(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 430 582 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **90312718.1**

(51) Int. Cl.[5]: **D21H 19/40**, D21H 17/68

(22) Date of filing: **22.11.90**

(30) Priority: **22.11.89 US 440533**

(43) Date of publication of application:
05.06.91 Bulletin 91/23

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE
Bulletin

(71) Applicant: **ENGELHARD CORPORATION**
101 Wood Avenue
Iselin, New Jersey 08830-0770(US)

(72) Inventor: **Nemeh, Saadallah**
74 Linden Avenue
West Long Branch, New Jersey 07764(US)
Inventor: **Berube, Richard R.**
8 Regal Court
Holmdel, New Jersey 07733(US)
Inventor: **Kostelnik, Robert J.**
7 Pembroke Terrace
Belle Mead, New Jersey 08502(US)
Inventor: **Mack, Stanley S.**
18 Albright Circle
Madison, New Jersey 07940(US)

(74) Representative: **Geering, Keith Edwin et al**
REDDIE & GROSE 16 Theobalds Road
London WC1X 8PL(GB)

(54) Structured kaolins used to fill paper.

(57) An opacifying pigment for filling paper comprising particles obtainable by flocculating hydrous kaolin clay in the presence of water with cationic polyelectrolyte flocculant in amount in excess of that necessary to achieve flocculation but insufficient to redeflocculate said kaolin, said flocculated particles of clay when dry having scattering values at 577 nm higher than that of said clay flocculated with minimal amount of said polyelectrolyte.

EP 0 430 582 A1

STRUCTURED KAOLINS USED TO FILL PAPER

This invention relates to improving the properties of paper filling pigments obtained by bulking kaolin clay by addition to the clay of a cationic polyelectrolyte,e.g. as a polyamine or a quaternary ammonium polyelectrolyte. More specifically, this invention relates to improvements in cationically bulked kaolin of the type described in U.S. 4,738,726, Pratt et al, U.S. 4,767,466, Nemeh et al, and U.S. 4,772,332, Nemeh et al.

It is conventional practice in the paper making art to improve the opacifying and/or hiding power of kaolin-based paper coating and paper filling pigments by blending the kaolin clay pigments with more costly pigments having greater opacifying power, such as TiO_2. The industry has long sought a kaolin clay pigment which imparts improved opacity and brightness to coated and filled paper without sacrificing runability, gloss, abrasion and printability and which can preferably be used in the absence of other more expensive pigments.

Coated printing paper possessing superior printability especially by rotogravure and offset methods, has been obtained by coating with coating formulations containing bulked pigments.

Cationically bulked kaolin is enjoying widespread commercial success for coating paper, but the desired degree of improvement in opacification when used to fill paper has not been realized - see, for example, data in EXAMPLE VI of US-A-4738726, supra.

High bulking clay pigments offer the opportunity of maintaining or improving the opacity, brightness, gloss and printability of coated paper having lower coating weights, thereby reducing the pigment cost for coating colors; and improving the opacity of paper filled with kaolin. Generally, bulking is achieved by introducing voids in a pigment structure which contribute to increased light scatter. Controlled calcination of kaolin clays results in one type of bulking clay pigment. Calcined bulked kaolin clay such as the material supplied under the registered trademark ANSILEX has enjoyed widespread commercial success for more than a decade especially as paper filler. For many years attempts have been made to bulk hydrous kaolin clays, thereby avoiding the increase in pigment abrasivity that appears to be an inherent result of calcination. U.S. Patent Nos. 4,075,030, 4,076,548 and 4,078,941 teach procedures for increasing the opacifying power of hydrous kaolin clays by "selectively flocculating" ultrafine clay particles with a low molecular weight polyamine flocculating agent (e.g., ethylene diamine or hexamethylene diamine) or with long carbon chain amines or certain quaternary ammonium salts (e.g. "ditallowdimethyl" ammonium chloride) in the presence of a mineral acid flocculating agent, e.g., sulfuric acid, and optionally with the adding presence of citric acid or mica or both. The selective flocculation treatment allegedly incorporates voids in the clay to form a low density, high-bulking pigment which when used as a coating color pigment improves the opacity of paper coated therewith. U.S. Patent No. 4,640,716 teaches the use of certain zirconium compounds such as zirconium ammonium carbonate to bulk clay.

