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(71) Applicant: ANGLO-AMERICAN CLAYS CORPORATION [US/US]; 5775 Peachtree-Dunwoody Road, N.E., Atlanta, GA 30342 (US).

(72) Inventors: JONES, Philip, E., J. ; Route 1, Box 52, Sandersville, GA 31082 (US). RAYTHATHA, Rasik, H. ; 321 Franklin Street, Tennille, GA 31089 (US). SALINAS, Jorge, E. ; 711 West Church Street, Sandersville, GA 31082 (US). GEHO, Keryn, N. ; 272 Indian Forest Road, Jasper, GA 30143 (US). DUNAWAY, Weyman, H. ; Route 2, Box 208, Sandersville, GA 31082 (US).

(74) Agent: KLAUBER, Stefan, J.; Stefan J. Klauber & Associates, One University Plaza, Hackensack, NJ 07601 (US).

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(54) Title: STRUCTURED KAOLIN PIGMENTS

(57) Abstract

A structured kaolinitic pigment having improved physical and optical characteristics when incorporated as a filler or coating pigment in paper. When used in paper coating applications, it results in a coated paper of improved optical and printing qualities. The pigment consists of porous aggregates of kaolin particles which are chemically bonded together. The pigment may be produces by chemically reacting a particulate kaolin with a metal chloride, such as silicon tetrachloride. The process is conducted under conditions such that the kaolinite structure is not impaired.

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Description

Structured Kaolin Pigments

Technical Field

This invention relates generally to kaolin products, and more specifically relates to a structured kaolin pigment and methods of manufacture of same. The pigment is useful as a filler in proper products and enables preparation of paper coating formulations which yield resultant coated paper products of surprisingly enhanced properties.

Background Art

In the course of manufacturing paper and similar products, including paperboard and the like, it is well-known to incorporate quantities of inorganic materials into the fibrous web in order to improve the quality of the resulting product. In the absence of such "fillers", the resulting paper can have a relatively poor texture due to discontinuities in the fibrous web. The said fillers are also important in improving the printing qualities of the paper, i.e. by improving the surface characteristics of same. The use of appropriate such fillers, further, vastly improves the opacity and the brightness of a paper sheet of a given weight.

A number of inorganic materials have long been known to be effective for many of the aforementioned purposes. Among the best of these materials is titanium dioxide, which can be incorporated into the paper in the form of anatase or of rutile. Titanium dioxide, however, is among the most expensive materials which are so useable. Thus despite the effectiveness of such material as a filler, its use is limited and satisfactory replacements have been much sought after.

Among the materials which have found increasing acceptance as paper fillers are calcined kaolins. Materials of this type are generally prepared by calcining a crude kaolin which may have been initially subjected to prior beneficiation steps in order to remove certain impurities, e.g. for the purpose of improving brightness in the ultimate product. Reference may usefully be had to Proctor U.S. Patent No. 3,014,836, and to Fanselow et al, U.S. Patent No. 3,586,823, which disclosures are representative of the prior art pertinent to calcined kaolins.

Those properties which render a kaolin pigment particularly valuable for use as a filler are also well-known. These include a low abrasion value, and high brightness and opacifying characterisitics. The low abrasion is significant in order to assure that the resultant paper product may be manufactured and processed using conventional machinery without damaging same. The brightness and opacifying characteristics are important in producing an acceptable paper sheet, one which incorporates

whiteness, high opacity, good printability, and light weight.

Both the brightness characteristics of the given kaolin and the opacifying properties of same when incorporated as a filler in paper, may be quantitatively related to a property of the filler identified as the "scattering coefficient S". The said parameter, i.e. the scattering coefficient S of a given filler pigment, is a property well-known and extensively utilized in the paper technology art, and has been the subject of numerous technical papers and the like. The early exposition of such measurements was made by Kubelka and Munk, and is reported in Z. Tech Physik 12:539 (1931). Further citations to the applicable measurement techniques and detailed definitions of the said scattering coefficient are set forth at numerous places in the patent and technical literature. Reference may usefully be had in this connection, e.g. to U.S. patents Nos. 4,026,726 and 4,028,173. In addition to the citations set forth in these patents, reference may further be had to Pulp and Paper Science Technology, Vol. 2 "Paper", Chapter 3, by H. C. Schwalbe (McGraw-Hill Book Company, N.Y.).

It is well-known that in order to obtain high light scattering and opacity, the major portion of filler should be in the range of one micrometer. However, good light scatter cannot be achieved solely by using a kaolin having the said size characteristics: an essential further characteristic needed is that

the kaolin be structured, i.e., formed from an assemblage of platelets interconnected or bonded to provide aggregates which include a network of the platelets.

Aggregation can be of interest for additional reasons. In particular, many kaolin crude reserves are considerably finer than preferred by the paper industry; i.e., they have an unduly high proportion of particles with E.S.D.'s below 0.25 micrometers. Typical Cretaceous kaolins, e.g., include 25 to 30% by weight of particles below 0.25 micrometers; and typical Tertiary kaolins can include 50 to 60% by weight of particles below 0.25 micrometers E.S.D. The presence of such large quantities of very fine particles can have detrimental effects upon paper strength, and in other respects are undesired by the paper manufacturer. While the said extreme fines can be removed by various separation processes, such as high speed centrifuging, such removal is very expensive and entails high capital investment; this quite aside from the possible loss of high proportions of the input feed.

One method for achieving aggregation is to utilize calcining. Thus, in U.S. Patent No. 4,381,948 to A.D. McConnell et al, a calcined kaolin pigment is disclosed and a method for manufacture of same. The said pigment consists of porous aggregates of kaolin platelets, and exhibits exceptionally high light scattering characteristics when incorporated as a filler in paper. This pigment, which substantially corresponds to the

commercially available product ALPHATEX® of the present assignee Anglo-American Clays Corporation (Atlanta, Georgia), is prepared by first blunging and dispersing an appropriate crude kaolin to form an aqueous dispersion of same. The blunged and dispersed aqueous slurry is subjected to a particle size separation from which there is recovered a slurry of the clay, which includes a very fine particle size; e.g. substantially all particles can be smaller than 1 micrometer E.S.D. The slurry is dried to produce a relatively moisture-free clay, which is then thoroughly pulverized to break up agglomerates. This material is then used as a feed to a calciner; such feed is calcined under carefully controlled conditions to typical temperatures of at least 900°C. The resulting product is cooled and pulverized to provide a pigment of the porous high light scattering aggregates of kaolin platelets as described.

Calcined kaolins have also found use in paper coating applications. Reference may be had to the paper by Hollingsworth, Jones, and Bonney, "The Effect of Calcined Clays on the Printability of Coated Rotogravure and Offset Printing Papers", TAPPI Proceedings, pages 9-16, 1983 Coating Conference, discussing the advantages of incorporating small quantities of calcined kaolins into conventional kaolin-based coating formulations. Brightness and opacity of the paper both increase with increased calcined kaolin content, as may be expected from a pigment with

high light scatter, and in some formulations gloss may show a slight increase with increasing calcined kaolin content.

Calcined kaolin products, including those of the aforementioned ALPHATEX® type, are seen to be manufactured by relatively complex techniques involving a multiplicity of steps, including specifically a calcining step, plus various preparatory steps and post-calcining steps. Thus, the said product is relatively expensive to produce; and requires considerable investment in complex apparatus and the like -- e.g. highly regulated calciners etc. It can indeed be noted that the conditions of preparation of these materials must be very carefully controlled in order to keep abrasion acceptably low in the calcined product. For example the calcination operation tends per se to produce an abrasive product -- in consequence of overheating -- if great care is not taken to preclude such a result.

It is further to be noted that in order to produce a low abrasion calcined product, the particle size in the feed to the calciner must be carefully controlled -- even a relatively small increase in coarseness of such feed can have very marked detrimental effect on Valley abrasion.

