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(54) Composite kaolin pigment for paper.

(57) A filling or coating pigment for paper comprises mixed particles of chemically bulked hydrous kaolin pigment and low abrasion calcined kaolin pigment, the weight ratio of chemically bulked to calcined kaolins preferably being from 9 :1 to 1 :9.

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COMPOSITE KAOLIN PIGMENT FOR PAPER

This invention relates to pigments containing a mixture of kaolins, and to their use in filling paper and in coating paper and paperboard.

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 kaolin clay pigments which impart 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.

Highly bulked clay pigments offer the opportunity of maintaining or improving the opacity, brightness, gloss and printability of coated paper at lower coating weights, and possibly reducing the pigment cost for coating colors. Such pigments also offer promise to improve the opacity of paper filled with kaolin. Generally, bulking optimizes the particle size distribution of a pigment and introduces voids in a pigment structure both of which contribute to increased light scatter. Controlled calcination of kaolin clays results in one type of bulked clay pigment. Calcined bulked kaolin clays such as the material supplied under the registered trademark ANSILEX have enjoyed widespread commercial success for more than a decade, especially as paper filler. For many years attempts have been made to bulk hydrous (uncalcined) kaolin clays, thereby avoiding the increase in pigment abrasivity that appeared to be an inherent result of calcination. US-A-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" ammomium chloride) in the presence of a mineral acid flocculating agent, e.g., sulfuric acid, and optionally with the added 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. US-4,640,716 teaches the use of certain zirconium compounds such as zirconium ammonium carbonate to bulk clay.

US-A-4,738,726, -4,767,466 and -4,772,332 describe 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. The pigments are obtained by flocculating slurries of hydrous kaolin with cationic polymeric polyelectrolytes such as poly (diallyldimethyl ammonium chloride). 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. These 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 having properties comparable to higher basis weight sheets. However, 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-4,738,726.

EP Application No. 90312718 (EP-A-) provides means for improving the opacifying properties of cationically bulked kaolin clay pigments when used as fillers for paper and paperboard. In accordance with this teaching, a bulked hydrous kaolin clay paper filler is prepared by adding a water soluble cationic organic material such as a polyamine or a quaternary ammonium polyelectrolyte, in an amount in excess of that required to flocculate the kaolin but insufficient to redeflocculate the previously flocculated kaolin.

In an increasingly competitive market environment, printers 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 filling paper 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 those of higher basis wheights. The pigment compensates for the reduction in fiber content of the lighter papers and the consequent loss of opacity and printing properties.

When used as coating pigment for paper and paperboard, bulked kaolins enhance a number of aesthetic and functional paper properties. In LWC (lightweight coated) paper, surface roughness is reduced and rotogravure printability is significantly improved. The highly light scattering and porous coating structure formed by bulked kaolin increases paper opacity, paper brightness, the hiding power of the coating and ink receptivity, while maintaining or improving ink gloss. The porous coating structure is also beneficial in reducing the blistering tendency of heavy coat weight merchant paper. The ability of bulked kaolin to increase hiding power of the coating enhances LWC paper and paper board brightness by more effectively hiding the poor color of the coating basestock when such basestocks are used.

The present invention provides a composite kaolin opacifying pigment for paper comprising a particulate mixture of calcined kaolin pigment and chemically bulked hydrous kaolin pigment, the latter preferably being the major pigment component. The dry weight ratio of the chemically bulked hydrous kaolin to the calcined kaolin is preferably from 9 :1 to 1 :9, more preferably from 3 :1 to 1 :3, and most preferably from 3 :2 to 2 :3. Pigments according to the invention function to increase unexpectedly the opacity of paper and paperboard filled or coated therewith.

The preferred chemically bulked hydrous kaolin pigments for use in the invention are those obtained by flocculating kaolin with an organic cationic polyelectrolyte such as a quaternary ammonium polyelectrolyte ; an example is the material commercially available under the registered trademark EXSILON. Commercial low abrasion calcined kaolin pigments, e.g. those available under the trademarks ANSILEX, ANSILEX 93 and SPECTRAFIL, may be employed as the calcined kaolin component in the pigment of the invention ; low abrasion is important and Valley abrasion values of 50m^2/g or less are preferred.

In producing a paper filling pigment according to this invention, we prefer to prepare separate aqueous slurries of the kaolin components of the blend and then thoroughly mix the slurries before adding the resulting mixed pigment slurry to paper pulp, followed by sheet formation. Conventional paper (and paperboard) forming and handling methods can be utilized.

Pigment blends of the invention have resulted in filled paper that is significantly more opaque than would be expected from the performance of the chemically bulked hydrated kaolin component. Opacity achieved using the blends is less than that achievable using an equivalent level of calcined kaolin but greater than that expected by the additive effect as predicted by the Kubelka-Munk theory.