U.S. 4,738,726, Pratt et al, supra, describes new relatively inexpensive kaolin pigments with a stable bulked structure but also capable of being mixed with water and dispersants to form clay-water slurries and coating colors having usable low and high shear viscosity. Although aqueous suspensions of such bulked clay contain added deflocculant to increase fluidity, these suspensions are not truly in a fully deflocculated or dispersed condition because the bulked, flocced structure is retained. Thus, these slurries can be termed "partially deflocculated" or "partially dispersed" slurries or suspensions. The new bulked pigments, obtained using high charge density cationic polyelectrolytes to bulk the clay, can also be applied to paper at lower coat weights, to produce lower basis weight papers showing properties comparable to higher basis weight sheets.

In an increasingly competitive market environment, printer and publishers are requiring paper with improved optical and printing properties. These properties sometimes cannot be achieved without the aid of filler pigments.

Another primary reason behind the increased use of pigments in bulking is related to the modification and conversion of older, less efficient newsprint machines to produce more profitable groundwood specialties. The superior optical and printing properties of these products command a higher price, but they also, require the use of filler pigments to meet the higher standards.

Another reason for the use of filler pigments is the desire to produce lighter basis weight papers with optical and printing properties comparable to higher basis weights. The pigment compensates for the reduction in fiber content of the lighter papers and the consequent loss of opacity and printing properties.

Advances in pulping technology have produced a new generation of mechanical pulps that are stronger and higher in yield, but lower in scattering coefficient than conventional pulps. As industry acceptance of these new, less optically efficient products grows, filler pigments will be needed to improve opacity, brightness and print-through resistance. Superior optical properties are perceived as an indication of superior product quality by the paper industry and by users of newsprint and mechanical pulp containing paper.

The present invention provide means for improving the opacifying properties of cationically bulked kaolin clay pigments when used as fillers for paper and paperboard. In accordance with this invention, a bulked hydrous kaolin clay paper filler is prepared by adding water soluble cationic organic material such as polyamine or quaternary ammonium polyelectrolyte, in amount in excess of that required to flocculate the kaolin, but insufficient to redeflocculate the previously flocculated kaolin.

The median particle size of the clay particles that are treated with the cationic polyelectrolyte preferably ranges from 0.4 to 0.7 micrometers, equivalent spherical diameter (e.s.d), more preferably 0.5 to 0.6 micrometers, as determined by conventional sedimentation techniques using the SEDIGRAPH particle size analyzer, supplied by Micromeritics, Inc. From about 50 to 95 wt.% of the particles are preferably finer than 2 micrometers, e.s.d. The content of fines below 0.3 micrometer e.s.d. may be below 35 weight percent, preferably below 25 weight percent, and most preferably 20 weight percent or below. It should be understood that the measurements of the size of clay particles that are 0.3 micrometer or finer are of limited reproducibility. Thus, when a SEDIGRAPH analyzer is employed, the value for weight percent may be ±5% when tested by another operator or a different SEDIGRAPH analyzer is employed. Most preferably, median particle size is 0.5 to 0.6 micrometers, e.s.d., with 85 to 90% by weight of the particles finer than 2 micrometers, e.s.d., and less than about 20% by weight or less finer than 0.30 micrometers, e.s.d. Especially preferred is the use of a hydrous kaolin fraction that is about 80 to 88% finer than 2 micrometers. Most preferably, about 80 to 85% finer than 2 micrometers with from 10% to 19% by weight finer than 0.3 micrometers.

The amount of cationic polyelectrolyte employed is carefully controlled to be sufficient to achieve maximum opacification potential of the clay as a result of forming a bulked (aggregated) structure in which the aggregates are sufficiently strong to survive mechanical forces exerted during manufacture and end use and is carefully controlled. The amount of cationic polyelectrolyte exceeds that required to flocculate the kaolin, but is insufficient to redeflocculated the previously flocculated clay.

The specific amount of the cationic polyelectrolyte salt used to treat the kaolin clay may vary with characteristics of the polyelectrolyte, the particle size distribution of the clay and solids content of the clay slurry to which the polyelectrolyte is added. Using the presently preferred dimethyldiallyl ammonium salt polyelectrolyte with clay having a median size in the range of about 0.5 to 0.6 micrometers, and having less than 20% finer than 0.3 micrometers and adding polyelectrolyte to a previously deflocculated clay-water suspension having a clay solids content of about 20-40% by weight, useful amounts range from about 0.12% to about 0.20% by weight of the moisture free weight of the clay, most preferably about 0.15% to about 0.16% by weight. An excessive amount of the polyelectrolyte will redeflocculate the clay.