It has heretofore been known to utilize uncalcined (sometimes referred to as "hydrous") kaolin both as paper fillers and for paper coating. Because the uncalcined material usually does not possess high light scattering qualities or good

opacity, its usefulness, especially as a filler, is limited; and this (in addition to improving brightness) is indeed the particular advantage of calcined products of the ALPHATEX® type; i.e. by virtue of the aggregated structures of same, high light scattering properties are provided and good opacity.

With respect further to terminology, it is noted that the prior art literature, including numerous of the prior art patents relating to the field of kaolin products and processing, often uses the term "hydrous" to refer to a kaolin which has not been subjected to calcination -- more specifically, which has not been subjected to temperatures above about 450°C, which temperatures serve to impair the basic crystal structure of kaolin. These so-called "hydrous" clays may have been produced from crude kaolins, which have been subjected to beneficiation, as, for example, to froth flotation, to magnetic separation, to mechanical delamination, grinding, or similar comminution, but not to the mentioned heating as would impair the crystal structure.

In an accurate technical sense, the description of these materials as "hydrous" is, however, incorrect. More specifically, there is no molecular water actually present in the kaolinite structure. Thus, although the composition can be (and often is) arbitrarily written in the form $2\ H_2O.Al_2O_3.2SiO_2$, it is now well-known that kaolinite is an aluminum hydroxide silicate of approximate composition $Al_2(OH)_4Si_2O_5$ (which equates to

the hydrated formula just cited). Once the kaolin is subjected to calcination, which, for the purposes of this specification means being subjected to heating of 450°C or higher for a period which eliminates the hydroxyl groups, the crystalline structure of the kaolinite is destroyed. Therefore, such material, having been thus calcined, cannot correctly be referred to as a "kaolin". Accordingly, it should be appreciated that henceforth in this specification, when the term "kaolin" or "kaolinite" is utilized, such term necessarily implies that the original structure of the material is intact. Thus, the term "kaolin" as used herein, can be considered to be equivalent to the technically inaccurate (but oft-occurring) prior art usage, "hydrous kaolin" or sometimes simply "hydrous clay."

From time to time, it has been proposed to provide structured kaolin agglomerates by methods unrelated to calcining, the objective being to produce a high light scattering pigment, one with good opacifying properties, without the need for calcination.

Thus, in U.S. Patent No. 4,346,178 to Peter Economou, a structured kaolin agglomerate is disclosed wherein the clay platelets are stabilized or frozen in position by the addition thereto of a urea-formaldehyde prepolymer.

Further relevant art includes U.S. Patent No. 4,072,537 to F. L. Kurrle. Disclosed therein is a composite silicate pig-

ment prepared by a precipitation reaction where spherical hydrous metal silicate particles are precipitated on the planar surfaces of clay particles having a platelet-type structure. The metal silicate pigment component is comprised of the reaction product of a water soluble alkali metal silicate such as sodium silicate and a water soluble salt of a polyvalent metal, such as calcium chloride.

In United States Patents Nos. 3,853,574; 3,864,140; and 3,856,545, all to Thomas H. Ferrigno, pigmentary compositions are disclosed wherein comminuted minerals such as kaolins are combined with inorganic binders, and formed into agglomerates, which when calcined produce compositions embodying numerous particles of the minerals bonded together and presenting internal voids and multiple light reflecting surfaces. The resulting pigmentary compositions are useful in applications requiring high visible light reflectance. These products, however, are, as indicated, produced by calcining, and based upon inorganic binders such as a glassy material, e.g. an alkali metal silicate or the like.

In accordance with the foregoing, it may be regarded as an object of the present invention, to provide a structured kaolin pigment product, which possesses improved light scattering characteristics, and hence is useful as an opacifier and light scattering filler for paper and paper products, and which

may similarly be used in other paper manufacturing applications, including in the coating of same.

It is also an object of the invention to provide improved coated papers and paperboard products for printing purposes such as for offset printing, gravure printing and other types of printing, using a structured kaolin pigment.

It is a further object of the present invention, to provide a pigment product of the foregoing character, which is prepared without calcination and therefore without subjecting the kaolin to high temperatures, and which accordingly possesses low abrasiveness in accordance with the kaolin feed from which it is produced.

It is a yet further object of the invention, to provide a pigmentary product of the foregoing character, which is composed of structured aggregates of minute kaolin particles which are bonded together chemically, i.e. without the use of calcination or other high temperature techniques.

It is a still further object of the invention to provide a high light scattering pigmentary kaolin product, which may be produced at lower costs than calcined kaolins, and which can therefore provide a lower cost replacement for many applications in which calcined kaolin products or other high cost fillers are presently utilized.

It is a yet further object of the invention, to provide a process for producing a pigmentary high light scattering kaolin product, which process utilizes chemical aggregation techniques, and may be carried out without the use of a calcining step or of other high temperature processing conditions or equipment.

It is a yet further object of the present invention, to provide a process for producing structured kaolin pigments as aforementioned, which consists of a minimal number of simply conducted steps, which utilize relatively simple and inexpensive apparatus, and which introduce minimal foreign elements into the final product produced by same.

A still further object of the invention is to provide a process for producing structured kaolin pigments as aforementioned, from a feed crude containing high percentages of extremely minute particles, e.g., less than 0.25 micrometers, to thereby convert a crude having limited value to the paper maker to one which can be readily and economically used in paper products.

A yet further object of the invention, is to provide a process as aforementioned, which enables low abrasion structured kaolin pigments to be produced from coarser process feeds than can normally be employed in calcination to produce a product of comparable low abrasion.

It is a further object of the invention to provide bulky structured kaolin pigments which are eminently suitable for paper coating applications.

It is a still further object of the invention, to provide kaolin pigment-based coating compositions and related methods, which in comparison to use of conventional kaolin pigment-based coating compositions, improves the coating structure and coverage in papers coated with such compositions, as shown by optical properties such as gloss, brightness and opacity, and as shown by printability properties such as offset print gloss, ink receptivity, better K & N and less mottle, and fewer missing gravure ink dots.

A yet further object of the invention, is to provide improved papers of the type provided with a coating composition comprising a kaolin pigment and an adhesive binder, which papers, when manufactured pursuant to the invention, have improved optical and printability properties over a very wide range of coating weights.

It is a further object of the invention to provide paper and paperboard coating compositions which under calendaring conditions used with conventional coating compositions provide improved gloss, and alternatively with reduced calendaring, result in less coating structure collapse than with conventional

coating compositions, and which compositions, further, provide smoother surfaces on papers coated therewith.

A still further object of the invention, is to provide improved paper and paperboard coating compositions, which so enhance coverage in relation to coating weight, as measured by gloss and other optical properties in resultant coated papers, as to enable a significant reduction in the coating weight, while yet maintaining the coverage, i.e. the gloss and other optical properties.

Disclosure of Invention

In accordance with the method of the present invention, a fine particle size kaolin feed is reacted in particulate form with a metal chloride, such as silicon tetrachloride, to form a chemically aggregated structured kaolin pigment. Free moisture present in the particulate feed is sufficient to hydrolyze the metal chloride, but below levels at which the metal oxide will precipitate. A free moisture level of from about 0.4% to 1.0% by weight of the feed is preferred. The indicated steps are conducted under conditions such that the kaolinite structure is not impaired. Heating may optionally be used to shorten the reaction time. When so used, temperatures generally will not, however, exceed about 150°C. In order to complete the polymerization and condensation which is believed to occur pursuant to the inven-

tion, it is preferable to age the resulting product for a period, typically at least three days.

The kaolin feed is preferably dry-milled prior to the reaction step with the metal chloride.

The metal chloride utilized in the invention can be one or more of the chlorides having the general formula MCl_x, where M is Si, Ti or Al; and x is 3 or 4 in accordance with M. The quantity of metal chloride utilized is preferably from about 20 to 35 pounds per ton of dry mixture. More generally at least 10 lbs. per ton of the metal chloride can be used, with the level selected depending upon the desired scattering improvement, except that a plateau is reached about 35 to 40 lbs/ton, above which scattering increases are very limited.