Filler pigments of the invention are of special value in enhancing brightness, shade, print-through resistance and smoothness of standard newsprint and groundwood specialties. The pigment permits newsprint mills to achieve economically optical properties superior to those of unfilled newsprint and results in optical and printing properties of lighter basis weight papers that are comparable to the performance of higher basis weight papers. The mixed filler pigment thus provides a cost effective means to upgrade newsprint. Generally, the composite filler pigment is used in the manufacture of paper using mechanical-pulp containing furnishes at retained loading levels up to 6 wt.%. The abrasion of the blend is lower than that of low abrasion calcined kaolin, resulting in a sheet with lower abrasion than those filled with calcined kaolin at equivalent levels.

Coating pigments of the invention are of special value in enhancing brightness, opacity and printability and the pigments have lower pigment abrasion than available forms of calcined kaolin pigments. An important commercial advantage is that this composite pigment, when spray dried, has a bulk density much greater than that of calcined kaolins and typical of spray dried hydrous clays - 0. 6 kg/m^3 (45 lbs/ft^3) firmly packed. This increase in density can result in reduced freight costs. Another important advantage of the composite pigment of the invention, when supplied in spray dried form, is that it can be loaded and unloaded from shipping containers by sparging equipment which cannot be used with commercially available spray dried forms of chemically bulked kaolin coating pigments. Sparging involves introducing water and air into a rail car compartment to make a slurry (typically 30% solids) of the dry material to facilitate unloading.

PREFERRED EMBODIMENTS

Chemically Bulked Kaolin Component

Preferred chemically bulked hydrous kaolin pigments are prepared using procedures and reagents described in US-A-4,738,726, to which attention is directed for detail.

In this known bulking method the median particle size of the kaolin particles that are treated with the cationic polyelectrolyte should range from 0.4 to 0.7 micrometers, equivalent spherical diameter (e.s.d.), 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 80% to 95% by weight of the particles should be finer than 2 micrometers, e.s.d. The content of fines below 0.3 micrometers e.s.d. should be below 35 wt.%, preferably below 25 wt.% and most preferably 20 wt.%or below. It should be understood that the measurements of the size of clay particles of 0.3 micrometer or finer are of limited reproducibility. Thus, when a SEDIGRAPH analyzer is employed, the value for wt.% 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, with 85 to 90 wt.% of the particles finer than 2 micrometers, e.s.d., and about 20 wt.% 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 wt.% finer than 2 micrometers with from 10 to 19 wt.% finer than 0.3 micrometers.

The amount of cationic polyelectrolyte employed can be 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. The amount of cationic polyelectrolyte may exceed that required to flocculate the kaolin, but is insufficient to redeflocculate the previously flocculated clay.

The specific amount of cationic polyelectrolyte 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 wt.% finer than 0.3 micrometers, and adding polyelectrolyte of a previously deflocculated clay-water suspension having a clay solids content of about 20-40 wt.%, useful amounts range from about 0.04% to about 0.20% of the moisture free weight of the clay, e.g. about 0.08% or about 0.15 or 0.16 wt.%.

The polyelectrolyte, which is water soluble, is 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 65-80°C (150° to 180°F.) The cationic polyelectrolyte flocculants that are used have closely spaced charge 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 with 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 ends 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-A-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. Diallyldimethyl quaternary ammonium salt polymers of molecular weight in the range $1x10^3$ to $1x10^6$ are suitable. A diallyldimethyl quaternary ammonium chloride polymer commercially available under the trademark designation Polymer 261LV from the Calgon Corporation having a molecular weight estimated to be 50,000-250,000 has been found particularly useful in the practice of the present invention. However, there is no limitation to Polymer 261 LV since other cationic flocculants appear to provide equivalent, if not superior results. In addition to the dialkyldiallyl quaternary ammonium salts, other quaternary ammonium cationic flocculants are obtained by copolymerizing aliphatic secondary amines with epichlorhydrin - see US-A-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 an N, N, $N^{(1)}$, $N^{(1)}$ tetraalkylhydroxy-alkylenediamine and an organic dihalide such as a dihydroalkane or a dihaloether with an epoxy haloalkane. Such polyelectrolytes and their use in flocculating clay are disclosed in US-A-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.

Satisfactory results can be realized when the polyelectrolyte is added to deflocculated clay suspensions having pH values of 6 to 9. After addition of polyelectrolyte, the suspension is substantially thickened as a result of flocculation. The resulting thickened system is then acidified, typically to pH 2 to 6, preferably 3 to 5, and optionally bleached using a conventional 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 it can be washed if necessary to remove ions in the flocculated clay suspension. Normally dewatering is carried out on a filter, for example a rotary vacuum filter. When a brighter composite pigment is desired the kaolin clay feed is further improved in brightness by subjecting it to froth flotation or high intensity magnets to physically remove impurities prior to bulking.

Typically, the suspension of bulked kaolin is dewatered to a moist filter cake having a solids content of about 50 to 60 wt.%. The filter cake (optionally washed to remove soluble material), after addition of suitable dispersing agent to fluidize the cake, can be spray dried to provide pigment in dry form. The dispersed cake and/or spray dried material can be slurried to provide an aqueous slurry suitable for shipment.

