11	1.89	75.3	2	280	3.47	1.72	80.7	5	Excellent (grade become acceptable as a result of acid treatment).
12	1.98	68.0	3	340	3.03	1.89	78.2	7	Do.
13	1.35	64.7	4	168	3.69	1.32	70.4	8	Poor.
14	2.29	70.8	3	400	3.42	1.57	73.8	6	Excellent (grade become acceptable as a result of acid treatment).
15	1.35	68.7	2	295	3.20	1.33	78.9	4	Poor (decolorizing property good).

Testing procedures.

The several tests indicated in Table I were conducted in the following manner:

1. Preparation of the specimen.

After the dried color former has been fully comminuted in a mortar or pot mill, it is winnowed and prepared such that at least 85 percent by weight of the total particles are those having a particle diameter 10 microns or less and not more than 35 percent by weight are those of a particle diameter one micron or less. Five grams of this powder are then weighed into a weighing bottle, dried for one hour in a 110°C. constant temperature dryer and, thereafter, allowed to cool in a desiccator.

2. Acid treatment conditions.

1. Specimens Nos. 1–8.

Fifty gram samples of the clay on a dry basis are weighed into six 500-ml conical beakers. After adding 300 ml of 16.2 wt. percent hydrochloric acid to each beaker, they are heated in a 85°C. water bath. After the passage of each hour one of the beakers is taken out from the water bath, and the contents are water-washed until no chloride ion remains, then dried at 110°C., comminuted and winnowed to obtain the specimen. Of these 6 specimens, the tests were conducted on (A) those demonstrating the greatest decolorizing property when a lubricating oil was decolorized at 250°C., and (B) those demonstrating the greatest decolorizing property when soybean oil was decolorized at 110°C.

2. Specimens Nos. 9–15.

76.5 gram samples of the clay on a dry basis were weighed into eight 500-ml conical beakers. After add-

ing 200 ml of 34 wt. percent sulfuric acid to each beaker, they are heated in a 85°C. water bath. After the passage of each hour, one of the beakers is taken out from the hot water bath and the contents are water-washed until no sulfate ion remains, followed by drying at 110°C., comminution and winnowing to obtain the specimens. Of these specimens, the tests were conducted on (A) those demonstrating the greatest decolorizing property when a lubricant was decolorized at 250°C. and (B) those demonstrating the greatest decolorizing property when soybean oil was decolorized at 110°C. These (A) and (B) specimens are indicated in Table I as acid-treated specimens (A) and (B), respectively.

3. Specific surface area.

The specific surface area of the several specimens were determined by the BET method which is based on the adsorption of nitrogen gas. For details of this method, reference is made to the following literature:

S. Brunauer, P. H. Emmett, E. Teller,

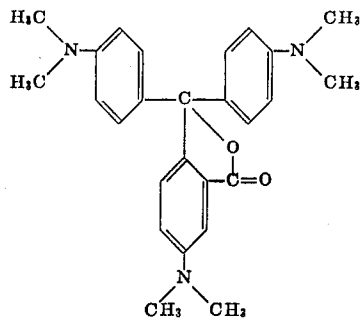
J. Am. Chem. Soc., 60,309 (1938) The specific surface area, as indicated herein, has been determined by the foregoing method.

4. Method of measuring the primary color development property.

1. Preparation of the solution of the color development coloring matter.

Crystal voilet lactone, a triphenylmethane coloring matter, is used as the primary color development coloring matter. 0.5 Gram of this coloring matter is dissolved in 99.5 grams of g.p. benzene. The chemical nomenclature and structural formula of crystal violet lactone are as follows:

Crystal voilet lactone [3,3-bis(p-dimethylaminophenyl)-6-dimethylphthalide]



2. Color development conditions.

Two grams of the hereinbefore described dried specimen are weighed into a watch glass 8 cm in diameter and spread out thinly, after which 4 ml of the crystal violet lactone benzene solution are dropped onto the specimen in such a manner that the entire specimen becomes completely wet. This is followed by mixing the specimen with a spatula to achieve a homogeneous mixture and allowing the mixture to stand for one hour in a room temperature of 15° – 20°C. into which direct rays of sunlight do not shine. In this way, the specimen is obtained for measuring the color development. When the oil absorption of the specimen is great and complete wetting is not obtained by 4 ml of the solution, the same operation is carried out after first having added the necessary amount of benzene to the coloring matter solution.

