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(54) **Calcium carbonate pigment for heat-sensitive recording paper, process for preparing same, coating composition for heat-sensitive recording paper and heat-sensitive recording paper.**

(57) Disclosed are a calcium carbonate pigment for heat-sensitive recording paper, the pigment having a BET specific surface area of about 17 to about 55 m^2/g, an oil absorption of about 90 to about 220 ml/100 g as determined by the Ogura method and a surface acidity of solid substantially represented by the following equation (Z) :

$$y=0.13\ x + 31 \quad (Z)$$

wherein x is a BET specific surface area (m^2/g) and y is a surface acidity of solid (μmol/g) ; a process for preparing the pigment ; coating compositions comprising said pigment each for forming an intermediate layer of heat-sensitive recording layer, and for a heat-sensitive recording layer thereof : and heat-sensitive recording papers obtained by application of the coating compositions.

EP 0 456 413 A2

BACKGROUND OF THE INVENTION

The present invention relates to an anti-fogging and surface-treated calcium carbonate pigment for the coating layer of heat-sensitive recording paper, a process for preparing the same, a coating composition comprising the calcium carbonate for heat-sensitive recording paper, and heat-sensitive recording paper coated with the composition.

Calcium carbonates include light calcium carbonate and heavy calcium carbonate which are up to 10 m^2/g in BET specific surface area, and fine calcium carbonate in excess of 10 m^2/g in BET specific surface area. Calcium carbonate is widely used as a pigment for papers, coating compositions, inks, etc. and also as a filler for rubbers, plastics, papers, sealing materials, etc.

In recent years, calcium carbonate is increasingly used also as a pigment for the coating layer of information recording papers such as heat-sensitive recording paper, ink-jet recording paper, etc.

Calcium carbonate is incorporated into coating compositions for heat-sensitive recording paper generally in order to improve the whiteness, non-transparency, surface-smoothness, writablity and like properties of heat-sensitive recording paper as in the case of usual papers. Yet the main object of incorporation of the calcium carbonate is to give the following effects. When heat-sensitive recording paper is heated by the thermal head of a heat-sensitive facsimile system or heat-sensitive printer to develop a color for recording, a higher fatty acid amide or like chromogenic sensitivity adjusting agent, crystal violet lactone or like dye, etc. adhere to the thermal head as residual matter (hereinafter referred to as "residue") to obscure the recorded characters or to reduce the runnablity, i.e., the ability of recording paper to smoothly pass, so that calcium carbonate is incorporated in the coating composition for such paper to inhibit or prevent the adhesion of the residue (hereinafter referred to as "effect to remove residue") and also to achieve heat transfer with enhanced efficiency from the thermal head to the surface of heat-sensitive recording paper.

Heat-sensitive recording paper is a recording material comprising a chromogenic material, a color developer, a pigment and other components, and is required to have:

(1) an ability to give an image of distinct color;

(2) a background having high whiteness, i.e. free of fogging;

(3) an ability to produce an image exhibiting a high weatherability even during long-term storage.

Use of highly oil-absorbent calcium carbonate pigment has been considered desirable for improvement of the effect to remove residue. Such known calcium carbonates include, for example, bodies of intertwined needle- to pillar-like calcium carbonate particles as disclosed in Japanese Examined Patent Publication No.8048/1988 and highly oil- and water-absorbent calcium carbonate as described in Japanese Unexamined Patent Publication No.230424/1989. These calcium carbonates are excellent in the effect to remove residue, but are not always fully satisfactory in anti-fogging property, ability to form images with high resistance to weather, especially to light, heat transfer efficiency, etc.

Currently attempts are being made in the art to develop a heat-sensitive recording paper which is able to achieve speedy recording, and there is a tendency to use more highly oil-absorbent calcium carbonates capable of producing an improved effect to remove residue and giving a higher heat transfer efficiency. Nevertheless calcium carbonate has yet to be developed which is fully satisfactory in anti-fogging property of heat-sensitive recording paper, ability to form images of high weatherability, etc.

It is an object of the invention to provide a calcium carbonate pigment which is sufficiently highly oil-absorbent to provide an improved effect to remove residue, and also outstanding in anti-fogging property, ability to form images of high weatherability, etc.

We thought that the above object might be accomplished by surface-treating a highly oil-absorbent calcium carbonate pigment with a certain substance. For investigation, we conducted extensive research to provide a surface-treated calcium carbonate which, when used as a pigment for the coating layer of heat-sensitive recording paper, exhibits not only an excellent effect to remove residue and a high chromogenic sensitivity, but also an excellent property of forming images of high weatherability with substantially no fogging. As a result of the research, we found the following. When a specific calcium carbonate surface-treating agent is added to an aqueous suspension of calcium carbonate particles having a BET specific surface area of about 17 to about 55 m^2/g, and the mixture is stirred to surface-treat the carbonate, the thus treated carbonate is given a surface acidity of solid of about 33 to about 38 μmol/g with substantially no reduction of oil absorption of the starting calcium carbonate, and is rendered able to achieve remarkable effects unattainable by known calcium carbonates. The present invention has been accomplished based on this novel finding.

According to the present invention, there is provided a calcium carbonate pigment for heat-sensitive recording paper, the pigment having a BET specific surface area of about 17 to about 55 m^2/g, preferably about 19 to about 55 m^2/g, an oil absorption of about 90 to about 220 ml/100 g as determined by the Ogura method and a surface acidity of solid substantially represented by the equation (Z):

$$y = 0.13\,x + 31 \quad (Z)$$

wherein x is a BET specific surface area (m^2/g) and y is a surface acidity of solid (μmol/g).