Preferred dispersants for use with kaolin bulked with a cationic polymer are disclosed in US-A-4,772,332, to which reference is directed for detail. The dispersant is a combination of an anionic lignosulfonate, anionic naphthalene sulfonate complex and polyacrylate salt.

Also useful in the practice of this invention are kaolins bulked with more cationic polyelectrolyte than is needed to flocculate the pigment. An example is the "Experimental Pigment" used in Example 1.

Calcined Kaolin Component

Low abrasion calcined kaolin opacifying pigments (usually of a Valley abrasion value of $50m^2/g$ or less) are known in the art - see US-A-3,586,523, to which reference is directed for detail. The crudes, known as "hard" kaolins, are of Tertiary origin and are characterized by containing extremely fine particles (e.g., average particle size below 1/2 micron). When examined by X-ray these clays appear to be less well crystallized than so-called "soft" kaolins. Generally, the iron content of these ultrafine Tertiary clays is of the order of about 0.7 to 0.9 wt.% (expressed as Fe_2O_3) and in many but not all cases the uncalcined clay has a distinctly grey color, hence the designation "grey kaolin". When calcined in powder form these unique sedimentary kaolins aggregate to produce coarser particles possessing remarkably high opacifying power, but without the high abrasion generally characteristic of earlier calcined kaolins. The crudes found to be useful in the production of high brightness low abrasion calcined kaolin pigments are frequently lower in G.E. brightness, e.g., about 85%, than quality crudes used to provide high brightness uncalcined pigments. Nevertheless, when calcined,products with G.E. brightness of at least 90% are produced. It is within the scope of the invention, however, to employ calcined kaolin opacifying pigments having a brightness below 90%, e.g., as low as 75 or 80 or 85%. When used as filler pigments, the low abrasion calcined kaolin fillers also provided desired print-through resistance and color at acceptable burst levels.

Processing schemes presently commercially used to produce low abrasion calcined kaolin pigments involve preliminary upgrading of fine particle size crude kaolin, dispersion in water to form a pulp, and removal of coarse particles (so-called "grit") usually followed by fractionation of the degritted pulp to recover the desired ultrafine particle size fraction, generally at least 100 wt.% finer than 2 microns and at least 90 wt.% finer than 1 micron. The fractionated kaolin is dried, pulverized, and then partially calcined to metakaolin state or it is fully calcined. The calcined kaolin is then repulverized.

The Composite Pigment

In producing pigment composites of this invention, aqueous slurries or sites can be prepared. The specific technique for preparing the composite will vary depending upon the mode of shipment contemplated as well as the equipment that is available and the availability of slurried or dry components. Whether dry or slurry methods are used, the best coating properties are achieved using composites containing 90% chemically bulked hydrous kaolin/10% calcined kaolin to 10% chemically bulked hydrous kaolin/90% calcined kaolin, preferably in the range of about 75% bulked hydrous kaolin and about 25% calcined kaolin to about 25% bulked hydrous kaolin and 75% calcined kaolin, and most preferably in the range of about 60% bulked hydrous kaolin and 40% calcined kaolin to about 40% bulked hydrous and 60% calcined kaolin, based on the total dry weight of said kaolins.

Those familiar with handling dry kaolins, calcined kaolins and chemically bulked hydrous kaolins are aware of the differences in bulk density between the materials. The bulk density of the chemically bulked hydrous kaolin is generally from two to three times greater than that of calcined kaolin. Testing to simulate rail car shipping conditions indicates that the components of pigments of the invention will remain mixed during shipping. Thus, commercially available dry blending techniques can be used in the practice of the invention.

Any of the conventional dry packaging, bulk, bulk bag, or paper bag methods may be used for shipping the dry composite pigment. In addition any mode of shipment, truck, rail or cargo ship or barge may be used. Sparger rail car may also be used for the shipment of the composite pigments. Those familiar with shipping chemically bulked hydrous kaolin are aware that hydrous kaolins will not sparge. However, testing has shown that composites of calcined kaolin and chemically bulked hydrous kaolin can be sparged.

Aqueous slurry can be made by compositing dry calcined kaolin pigment with a slurry of chemically bulked hydrous (uncalcined) kaolin pigment or dry chemically bulked hydrous (uncalcined) kaolin can be mixed with a slurry of calcined kaolin. Alternatively, slurries of both components can be composited.