3. Method of measuring the degree of color development.

The degree of color development of the specimen whose color has been developed under the hereinbefore indicated conditions is measured using a spectrophotomer. The specimen is packed in a quartz cell having a diameter of 21 mm and a height of 10 mm, and with the width of the slit of 1 mm the reflectances at wavelengths 390, 550, and 590 m μ are measured. The reflectance is indicated in precent using as the basis 100 percent for the reflectance of an alphaalumina shaped article.

4. Method of indicating the primary color development property.

When the reflectances at 390, 550, and 590 m μ are respectively designated R_{390}, R_{550}, and R_{590}, the primary color development property, K_1, is defined by the following equation:

$$K_1 = R_{390}/R_{590} + \tfrac{1}{2}\,(1-R_{550})$$

Thus, it can be said that the larger the value of K_1, the better the primary color development property. It has been determined that there is very good agreement between the determinations of the color development property as expressed by the value of K_1 and the results obtained by determinations by means of the naked eye.

5. Method of measuring the secondary color development property.

The method of measuring and indicating this property, as previously described herein, is used.

6. Decolorizing property.

Fifty grams of unrefined soybean oil are weighed into a hard glass 150-ml test tube, to which one gram of the specimen is then added. The test tube is then immersed in an oil bath heated at 110°C. and the contents are stirred vigorously for 20 minutes. The specimen is then filtered with a filter paper, after which the clarified oil is placed in a 20-mm cell. White light is directed against this cell and the light transmittance is measured with a photoelectric colorimeter. The light transmittance is indicated in percent on the basis of 100 percent for the light transmittance of distilled water. The decolorizing property of oil when its light transmittance is T percent is defined by the following equation:

$$\text{Decolorizing property (\%)} = T - 56/100 - 56 \times 100$$

where 56 percent is the light transmittance of the unrefined soybean oil used in the present experiment.

7. Criterion of suitability.

Those having a secondary color development property above 1.40 and a specific surface area above 180 m^2/g are considered as being acceptable.

The following facts can be understood from the results of Table I. Namely, 1) the natural clay minerals other than the dioctahedral montmorillonite clay minerals used in the present invention are all inferior in their primary and secondary color development properties, the only exception being attapulgite (see specimen Nos. 2, 3, and 4 in Table 1). Even though the specific surface area of other minerals is increased by an acid treatment, there is not much improvement of their primary color development property (see specimen No. 3 in Table I).

2. While attapulgite demonstrates considerably good primary and secondary color development properties in its as-obtained natural state, its specific surface area is not increased to as much as 180 m^2/g even though it is subjected to the acid treatment, and its primary color development property is also scarcely improved (see specimen No. 1 in Table I).

3. On the other hand, a certain class of dioctahedral montmorillonite clays demonstrates good secondary color development property, which when acid treated increases its specific surface area greatly to also demonstrate, concomitantly, a marked improvement in its primary color development property as well (see specimen Nos. 7, 9, 11, 12, and 14 in Table I).

4. However, certain dioctahedral montmorillonite clay minerals are unsuitable for use as the color former of the present invention because they are inferior in their secondary color development property although they excel in their specific surface area, primary color development property and decolorizing property (see specimen Nos. 10, 13, and 15).

5. Further, certain dioctahedral montmorillonite clay minerals excel in their secondary color development property as in the case with attapulgite but their specific surface area does not increase by means of the acid treatment and, accordingly, their primary color development property is not improved (see specimen No. 8 in Table I).

From the foregoing results, it can be understood that the following general principles hold in the case of the dioctahedral montmorillonite clay minerals.

a. The secondary color development property being an inherent property of the material clay itself cannot essentially be improved though some improvement can be had by the acid treatment.

b. The primary color development property increases in proportion to an increase in the specific surface area by means of the acid treatment, the desirable primary color development property ($K_1 = 2.60$) being attained when the specific surface area reaches or exceeds 180 m^2/g.

c. The decolorizing property is not related at all to the secondary color development property.