The present invention also provides a process for preparing the foregoing calcium carbonate pigment for heat-sensitive recording paper, the process comprising the steps of (i) adding a calcium carbonate surface-treating agent to an aqueous suspension of calcium carbonate having a BET specific surface area of about 17 to about 55 m^2/g, preferably about 19 to about 55 m^2/g, the surface-treating agent being at least one member selected from the group consisting of hydroxide of alkaline earth metal, hydroxide of alkali metal, carbonate of alkali metal, bicarbonate of alkali metal, sodium aluminate, aluminum acetate and C_{4-14} aliphatic amine acetate; and (ii) stirring the mixture.

The invention further provides a coating composition for heat-sensitive recording paper characterized in that the composition contains the above calcium carbonate pigment for heat-sensitive recording paper.

Throughout the specification and claims, the BET specific surface area was determined by the low-temperature nitrogen adsorption method (see "Particle Size Determination Techniques," edited by the Research Association of Powder Technology, Nikkan Kogyo Press, 1st edition, 1975, pp. 299-305). The surface acidity of solid was determined by an amine titrimetric determination method (see Kozo Tabe and Tsuneichi Takeshita, "Acid-base Catalyst," Sangyo Tosho, 1st edition, 1966, pp.164-167). The method comprises titrating a calcium carbonate pigment as a solid acid in benzene with p-dimethylamino-azobenzene (dimethyl yellow) as an indicator using normal butyl amine. The oil absorption was determined by the Ogura method (see Junzo Matsumoto and Masateru Ogura, "Pigments, Coloring Materials and Inks," Kyoritsu Shuppan Co., Ltd., 4th print, 1950, pp. 66-67, with use of boiled linseed oil according to JIS K 5421).

Table 1 below shows the physical properties of the calcium carbonate pigment of the invention for heat-sensitive recording paper in comparison with those of known calcium carbonates.

Table 1

Properties	Calcium carbonate of the invention	Known calcium carbonate			
		(i)	(ii)	(iii)	(iV)
BET specific surface area (m^2/g)	17-55	25-55	17	6	5-15
Surface acidity of solid (μmol/g)	33-38	44-47	43	23	30-40
Oil absorption (ml/100g)	90-220	120-220	95	59	80-100
Bulk (ml/g)	6.5-15	8-15	6	5	6.5-10
Sedimentation volume (ml/60min.)	55-98	60-90	52	18	20-60
Hiding power (cm^2/g)	35-55	30-40	13	20	27-35
True specific gravity	2.56-2.64	2.58-2.62	2.60	2.60	2.75-2.93
Crystal system	Calcite	Calcite	Calcite	Calcite	Aragonite
Mean particle size (μm)	0.5-6	0.5-5	4	5	0.5-6

EP 0 456 413 A2

The known calcium carbonates (i) to (iv) listed in Table 1 are as follows.

(i) Highly oil- and water-absorbent calcium carbonate as disclosed in Japanese Unexamined Patent Publication No.230424/1989

(ii) Fine precipitated calcium carbonate

(iii) Light calcium carbonate

(iv) Bodies of intertwined needle-like to pillar-like calcium carbonate particles as disclosed in Japanese Examined Patent Publication No.8048/1988

The properties such as bulk in Table 1 were determined by the following methods.

Bulk:	Pigment-testing method according to JIS K 5101
Sedimentation volume:	5 g of calcium carbonate was placed into a 100 ml measuring cylinder, and water was added to make 100 ml of a suspension. After shaking for 20 seconds, the suspension was left to stand for 60 minutes to determine the volume of sediment.
Hiding power:	Pigment-testing method according to JIS K 5101
True specific gravity:	Pigment-testing method according to JIS K 5101
Crystal system:	Determined by X ray diffraction method
Mean particle size:	Median particle size as measured by light transmission particle size determination method.

Table 1 shows that the surface-treated calcium carbonate pigment of the invention has a surface acidity of solid of as low as 33 to 38 μmol/g compared with the known calcium carbonate (i) having a BET specific surface area of about 25 to 55 m^2/g, and retains high oil absorption which is another important property of calcium carbonate pigment for heat-sensitive recording paper.

Our research revealed that calcium carbonate having a BET specific surface area of about 17 to about 55 m^2/g has the problem of being generally not always satisfactory in the anti-fogging property presumably because of its high surface acidity of solid due to its great BET specific surface area irrespective of the other physical properties such as particle shape, sedimentation volume, etc. In other words, generally calcium carbonates having a BET specific surface area of about 17 to about 55 m^2/g would be likely to cause fogging when used as a pigment for heat-sensitive recording paper. Therefore the surface-treating method of the invention shows a particular significance when employed to treat calcium carbonates having a BET specific surface area of about 17 to about 55 m^2/g, preferably about 19 to about 55 m^2/g. The method of the invention reduces the surface acidity of solid of calcium carbonate to the specific range of about 33 to about 38 μmol/g in the specific relation represented by the above-defined equation (Z) with substantially no decrease in the BET specific surface area or in the oil absorption.