It is known that slurries of calcined kaolin require high levels of shear during makedown to achieve adequate dispersion. When using slurry blending techniques this characteristic of the calcined kaolin can be accommodated using high shear makedown equipment such as Cowles dissolvers, preferably in three consecutive stages. The desired high solids slurry concentration of the calcined kaolin pigment component is typically 50-53 wt.% solids. In the first stage, the calcined kaolin pigment and water are mixed to the desired solids level. Also added are chemical dispersants (e.g., sodium polyacrylate or tetrasodium pyrophosphate, typically added in amount of 0.05-0.10 wt.% on active chemical basis to dry calcined kaolin pigment weight), thickening agent (e.g., 1% CMC solution, 0.10-0.15% active on dry weight) and biocide treatment (e.g., 750 ppm PROXEL GXL biocide). An additional two stages are required to completely disperse the calcined kaolin and impart adequate work to meet rheology specification. Approximately 24-30 kW.hr/10^3kg (35-45 hp.hr/ton) is generally necessary to achieve a desired Hercules End Point of 400 RPM/16 dyne-cm x 10^5 ("A" bob, 27°C (80°F), 100,000 dyne springs at 50% solids).

Production of a slurry of chemically bulked hydrous kaolin requires moderate levels of shear to achieve adequate dispersion. This can be accomplished in typical makedown equipment (Cowles dissolvers of Cellier equipment, for example). Two stages of Cowles dissolvers are recommended for use in the production of chemically bulked hydrous kaolin. The desired slurry concentration of this component is 62-64% solids. In the first stage the chemically bulked kaolin and water are mixed to the desired solids level, optionally with biocide treatment (e.g., 750 ppm PROXEL GLX biocide). Additional dispersant is not added when the pigment is predispersed as described, for example, in US-A-4,772,332. The chemically bulked pigment will wet out quickly and requires only moderate levels of shear, e.g., about 7-10 kW.hr/10^3kg (10-15 hp.hr/ton). Excessive work input will adversely affect the optical properties of the chemically bulked hydrous kaolin pigment.

As mentioned, in producing a composite slurry pigment, the ratio of hydrous to calcined kaolin can be chosen to achieve the desired coating properties. Composites obtained by slurrying techniques can have the same proportions of chemically bulked hydrous kaolin and calcined kaolin as composites obtained using the dry technique. The final composite slurry preferably has a solids levels of 50% or above but below 65% in order to assure that the optical properties of the composite pigment are not impaired. The preferred solids level of the final blended pigment is 57-63% and most preferably about 59%, e.g., 58-60%. It is apparent that slurries of composite pigments can be provided at higher solids than are feasible for slurries of calcined kaolin. This is a benefit of significant commercial importance.

If both components are in slurry form, compositing can be accomplished by adding the components in the proper ratio to a storage tank and agitating to achieve a homogeneous mixture. Adding a dry component into a slurry requires the use of moderate to high levels of shear. Enough agitation through the use of typical makedown equipment (Cowles dissolver, for example) is required to properly wet out the dry component to achieve a homogeneous mixture.

The composite pigment of the invention can be used as the sole paper coating pigment but usually it will be employed as an extender with conventional paper coating pigments, such as No. 1 or No. 2 coating kaolins or delaminated kaolins, alumina hydrate, calcium carbonate or talc. Titania pigments may also be present. Generally, from 2 to 20 or 40, usually 5 to 15, and most usually 8 to 12 parts by weight of composite pigment is used per 100 parts by weight of the total pigment.

To coat paper, the coating and extender pigments are disrsed in water and mixed with appropriate adhesives, biocides, etc., to prepare so-called "coating colors" which are then applied to paper. Coating color formulations vary with the grades of paper being coated and the method of printing to be used. Typical coating formulations appear in the accompanying illustrative Examples.

The coating colors can be applied to paper sheets or paperboard in known manner, using conventional coating, drying and finishing equipment (e.g., supercalenders, etc).

The mixed bulked hydrous kaolin/calcined kaolin filler pigment of the invention enhances opacity, brightness, shade, print-through resistance and smoothness of standard newsprint, groundwood specialties and wood-free grades. The pigment permits mills to achieve optical properties superior to that of unfilled paper at relatively low cost and results in optical and printing properties of lighter basis weight papers (e.g., 45 to 48 g/m^2) that are comparable to the performance of higher basis weight papers. In other words the mixed filler pigment provides cost effective means to upgrade newsprint ; generally, it is used in the manufacture of paper using mechanical pulp containing furnishes at retained loading levels up to 6 wt.%. The newer mechanical pulps being used by the paper industry result in products that are stronger and brighter than products obtained with older forms of mechanical pulp but the paper products obtained with the current mechanical pulps tend to have lower light scattering efficiency and/or absorptive coefficients. Thus, the papers are less opaque and have poorer print-through resistance. The higher light scattering ability of pigments of the invention can compensate for the effects of lower light scattering and adsorption of the newer pulps.

Filler pigments of this invention are also useful in other mechanical papers such as highly filled supercalendered (SC) grades, directory grades and coating basestock for lightweight coated (LWC) grades. The new filler pigment will also enhance the opacity, brightness and printing properties of non-mechanical pulp paper and board grades.