Therefore, according to the present invention, a dioctahedral montmorillonite clay mineral having the highest possible K_2 value, at least above 1.40, and preferably above 1.60, is first chosen. This clay mineral is then subjected to an acid treatment so as to increase its specific surface area to above 180 m^2/g while ensuring that its K_2 value does not fall to below 1.40, and preferably not below 1.60. Thus, it becomes possible to produce a color former having extremely satisfactory primary and secondary color development properties. The dioctahedral montmorillonite clay minerals which can be utilized are the natural clay minerals such, for example, bentonite, sub-bentonite, fuller's earth, Florida earth, and Japanese acid clay. However, the dioctahedral montmorillonite clay minerals, as used herein, are not limited to only those which have been illustrated.

On the other hand, the acid to be used in the acid treatment that is carried out to produce the color former of the pressure sensitive recording paper of the present invention may be any inorganic or organic acid which is able to increase the specific surface area of the montmorillonite clay minerals to above 180 m^2/g. However, inorganic acids are generally preferred over the organic acids for reasons of cost and ease of handling. Of the inorganic acids, sulfuric and hydrochloric acids are particularly convenient.

Further, no particularly strict conditions are involved in the acid treatment. If an acid of dilute concentration is used, either the treatment time becomes longer or the quantity of the acid required becomes greater. Whereas if the concentration is high, either the treatment time becomes shorter or the quantity of the acid required becomes less in correspondence to the increase in concentration. Again, if the treatment temperature becomes higher, the treatment time is correspondingly shortened. Accordingly, the acid concentration may be conveniently within the range of 1–80 percent, but from the standpoint of convenience in handling, the acid treatment is preferably carried out at a concentration of the order of 15–45 percent and a temperature ranging between 50° and 105°C. In short, in this invention, it is only important that the acid treatment of the dioctahedral montmorillonite clay mineral be conducted until its specific surface area becomes at least 180 m^2/g.

However, one thing which must be cautioned against in carrying out the acid treatment is that there are instances in which the secondary color development property makes a marked decline when the acid treatment proceeds to an excessive degree. For this reason, it is preferred that the acid treatment conditions be so controlled that the specific surface area of the clay after treatment comes within the range between 180 m^2/g and 350 m^2/g.

Next, Table II shows the changes in the specific surface area and the primary and secondary color development properties of acid-treated clay depending upon the degree of acid treatment given.

TABLE II

Sulfuric acid treatment time (hr.)	Japanese acid clay A			Japanese acid clay B		
	Specific surface area (m^2/g.)	Primary color development property	Secondary color development property	Specific surface area (m^2/g.)	Primary color development property	Secondary color development property
0 (untreated clay)	75	2.45	2.13	62	2.36	1.62
0.5	102	2.55	2.15	103	2.42	1.68
1	108	2.60	2.15	142	2.50	1.75
2	235	2.99	2.17	163	2.84	1.70
3	265	3.28	2.24	187	3.09	1.65
4	295	3.39	2.31	230	3.21	1.50
5	307	3.47	2.24	242	3.30	1.38
6	325	3.51	2.15	248	3.38	1.30
8	346	3.60	1.88	263	3.42	1.28
10	370	3.68	1.65	271	3.45	1.25
12	384	3.74	1.60	280	3.48	1.20

As shown in Table II, above, the dioctahedral montmorillonite clay minerals used in the present invention are increased in their specific surface area by means of the acid treatment, and it can be seen that the primary color development property becomes good when the specific surface area becomes greater than 180 m^2/g. When the specific surface area increases in this manner, the capacity to absorb and adsorb oil increases at the same time. Hence, the acid treatment is necessary and indispensable in the present invention.

It has also been found that the particle size of the color former to be used in the present invention is also a very important factor. That is, when the particle size of the color former becomes too large, there is an increase in the smudging phenomenon, whereas if there is an increase in those particles which are too small, the particles after having been applied to paper tend to exfoliate. Moreover, if considered from the standpoint of the color development effect, a greater color development effect is obtained when the particles of the color former are smaller in both cases of the primary and secondary color development properties.

It has been discovered that by making the particle size of the color former such that the particles of a diameter 10 microns or less are present in an amount of at least 75 percent by weight, and preferably at least 85 percent by weight of the total particles and those of a diameter one micron or less are present in an amount not exceeding 45 percent by weight, and preferably not exceeding 35 percent by weight of the total particles, the color development effect is greatly enhanced to yield an excellent color former for pressure sensitive recording paper in which the undesirable tendency to smudging and exfoliation of the applied particles is less.