Now we turn to the properties of the calcium carbonate pigments of the invention. The calcium carbonate pigments less than 17 m^2/g in BET specific surface area have an inherently low surface acidity of solid like the starting calcium carbonate and are virtually free of fogging problem, but tend to have a low effect to remove residue because of generally low oil absorption. On the other hand, the treatment of calcium carbonate pigments more than 55 m^2/g in BET specific surface area requires an increased amount of a surface-treating agent which is needed in order to diminish the high surface acidity of solid of the starting calcium carbonate to 38 μmol/g as specified above according to the equation (Z), so that the obtained calcium carbonate tends to have a decreased oil absorption. Therefore such calcium carbonates are undesirable. To give a surface acidity of solid of less than 33 μmol/g to calcium carbonate, an increased amount of surface-treating agent is required, resulting in reduction of oil absorption. Thus such calcium carbonates are undesirable. In this case, presumably due to the relatively high surface basicity of solid, the obtained heat-sensitive recording paper is apt to form images of low weatherability. Above 38 μmol/g of a surface acidity of solid, a fogging problem may arise.

The calcium carbonate pigment of the invention is usually prepared by the following process. To an aqueous suspension of calcium carbonate having a BET specific surface area of about 17 to about 55 m^2/g is added at least one calcium carbonate surface-treating agent selected from the group consisting of hydroxide of alkaline earth metal, hydroxide of alkali metal, carbonate of alkali metal, bicarbonate of alkali metal, sodium aluminate, aluminum acetate and acetic acid salt of C_{4-14} aliphatic amine. Then the mixture is stirred to treat the surface of the pigment particles.

Useful starting calcium carbonates having a BET specific surface area of about 17 to about 55 m^2/g include a variety of known calcium carbonates. Among them, it is desirable to use those as disclosed in Japanese Unexamined Patent Publication No.230424/1989 and Japanese Examined Patent Publications No.31530/1982 and No.30815/1982.

More desirable among these starting calcium carbonate pigments are the calcium carbonate pigment as disclosed in Japanese Unexamined Patent Publication No.230424/1989 which is 25 to 55 m^2/g in BET specific surface area, between 5 and 110 in the ratio of BET specific surface area (m^2/g)/mean particle size (μm), at

least 120 ml/100 g in oil absorption as determined by the Ogura method and at least 1.8 g/g in water absorption, and the calcium carbonate pigment which is 17 to 55 m^2/g, preferably 19 to 55 m^2/g, in BET specific surface area, among the bodies of intertwined needle-like calcium carbonate particles as disclosed in Japanese Examined Patent Publication No.31530/1982, the particles being formed of bodies of needle-like primary particles of calcium carbonate three-dimensionally intertwined irregularly and having mean dimensions of 0.5 to 10 μm in length (L) and 0.05 to 0.2 μm in width (W) as observed under an electron microscope, an aspect ratio (L/W) of from 10 to 50, a void volume of 1.8 to 3.3 ml/g as measured by a porosimeter (mercury intrusion porosimetry) and an oil absorption of 50 to 100 ml/100 g as measured according to JIS K 5101.

The oil absorption of calcium carbonate pigment contributes to the effect to remove residue. From the viewpoint of the effect to remove residue, it is suitable in the invention to use starting calcium carbonate pigments of preferably about 90 to about 220 ml/100 g, more preferably about 93 to about 220 ml/ 100 g, in oil absorption. It is preferable that the starting calcium carbonate pigments are those having a bulk of about 6.5 to about 15 ml/g, preferably about 7 to about 15 ml/g.

Of calcium carbonate surface-treating agents useful in the invention, typical hydroxides of alkaline earth metals are hydroxides of magnesium, calcium or like metals, preferable hydroxides, carbonates or bicarbonates of alkali metals are sodium or potassium hydroxides, carbonates or bicarbonates, and preferred C_{4-14} aliphatic amine acetic acid salts are butyl amine, octyl amine and lauryl amine acetic acid salts. The amount of the calcium carbonate surface-treating agent which is added to the aqueous suspension of calcium carbonate of 17 to 55 m^2/g in BET specific surface area is in the range of about 0.1 to about 5 parts by weight, preferably about 0.2 to about 4 parts by weight, per 100 parts by weight of the calcium carbonate. When the amount is less than 0.1 part by weight, the surface acidity of solid can not be suppressed as contemplated and the heat-sensitive paper incorporating the treated carbonate is not imparted an improved anti-fogging property. When the amount is more than 5 parts by weight, the obtained heat-sensitive paper has an improved anti-fogging property but tends to have an impaired effect to remove residue due to reduced oil absorption. Therefore the amount of surface-treating agent outside the above range is undesirable.

The concentration of solids in the aqueous suspension of starting calcium carbonate is not specifically limited, but is usually in the range of about 5 to about 30% by weight, preferably about 7 to about 25% by weight. The mixture is stirred for surface treatment preferably at a temperature of about 15 to about 35°C. The aqueous suspension of starting calcium carbonate is stirred by stirring means which can stir uniformly the whole suspension, such as a propeller-type stirrer, high-speed impeller dispersing means, an oar-type stirrer, turbine-type stirrer, a stirrer of the type capable of blowing air or like gas, etc. The stirring time is not specifically limited, but is preferably in the range of about 10 to about 30 minutes.

The calcium carbonate pigment of the invention having the BET specific surface area and the surface acidity of solid related to each other as represented by the equation (Z) is prepared by surface-treating the starting calcium carbonate of the above-specified BET specific surface area under the above conditions. As compared with the starting calcium carbonate, the obtained calcium carbonate is slightly reduced or increased, but not substantially reduced to an unacceptable degree, in oil absorption, and has suppressed surface acidity of solid in the range of about 33 to about 38 μmol/g.

The calcium carbonate pigment obtained by the above surface treatment may be used in the form of a paste which is obtained by dewatering the suspension resulting from the surface treatment by a filter press or like dewatering means, or in the form of a powder prepared in the conventional manner by drying the paste, pulverizing the solid and classifying the particles.