The polyelectrolyte, which is water soluble, is best added to the slurry as a dilute aqueous solution, e.g., 0.25-2.0 wt.% concentration, with agitation to achieve good distribution in the slurry. Ambient temperature can be used. It may be advantageous to heat the slurry of clay, solution of polyelectrolyte, or both to about 150° to 180°F. The cationic polyelectrolyte flocculants that are used have closely spaced charged centers and therefore represent high charge density material. Because of this, the reaction with the clay mineral is extremely rapid and appears to be complete in a relatively short time. While not wishing to be limited by any particulars of the reaction mechanisms, it is believed that the clay mineral cations such as H^+, Na^+, and Ca^+, are replaced by the positively charged polymeric portion of the cationic polyelectrolyte at the original mineral cation location and that this replacement reduces the negative charge on the clay particles which in turn leads to coalescence by mutual attraction. Charge centers near the end of the polymer chain react and bridge with neighboring particles until the accessible clay cation exchange centers or the polymer charge centers are exhausted. The bridging strengthens the bond between the particles, thereby providing a highly shear resistant, bulked clay mineral composition. The amount of polyelectrolyte added is less than that calculated to provide a monolayer on the surface of clay particles. Present experience based on measurements of particle charge by electrophoretic mobility indicates that the bulked clay does not have a cationic charge when the clay is not redeflocculated.

Water soluble cationic polyelectrolyte flocculants are well known in the art and many are known to increase the rate at which clay slurries filter. See, for example, US. Patent No. 4,174,279. Cationic polyelectrolyte flocculants are characterized by a high density of positive charge. Positive charge density is calculated by dividing the total number of positive charges per molecule by the molecular weight. Generally the high charge density of polyelectrolyte flocculants exceeds $1X10^{-3}$ and such materials do not contain negative groups such as carboxyl or carbonyl groups. In addition to the alkyl diallyl quaternary ammonium salts, other quaternary ammonium cationic flocculants are obtained by copolymerizing aliphatic secondary amines with epichlorohydrin - see U.S. Patent No. 4,174,279. Still other water-soluble cationic polyelectrolytes are poly(quaternary ammonium) polyether salts that contain quaternary nitrogen in a polymeric backbone and are chain extended by ether groups. They are prepared from water-soluble poly(quaternary ammonium salts) containing pendant hydroxyl groups and bifunctionally reactive chain extending agents; such polyelectrolytes are prepared by treating N, N. $N^{(1)}$, $N^{(1)}$ tetraalkylhydroxyalkylenediamine and organic dihalide such as dihydroalkane or dihaloether with epoxy haloalkane. Such polyelectrolytes and their use in flocculating clay are disclosed in U.S. Patent No. 3,663,461. Other water soluble cationic polyelectrolyte flocculants are polyamines. Polyamine flocculants are usually supplied commercially under trade designations; chemical structure and molecular weight are not provided by the suppliers.

A diallyl dimethyl quaternary ammonium chloride polymer commercially available under the trademark designation Polymer 261LV from the Calgon Corporation having a molecular weight estimated to be between 50,000-250,000 has been found particularly useful in the practice of the present invention. However, the invention is not limited to Polymer 261 LV since other cationic flocculants appear to provide equivalent, if not superior results.

Satisfactory results have been realized when the polyelectrolyte was added to deflocculated clay suspensions having pH values in the range of 6 to 9. After addition of polyelectrolyte, the suspension is substantially thickened as a result of flocculation. The resulting thickened system can then be acidified, typically to pH 2 to 6, preferably 3 to 5, and bleached using a convention bleach reagent (hydrosulfite salt such as sodium dithionite) and then at least partially dewatered to remove free water and place the recovered bulked clay in a form such that is can be washed to remove ions in the flocculated clay suspension. Normally dewatering is carried out on a filter, for example a rotary vacuum filter.

Bleaches are usually preferred which reduce any color forming ferric iron constituents to a more water soluble and therefore more easily removable ferrous state (Fe^{2+}) suitable bleaching agents include water soluble dithionite salts, and borohydride salts which are advantageously added to the clay mineral slurry in an amount in the range of from 1 to 15 lbs., most preferably about 4 to 6 lbs., of bleaching agent per ton of dry clay. The slurry of polymer treated clay can be acidified before filtration to enhance filtration even if bleaching is not carried out. Viscosity stability of bulked kaolin products is poor unless bleach residues are removed by washing or sulfonates are used as dispersants.

The clay suspension can be dewatered by filtering to a moist filter cake having a solids content of about 50 to 60% by weight. The filter cake can be washed to remove soluble material and then fluidized by the addition of a secondary dispersing agent which, in accordance with a preferred embodiment of the invention, comprises a mixture of anionic sulfonates and polyacrylate salt described in U.S. 4,772,332. If the previously described acid bleaching step is omitted, only minimal if any pH adjustment may be necessary to bring pH into the desired range of 6.0 to 7.5 pH can be adjusted to a value between 6.0 and 7.5, preferably 6.8 to 7.5, using a suitable base such as sodium hydroxide.