Blends of chemically bulked kaolin and calcined kaolin pigments can also be used to coat paper and paperboard. In this case, the blend of pigment is normally used as a portion, e.g., 2 or 5 to 40% by weight, of the total coating pigment, the balance being other pigments conventionally used in combination with calcined kaolin pigments in paper and board coating formulations, e.g., hydrous kaolin, titanium dioxide, calcium carbonate and mixtures thereof. In these coating pigmentations the weight ratio of calcined kaolin (exemplified by ANSILEX^R or ANSILEX 93^R pigment) to chemically bulked hydrous kaolin (exemplified by EXSILON^R or EXSILON 90 pigment) is as previously indicated, preferably about 40/60 to 60/40. When used in the preferred range, a 58-62% solids slurry of the pigment of the invention will enhance paper performance properties to the same levels as coating pigmentations containing an equivalent amount of calcined kaolin slurried at 50% solids. Thus, an advantage of using the blends, which is of considerable commercial value to a paper mill, is that higher solids pigment slurries can be utilized and higher solids paper coating formulations (so-called "coating colors") can be prepared. This permits the coater to lower shipping costs, increase coating speeds when limited by drying capacity, use more extender when previously limited by 50% solids calcined kaolin slurry, and use extender pigments in certain paper grades that currently cannot use low solids kaolin slurries.

In preparing blends for use in coating paper, the components can be separately slurried in water, using appropriate dispersants and solids, and the slurries mixed. For example, a 53% solids slurry of ANSILEX pigment can be provided using a conventional sodium polyacrylate dispersant and a separate slurry of EXSILON pigment can be provided at 63% solids using an appropriate dispersant, most preferably a mixture of polyacrylate salt, lignosulfonate and naphthalene sulfonate as disclosed in US-A-4,772,332, to which reference is directed for detail. Alternatively, dry pigments can be mixed and dispersed and made down with water to a desired solids level, e.g., 60%. A third method would be to add dry calcined kaolin to a slurry of chemically bulked hydrous kaolin and make down to a solids of 57-63%.

Coating pigment blends of the invention provide the following benefits : opacity, brightness, rotoprintability, smoothness, good base stock coverage and hiding and improved printability for offset.

All particle sizes used herein are determined with the SEDIGRAPH 5000 particle size analyzer and are reported as equivalent spherical diameters (e.s.d.) on a weight percentage basis. All percentages quoted herein are by weight unless otherwise specified.

EXAMPLES

Example 1

In this Example, the cationically bulked hydrous kaolin designated "Experimental Pigment" was prepared as follows. 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. each of sodium silicate and sodium carbonate were used per ton of dry clay (about 0.6-0.9 kg each per 10^3kg 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 then passed through a high intensity magnetic separator for purification. CALGON 261 LV polymer was added to the suspension of purified clay at the 0.16% level, based on dry weight of clay. The polyelectrolyte was added as an aqueous solution of 0.5% (wt.) concentration.

The bulked slurry was mixed for one half hour, bleached with about 2 kg/ 10^3kg (5 lb/ton) K-brite (sodium hydrosulfite) at pH 3.0, aged for about 18 hours, filtered, washed, and then dispersed with a mixture of sulfonates and sodium polyacrylate dispersant at 55% solids as described in US-A-4,767,466.

The calcined kaolin used in this Example was ANSILEX 93 pigment supplied by Engelhard Corporation. G.E. brightness was 93%.

The chemically bulked kaolin was EXSILON pigment suppliedby Engelhard Corporation and prepared substantially as described in Example 1 of US-A-4,738,726. G.E. brightness was 86%.

A paper making trial, utilizing EXSILON pigment, ANSILEX 93, Experimental pigment and blends of ANSILEX 93/EXSILON and ANSILEX 93/Experimental pigment, was conducted. A fresh truckload of 100% thermomechanical pulp (TMP) pulp was used for each trial day. Unfilled (blank) newsprint was run each day followed by newsprint containing the selected pigments.

EXSILON pigment (dry product) was made down as is without additional dispersant at 50% solids, using a Cowles mixer. The slurry was mixed at 2200 rpm for one minute. ANSILEX 93 pigment in slurry form was also made down at 50% solids. The Experimental pigment, provided as 50% solids slurry, was mixed using a Lightnin' mixer prior to paper making.

The following pigments or pigment mixtures were then prepared to be used in the paper making. Mixtures were made by blending appropriate weights of slurries (ANSILEX 93 and EXSILON or ANSILEX 93 and the Experimental pigment) :

1. EXSILON 100%
2. ANSILEX 93 100%
3. ANSILEX 93/EXSILON AT 50/50
4. ANSILEX 93/EXSILON AT 40/60
5. ANSILEX 93/EXSILON AT 33/66
6. ANSILEX 93/EXSILON AT 20/80
7. Experimental Pigment
8. ANSILEX 93/Experimental Pigment at 40/60