It is preferable in order to obtain high light scattering characteristics, to utilize in the process of the invention a fine particle size kaolin,, preferably one in which the particle size distribution is such that from about 70 to about 100% by weight of same are of less than one micrometer E.S.D. (equivalent spherical diameter). Where the pigment is primarily of interest for use as a filler (as opposed to use in paper coating) and where light scattering qualities are not a primary consideration, coarser feeds can be effectively utilized, e.g., up to 70% by weight less than 2 micrometers E.S.D.

In a further aspect of the invention, it is preferable to intermix with the kaolin feed, small quantities of an aggregation enhancing agent. Such agent is selected from one or more members of the group consisting of the alkaline earth metal carbonates or hydroxides, or lithium carbonate.

The aggregation enhancing agent mixed with the kaolin preferably should provide from about 5 to 120 millimoles of alkaline earth metal or lithium ions per 100 parts by weight of kaolin. This equates to from about 0.5 to 12% by weight kaolin of a particulate alkaline earth metal carbonate or hydroxide or lithium carbonate. Where the particularly preferred calcium carbonate or hydroxide are used, a more preferable addition range is from about 1.5 to 4% by weight of kaolin.

The mixture of kaolin and aggregation enhancing metal ion source subjected to the reaction with the metal chloride, should have a free moisture content of between about 0.4 and 1% by weight of the total mixture.

In a further aspect of the invention,, ammonia is desirably added at addition levels of from about 8 to 16 pounds per ton of the feed mixture, the ammonia being added to the previously combined kaolin and metal chloride. Additional improvements in the products are found to occur when the steps of metal chloride and ammonia addition are sequentially repeated, following the initial sequence just mentioned. However, when the pig-

ment products are to be used in the coating of paper, it is preferred to use the ammonia treatment only after the second, sequential addition of the metal chloride.

The kaolin utilized as a feed for the invention, can be the product of wet processing, wherein various conventional beneficiation steps known to kaolin wet processing are utilized; or in accordance with a further aspect of the invention, the kaolin can be the product of air classifying a kaolin crude, preferably to at least 88% less than two micrometers -- depending upon the light scattering characteristics desired in the final product; except that where the product of the invention is to be used in coating formulations, the classification is preferably to at least 94% less than 2 micrometers.

The aggregated products of the invention are found to have a pore volume which is higher than the feed kaolin used to form same, although lower than a calcined kaolin formed from the same feed. The pore void volumes of products of the present invention when prepared from fine particle size feeds are found to range from 0.4 to 0.8 cm^3/g.

The products of the invention are accordingly found to have increased oil absorption in comparison to the unaggregated feed, although the oil absorption is not so high as that of a calcined kaolin prepared from the same feed. The increased oil

absorption characteristics provides enhanced printing qualities in papers in which the product is incorporated.

The process of the invention, very importantly, serves to aggregate the very fine particles (i.e. the sub 0.25 micrometer particles) present in very fine feeds of the type heretofore discussed. These minute particles can indeed serve in the aggregates as bridges between larger (e.g. micrometer-sized) particles to which they are chemically bonded. Thus, one important advantage to the paper manufacturer is that the otherwise large percentages of troublesome extremely fine particles have been effectively removed as separate entities, but without the need for separation steps, together with the costly equipment required for such operations.

The structured kaolin pigments produced by the foregoing process, have been unexpectedly found to enable preparation of surprisingly improved coated papers, and paperboard products. More specifically, coating formulations providing a bulky structured coating giving improved coverage, enhanced brightness, opacity and particularly gloss at given coating weights, are achieved by use of the said pigment. With respect to the final paper product, these benefits may be taken in the form of either improved sheet properties or significantly reduced coat weights. The resultant coated papers are found to have enhanced properties when used in the course of offset, gravure, letterpress, and similar contact printing.

When used in paper coating applications, the structured kaolin pigments of the invention comprises from about 5 to 60% and preferably from about 10 to 30% by weight of the total pigment component of the coating composition. The balance of the pigment can comprise any of the known coating pigments, such as coating grades of kaolins, calcium carbonate, titanium dioxide, plastic pigments, etc. The coating compositions, in addition to the pigment component, include conventional components, such as an adhesive binder, dispersants, and other known additives.

Where the structured kaolin pigments are used in the coating of paper as aforementioned, it has been found that the increase in gloss in the resultant coated papers, is in part a function of the particle size characteristics of the feed kaolin used to prepare the structured kaolin pigments. Thus, too coarse a feed can be undesirable in these instances. The said feed should preferably be at least 94% less than 2 micrometers E.S.D.

Brief Description of Drawings

In the drawings, Figures 1 and 2 have reference to use of the structured kaolin pigment of the invention as a filler, and Figures 3 to 12 to its use in the coating of paper.

FIGURE 1 is a graph, illustrating the effects upon scattering properties which result from varying the level of aggregation enhancing agent in the feed mix for the process of the invention;

FIGURE 2 is a graph, illustrating the effects upon scattering properties which result from varying the fineness of the kaolin used in the feed mix for the process of the invention;

FIGURE 3 is a graph illustrating the effect on brightness of a coated paper sheet by varying the percent addition to a conventional kaolin pigment, Betagloss®, of a pigment designated W and prepared according to the invention, in a coating composition applied to the paper, for offset printing; FIGURE 4 similarly shows the effect on opacity; FIGURE 5 on gloss; FIGURE 6 on print gloss; FIGURE 7 on litho print gloss, and FIGURE 8 on K & N (wax test);

FIGURE 9 is a graph showing the effect on sheet brightness of varying the coat weight, in g.s.m., grams per square meter, g/m^2, when using coating formulations with different ratios of the pigment of the invention to the control pigment; and FIGURE 10 similarly shows the effect on gloss;

FIGURE 11 is a graph showing the effect on sheet brightness of varying the coat weight, in g.s.m, grams per square meter, g/m^2, when using coating formulations including the pigment of the invention, in comparison to a control pigment, where the latter is a somewhat coarser grade of coating kaolin; and FIGURE 12 similarly shows the effect on gloss.

Best Modes For Carrying Out the Invention

In a presently preferred method, the said structured pigment may be produced by chemically reacting a classified and pulverized kaolin to which from about 0.4 to about 12% by weight of calcium carbonate or hydroxide has been incorporated, as an aggregation enhancer, with silicon tetrachloride, the latter being intermixed with the clay at room temperature (25°C) and at the rate of approximately 20 to 35 lbs. per ton of dry feed.

The free moisture content of the feed is preferably in the range of from about 0.4% to 1% by weight. These levels are sufficient to hydrolyze the $SiCl_4$ to initially produce monosilicic acid, without, however, being sufficient to precipitate free silica.

The silicon tetrachloride may be intermixed in liquid or vaporous form. The intermixing is effected by any suitable mixing apparatus capable of effecting rapid and intimate contact between the reactants. Low shear mechanical mixers, including paddle mixers and other known mixing devices, are suitable for this purpose.

The mixture of feed and silicon tetrachloride is then exposed to ammonia, e.g., by addition of gaseous ammonia at the rate of about 8 to 16 pounds per ton of feed. The ammonia serves to neutralize the acidic byproducts and contributes to the bonding process by formation of $Si_n-(NH)_n$ type polymers.

During mixing, a rapid initial reaction occurs between the kaolin particles and the reagents. The subsequent process of aggregation and bond formation is a relatively slow one, which levels off in about three days. Heating to temperatures of up to about 150°C after incorporation of the reagents into the feed mixture, can help to expel volatile undesired products, but such heating is not a necessary condition for the present process, which proceeds effectively without the need for any heating.