The relationship between the particle diameter of the color former and its primary and secondary color development properties and the relationship between the particle diameter and smudging are shown in Table III, below. It becomes apparent from these results that the color former should preferably be one containing at least 75 percent by weight of particles of a diameter 10 microns or less to achieve the color development effect and prevention of the smudging phenomenon.

The specimens submitted to the experiment whose results have been presented in Table III were those prepared by adjusting the particle size by winnowing of the acid-treated specimen (B). (No. 12) of the previously given Table I.

TABLE III

Specimen No.	Content of particles 10 μ or less (wt %)	Color Development Property Primary	Secondary	Soil-resistant property (%)
1	18.2	2.75	1.75	40.8
2	26.6	2.77	1.77	43.7
3	35.8	2.80	1.80	47.5
4	69.0	2.91	1.80	52.5
5	75.4	2.93	1.82	85.8
6	85.2	3.03	1.89	88.5
7	93.9	3.18	1.90	92.3
8	97.9	3.18	1.90	94.5

Method of measuring the soil-resistant property.

One hundred grams of the color former are suspended in 250 ml of water, to which 10 grams of starch are then added. This suspension is applied to paper of fine quality in an amount such that 7 grams of the color former are adhered per square meter of the paper, after which the paper is dried to obtain a coated front sheet. A coated back sheet is superposed on this coated front sheet, and a stainless steel cylinder 5 cm in diameter and weighing 4 kg is then placed on top of the superposed sheets and gently pulled across the sheets. The soiling of the coated front sheet which results is measured for its reflectance of light of a wavelength 430 m μ using a spectrophotometer. The soil-resistant property is defined by the following equation:

soil-resistant property (%) = reflectance of solid coated front sheet/reflectance of unsoiled coated front sheet × 100

The greater the numerical value of the soil-resistant property (%), the less is the soiling.

It is apparent from the results in Table III that a marked decrease in the smudging phenomenon takes place when the content of particles of a diameter 10 microns or less is at least 75 percent by weight, and preferably at least 85 percent by weight of the total particles. It is also seen that the primary and secondary color development effects are also superior with this particle size.

A relationship between the particle diameter of the color former and the exfoliation property of the coated front sheet, such as shown in Table IV, below, is observed. In this experiment, the I.G.T. (Instrturt voor Grafische Techniek) test was employed for investigating the exfoliation property. In this test the tendency to exfoliation is less as the number becomes greater. The specimen used are those whose particle diameter has been adjusted as in Table IV by winnowing the acid-treated specimen (A) (No. 12) of Table I.

TABLE IV

Specimen No.	Content of particles 1 μ or less (wt %)	Color Development Property Primary	Secondary	IGT Test (cm/sec)
1	15	3.15	1.88	180
2	28	3.15	1.90	160
3	35	3.19	1.92	150
4	40	3.21	1.93	120
5	45	3.22	1.96	115
6	50	3.22	1.96	90
7	60	3.23	1.97	60

The foregoing I.G.T. test was conducted on the specimen prepared in the following manner in accordance with the below-described measurement method. One hundred grams of the color former are suspended in 250 ml of water, and then 10 grams of starch are added. This suspension is applied to high quality paper such that the adhesion of the color former to the paper amounts to 7 grams per square meter, followed by drying the paper to obtain the coated front sheet. This sheet is submitted to the I.G.T. test and the rate at which the exfoliation of the color former takes place is measured. It can be seen that when the content of particles one micron or less in size exceeds 45 percent by weight the results of the I.G.T. test suddenly become worse.

It can be understood from the foregoing results that according to the present invention it is preferred from the standpoint of the color development effect obtained and smudging that of the total particles at least 75 percent by weight, and preferably 85 percent by weight, are those whose particle size is 10 microns or less; and moreover that from the standpoint of the exfoliation property of the color former it is preferred that of the total particles not more than 45 percent by weight, and preferably not more than 35 percent by weight, are those one micron or less.

This exfoliation property is a considerably important matter in making good quality transfer sheets, because if the exfoliation of the color former is great a large amount of paste must be used for preventing this, with

the consequence that a marked decline in the color development effect takes place.