The dewatered and washed filter cake may be fluidized by adding a deflocculant and supplied for shipment in slurry form as mentioned above. Alternately, the filter cake can be fluidized by addition of a deflocculant and then spray dried to produce a dry so-called "predispersed" product in dustless form.

The resultant bulked polyelectrolyte treated clay product can be used as a filler for paper webs by making a furnish comprising pulp, kaolin, retention aid and other ingredients. When forming a clay slurry having a higher solids content than the filter cake, it will be necessary to add dry, previously bulked clay to build up the solids content of the slurry obtained by adding dispersants to fluidize the filter cake. For example, when the filter cake is recovered at 55% solids and it is desired to fluidize the filter cake to form a slurry having a solids content of 62% for shipment, dry previously bulked clay should be mixed with the dispersed filter cake. Since the spray dried bulked clay already contains dispersant, only a little or no dispersant need be added to the mixture of dispersed filter cake and dry clay to obtain 62% solids slurry. The solids concentration of the slurry that is acceptable to the papermaker depends upon the properties that the pigment will impart to the paper.

We prefer to prepare fluidized slurries of bulked clay that do not contain condensed phosphate salts as dispersants because of the lack of hydrolytic stability of such materials. Thus, while we prefer to prepare phosphate free high solids slurries, traces of phosphate dispersants can be present.

The kaolin clay pigments bulked in accordance with practice of the present invention are especially useful in filling paper, but are generally not optimized for use in coating paper, due to difficulties in making high solids coating colors.

Typical pigments of the invention have the following properties:

G.E. Brightness, % +325 mesh residue, wt %	At least 76 Less than 0.025
Particle Size	
% Finer than 2 micrometers Average size, micrometer	At least 80% 0.6-0.8
Scattering coefficient, m^2/g	
@ 457 nm @ 577 nm	At least 0.17 At least 0.13
Brookfield viscosity of slurry, cps.	
@ 20 rpm @ 100 rpm Hercules viscosity end point. "A" bob (r.p.m./dyne-cm X10^5)	Below 1000 cps, preferably below 500 cps, most preferably 300 cps. No greater than at 20 rpm Above 500 rpm, preferably above 800 rpm and, most preferably, no greater than 16 X 10^5 dyne-cm at 1100 rpm.

We expect the Einlehner abrasion and paper abrasion (as measured by needle abrasion) of bulked kaolin of the invention to be comparable to standard filler kaolin and significantly lower than fine calcined kaolins.

All particle sizes used in the specification and claims are determined with the SEDIGRAPH 5000 particles size analyzer and are reported as equivalent spherical diameters (e.s.d.) on a weight percentage basis.

Light scattering is assessed by coating the kaolin clay suspensions onto black glass plates at a coat weight of 7.0-14.0 g/m^2 (expressed as dry clay). The reflectance of the coatings after drying in air is measured at wavelengths 457 nm and 577 nm by means of an Elrepho reflectometer. The reflectance values are converted by the use of Kubelka-Munk equations to light scattering values (m^2/g). The light scattering values are a measure of the opacity potential of the clay because the higher values indicate that light, rather than passing through the pigment coating, is reflected and scattered back. The higher the light scattering value, the higher the opacity potential of the clay. Reflectance is measured at two different wavelengths. The 457 nm wavelength used is the TAPPI brightness measurement, and the 572 nm wavelength is used to measure opacity.

In preparing slurries for measurement of high shear (Hercules) and low shear (Brookfield) viscosity, the procedure described in U.S. 4,772,332 were used.

EXAMPLE 1

A high purity kaolin crude clay from a deposit in Washington County, GA., known as North Jenkins crude, was degritted, after dispersion at approximately 35% solids in water having dissolved therein sodium silicate having a Na_2O/SiO_2 weight ratio of about 3/2 and sodium carbonate. Approximately 1.5-2.0 lbs. of sodium silicate and 1.5-2.0 lbs. of carbonate were used per ton of dry clay. The suspension was then degritted and fractionated in a centrifuge to 87% finer than 2 micrometers. The median size of the fractional suspensions was 0.59±0.03 micrometers; weight percentage finer than 0.3 micrometers was 17%. Solids were about 20% and pH about 7. The suspension was then passed through a high intensity magnetic separator for purification. CALGON 261 LV polymer was added to the suspension of purified clay at the 0.08, 0.10, 0.12, 0.16 and 0.20% level, based on dry weight of clay. The polyelectrolyte was added as an aqueous solution of 0.5% (wt.) concentration.