Additional beneficiation steps can be utilized in the process prior to the intermixing of the clay with silicon tetrachloride. Such steps will be utilized depending upon the characteristics of the initial crude kaolin and upon the intended end use of the resultant product. For example, if the initial crude is already of satisfactory whiteness and brightness, and is otherwise devoid of deleterious contaminants, then minimal or no such beneficiation is necessary; i.e., in many instances mere particle size classification will suffice. Among other things, it should be appreciated that since the process of the present invention does not utilize high temperature heating as occurs during calcining, impurities which are considered highly undesirable in processing by calcining, such as glass forming oxides, are of no major concern in the present process. This indeed is one of the principal advantages of the present process, in that minimum beneficiation of the crude clay is necessary. Since no high temperature heating is utilized, the product of the inven-

tion displays an abrasion value which is in accord with the feed kaolin used in the process. Indeed typical abrasions for products of this invention are well under 15, where all abrasions are Valley abrasions determined by the Institute of Paper Chemistry Procedure 65.

Since further, the process of this invention can be carried out, as aforementioned, without substantially altering the feed material, i.e., as would result from heating to calcining temperatures, one may utilize a wide variety of crude kaolins -- or more specifically one may utilize a wide variety of feed kaolins for the present process, without enormous concern for the specific impurity levels that may be present in the kaolin, such as the aforementioned glass forming oxides, iron content or the like; i.e. the primary concern is rather one with the whiteness and brightness of the feed and the abrasion properties of same.

Especially where the objective is to attain a very high scattering coefficient in the product, classification of the starting crude kaolin can be an important consideration in the present invention, since as is the case in the aforementioned McConnell et al, U.S. Patent No. 4,381,948, the resulting aggregates possess light scattering qualities (and consequent opacity when utilized in papers) partially as a function of the fineness and uniformity of the particles which comprise the aggregates. So, for example, use of a finely classified clay fraction, one

e.g. where a very high percentage of same are below 1 micrometer in equivalent spherical diameter (E.S.D.) produces an unusually excellent product in the present invention for the same reasons as are set forth in the McConnell et al patent. Classification to such a fine degree may not, however, be necessary or appropriate where the desired end product need not have unusually high light scattering or opacifying properties. Thus, more generally where classification of the kaolin crude is considered desirable, a feed fraction for the present process may be provided wherein at least 88% by weight of the particles are less than 2 micrometers ESD. (Except that as aforementioned, where the product is intended for paper coating applications, the feed fraction should preferably have at least 94% by weight of the particles, less than 2 micrometers, ESD). Classification can be conducted by various techniques known in the art, including air classification or by aqueous classification techniques.

It should be appreciated from the foregoing that whereas excessive fines are undesirable for papermaking, as previously discussed, they are desirable in the feed used in the process of the present invention, where they serve to improve the properties of the resultant aggregates.

In some instances, the particular kaolin crude utilized may already have sufficient uniformity of particle size, and be of sufficiently fine size to begin with, that there is no essen-

tial need to effect classification; i.e. the crude in its "natural" condition is adequately classified to achieve the results discussed above. In addition, in other instances where particularly high light scattering characteristics are not an essential attribute of the final product, classification may not be required by virtue of the diminished need for high light scattering. In any event, it is found in accordance with the invention that regardless of the particular classification and size characteristics of the feed material processed by this invention, the light scattering characteristics will be improved relative to the starting material.

The brightness of pigment products yielded by the invention are primarily dictated by the starting crude kaolin and by the beneficiation, if any, to which the kaolin is subjected prior to being processed in accordance with the present invention. Depending on the particular end use to which the pigment products of the invention are to be applied, final GE brightness can range from 75 to over 90. Where the pigment products are used for coating applications, the kaolin feed for the process producing the structured pigments can have a GE brightness in the range of from about 80 to 92.

The chemical reaction step, instituted by the intermixing of the kaolin feed mix with silicon tetrachloride, is carried out by adding the silicon tetrachloride while the mixing

operation proceeds. Once the intermixing operation is completed, the resultant product is aged, preferably for a period of at least 3 days, to enhance the scattering properties of the aggregated kaolin particles.

The quality of the resultant products produced by the process of the invention depend, in part, upon the physical and chemical properties of the crude kaolin serving as the source for the feed. A wide range of crude kaolins can be utilized in the invention. The crude can be processed by conventional methodology known in the art, including by so-called "dry" processing and/or by so-called "wet" processing. Where wet processing is utilized, it can be, in some cases, limited to aqueous classification. In other instances, depending upon the nature of the crude, and the product desired, additional known beneficiation techniques can be used to remove undesired elements or contaminants from the kaolin. Similarly, classification can be effected as a part of the wet processing treatment. In a typical known sequence for wet processing for example, the crude can be blunged and dispersed, and then subjected, e.g. by centrifuging, to a particle size separation as an aqueous slurry or dispersion, from which is recovered a slurry of the clay, wherein a desired percentage of the particles are beneath a specified limit. This slurry can then be dried to produce a clay having very low moisture content, normally one wherein less than 1% moisture by

weight is present. Drying in this instance is preferably effected by use of spray drying. The calcium carbonate or hydroxide addition is preferably effected by mixing in the said material prior to the spray drying.

By virtue of its relatively low cost and ready availability, silicon tetrachloride is a presently preferred reagent for use in the process of the present invention. However, other metal chlorides can be effectively utilized in the invention. More specifically, metal chlorides having the general formula MCl_x, where x can be 3 or 4 in accordance with M, and M is Si, Al, and/or Ti. The hydrolyzed products of the indicated metal chlorides have an appropriate structure as will enable them to fit within the crystalline tetrahedra structure of kaolin. Similarly, while calcium carbonate is a preferred aggregation enhancing agent for use in the process of the invention, other alkaline earth metal carbonates or hydroxides, or lithium carbonate, are utilizable in the invention.

A preferable range of addition for the aggregation enhancing agent is from 1.5 to 4% by weight of the feed mixture.

Coarse calcium carbonates or hydroxides are less effective in the present invention, where it is preferable rather to use the so-called paper grades of fine ground or precipitated calcium carbonate, i.e. the grades of same which are used for paper filling and paper coating. A suitable material for use in

the process of the invention is the CARBITAL 50 or CARBITAL 90 product of Atlantic Carbonates of Baltimore, Maryland. These products have respectively particle size distribution such that 50 and 90% thereof by weight are of less than 2 microns E.S.D.

While the applicant does not wish to be bound by any specific theory of the present invention, it is hypothesized that the effectiveness of the present invention partially may result from the hydrolysis of the silicon tetrachloride, which leads to monosilicic acid, which either reacts with the kaolin surface immediately or polymerizes and then reacts with the kaolin particles. However, the immediate reaction is believed to be more likely. Addition of ammonia helps to neutralize the acid resulting from the above, first indicated reaction, and enhances the condensation reactions of the monosilicic acid. The ammonia also forms silicon-amine type polymers, which further enhance and bond the particles. Enhancement of the present process is effected by the addition of the enhancing agent metal ion, which is believed to result in the formation of metal silicates, which function as binding agents, yielding stronger aggregates, and which also helps to neutralize the acidic by-products.

The invention is further illustrated by the following Examples, which are to be regarded as only illustrative of the present invention, and not delimitive thereof:

Example I

For purposes of this Example, a kaolin crude was utilized as a starting material, which was derived from northeast Georgia, and which comprised a very fine particle size, material. The GE brightness of the said crude was thus in the range of 82 to 87 (in all instances in this specification it will be understood that brightness values are obtained according to the standard specification established by TAPPI procedure T-646 os-75).

The said crude was dried, micropulverized and then air classified into a fine and a coarse fraction. The fine fraction was once again micropulverized, and included approximately 97% by weight of particles having an E.S.D. (equivalent spherical diameter) of less than 1 micrometer. Particle size determinations as set forth herein are determined by Sedigraph analysis, i.e. by the instrument of such type available from Micromeritics Instrument Corporation of Norcross, Georgia.

The said fine fraction was dried at about 150°C for a period of 15 minutes to bring the moisture to about 1% or less. The dried and classified feed was thereupon loaded into a Waring blender. Liquid silicon tetrachloride was then added at the rate of 30 pounds per ton of dry clay, corresponding to approximately 1.5% by weight of the clay. This addition was carried out while the Waring blender was operating, and the silicon

tetrachloride was added at the rate of about 1/2 ml in 25 to 30 seconds. The blender was maintained operational for an additional 1 to 2 minutes. The clay was then dried in an oven which was open to air and ambient conditions, at about 150°C for 5 minutes. No post-milling of any type was involved in the present Example.