Thus, according to the present invention, success was achieved in the production of a color former for pressure sensitive recording paper by a procedure comprising choosing from among the dioctahedral montmorillonite clay minerals one whose secondary color development property, K_2, value, relative to benzoyl leuco methylene blue as measured in accordance with the hereinbefore described measurement method, is at least 1.40, and preferably at least 1.60, subjecting this chosen montmorillonite clay mineral to an acid treatment to increase its specific surface area to at least 180 m^2/g, and preferably to a value in the range between 180 m^2/g and 350 m^2/g and moreover ensuring that the foregoing secondary color development property, K_2, value does not become less than 1.40, and preferably not less than 1.60, followed by water-washing and drying, and thereafter either comminuting or classifying the foregoing clay mineral to render it into particle sizes in which, of the total particles, at least 75 percent by weight are those having a particle diameter 10 microns or less and moreover not more than 45 percent by weight of the total particles are those one micron or less in diameter.

In producing the color former of the pressure sensitive recording paper of the present invention, the procedure described above need not necessarily be followed since it is also possible to produce it by the following method.

The color former can also be produced by mixing (A) a dioctahedral montmorillonite clay mineral which has been acid treated until its specific surface area is at least 180 m^2/g, and preferably at least 220 m^2/g, with (B) a dioctahedral montmorillonite clay mineral or an acid-treated product thereof whose secondary color development property, K_2, has a value of at least 1.40, and preferably at least 1.80 to obtain as a whole a specific surface area of at least 180 m^2/g and a value for K_2 of at least 1.40, and comminuting or classifying clay minerals (A) and (B) either before or after their mixture, either separately or at the same time to render the mixture into particle sizes in which at least 75 percent by weight of the total particles are particles having a diameter 10 microns or less and moreover not more than 45 percent by weight of the total particles are those 1 micron or less in diameter.

When the hereinabove described method of the present invention is followed, clay mineral (A) need not necessarily be one whose K_2 value is at least 1.40. On the other hand, clay mineral (B) or its acid-treated product need not necessarily be one whose specific surface area is at least 180 m^2/g.

The color former prepared as hereinbefore described can be applied to paper using the natural or artificial pastes such as, for example, starch, casein, tragacanth gum, CMC, synthetic latex having a bonding property, such as styrene-butadiene latex and butadiene-acrylonitrille resin latex and polyvinyl alcohol to make the coated front sheet of pressure sensitive recording paper. Thus, a good quality coated front sheet is obtained whose primary and secondary color development effects during copying are exceedingly good and moreover in which smudging is held to a minimum.

Further, to improve the color development effect still further or to increase the amount of color former added, it is possible to suitably add such additives as other natural clay minerals or synthetic inorganic substances, e.g., calcium carbonate, silica, silicate; organic or inorganic pigments, e.g., ultramarine, persian blue, chrome yellow, iron oxide, Indanthrene, Rhodamine, and Methyl violet; dyestuffs such as fluorescent bleaching agent, e.g., diaminostilbene and benzoimidazole; oxidants, e.g., chloro-anyl, persulfates, dichromates, perhydrochlorides, permanganates, cupric salts, ferric salts, iodine, potassium ferrocyanide and organic acid peroxides; reducing agents, e.g., calcium sulfide and solid organic amines; solid acids, e.g., alumina, siloca, titania, zinc oxide, zinc chloride, titanium phosphate and zirconium phosphate; and alkaline substances such as sodium silicate, sodium pryophosphate and alkaline earth metal hydroxides, e.g., slaked lime.

The present invention will now be illustrated by reference to the following specific examples which are presented for purposes of illustration only and the present invention is in no way to be deemed as limited thereby.

EXAMPLES 1–5

The material clays indicated in Table V were chosen, dried, comminuted and winnowed to prepare them into specimens in which 90 percent of the total weight were particles whose diameter was 10 microns or less and 30 percent of the total weight were those whose diameter was one micron or less.

When the test for secondary color development property, as fully described herein, was conducted on the foregoing specimens, the K_2 values shown in Table V were obtained.

TABLE V

Specimen No.	Material clay and locale of its production		Secondary color development property K_2
1	Japanese acid clay-Nakajo, Niigata Pref., Japan	A	2.15
2	do	B	1.63
3	do	C	1.31
4	Japanese acid clay-Tsuruoka, Yamagate Pref., Japan	A	2.15
5	do	B	1.39
6	do	C	1.35
7	Japanese acid clay-Shibata, Niigata Pref., Japan	A	1.29
8	do	B	1.25
9	do	C	1.30
10	bentonite-Tsugawa, Niigate Pref., Japan		1.70
11	sub-bentonite, Mississippi, USA		1.80

The value of K_2 of specimen Nos. 1, 2, 4, 10, and 11 in Table V were above 1.40. Accordingly, the acid treatment of these was carried out under the following conditions.