The thus obtained calcium carbonate pigment of the invention, when used for forming a coating layer in heat-sensitive recording paper, was found to exhibit, due to the above specific properties of the surface, the excellent properties which have not been found in known calcium carbonates. Therefore, the present invention also relates to coating compositions for heat-sensitive recording paper which comprise about 5 to about 90% by weight of the above-obtained calcium carbonate pigment based on the total solids. Given below are examples of coating compositions of the invention.

(1) Composition for forming a heat-sensitive recording layer of heat-sensitive recording paper

This composition comprises about 5 to about 60 wt. % of the calcium carbonate pigment of the invention as admixed with a known colorless to pale-colored basic dye, a color developer such as phenolic compound for causing the dye to produce a color when heated, a chromogenic sensitivity adjusting agent, a binder, etc. The heat-sensitive recording papers obtained with use of the composition are comparable to those incorporating the conventional calcium carbonate in the effect to remove residue and are superior to the latter in color density, anti-fogging property, resistance to light, etc.

The components of the coating composition for heat-sensitive recording paper other than the above calcium carbonate pigment, i.e. the basic dye, color developer, chromogenic sensitivity adjusting agent, binder, and the like can be a wide variety of those conventionally used for heat-sensitive paper. Typical examples of these components are as follows.

(a) Colorless to pale-colored basic dyes

Triarylmethane dyes such as 3,3-bis(p-dimethylaminophenyl)-6-dimethylaminophthalide, fluoran dyes such as 3-diethylamino-6-methyl-7-anilinofluoran, spiropyran dyes such as 3-methyl-spiro-dinaphthopyran, diphenylmethane dyes such as N-halophenyl-leucoauramine, thiazine dyes such as benzoylleucomethyleneblue, etc.

(b) Color developers

Phenolic compounds such as 4-tert-butylphenol, 4-hydroxydiphenoxide, 4,4'-isopropylidenediphenol (bisphenol A), 2,2'-methylenebis(4-chlorophenol) and novolak-type phenolic resins, aromatic carboxylic acids or derivatives thereof such as benzoic acid, p-tert-butyl-benzoic acid, p-hydroxybenzoic acid, methyl p-hydroxybenzoate, isopropyl p-hydroxybenzoate, benzyl p-hydroxybenzoate, lauryl gallate, stearyl gallate, salicylanilide, 5-chlorosalicylanilide, 5-tert-butylsalicylic acid, hydroxynaphthoic acid and zinc or like metal salts of these acids or derivatives thereof.

(c) Chromogenic sensitivity adjusting agents

Higher fatty acid amides such as palmitic acid amide, stearic acid amide, oleic acid amide, hydroxystearic acid amide, methylolated fatty acid amide, ethylenebis fatty acid amide and methylenebis fatty acid amide.

(d) Binders

Water-soluble high-molecular-weight compounds such as polyvinyl alcohol, methyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxpropyl cellulose, starch, casein, gelatin and gum arabic.

When required, various auxiliary agents for use in known coating compositions for heat-sensitive paper can be further incorporated into the composition of the invention. Examples of such additives are release agents, defoaming agents, ultraviolet absorbers, fluorescent dyes, coloring dyes, preservatives, etc. When required, another pigment can be added in an amount of up to about 20% by weight, based on the total amount of the composition. Examples of useful other pigments are aluminum hydroxide, silica, calcined kaolin, kaolin, talc, urea resin, etc.

The components of the coating composition according to the invention and the proportions (solid contents) thereof can be changed according to the contemplated purpose. Usually, the composition comprises the following proportions (solid contents) of components based on the total solids.

Basic dye	about 3 to about 10 wt.% (preferably about 5 to about 10 wt.%)
Color developer	about 15 to about 50 wt.% (preferably about 20 to about 40 wt.%)
Chromogenic sensitivity adjusting agent	about 6 to about 30 wt.% (preferably about 10 to about 30 wt.%)
Binder	about 16 to about 22 wt.% (preferably about 16 to about 20 wt.%)
Calcium carbonate pigment of the invention	about 5 to about 60 wt.% (preferably about 10 to about 55 wt.%)

The coating composition of the invention can be prepared in a known manner, for example, by the following method. First, the basic dye, color developer and chromogenic sensitivity adjusting agent are each separately milled in an aqueous solution of binder. When a ball mill, for example, is used for this purpose, each component is added to the binder solution usually to a solids concentration of about 15 to about 30 wt. %, and the mill is operated for 2 days to obtain fine particles of about 1 to about 5 μm in size. The calcium carbonate pigment of the invention, when required together with other pigments, is dispersed in an aqueous solution of binder in the usual manner using a dispersant to prepare a pigment dispersion containing about 20 to about 30 wt. % of solids. Subsequently, the pigment dispersion and the aqueous suspensions of finely divided components are mixed together in the conventional manner, giving a coating composition for forming a heat-sensitive recording layer of heat-sensitive paper according to the invention. The composition is in the form of a dispersion containing about 15 to about 30 wt. % of solids.

The composition is applied to a substrate and dried in the usual manner, and the coated substrate is calendered when required to give heat-sensitive paper. The coating composition of the invention is applied usually in an amount of about 3 to about 15 g/m^2, preferably about 5 to about 10 g/m^2, calculated as dry weight, although the amount is variable, for example, with the properties of the heat-sensitive paper to be obtained.

Thus, the present invention provides a heat-sensitive recording paper which is characterized in that it comprises a substrate and a heat-sensitive recording layer formed thereon by applying the above coating composition and drying the resulting coating. Examples of useful substrates are various papers, synthetic resin sheets or films and the like which are conventionally used in the art.