The pigment product yielded by this Example was subjected to tests to determine the light scattering coefficient of the pigment when same was used as a filler in paper at a 10% loading factor by weight. More specifically, the pigment was tested at 10% loading in Storafite (trademark of Nova Scotia Forest Industries) bleached sulphite pulp beaten to a CSF (Canadian Standard Freeness) of 300-350. Deionized water was used in the sheet formation, together with 20 lbs/ton alum, and Percol 292 (trademark of Allied Colloids) as a retention aid. The tests thus performed showed a scattering coefficient (at 10% filler) in the general range of 555 to 560 cm^2/gram, the average being approximately 557 cm^2/gram. GE brightness was 86.3.

This 10% value was derived by nominally loading the material at 5, 10, and 15%, obtaining the sheet scatter for the three sets of sheets, fitting the points to a straight line by a least square analysis, and calculating the 10% level by the equation generated.

As a control, the aforementioned Alphatex® product of

Anglo-American Clays Corporation was used at 10% loading under otherwise identical conditions. The average scattering coefficient determined with the use of Alphatex® was 720 to 730 cm^2/gram.

A further control was determined by evaluating the scattering coefficient for the starting feed material, i.e. the classified clay fraction utilized in the present Example, i.e. without the chemical aggregation. When prepared under identical conditions as aforementioned, it displayed a scattering coefficient of 528 cm^2/gram.

Example II

In this Example, the same general procedure was utilized as in Example I. The starting feed material, however, was a Georgia kaolin having a crude GE brightness of 87 to 88, which had been wet classified to 97% less than one micrometer E.S.D., and to 100% less than 2 micrometers E.S.D., and spray-dried. The procedure utilized in adding the metal chloride and evaluating the samples were similar to that of Example I, and two further metal chlorides were evaluated, i.e., titanium chloride and anhydrous aluminum chloride. The pigment products yielded in this Example were subjected to tests in accordance with the procedure of Example I, and the scattering coefficients were evaluated at 10% filler level. Samples of the aforementioned Alphatex® were also evaluated for comparison, and samples of the same

feed were also evaluated as fillers without being subjected to the aggregation process of the invention. It was found that the untreated samples produced a scattering coefficient of 540 cm^2/gram. The product prepared with silicon tetrachloride had a scattering coefficient of 555 cm^2/gram, the product prepared with titanium chloride a scattering cross-section of 556 cm^2/gram; and the product prepared with aluminum chloride, a scattering cross-section of 548 cm^2/gram. The Alphatex® product had a scattering of 689 cm^2/gram.

Example III

The crude used in this Example was the same as that of Example I, except that the crude was wet-classified to 96% less than 2 micrometers to provide the feed for testing. The said feed samples were processed with silicon tetrachloride according to the procedure of Example I, except that following the intermixing of the feed with silicon tetrachloride the mixture was exposed to a slight vacuum and was then reacted with 12 pounds of gaseous ammonia per ton of clay. The sequence of silicon tetrachloride and ammonia addition was repeated, and the resultant product dried at 150°C.

For comparison, identical samples were processed as indicated, except that no ammonia was added. Table I sets forth scatter levels achieved at 10% filler level for the two sets of samples. In this and subsequent Examples, all scattering data

are normalized by comparison to the scattering coefficient of samples of the aforementioned Alphatex®. Ideally in a study of the present nature, the same batch of beaten pulp should be used throughout. As this is not practical, the method adopted was to fill one set of sheets in each series of tests using the same Alphatex® from series to series. Statistically, the Alphatex® filled samples at 10% filler had a scattering coefficient of 700 cm^2/gram, and in each series in which Alphatex® differed from 700, the scattering coefficients of the experimental samples were accordingly adjusted proportionally to the adjustments which the Alphatex®-containing paper required to bring its value to 700 cm^2/gram. This procedure, which was used in subsequent examples, is from time to time referred to in the specification as "normalizing" the scattering coefficients.

It is seen that the addition of the ammonia yielded significant further increases in the light scattering properties of the final product. In particular, the scatter at 10% filler level was well over 570 cm^2/gram.

In general, it has been found that repeating the metal chloride treatment increases scattering coefficient by about 10 units, while repeating the metal chloride, ammonia treatment sequence, as was done in this Example, enhances the light scattering coefficient by about 15 units.

Table I

COMPARATIVE SCATTER DATA

Sample	Scatter Coefficient at 10% Filler Level for Product Without NH_3	Scatter Coefficient at 10% Filler Level for Product With NH_3
1	560 cm^2/g	576 cm^2/g
2	556	578
3	551	573
4	559	573

Example IV

The crude kaolin utilized in this Example was a blend of northeast Georgia Kaolins of fine particle size and G.E. brightness of about 87. The said crude was wet-classified to 96% less than 2 micrometers, and was then processed in a manner substantially identical to the samples of Example III, except that the metal chloride was titanium chloride, which was added at a dosage rate of 20 pounds per ton of feed clay. Ammonia was added as in Example III. The resultant products were then evaluated at 10% filler as aforementioned. It was found that the scatter levels achieved at the mentioned filler level was 544 cm^2/g. A control sample not subjected to the process of the invention, displayed a scatter of 522 cm^2/g when similarly processed.

Example V

Feed clays were prepared as described in Example II. These clays were treated with various rapidly hydrolyzing metal chlorides, at addition levels of 30 lbs/ton of clay. The chlorides used were titanium tetrachloride, anhydrous aluminum chloride, and silicon tetrachloride, as described in Example III. Aggregation was found to occur with all of these metal chlorides. A control sample of feed, which was not subjected to the process of the invention, displayed scatter of 522 cm^2/g. Utilizing the process of the invention and the procedure of Example IV, provided a scatter at 10% filler of 565 cm^2/gram with silicon tetrachloride, and 556 cm^2/gram with titanium chloride. Utilizing a different pulp which exhibited a control scattering of 526 cm^2/gram, the process of the invention (practiced as in Example IV) and using aluminum chloride, produced a product having a scatter of 536 cm^2/gram.

Example VI

The same crude kaolin as in Example I was used to prepare feed samples as in Example III. Moisture levels in the final feed were adjusted to be in the range of 0.05% to 3.0% by weight, and the resultant samples were evaluated as in Example I. The scattering coefficient improvements at 10% loading were evaluated, and are shown in Table II as a function of moisture

levels. The Table sets forth the increase in scattering over that yielded by an untreated sample of feed kaolin.

Table II

Improvement of Scattering Coefficient as a Function of Moisture Level of the Feed Kaolin

Percentage Moisture	Increase in Scattering Coefficient at 10% Filler Compared to Scatter of Untreated Feed Kaolin
0.05	3
0.85	24
1.15	8
3.00	7

Example VII

In this Example, the kaolin feed was a blend of two fine northeastern Georgia Kaolins. The feed was wet-classified to 96% less than 2 micrometers. The beneficiated, spray-dried and pulverized feed kaolin was mixed with 3% calcium carbonate dry weight, in slurry form. The calcium carbonate was a paper coating grade having a 90% less than 2 micrometers by weight P.S.D. The feed mixture was dried at 150°C for 5 minutes, to bring the moisture level to about 0.7%, and pulverized once more. Samples of this feed were treated with silicon tetrachloride and ammonia, and other samples with titanium chloride and ammonia

according to Example IV. The resultant products displayed at 10% filling, light scattering of 588 and 576 cm^2/gram, respectively for the silicon tetrachloride and for the titanium tetrachloride prepared products. The untreated feed samples for the $SiCl_4$ test had a scatter of 528, and for the $TiCl_4$ had a scatter of about 522 cm^2/g.