Fifty grams on a dry basis of each of the foregoing five classes of clays were weighed into 500-ml conical breakers and their acid treatment was carried out under the conditions indicated in Table V, followed by water-washing, drying at 110°C., comminuting and winnowing to prepare the specimens. The particle size of each specimen was in all cases 90 percent of particles 10 microns or less in diameter and 25 percent of those one micron or less.

TABLE VI

Ex. No.	Specimen No. in Table V	Acid treatment conditions: Class of acid	Temperature (° C.)	Concentration (wt. percent)	Time (hr.)
1	1	Sulfuric acid	85	34	2
2	2	do	85	34	3
3	4	Hydrochloric acid	70	16	3
4	10	Nitric acid	60	26	4
5	11	Acetic acid	85	27	6

The properties of the several specimens obtained by the foregoing acid treatment are shown in Table VII, below.

TABLE VII

Example No.	Specimen No. in Table V	Specific surface area ($m.^2/g.$)	Color development value K_1	Color development value K_2	Decolorizing ability (percent)	Soil-resistant property (percent)	I.G.T. (cm./sec.)
1	1	200	3.15	1.80	75.3	93.4	162
2	2	240	2.70	1.89	68.0	93.0	160
3	4	350	3.21	2.29	70.8	92.8	158
4	10	185	3.10	1.82	73.2	93.1	161
5	11	280	3.04	2.22	70.7	92.8	157

As apparent from the foregoing description, when those having a K_2 value of at least 1.40 are chosen from the various classes of the dioctahedral montmorillonite clay minerals and these chosen minerals are subjected to an acid treatment under suitable conditions as specified by the present invention, minerals which excel in both primary and secondary color development properties are obtained, and those having particle sizes as specified by the present invention also excel in soil-resistant and exfoliation resistant properties.

EXAMPLE 6

65 percent by weight of the Japanese acid clay specimen B of Table II which had been acid treated for 12 hours and 35 percent by weight of specimen No. 8 of Table I were mixed and then comminuted. This comminuted mixture was then winnowed and a specimen having the following particle size was prepared; i.e., 92 percent by weight of particles whose diameter was 10 microns or less and 23 percent by weight of particles whose diameter was one micron or less. When the properties of this specimen were tested by the methods fully described in connection with Table I, the following results were obtained.

specific surface area	197 m^2/g
K_1	3.05
K_2	1.58

EXAMPLE 7

Specimen I (specimen No. 1 of Table I) and specimen II (Japanese acid clay specimen B of Table II which had been acid treated for 12 hours) were each winnowed and specimens having the following particle sizes were prepared.

Specimen	10 or less	1 or less
I	90 wt. %	21 wt. %
II	93 wt. %	24 wt. %

Next, 20 percent by weight of specimen I and 80 percent by weight of specimen II were well mixed, after which the properties of the mixture were tested by the methods fully described in connection with Table I, with the following results:

specific surface area	310 m^2/g
K_1	3.02
K_2	1.67

EXAMPLE 8

The acid-treated specimen (B) (specimen No. 11 of Table I) was winnowed and a specimen having the following particle size was prepared.

10 microns or less	92 wt. %
1 micron or less	26 wt. %

Then 0.25 gram of e.p. sodium perborate as an oxidant was added to 50 grams of the specimen followed by thorough mixing. When this mixture was tested for its properties in accordance with the testing methods fully described in connection with Table I, the following results were obtained.

specific surface area	280 m^2/g
K_1	3.40
K_2	2.28

EXAMPLE 9

The acid-treated specimen (B) (specimen No. 12 of Table I) was winnowed and a specimen having the following particle sizes was prepared.

10 microns or less	93 wt. %
1 micron or less	21 wt. %

Then, 4 grams of slaked lime as an alkaline substance were added to 100 grams of the specimen, followed by thorough mixing. When this specimen was tested for its properties by the test methods fully described in connection with Table I, the results obtained were as follows:

specific surface area	340 m^2/g
K_1	3.15
K_2	1.89

While the present invention has been described primarily with regard to the foregoing exemplifications, it should be understood that the present invention is in no way to be deemed as limited thereto but, rather, must be construed as broadly as all or any equivalents thereof.