Coating composition for forming an intermediate layer between heat-sensitive recording layer of heat-sensitive recording paper and substrate thereof

Our research has revealed that when the composition containing about 5 to about 40 parts by weight of a binder per 100 parts by weight of the calcium carbonate pigment of the invention is applied to a substrate to form an intermediate layer and a heat-sensitive recording layer is formed over the intermediate layer, the resulting paper is higher in color density, anti-fogging property, resistance to light, and the like than when the conventional calcium carbonate is used.

The binder to be used for the coating composition for forming the intermediate layer can be any of the binders already mentioned in item (1) for the heat-sensitive recording layer. Also useful are latices of styrene-butadiene copolymer, polyvinyl acetate, polyurethane, polyacrylic acid, polyacrylate, vinyl chloride-vinyl acetate copolymer, polybutyl methacrylate, ethylene-vinyl acetate copolymer, styrene-butadiene-acrylic copolymer and the like. When required, the coating composition may have further incorporated therein other pigments (such as calcined kaolin, silica, etc.), dispersants, surfactants, defoaming agents, coloring dyes, preservatives, etc.

While the proportions of components (calculated as solids) of the coating composition for forming the intermediate layer are variable over a wide range, a binder is used preferably in an amount of, calculated as solids, about 5 to about 40 parts by weight, preferably about 10 to 35 parts by weight, per 100 parts by weight of the calcium carbonate pigment of the invention. The amount of another pigment to be added when required is up to about 40 parts by weight, preferably about 10 to about 40 parts by weight, per 100 parts by weight of the combined amount of the calcium carbonate pigment of the invention and the binder calculated as solids.

The coating composition for the intermediate layer can be prepared by uniformly dispersing the calcium carbonate pigment of the invention and another pigment when so required in an aqueous solution of binder in the usual manner using a dispersant or the like to obtain a pigment dispersion containing about 25 to about 35 wt. % of solids. The composition can be applied to a substrate by various methods, for example, by a coater such as steel blade, air knife, roll, flexographic press, Mayer bar or the like. The amount of the composition to be applied, although widely variable, is generally about 1 to about 15 g/m^2, preferably about 3 to about 10 g/m^2, calculated as dry weight. The coating, when dried, is preferably calendered.

A heat-sensitive recording layer is formed by applying the coating composition for forming a heat-sensitive recording layer as stated above in item (1) in the conventional manner to the intermediate layer thus formed, and drying the coating layer, whereby a heat-sensitive recording paper is obtained which is excellent in effect to remove residue, anti-fogging property, color density, resistance to light and other properties.

Accordingly, the present invention further provides a heat-sensitive recording paper comprising a substrate, the above intermediate layer formed thereon and the heat-sensitive recording layer formed over the intermediate layer from the coating composition for a heat-sensitive recording layer which composition contains the calcium carbonate pigment of the invention as described above in item (1). Examples of useful substrates are paper, synthetic resin film and the like which are conventionally used in the art. The heat-sensitive recording layer can be any of those heretofore known other than those described above in item (1), such as one containing a colorless to pale-colored basic dye, color developer, chromogenic sensitivity adjusting agent, binder and the like as exemplified in item (1), and various other layers.

The reason still remains to be clarified why the above calcium carbonate pigment of the invention used for the coating layer of heat-sensitive recording paper produces the above excellent effects. However, the reason could presumably be explained as follows. Calcium carbonate has some characteristics of solid acid as its surface properties, and the surface acidity of solid thereof is considered to be associated with the anti-fogging property of heat-sensitive recording paper. While the surface of particulate calcium carbonate is relatively low in surface acidity of solid, calcium carbonates of greater BET specific surface area tend to have a higher surface acidity of solid. It is assumed accordingly that in a heat-sensitive recording layer, the calcium carbonate pigment of greater BET specific surface area has a larger surface area in contact with a basic dye acting as a chromogenic material, resulting in reduction of anti-fogging property. Calcium carbonate pigments for heat-sensitive paper are also required to have a high oil absorption which is another important property of such pigment.

Presumably, by surface-treating the calcium carbonate of about 17 to about 55 m^2/g in BET specific surface area according to the specific surface-treating method of the invention which induces substantially no reduction in the BET specific surface area or the oil absorption, the calcium carbonate pigment of the invention is endowed with a surface acidity of solid in the specific range, and thereby a heat-sensitive recording paper improved in anti-fogging property, color density and effect to remove residue is obtained. The calcium carbonate of the invention used also provides a heat-sensitive recording paper with higher resistance to light. However, the effect is unpredictable from the relation with the surface acidity of solid, and the reason for this improvement remains unclear.

Furthermore, the calcium carbonate of the invention used for heat-sensitive paper can enhance the whiteness and non-transparency of the paper.

The calcium carbonate pigments of the invention also have the following advantages.

1) When used as a filler for paper, the calcium carbonate of the invention can increase the retention of filler and enhance the whiteness and non-transparency of paper.

2) When incorporated into a coating composition for coat paper, the pigment of the invention gives a coating layer having a porous surface which can effectively absorb the applied printing ink, thereby accelerating the drying.

Examples

The present invention will be described below in more detail with reference to the following examples. In the following examples, "parts" and "percentages" are all by weight unless otherwise specified.