Example VIII

Feed kaolins were prepared as in Example VII, incorporating varying amounts of the aforementioned calcium carbonate in the range of from about 0 to 12% by weight of the total feed mixture. The calcium carbonate used was in 75% solids slurry form. The light scatter improved with the level of calcium carbonate addition, and is depicted in the graph of Figure 1, which shows scatter coefficient as a function of calcium carbonate addition level.

Example IX

The procedure described in Example VIII was repeated with varying dosages of the silicon tetrachloride, ranging from 15 lbs/ton to 35 lbs/ton of feed. For a given feed clay, aggregation and light scatter was found to increase with the amount of silicon tetrachloride utilized. The feed containing 3% calcium carbonate had a resultant light scatter when used at 10% filler of 585 and 610 cm^2/gram when treated with 15 and 30 lbs/ton

silicon tetrachloride, respectively. The scatter was found to be somewhat further improved by application of much higher dosage levels. Thus, at 300 lbs/ton of silicon tetrachloride, scatter at 10% filling was 630 cm^2/gram.

Example X

The procedure described in Example VII was repeated utilizing calcium carbonate of various fineness of particle sizes in the range of 10% less than 2 micrometers by weight to 90% less than 2 micrometers by weight. In general, it was found that in this range of calcium carbonate particle size there was little variation in achieved scatter improvement -- the scattering coefficient improvements due to the addition of the $CaCO_3$ ranged from about 35 to 55 units. For paper industry applications, it is, however, preferable to use a finer grade of calcium carbonate, typically 90% less than 2 micrometers, to reduce abrasion in the event any residual materials remain in the final products of the invention.

Example XI

A series of samples were prepared using starting kaolin crudes and general procedures as in Example VII, and various aggregation enhancing agents were used, including calcium hydroxide, barium carbonate, magnesium carbonate, and lithium carbonate. In each instance, the enhancing agent was added at 3%

dosage level, and the test samples were processed and evaluated as in the procedures in Example VII. The resulting data appear in Table III below.

Table III

Aggregation Enhancing Agent	Scattering Coefficient at 10% Filler Level
Calcium Hydroxide	581
Barium Carbonate	600
Magnesium Carbonate	591
Lithium Carbonate	599

Example XII

In order to illustrate the effects of feed particle size on the resultant products of the invention, feed kaolins derived from the crudes used in Example IV were wet-classified in the range of 88% less than 2 micrometers to 100% less than 2 micrometers. The classified feeds were then spray-dried, blended with 3% calcium carbonate slurry, and subjected to reactants according to the procedure of Example VII. The uppermost curve in Figure 2 depicts the variation in scattering properties as a function of particle size. Scatter generally increased with the fineness of the feed clay. It will be noted, however, that even with a somewhat coarser feed (e.g. 88% less than 2 micrometers) good results are achieved. For comparison, scatter coefficients

for the kaolin without the added calcium carbonate, and for the feed kaolin containing the calcium carbonate, are also shown.

Example XIII

The process of the present invention is one which provide porous structured aggregates. Aggregates thus produced by the procedures of Examples I and IV were analyzed for pore void volume by use of mercury porosimetry. The sample with higher measured porosity was deemed to have the higher intraaggregate pore void volume. Results are set forth in Table IV. The scatters were in the range of 585 to 630 cm^2/g and pore void volume ranged from about 0.4 to 0.7 cm^3/g.

Table IV

Sample No.	Procedure	Aggregated Pore Void Volume in cm^3/g	Scatter at 10% Filling in cm^2/g
1	Example IV	0.635	623
2	Example IV	0.685	630
3	Example I	0.378	585
4	Example I	0.530	608
5	Example IV	0.660	606

Example XIV

The same feed as described in Example VII, was milled several times, specifically 2 to 8 times, using a micropulverizer. The resultant feed samples were treated by the procedure of Example VII. It was found that increasing the number of passes through the micromill led to enhanced light scatter for the aggregated products. Specifically, utilizing 2, 4, 6 and 8 passes, provided light scatter respectively of 583, 595, 598 and 606 cm^2/gram.

Example XV

This Example illustrates the effects of aging upon the resultant products of the invention. In particular, structured kaolin products prepared by the procedure of Example III, were allowed to age for various lengths of time, after which the light scattering increases were evaluated at a 10% filler level. In preparing the samples, no heating or drying was utilized, but simply the aging of the intermixed metal chloride and feed. The light scatter was found to increase with time, and reached a plateau level after approximately three days. Specifically, scatter in a representative sample increased from 585 to 600 cm^2/gram, by increasing the aging period of the product from 1 day to 3 days at room temperature.

Example XVI

Paper Coating Properties of Pigment of the Invention

This Example demonstrates the use of a structured kaolin pigment, prepared according to the invention, and designated here as "Pigment W" to enhance the brightness, opacity, and gloss of an offset coating formulation. These improved qualities can be used to provide lighter weight coatings having optical and printing properties comparable to those which in the prior art could be obtained only with higher coat weights, or by use of expensive additives such as plastic pigments, titanium, dioxide or the like.

The Pigment W was prepared according to the procedures of Example III, using a kaolin feed as in Example VII. The said pigment was found to possess unique properties in its ability to enhance the coverage of a paper coating.

In order to demonstrate its usage, measured amounts have been added to an offset coating formulation based on Betagloss® (a regular brightness fine #1 coating clay) of properties given in Table V.

Table V. Physical Properties of Betagloss®

Brightness	87.1
pH	6.5
-10 Micrometers	100% by wt.
-2 Micrometers	96% by wt.
-1 Micrometers	90% by wt.
-1/2 Micrometers	84% by wt.
-1/4 Micrometers	75% by wt.
Brookfield Viscosity cps @ 20 rpm	300
Hercules Viscosity	
dynes @ rpm	1.2/1100
dynes @ rpm	7.5/4400

In general, the essential ingredients of a coating formulation are a pigment and an adhesive binder, with minor amounts of other ingredients.

The formulation used comprised:

100	parts	pigment
7	parts	Penford Gum 280 (starch binder)
0.5	parts	Nopcote C 104 (calcium stearate)**
1.4	parts	Sunrez® 666 (insolubilizer)
7	parts	Dow 620, latex adhesive binder

**coating lubricant, product of Diamond Shamrock

The coating formulation was prepared by mixing the ingredients in the following order of addition. Mix coating clay in water, followed by Pigment W, and mix to 45°C. Add dispersant, (Dispex® N-40, trademark of Allied Colloids, Great Britain for sodium polyacrylate), starch, calcium stearate, insolubilizer and latex. The amount of dispersant was controlled to give appropriate rheology. The solids in the coating formulation were nearly 62% by weight, as determined by moisture balance.

The control coating formulation employed Betagloss® (BG) as the sole pigment. For comparison purposes, other coatings were prepared with addition of 10, 20, and 30% of pigment W to the Betagloss.

Because of its unique structure and surface chemistry, pigment W in this Example, required additional quantities of dispersants (up to 1%), and coating formulation solids were reduced to maintain a usable rheology. In consequence, the control coating formulation had a solids content of up to 4% higher than the coating formulation with pigment W.

Coatings were applied on a publication base stock (brightness 67, opacity 90.6, gloss 6) using a coating machine, the Helicoater, running at 1500 ft/min for a target coat weight of 8 gsm (grams per square meter). The Helicoater is a pilot blade coater, details of which are described in N.O. Clark, et al. Paper Trade Journal, September 19, 1966.

The conditioned coated papers were calendered for 10 nips at 1500 psi and 150°F. It was found that the pigment responds to calendering very well to give good gloss properties. Also, it responded at lower pressure than usual.