EXAMPLE 10

This Example illustrates instances where various types of color formers are coated on paper, laid on a coloring matter paper, and then a color is developed under pressure.

As color formers, an acid-treated specimen No. 11A, prepared from specimen No. 11 described in Table 1, and the comminuted mixture specimen described in Example 6 were used. Further, specimens No. 13A, No. 8A, and No. 2A described in Table 1 were selected

and used as comparative examples. The specific surface areas and k_1 and k_2 values of the color formers are shown in Table VIII.

Each of the 5 types of samples was coated on a sheet of paper as follows, and then color was developed.

50 g. of each same were added to 70 g. of an aqueous solution in which 0.5 g. of sodium hexametaphosphate and 0.75 g. of sodium hydroxide had been dissolved, and then the mixture was sufficiently stirred for 1 hour in a 500 r.p.m. stirring machine to obtain a slurry. The pH of this slurry was adjusted to 9.5 ± 0.3 with a 10% NaOH solution, 15 g. (solid 50 percent) of SBR (styrene-butadiene rubber) latex (DOW No. 636) were added thereto as an adhesive, and then the mixture was stirred for 15 minutes. The slurry thus prepared was coated on a sheet of paper so that the amount of the color former might be 7–9 g/m² with the aid of a coating rod No. 12 manufactured by R. D. Specialities Laboratory. This coated paper was dried at 110°C. for 5 minutes in a thermostat, and a so-called CF (coated front) papers, on which the color former were coated, were obtained.

On the other hand, sheets of CB (coated back) paper, or sheets of paper on which a predetermined primary color development coloring matter (crystal violet lactone), a predetermined secondary color development coloring matter (benzoyl leucomethylene blue) and a mixture thereof were coated, respectively, were prepared.

The color formed-coated CF paper and the coloring matter-coated CB paper were laid one on the other, interposed between a rotary double roller, and a pressure of 500 kg/cm² was applied thereto to develop color.

After 24 hours had elapsed, the density of the color developed was measured with a densitometer to examine the color development effect. In this case the higher the color density, the larger its value.

The results were as shown in Table VIII.

TABLE VIII

Specimen No.	11A	Ex.6	13A	8A	2A
Specific surface area (m²/g)	200	197	100	100	40
Primary color development (k_1)	3.15	3.05	3.43	2.22	2.38
Secondary color development (k_2)	1.89	1.58	1.35	1.82	1.22
Color density					
Primary	69	68	45	42	18
Secondary	22	21	16	14	10
Mixture	72	68	50	35	20

From the above results, it is understood that a good color development effect can be obtained when a color former having a specific surface area of not less than 180 m²/g and a k_2 value not less than 1.40 is coated on paper, and then color is developed under pressure.

We claim:

1. In a pressure sensitive recording paper comprising a paper substrate and a coating of a color former formed thereon, the improvement wherein said color former consists essentially of particles of a member selected from the group consisting of acid-treated dioctahedral montmorillonite clay minerals and mixtures of a major proportion of said minerals with a minor proportion of natural dioctahedral montmorillonite clay minerals, said minerals being characterized by the following: (a) a specific surface area of at least 180 m²/g; (b) at least 75 percent by weight of the total particles being of a particle diameter of 10 microns or less; (c) not more than 45 percent by weight of the total particles being of a diameter of one micron or less; and (d) a secondary color development property, K_2, of at least 1.40, the value of K_2 being represented by the formula

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

wherein R_{430} and R_{550} are reflectances of light having wavelengths 430 mμ and 550 mμ, respectively, when the said minerals are developed by benzoyl leuco methylene blue.

2. The pressure sensitive recording paper of claim 1 wherein said minerals have a specific surface area within the range of 180 – 350 m²/g.

3. The pressure sensitive recording paper of claim 1 wherein the value of K_2 is at least 1.60.

4. The pressure sensitive recording paper of claim 1 wherein of the total particles of said color former at least 85 percent by weight of said particles have a diameter of 10 microns or less and not more than 35 percent by weight of said particles have a diameter of 1 micron or less.

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