Example 1

A 100 kg quantity of an aqueous suspension of calcium carbonate having a BET specific surface area of 20 m^2/g, adjusted to a concentration of 20 wt.% and a temperature of 20°C, was placed into a reactor equipped with an impeller disperser. Thereafter, 1.4 kg of an aqueous solution of sodium aluminate adjusted to a concentration of 10 wt.% was added to the aqueous suspension with stirring at 500 r.p.m., and the resulting mixture was further agitated for 15 minutes. After completion of the agitation, the aqueous suspension of calcium carbonate was dewatered by a filter press. The solid product obtained was dried, pulverized and classified, giving 20 kg of a calcium carbonate pigment for heat-sensitive recording paper of the present invention.

Examples 2 to 7

Calcium carbonate pigments for heat-sensitive recording paper of the invention were prepared in the same manner as in Example 1 with the exception of using the conditions listed in Table 2. Table 2 also shows the conditions employed in Example 1.

Table 2

Example	Calcium carbonate pigment as starting material		Aqueous solution of surface-treating agent			Amount of product (kg)
	BET specific surface area (m^2/g)	Surface acidity of solid ($\mu mol/g$)	Kind	Concentration (wt.%)	Amount added (kg)	
1	20	42	Sodium aluminate	10	1.4	20
2	20	40	Potassium carbonate	10	2.4	20
3	35	45	Sodium hydrogencarbonate	10	2.0	20
4	35	45	Magnesium hydroxide	15	0.6	20
5	35	45	Acetic acid salt of butylamine	2	35.0	20
6	55	47	Sodium hydroxide	10	1.0	20
7	55	47	Acetic acid salt of laurylamine	2	25.0	20

In Table 2, the calcium carbonates used as starting materials in Examples 1 and 2 were prepared by a process disclosed in Japanese Examined Patent Publication No. 31530/1982, and those used in Examples 3 to 7 were produced by a process set forth in Japanese Unexamined Patent Publication No. 230424/1989.

Comparative Examples 1 to 5

Comparative calcium carbonate pigments were prepared in the same manner as in Example 1 with the exception of employing the conditions as described below in Table 3. The calcium carbonates used as starting materials in Comparative Examples 1 and 2 were produced by a process disclosed in Japanese Examined Patent Publication No. 31530/1982, and those used in Comparative Examples 3 to 5 were obtained by a process described in Japanese Unexamined Patent Publication No. 230424/1989.

In Comparative Examples 2, 3 and 5, no surface-treating agent was used.

Table 3

Comparative Example	Calcium carbonate pigment as starting material		Aqueous solution of surface-treating agent		
	BET specific surface area (m^2/g)	Surface acidity of solid ($\mu mol/g$)	Kind	Concentration (wt.%)	Amount added (kg)
1	20	42	Sodium aluminate	10	0.14
2	20	40	-	-	-
3	35	45	-	-	-
4	35	45	Acetic acid salt of butylamine	2	65
5	55	47	-	-	-

Table 4 below shows the physical properties of the calcium carbonate pigments obtained in Examples 1 to 7 and Comparative Examples 1 to 5.

Table 4

	BET specific surface area (m^2/g)	Surface acidity of solid (μmol/g)	Oil absorption (ml/100 g)	Bulk (ml/g)	Sedimentation volume (ml/60min)	Hiding power (cm^2/g)	Crystal form
Example 1	20	34	95	9	56	38	Calcite
Example 2	19	34	93	10	59	39	Calcite
Example 3	35	35	140	14	73	48	Calcite
Example 4	35	36	145	11	70	45	Calcite
Example 5	32	36	130	15	65	42	Calcite
Example 6	55	38	160	15	87	39	Calcite
Example 7	53	37	155	17	94	37	Calcite
Comp. Ex. 1	20	42	100	8	52	34	Calcite
Comp. Ex. 2	20	40	110	8	50	33	Calcite
Comp. Ex. 3	35	45	135	10	60	40	Calcite
Comp. Ex. 4	28	35	60	10	62	36	Calcite
Comp. Ex. 5	55	47	150	11	75	38	Calcite

From the results with respect to Examples 2 and 3 and Comparative Examples 2 and 3 as shown in Table 4, it is revealed that the calcium carbonate pigments of the invention are somewhat increased or decreased in BET specific surface area and oil absorption as compared with calcium carbonate used as the starting material. However, substantially no problem is caused even in the case where the calcium carbonate pigment of the invention is decreased in BET specific surface area or oil absorption. This indicates that the surface acidity of solid of the calcium carbonate pigment of the invention is suppressed to a specific range.

Example I

Coating compositions for forming the heat-sensitive recording layer of heat-sensitive recording paper were prepared by the following procedure using the calcium carbonate pigments of the invention (those obtained in Examples 1, 3 and 7). The compositions were used for preparing heat-sensitive recording papers.

First, a colorless dye, phenolic compound and fatty acid amide were each separately milled into fine particles according to the following formulations A, B and C. For this purpose, ball mills were operated for 2 days.

Formulation A

3-Diethylamino-6-methyl-7-anilinofluoran (product of Yamamoto Kagaku Gosei Co., Ltd., trademark "ONE DYE BLACK")	100 parts
5% Aqueous solution of polyvinyl alcohol	500 parts

Formulation B

Bisphenol A	100 parts
5% Aqueous solution of polyvinyl alcohol	500 parts

Formulation C

Fatty acid amide (trademark "ARMID HT-P", product of Lion ARMER Co., Ltd., m.p. 98°C, mixture of 22% palmitic acid amide, 75% stearic acid amide and 3% of oleic acid amide)	100 parts
5% Aqueous solution of polyvinyl alcohol	500 parts

According to the following formulation D, the calcium carbonate pigment of the invention was made into a pigment dispersion containing 25% of solids using an impeller-type agitator.