Results

The measured properties of the resultant coated stock are set forth in Table VI, and in the graphs of Figures 3 to 10:

TABLE VI

Coated Sheet Properties @ 8 GSM (g/m^2)

BG = Betagloss®

ATEX = Alphatex®

W = Pigment W

	100% BG	90% BG 10% W	80% BG 20% W	70% BG 30% W	90% BG 10% ATEX	80% BG 20% ATEX
Brightness	67.2	67.8	68.7	70.5	68.1	69.4
Yellowness	7.3	8.0	7.0	6.2	7.1	6.5
Opacity	92.2	92.7	92.9	92.8	92.4	92.5
Gloss	51	58	55	62	52	49
Print Gloss	63	64	66	74	64	63
Litho P. Gloss	57	57	57	60	59	56
Delta Gloss	12	6	11	12	12	14
Print Density	1.54	1.48	1.51	1.56	1.47	1.47
Litho P. Density	1.48	1.44	1.42	1.28	1.46	1.43
Density Ratio	0.96	0.97	0.94	0.82	0.99	0.97
K&N	21	26	26	30	24	26
Pick, cm/s	60	41	56	50	53	50

TABLE VI (continued)

Comments:

Base Paper:		Print Gloss Conditions Using IGT AIC2 Print Tester:
Coated Wireside		0.3 mls. OR2050 Offset Ink
Basis Weight - 43.8 gsm		0.5 m/sec. printing speed
		Constant Mode
Brightness	67.0	15 kgf - Top Sector
Yellowness	7.2	50 kgf - Bottom Sector
Opacity	90.6	70# Offset Control
Gloss	6	(Print Gloss 80, Litho P. Gloss 75)
		(Print Density 1.58, Litho P. Density 1.52)

Brightness & Opacity

The increase in brightness and opacity are indicative of an increase in light scatter of the coating (Figure 3 and 4), and consequently suggests the presence of an enhanced pore structure.

Gloss

Gloss was measured using TAPPI procedure T480 om-85. Surprisingly, gloss increased with increasing usage of Pigment W (Figure 5), even though in this Example the coating solids were lower in the Pigment W formulation than in the control formulation. Usually gloss decreases when coating formulation solids are decreased. The fine No. 1 pigment used in this Example is usually regarded as an easy glossing clay, and hence the gloss improvement obtained with the use of Pigment W is very significant.

Also to be noted in Table VI is that two further controls wherein the coating formulations included respectively 90% Betagloss® plus 10% Alphatex®, and 80% Betagloss® and 20% Alphatex® (Alphatex being the previously described calcined pigment), did not yield the increases in gloss provided pursuant to the instant invention.

Offset print gloss also showed some evidence of increasing (Figures 6 and 7). ("Litho print gloss" is measured

from predamped printed surface).

It is also seen in Table V that the wet pick improved where the composition of the invention were used -- this being a measurement of missing points in the offset printed stock. At the same time, print density was substantially maintained.

Finally K&N (a measurement of ink receptivity) shows an increase with addition of Pigment W, and further indicates the development of a more open coating structure (Figure 8).

References for the terms "Litho Print Gloss", "Wet Pick", "K & N", etc. are found in the Hollingsworth et al paper, op. cit.

Variations With Coat Weights

In general, when lighter weight coatings are applied, the coverage on a sheet will usually be poorer, and optical properties such as brightness, opacity, and gloss will decrease. The use of Pigment W permits improvement in these properties at the same coat weight. Alternatively, a reduced coat weight of a coating containing Pigment W is seen to achieve the same properties as the coating pigment Betagloss® alone. For example, a coating of 80:20 Betagloss:Pigment W at 6.5 g/m^2 provides similar gloss as Betagloss® alone at 8 g/m^2. Brightness is significantly higher (Figures 9 and 10).

The use of Pigment W provides improvements in brightness, opacity, and gloss. Printability is similarly indicated to be improved. These benefits may be taken by the manufacturer in the form of either improved sheet properties or of significantly reduced coat weights.

Example XVII

In this Example, further paper coating formulations were prepared which included the same components specified in Example XVI, except that the control pigment instead of being a fine size coating kaolin such as Betagloss®, was a coarser grade coating kaolin, comprising 50 parts of a No. 2 coating kaolin (the KCS product of Georgia Kaolin Co.) and 50 parts of an 80% below 2 micrometers delaminated kaolin (the Alphaplate® product of Anglo-American Clays Corporation). The control formulation was coated at 62% solids.

In one test coating formulation (A), 20 parts of pigment W, as in Example XVI, were substituted, i.e. to provide a ratio of 20 parts W to 40 parts No. 2 coating clay, and 40 parts of the Alphaplate®. In the second test formulation, (B), the same ratio was used, except that instead of being blended into the coating formulation as pigment powders, the pigment W was added as a 50% solids slurry, which therefore included small amounts of additional dispersants (13 lbs/ton dry clay of carboxy methyl cellulose (CMC), 10 lbs/ton of TSPP, (tetrasodium pyro-

phosphate) and 10 lbs/ton of Dispex® N-40). The test formulations were coated at 58% solids.

The resultant improvements in paper brightness and gloss are seen in the graphs of Figures 11 and 12, from which it is seen that similar improvements obtain with the incorporation of the pigments of the invention into coarser kaolin coating grade formulations, as is the case where addition is effected to fine particle size grade coating kaolins.

Example XVIII

In a further formulation where a lower viscosity starch was used, i.e. Penford Gum 290 (instead of PG 280), the test formulation (D) was coated at about 62% solids with 10 parts of pigment W and 45 parts of KCS and 45 parts Alphaplate®.

Data for a control formulation (C) also appears. Coating procedures and evaluation were as in Example XVII. In this case, and as seen in Table VII, improvements were obtained comparable to use of 20 parts of pigment W at lower solids.

TABLE VII

	FORMULATION C	FORMULATION D
	50 parts Alphaplate®	45 parts Alphaplate®
	50 parts KCS	45 parts KCS
	(PG 280)	10 parts Pigment W (PG-290)
pH	7.8	7.8
Brookfield Visc. cps @10 rpm	8000	8800
Brookfield Visc. cps @20 rpm	4700	5100
Brookfield Visc. cps @50 rpm	2440	2480
Brookfield Visc. cps @100 rpm	1520	1460
Hercules Visc. "E-Bob" @400K Dynes	39	53
rpm	4400	4400
%Solids	61.8	61.9
Temp. Cel.	37	38

TABLE VII (continued)

	FORMULATION C		FORMULATION D
	50 parts Alphaplate®		45 parts Alphaplate®
	50 parts KCS		45 parts KCS
	(PG-280)		10 parts Pigment W (PG-290)
	Brightness	68.9	70.1
	Yellowness	7.5	6.9
	Opacity	92.9	93.2
	Gloss	40.1	44.5
	Print Gloss	57.4	62.3
	Litho P. Gloss	51.8	56.5
	Delta P. Gloss	17.3	17.8
	Print Density	1.48	1.54
	Litho P. Density	1.38	1.46
	P. Density Ratio	0.93	0.95
	K&N	24.6	26.8

Example XIX

Preparation of A Pigment Slurry

In order to effectively utilize the pigments of the invention in coating applications, it is often desirable to prepare same in the form of aqueous slurries. The presence of various inorganic salts as a result of the processes of preparation of the pigments tend to produce some difficulties in making up a slurry by use of conventional dispersing agents and techniques. In accordance with a further aspect of the invention, it has been found that fully satisfactory aqueous slurries can, however, be prepared by use of a combination of several dispersing agents, which have not commonly been used in these combinations heretofore. More specifically, it has been found that a combination of from about .4 to 1% of medium viscosity CMC (carboxymethylcelulose), in combination with from about .1 to .5% of TSPP, and from about 0 to .5% of Dispex® N-40 (a trademark of United Colloids of Great Britain for sodium polyacrylate salts), where all percentages indicated are expressed as weight percent of the dry pigment present in the said slurry, are found to be effective in yielding slurries of acceptable rheological properties for purposes of pumping and otherwise handling the slurry, up to a solids content of about 52%.

While the present invention has been particularly set forth in terms of specific embodiments thereof, it will be under-

stood in view of the instant disclosure, that numerous variations upon the invention are now enabled to those skilled in the art, which variations yet reside within the scope of the present teaching. Accordingly, the invention is to be broadly construed, and limited only by the scope and spirit of the claims now appended hereto.