Paper making was performed on a Fourdrinier papermaking machine with pulp that was provided at 3.5% solids. The paper was targeted to be produced at 45 g/m^2 and net mineral contents (NMC) of 1,2 and 4% for sheets filled with 100% ANSILEX 93, and 2, 4 and 6% for all other pigments. Paper making was conducted without the addition of retention aid and without pH adjustment. Formed sheets were machine calendered. The following machine parameters were measured during the paper making trial :

Machine Speed	60 meters/minute
Fan Pump	385-390 liters/minute
Stock Concentration	0.5-0.7% in water
Pulp Freeness Value	120-140ml

It was found that the opacity of the unfilled newsprint varied significantly depending upon the pulp used. Two pigments were run on day 1, four pigments on day 2 and two pigments on day 3. The opacity of the unfilled (blank) newsprint was significantly higher and the brightness was lower on day 1 than on days 2 and 3. Therefore, the change in opacity is referenced to the blank made on the same day as the trial pigments.

The results showed that significant, unexpected enhancement in newsprint opacity occured for blends of the calcined kaolin (ANSILEX 93) with EXSILON pigment and with the Experimental structured pigment. The improvement was most dramatic for 2 :3 and 1 :2 blends of ANSILEX 93 with EXSILON pigment and for a 2 :3 blend of ANSILEX 93 with the Experimental pigment. Lesser, but still significant, improvements in opacity were obtained with lower and higher levels of ANSILEX 93 in the pigment blends. Increased opacity will also occur with fine calcined kaolins such as ANSILEX and SPECTRAFIL.

The significant improvement obtained upon blending the calcined kaolin with the structured hydrous kaolin was not due to debonding as evidence by the fact that the burst indices, relative to the appropriate blanks, of the filled sheets were equivalent within experimental error. It was also apparent that the improvement in opacity was not due to absorption since the brightnesses of the sheets filled with the blends were at least equivalent to the brightness of the paper filled with the calcined kaolin alone.

Example 2

The following tests were used in this Example to evaluate performance of coating pigments of this invention:

Paper Brightness - Paper brightness (diffuse brightness) was measured using the Technibrite Micro TB-1C instrument ; six readings per sheet and five sheets per sample were used in this test. This procedure gives results similar to those obtained using TAPPI Standard T452 om-87.

Opacity - Paper opacity (TAPPI opacity) was measured using the Technidyne instrument using a procedure based on TAPPI standard T425 om-86 ; six readings per sheet and five sheets per sample were used in this test.

Gloss - Paper gloss (75 degree gloss) was measured using the Hunter Lab D 48-7 in accordance with a procedure based on TAPPI standard T480 om-85 ; six readings per sheet and five sheets per sample were used in this test.

K & N Ink Receptivity - This test is referenced in US-A-4,738,726.

IGT Pick - This is a dry pick test widely used in the industry.

Heliotest - The rotogravure printability of paper was measured using the IGT AC2 instrument, one reading per strip and ten strips per sample were used in this test - see US-A-4,772,332.

Print Gloss - The ink holdout of paper was measured using the Vandercook press (using Inmont's web offset heatset ink and 15 micron wedge). The 75° ink gloss was measured at 1.6 optical density. Five readings per sheet and three sheets per sample were used in this test.

Parker Print Surf (PPS) - The surface roughness of paper was measured by this test. A soft Black Neoprene Rubber backing and 10kg pressure were used during the test. Six readings per sheet and three sheets per sample were taken in this test.

Light scattering is determined by coating the clay suspensions at 50% solids onto black glass plates. 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 reflecance values are converted by the use of Kubelka-Munk equations to light scattering coefficients (m^2/g). The light scattering coefficients 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 577 nm wavelength is used to measure opacity.

The calcined kaolin used in the example was ANSILEX 93 pigment supplied by Engelhard Corporation. G.E. brightness was 93%.

The chemically bulked kaolin was EXSILON pigment supplied by Engelhard Corporation and prepared substantially as described in US-A-4,772,332. The pigment was predispersed with a mixture of sulfonates and sodium polyacrylate as described in that patent. The bulking polymer was Calgon 261 LV. G.E. brightness was 86%. Higher brightness versions of chemically bulked kaolin, such as EXSILON 90 pigment, with a 90% G.E. brightness, can also be used

Paper coating tests were conducted utilizing EXSILON pigment alone, ANSILEX 93 alone, and Experimental pigment. Commercial hydrous coating kaolin supplied under the trademarks HT, NUCLAY and ULTRAWHITE 90 were used as primary coating pigments in the paper coating formulations and were mixed with the calcined kaolin pigments (in controls) and the pigments of the invention.

A 68% solids slurry of NUCLAY kaolin, a 70% solids slurry of HT and a 70% solids slurry of ULTRAWHITE 90 were made down in accordance with PL-1, described in US-A-4,738,726, using sodium polyacrylate as dispersant. The 50% and 53% solids ANSILEX 93 slurries were made down in accordance with high shear procedures mentioned above. The 62% and 63% solids slurries of EXSILON pigment were made down using the procedure described as the PL-3 procedure in US-A-4,772,332.