Formulation D

Calcium carbonate pigment	100 parts
5% Aqueous solution of polycarboxylic acid dispersant	20 parts
5% Aqueous solution of polyvinyl alcohol	300 parts
Water	40 parts

The dispersions A to D prepared according to the formulations A to D were mixed together in the ratio by weight of A:B:C:D = 1:5:3:5 to prepare coating compositions of the invention for forming a heat-sensitive recording layer.

Using a coating rod, the coating composition thus prepared was applied to one surface of wood-free paper, weighing 50 g/m^2, in the usual manner in an amount of 6 g/m^2 on dry basis. After drying the coating at room temperature, the coated paper was calendered to obtain heat-sensitive paper.

Table 5 showing the characteristics of the paper thus obtained indicates that the paper retains substantially the same degree of whiteness before and after the heating of the paper and is excellent in anti-fogging property. Further, the paper is outstanding in resistance to light and has high effect to remove residue.

Comparative Example I

Comparative coating compositions for forming a heat-sensitive recording layer were prepared in the same manner as in Example I except that the comparative calcium carbonate pigments obtained in Comparative Examples 1 to 5 were used. The compositions were used for preparing heat-sensitive recording paper. Table 5 shows the characteristics of the paper obtained. Table 5 also shows the results obtained using known calcium carbonate (i) (which is disclosed in Japanese Unexamined Patent Publication No. 230424/1989). The physical properties of the known calcium carbonate (i) used are as follows. (The same applies in the following description.)

BET specific surface area	38 m^2/g
Surface acidity of solid	44 μmol/g
Oil absorption	140 ml/100 g
Bulk	10 ml/g
Sedimentation volume	75 ml/60 min
Hiding power	35 cm^2/g
True specific gravity	2.60

Example II

Calcium carbonate pigments of the invention (those obtained in Examples 1, 3 and 7) were used for forming the intermediate layer of heat-sensitive paper. More specifically, the calcium carbonate pigment was uniformly dispersed according to the following formulation to obtain a coating composition for forming the intermediate layer.

Calcium carbonate pigment	100 parts
5% Aqueous solution of polycarboxylic acid dispersant	20 parts
5% Aqueous solution of polyvinyl alcohol	300 parts
Styrene-butadiene latex (brand name "SN-307", product of Sumitomo Naugatuck Co., Ltd., solids content 48%)	20 parts
Water	40 parts

Using a coating rod, the coating composition was applied to one surface of wood-free paper, weighing 50 g/m^2, in the usual manner in an amount of 7 g/m^2 on dry basis. After drying the coating, the coated paper was falendered to obtain pigment-coated paper.

Dispersions A, B, C and D prepared according to the formulations A to D in Example I were mixed together in the ratio by weight of A:B:C:D = 1:5:3:1 to obtain a coating composition, which was then applied to the pigment-coated paper in an amount of 6 g/m^2 on dry basis using a coating rod. After drying the coating at room temperature, the resulting paper was calendered to obtain heat-sensitive recording paper having an intermediate layer. Table 5 showing the characteristics of the heat-sensitive recording paper thus prepared indicates that the paper retained substantially the same whiteness before and after the heating of the paper, and was outstanding in anti-fogging property and resistance to light. Further, the paper had sufficiently high effect to remove residue.

Comparative Example II

Comparative coating compositions for forming an intermediate layer were prepared in the same manner as in Example II except that the comparative calcium carbonates obtained in Comparative Examples 1 to 5 were used. Comparative heat-sensitive paper having an intermediate layer was obtained in the same manner as in Example II using each of the comparative coating compositions. The characteristics of the heat-sensitive recording paper thus obtained were shown in Table 5, which also shows the result achieved using known calcium carbonate (i) similarly.

Table 5

	Anti-fogging property [1] (whiteness, %)		Resistance to light [2]	Effect to remove residue [3]
	After heating	Before heating	Image retentivity (%)	
Example I				
Pigment of Ex. 1	79	81	96	A
Pigment of Ex. 3	78	82	93	A
Pigment of Ex. 7	78	81	91	A
Comp. Example I				
Pigment of Comp. Ex. 1	66	81	85	A
Pigment of Comp. Ex. 2	65	81	84	A
Pigment of Comp. Ex. 3	64	80	83	A
Pigment of Comp. Ex. 4	77	80	91	B
Pigment of Comp. Ex. 5	62	79	80	A
Known calcium carbonate (i)	64	80	83	A
Example II				
Pigment of Ex. 1	76	79	93	A
Pigment of Ex. 3	75	79	91	A
Pigment of Ex. 7	74	78	90	A
Comp. Example II				
Pigment of Comp. Ex. 1	64	77	82	A
Pigment of Comp. Ex. 2	63	78	81	A
Pigment of Comp. Ex. 3	61	79	80	A
Pigment of Comp. Ex. 4	74	79	90	B
Pigment of Comp. Ex. 5	60	77	79	A
Known calcium carbonate (i)	61	79	80	A

1) Test for anti-fogging property

A piece of heat-sensitive paper (white paper) was set in a test apparatus maintained at a temperature of 60°C and was allowed to stand for 24 hours. The degree of discoloration (fogging) of the paper was determined by checking the whiteness of the paper (degree of 0°-45° reflection was measured with a blue filter using a deformation photometer manufactured by Murakami Shikisai-Giken Co.) before and after the heating of the paper.