The bulked slurries were mixed for one half hour, bleached with 5 lb/ton K-brite at pH 3.0, aged for about 18 hours, filtered, washed with 0.5 to 1 water/dry kaolin and dispersed with a mixture of sulfonates and sodium polyacrylate dispersant as shown in Table 1. The slurries were then spray dried and made down at 55% solids without additional dispersant. Brookfield viscosity and black glass scattering of the sample were measured. As expected, scattering and Brookfield viscosities of bulking pigments increase with increasing the polymer dosage. At the bulking level of 0.2%, the viscosity of the aqueous slurry can be reduced by adding more dispersant as can be seen from data on Table 2.

TABLE 1

Pigment Preparation		
Level of Polymer	Bleach pH	Dispersant
0.08%	3.0	3 lb/ton
0.10%	3.0	3.5 lb/ton
0.12%	3.0	4 lb/ton
0.16%	3.0	4 lb/ton
0.20%	3.0	4.5 lb/ton

Dry samples were make down at 55% solids.

TABLE II

Product Properties

Pigment	Makedown pH	Brookfield 20rpm	Brookfield 100rpm	Scattering [1] S457	Scattering [1] S577
Exsilon[2]	6.3	30	42	.157	.116
.08% Polymer	6.6	45	45	.159	.130
.10% Polymer	6.8	45	60	.168	.135
.12% Polymer	7.0	75	60	.174	.142
.16% Polymer	7.1	475	180	.191	.153
Next day "	7.1	325	120	-	-
+.025 Dispersant	7.1	125	80	.189	.148
.20% Polymer	7.3	2325	575	.185	.161
Next day "	7.4	1500	-	-	-
+.025% Dispersant	7.4	500	-	.199	.158

1. An average of four reading (duplicates by two operators).

2. Commercial sample of EXSILON bulked kaolin pigment.

Claims

1. An opacifying pigment for filling paper comprising particles obtainable by flocculating hydrous kaolin clay in the presence of water with cationic polyelectrolyte flooculant in amount in excess of that necessary to achieve flocculation but insufficient to redeflocculate said kaolin, said flocculated particles of clay when dry having scattering values at 577 nm higher than that of said clay flocculated with minimal amount of said polyelectrolyte.

2. A pigment according to claim 1 which also contains less than 0.2% by weight of deflocculating agent.

3. A pigment according to claim 1 or 2 wherein said polyelectroyte is selected from quaternary ammonium polymer salts and diallyl ammonium polymer salts.

4. A pigment according to any preceding claim wherein said polyelectrolyte comprises dimethyl diallyl ammonium polymer salt having a molecular weight of 1×10^4 to 1×10^6 (e.g. between 50,000 and 250,000), said polymer salt preferably being present in an amount in excess of 0.15% but less than 0.40%

based on the dry weight of said kaolin clay.

5. A method for preparing a bulking pigment suitable for use in filling paper which comprises preparing a fluid aqueous suspension of particles of kaolin clay, adding thereto water-soluble cationic polyelectrolyte flocculant and at least partially dewatering said suspension to recover the resulting bulked clay, the amount of said cationic polyelectrolyte being in excess of that required to substantially thicken and flocculate said fluid and resulting in a clay pigment having improved opacification.

6. A method according claim 5 wherein said polyelectrolyte is selected from quaternary ammonium polymer salts and diallyl ammonium polymer salts.

7. A method according to claims 5 or 6 wherein said polyelectrolyte has a molecular weight between 50,000 and 250,000.

8. A method according to claims 6 or 7 wherein said polyelectrolyte comprises polydimethyldiallyl ammonium chloride in an amount in excess of 0.12% but below 0.40% based on the height of said kaolin.

9. A method according to any of claims 5 to 8 wherein the clay before flocculation has a particle size distribution such that less than 20 wt.% is finer then 0.3 micrometers e.s.d.

10. Paper, e.g newsprint paper, containing pigment according to any of claims 1 to 4 as a filler.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 31 2718

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,X	EP-A-0 245 553 (ENGELHARD CORPORATION) * claims 1-19 *	1	D 21 H 19/40 D 21 H 17/68
D,X	EP-A-0 260 945 (ENGELHARD CORPORATION) * claims 1-10 *	1	
D,X	US-A-4 772 332 (SAAD SEMEH ET AL) * claims 1-10 *	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

D 21 H

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	22 February 91	FOUQUIER J.P.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same catagory
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document