Dry experimental pigments were made down by first mixing dry ANSILEX 93 and EXSILON pigments in ratios of 75/25, 50/50 and 25/75, followed by wetting out with water in a Kitchen Aid Mixer. When the wet out was completed, the slurry was transferrd to a Waring Blendor mixer and sheared for one minute at 11,300 rpm (same as the agitation procedure for EXSILON pigment makedown).

The 60% ANSILEX 93/40% EXSILON composite was made down using 63% solids EXSILON pigment with 53% solids ANSILEX 93 pigment slurries in a ratio of 60/40.

Preparation of coating colors :

(1) LWC (lightweight coating) Roto Formulations

The roto pigmentations were prepared by blending 90 parts of NUCLAY hydrous kaolin with 10 parts of various extender clays. Extender for the formulation designation R-A was 50% solids ANSILEX 93 ; extender for R-B was 75% ANSILEX 93/25% EXSILON composite ; extender for R-C was 50% ANSILEX 93/50% EXSILON composite ; extender for R-D was 40% ANSILEX 93/60% EXSILON slurry composite ; extender for R-E was 25% ANSILEX 93/75% EXSILON composite.

The pigmentations consisting of 100 parts each, were then blended with 4 parts by weight of DOW-620 latex, 7 parts by weight of PG-280 starch binder and 0.5 parts of NOPCO C-140 calcium stearate. After blending all ingredients, dilution water and 10% NH_4OH were added to adjust the coating solids to 57% and pH 8. The starch was prepared at 31% solids.

(2) LWC Offset Formulations

The offset pigmentations were prepared by blending 45 parts of NUCLAY kaolin and 45 parts of HT kaolin with 10 parts of each extender. Extender for O-A was 50% solids ANSILEX 93 pigment ; extender for O-B was 75% ANSILEX 93/25% EXSILON composite ; extender for O-C was 50% ANSILEX 93/50% EXSILON composite ; extender for O-D was 40% ANSILEX 93/60% EXSILON composite.

The pigmentations [100 parts] were then blended with 8 parts of DOW-640 latex, 8 parts of PG-280 starch binder, 0.5 parts of NOPCO C-140 calcium stearate and 0.5 parts of SUNREZ 700 insolubilizer. After blending all ingredients, dilution water and 10% NH_4OH were added to adjust the coating solids to 57% and pH 8.

(3) Offset Merchant Formulations

The merchant pigmentations were prepared by blending 90 parts of ULTRAWHITE 90 kaolin with 10 parts of extender. Extender for M-A was 50% ANSILEX 93 ; extender for M-B was 75% ANSILEX 93/25% EXSILON composite ; extender for M-C was 50% ANSILEX 93/50% EXSILON composite ; extender for M-D was 40% ANSILEX 93/60% EXSILON composite.

The pigmentations [100 parts] were then blended with 12 parts of DOW-640 latex, 4 parts of PG-280 starch, 0.5 parts of NOPCO C-140 calcium stearate and 0.5 parts of SUNREZ 700 insolubilizer. After blending all ingredients, dilution water and 10% NH_4OH were added to adjust colors to 63% solids and pH 8.

Preparation of coated sheets :

Using a Keegan blade coater, the roto and offset colors were applied on the wire side of Blandin 11.8 kg (26 lb) paper rawstock at coating weight targets of about 6, 8 and 9 kg/10^{3}m^2 (4, 5.5 and 6 lbs/3300 sq. ft). The merchant color was applied on the wire side of Mead 21.8 kg (48 lb) rawstock at the coating weight target of about 13.5 kg/10^{3}m^2 (9 lbs/3300 sq. ft). After coating, the sheets were allowed to condition overnight at constant room temperature prior to coat weight measurement. Sheets having desired coat weight were calendered using a lab supercalender.

Coated LWC roto sheets were supercalendered through 3 nips at 60°C (140°F) and about 14 MPa (2000 psig) ; LWC offset sheets were supercalendered through 3 nips at 60°C (140°F) and about 11 MPa (1600 psig); and merchant sheets were supercalendered through 3 nips at 46°C (115°F) and about 10 MPa (1400 psig). All sheets were conditioned overnight in a constant temperature and humidity room before optical and printing tests were performed.

RESULTS

LWC Roto (Table 1)

In this evaluation, the pigmentation used as the standard industry control was R-A which was pigment wit 90 parts of NUCLAY (mechanically delaminated kaolin) and 10 parts ANSILEX 93 calcined kaolin. When con posites of ANSILEX 93/EXSILON were substituted for the ANSILEX 93 component at the 10 part level, brigl ness, opacity, gloss, and roto-printability as measured by Heliotest and Parker Print Surf (PPS) wer maintained. The only variations noted were the marginally inferior brightness and Heliotest of R-C and R-D, respectively. Composites with higher brightness chemically bulked kaolin will give higher brightness results.