2) Test for resistance to light

A piece of heat-sensitive paper on which images were formed with use of a commercially available facsimile machine (type G-III) was exposed to sunlight for 8 hours. The color densities of the images were measured before and after the exposure to sunlight using reflective densitometer (model DM-400, for black-and-white and color use, product of Dainippon Screen Co., Ltd.). The image retentivity was determined by the following equation.

$$\text{Image retentivity (\%)} = \frac{\text{Color density on color-developed side after exposure to sunlight}}{\text{Color density on color-developed side before exposure to sunlight}} \times 100$$

3) Effect to remove residue

Degree of stain (due to adhesion of residue) of the thermal head of commercially available facsimile machines was examined. The symbol "A" means that substantially no residue adheres to the head and the paper can be used without problem. The symbol "B" means that a large amount of residue adheres to the head and the paper is not practically usable.

As clear from the results shown in Table 5, the calcium carbonate pigment of the present invention is excellent not only in anti-fogging property but in resistance to light in comparison with known calcium carbonate pigments.

Claims

1. A calcium carbonate pigment for heat-sensitive recording paper, the pigment having a BET specific surface area of about 17 to about 55 m^2/g, an oil absorption of about 90 to about 220 ml/100 g as determined by the Ogura method and a surface acidity of solid substantially represented by the equation (Z):

$$y = 0.13x + 31 \quad (Z)$$

wherein x is a BET specific surface area (m^2/g) and y is a surface acidity of solid (μmol/g).

2. A calcium carbonate pigment according to claim 1 which has a BET specific surface area of about 19 to about 55 m^2/g.

3. A process for preparing the calcium carbonate pigment of claim 1 for heat-sensitive recording paper, the process comprising the steps of (i) adding a calcium carbonate surface-treating agent to an aqueous suspension of a calcium carbonate having a BET specific surface area of about 17 to about 55 m^2/g, the surface-treating agent being at least one member selected from the group consisting of hydroxide of alkaline earth metal, hydroxide of alkali metal, carbonate of alkali metal, bicarbonate of alkali metal, sodium aluminate, aluminum acetate and acetic acid salt of C_{4-14} aliphatic amine, and (ii) stirring the mixture.

4. A process according to claim 3 wherein the calcium carbonate has a BET specific surface area of about 19 to about 55 m^2/g.

5. A process according to claim 3 wherein the surface-treating agent is used in an amount of about 0.1 to about 5 parts by weight per 100 parts by weight of the calcium carbonate.

6. A process according to claim 3 wherein the surface-treating agent is used in an amount of about 0.2 to about 4 parts by weight per 100 parts by weight of the calcium carbonate.

7. A coating composition for forming a heat-sensitive recording layer of heat-sensitive recording paper characterized in that the composition comprises about 5 to about 60% by weight of the calcium carbonate pigment of claim 1 based on the total solids.

8. A coating composition according to claim 7 which comprises, calculated as solids, about 3 to about 10 wt.% of a basic dye, about 15 to about 50 wt.% of a color developer, about 6 to about 30 wt.% of a chromogenic sensitivity adjusting agent, about 16 to about 22 wt.% of a binder, and about 5 to about 60 wt.% of the calcium carbonate pigment of claim 1, based on the total solids.

9. A coating composition according to claim 7 which comprises, calculated as solids, about 5 to about 10 wt.% of a basic dye, about 20 to about 40 wt.% of a color developer, about 10 to about 30 wt.% of a chromogenic sensitivity adjusting agent, about 16 to about 20 wt.% of a binder, and about 10 to about 55 wt.% of the calcium carbonate pigment of claim 1, based on the total solids.

10. A coating composition for forming an intermediate layer between a heat-sensitive recording layer of heat-sensitive recording paper and the substrate thereof, characterized in that the composition contains a binder in an amount, calculated as solids, of about 5 to about 40 parts by weight per 100 parts by weight of the calcium carbonate pigment of claim 1.

11. A heat-sensitive recording paper which comprises a substrate and a heat-sensitive recording layer formed thereon and containing the calcium carbonate pigment of claim 1, a chromogenic sensitivity adjusting agent, a colorless to pale-colored basic dye, a color developer for causing the dye to produce a color when heated and a binder.

12. A heat-sensitive recording paper according to claim 11 characterized in that it is obtained by applying the coating composition of claim 8 to the substrate and drying the coating layer.

13. A heat-sensitive recording paper according to claim 11 characterized in that it is obtained by applying the coating composition of claim 9 to the substrate and drying the coating layer.

14. A heat-sensitive recording paper which comprises (i) a substrate, (ii) an intermediate layer formed thereon and containing the calcium carbonate pigment of claim 1 and (iii) a heat-sensitive recording layer formed on the intermediate layer and containing the calcium carbonate pigment of claim 1, a chromogenic sensitivity adjusting agent, a colorless to pale-colored basic dye, a color developer for causing the dye to produce a color when heated and a binder.

15. A heat-sensitive recording paper according to claim 14 which comprises (a) a substrate, (b) an intermediate layer formed by applying to the substrate the coating composition of claim 10 for forming an intermediate layer and drying the coating layer and (c) a heat-sensitive recording layer formed by applying the coating composition of claim 8 for forming a heat-sensitive recording layer to the intermediate layer and drying the coating layer.

16. A heat-sensitive recording paper according to claim 14 which comprises (a) a substrate, (b) an intermediate layer formed by applying to the substrate the coating composition of claim 10 for forming an intermediate layer and drying the coating layer and (c) a heat-sensitive recording layer formed by applying the coating composition of claim 9 for forming a heat-sensitive recording layer to the intermediate layer and drying the coating layer.