LWC Offset (Table 2)

In this evaluation, the pigmentation used as the standard industry control was O-A which was pigmented with 45 parts NUCLAY delaminated kaolin, 45 parts HT No. 2 coating kaolin and 10 parts ANSILEX 93 calcined kaolin. Brightness, gloss, print gloss and IGT pick resistance were unaffected by using 10 parts of the ANSILEX 93/EXSILON composites in place of ANSILEX 93 pigment. However, as demonstrated by O-C and O-D, replacing ANSILEX 93 pigment with these two composites reduced opacity and tended to reduce K+N ink receptivity. This effect on opacity is unexplained since this trend was not demonstrated to the same extent in the LWC roto and merchant paper evaluations. The reduction in K+N ink receptively is marginal, and this trend is also observed in the Merchant study (Table 3).

Merchant Study

In this evaluation, the pigmentation used as the standard industry control was M-A composed of 90 parts ULTRAWHITE 90 premium brightness No. 1 coating kaolin and 10 parts ANSILEX 93 calcined kaolin. Opacity, gloss, print gloss and pick resistance were unaffected by using ANSILEX 93/EXSILON composites. There were very slight marginal reductions in brightness and ink receptivity which were expected.

TABLE I

LWC ROTO SHEET PROPERTIES

ANSILEX 93/EXSILON COMPOSITES

	R-A A93* ___	R-B 75A 25E**	R-C 50A 50E	R-D 40A 60E	R-E 25A 75E
Brightness, %	73.2	73.1	72.7	73.2	73.4
Opacity, %	82.1	82.2	82.2	82.1	82.1
Gloss, %	50.7	50.8	50.6	51.3	50.3
Heliotest, mm	59	56	56	53	57
PPS, microns	1.32	1.34	1.31	1.33	1.37

Pigment Formulation: 90 parts NUCLAY was blended with 10 parts of each extender

* ANSILEX 93 as 50% solids slurry
** EXSILON

TABLE 2

LWC OFFSET SHEET PROPERTIES

ANSILEX 93/EXSILON COMPOSITES

	O-A	O-B	O-C	O-D
	A93*	75A	50A	40A
		25E**	50E	60E
Brightness, %	71.1	71.2	71.0	70.9
Opacity, %	80.9	80.8	80.3	80.3
Gloss, %	50.4	51.4	51.7	53.9
Print Gloss, %	69.9	70.0	69.2	71.4
IGT Pick, vvp	20	20	20	19
K&N, %	22	21	20	19

Pigment Formulation:
45 parts NUCLAY
45 parts HT
10 parts Extender

* ANSILEX 93 as 50% solids slurry
** EXSILON

TABLE 3

MERCHANT SHEET PROPERTIES

ANSILEX 93/EXSILON COMPOSITES

	M-A A93* ___	M-B 75A 25E**	M-C 50A 50E	M-D 40A 60E
Brightness, %	82.1	82.0	81.7	81.6
Opacity, %	90.8	90.7	90.5	90.6
Gloss, %	61.0	60.4	59.4	60.4
Print Gloss, %	77.5	76.2	76.7	77.5
IGT Pick, vvp	31	33	33	31
K&N, %	20	19	17	18

Pigment Formulation: 90 parts ULTRAWHITE 90
10 parts Extender

* ANSILEX 93 as 50% solids slurry
** EXSILON

Claims

1. An opacifying pigment for paper comprising mixed particles of calcined kaolin pigment and chemically bulked hydrous kaolin pigment.

2. A pigment according to claim 1 wherein the weight ratio of said chemically bulked kaolin to said calcined kaolin is from 9 :1 to 1 :9.

3. A pigment according to claim 2 wherein said ratio is from 3 :1 to 1 :3, preferably from 3 :2 to 2 :3.

4. A pigment according to any preceding claim wherein the bulked hydrous kaolin pigment is the major pigment component.

5. A pigment according to any preceding claim wherein the hydrous kaolin pigment is one bulked by treatment with cationic polyelectrolyte.

6. A pigment according to claim 5 wherein said polyelectrolyte comprises quaternary ammonium polymer salt or dialkyl diallyl ammonium polymer salt.

7. A pigment according to claim 6 wherein said polyelectrolyte comprises dimethyldiallyl ammonium polymer salt having a molecular weight of 1×10^3 to 1×10^6.

8. A pigment according to any preceding claim wherein said calcined kaolin clay pigment has a GE brightness of at least 75%, preferably at least 80%.

9. Paper or paperboard filled or coated with pigment according to any preceding claim.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 0668

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-245553 (ENGELHARD CORPORATION) * claims 1-19 * ---	1	D21H17/68 D21H19/40
D,X	EP-A-260945 (ENGELHARD CORPORATION) * claims 1-10 * ---	1	
D,X	US-A-4772332 (SAAD SEMEH ET AL) * claims 1-10 * -----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

D21H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	14 MAY 1991	FOUQUIER J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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
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