Claims

1. A process for producing a structured kaolin pigment having enhanced light scattering and opacifying properties when incorporated in paper; said process comprising the steps of

(a) forming a feed mixture of a fine particle size kaolin; and

(b) chemically reacting said feed mixture in particulate form with a metal chloride having the general formula $M Cl_x$, where M is Si, Al or Ti; and x is 3 or 4 in accordance with M, to aggregate the kaolin particles to form the structured pigment;

the moisture level present in the said feed mixture reacted in step (b) being sufficient to hydrolyze the metal chloride but being insufficient to precipitate the corresponding metal oxide; and

steps (a) and (b) being conducted under conditions such that the kaolinite structure is not impaired.

2. A process for producing a structured kaolin pigment having enhanced light scattering and opacifying properties when incorporated in paper; said process comprising the steps of:

(a) forming a feed mixture of a fine particle size kaolin; and

(b) aggregating the kaolin particles to form the structured pigment, by combining said feed mixture in particulate form with a metal chloride having the general formula $M\ Cl_x$ where M is Si, Al or Ti, and x is 3 or 4 in accordance with M; and then adding ammonia to the combined feed mixture and metal chloride;

the moisture level present in the said feed mixture reacted in step (b) being sufficient to hydrolyze the metal chloride but being insufficient to precipitate the corresponding metal oxide; and

steps (a) and (b) being conducted under conditions such that the kaolinite structure is not impaired.

3. A process for producing a structured kaolin pigment having enhanced light scattering and opacifying properties when incorporated in paper; said process comprising the steps of:

(a) forming a feed mixture of a fine particle size kaolin together with an aggregation enhancing agent selected from one or more members of the group consisting of any alkaline earth metal carbonate or hydroxide, and lithium carbonate, the enhancing agent being present in quantities to provide from about 5 to 120 millimoles of the enhancing agent metal ion species per 100 parts by weight of kaolin; and

(b) chemically reacting said feed mixture in particulate form with a metal chloride having the general formula M Cl_x where M is Si, Al or Ti; and x is 3 or 4 in accordance with M, to aggregate the kaolin particles to form the structured pigment;

the moisture level present in the said feed mixture reacted in step (b) being sufficient to hydrolyze the metal chloride but being insufficient to precipitate the corresponding metal oxide; and

steps (a) and (b) being conducted under conditions such that the kaolinite structure is not impaired.

4. A process for producing a structured kaolin pigment having enhanced light scattering and opacifying properties when incorporated in paper; said process comprising the steps of:

(a) forming a feed mixture of a fine particle size kaolin together with an aggregation enhancing agent selected from one or more members of the group consisting of an alkaline earth metal carbonate or hydroxide, and lithium carbonate, the enhancing agent being present in quantities to provide from about 5 to 120 millimoles of the enhancing agent metal ion species per 100 parts by weight of kaolin; and

(b) aggregating the kaolin particles to form the structured pigment, by combining said feed mixture in particulate form with a metal chloride having the general formula M Cl_x where

M is Si, Al or Ti; and x is 3 or 4 in accordance with M; and then adding ammonia to the combined feed mixture and metal chloride;

the moisture level present in the said feed mixture reacted in step (b) being sufficient to hydrolyze the metal chloride, but being insufficient to precipitate the corresponding metal oxide; and

steps (a) and (b) being conducted under conditions such that the kaolinite structure is not impaired.

5. A method in accordance with claims 1, 2, 3 or 4 wherein said metal chloride comprises silicon tetrachloride.

6. A method in accordance with claims 1, 2, 3 or 4 including the step of heating the reactants in step (b) to temperatures not higher than 150°C.

7. A method in accordance with claims 1, 2, 3 or 4 including the steps of aging the product of step (b) for a period of at least three days to enhance the scattering properties of the aggregated kaolin particles.

8. A method in accordance with claims 1, 2, 3 or 4, wherein said kaolin has a particle size distribution such that from about 70 to 100% by weight thereof is of less than 2 micrometers ESD.

9. A method in accordance with claims 1, 2, 3 or 4, wherein the feed mixture subjected to step (b) has a free moisture content of from about 0.4% to 1% by weight of the mixture.

10. A method in accordance with claims 1, 2, 3 or 4, wherein said kaolin utilized in step (a) is the product of air classifying a kaolin crude clay to at least as fine as 88% less than 2 microns.

11. A method in accordance with claims 3 or 4, wherein said aggregation enhancing agent comprises from about 0.4 to about 12% by weight of the kaolin, of a particulate alkaline earth metal carbonate or hydroxide.

12. A method in accordance with claim 11, wherein said enhancing agent comprises calcium carbonate.

13. A process in accordance with claim 12 wherein the feed mixture of kaolin and calcium carbonate is dry-milled prior to step (b).

14. A process in accordance with claim 13, wherein the said feed mixture is dry-milled by repetitive passes through a micromilling means.

15. A method in accordance with claims 2 or 4, wherein said ammonia is added at levels from about 8 to 16 lbs/ton of feed mix.

16. A method in accordance with claim 15, wherein the steps of metal chloride and ammonia addition are sequentially repeated.

17. A method in accordance with claims 1 or 3, wherein the step of metal chloride addition is sequentially repeated.

18. A structured kaolinitic pigment, comprising porous aggregates of kaolin particles which are chemically bonded to one another, by the process of any of claims 1, 2, 3 or 4.

19. The structured kaolinitic pigment produced by the process of any of claims 1, 2, 3 or 4.

20. A method of coating paper which comprises producing a structured kaolin pigment having enhanced light scattering and opacifying properties by a process comprising the steps of:

(a) forming a feed mixture of a fine particle size kaolin; and

(b) chemically reacting said feed mixture in particulate form with a metal chloride having the general formula MCl_x, in which M is Si, Al or Ti and x is 3 or 4 depending on the valence of M, to aggregate the kaolin particles to form the structured pigment;

the moisture level present in the said feed mixture reacted in step (b) being sufficient to hydrolyze the metal chlo-

ride but insufficient to precipitate the corresponding metal oxide;

steps (a) and (b) being conducted under conditions such that the kaolinite structure is not impaired; and

(c) coating the paper with a coating composition containing said structured kaolin pigment.

21. A method of coating paper which comprises producing a structured kaolin pigment having enhanced light scattering and opacifying properties by a process comprising the steps of:

(a) forming a feed mixture of a fine particle size kaolin; and

(b) aggregating the kaolin particles to form the structured pigment, by combining said feed mixture in particulate form with a metal chloride having the general formula MCl_x in which M is Si, Al or Ti and x is 3 or 4 depending on the valence of M, and then adding ammonia to the combined feed mixture and metal chloride;

the moisture level present in the said feed mixture reacted in step (b) being sufficient to hydrolyze the metal chloride but insufficient to precipitate the corresponding metal oxide; and

steps (a) and (b) being conducted under conditions such

that the kaolinite structure is not impaired; and

(c) coating the paper with a coating composition containing said structured kaolin pigment.

22. A method of coating paper which comprises producing a structured kaolin pigment having enhanced light scattering and opacifying properties when incorporated in paper by a process comprising the steps of

(a) forming a feed mixture of a fine particle size kaolin together with an aggregation enhacing agent selected from one or more members of the group consisting of any alkaline earth metal carbonate or hydroxide, and lithium carbonate, the enhancing agent being present in quantities to provide from about 5 to 120 millimoles of the enhancing agent metal ion species per 100 parts by weight of kaolin; and

(b) chemically reacting said feed mixture in particulate form with a metal chloride having the general formula $M\ Cl_x$ where M is Si, Al or Ti; and x is 3 or 4 in accordance with M, to aggregate the kaolin particles to form the structured pigment;

the moisture level present in the said feed mixture reacted in step (b) being sufficient to hydrolyze the metal chloride but being insufficient to precipitate the corresponding metal oxide;

steps (a) and (b) being conducted under conditions such

that the kaolinite structure is not impaired; and

(c) coating the paper with a coating composition containing said structured kaolin pigment.

23. A method of coating paper which comprises producing a structured kaolin pigment having enhanced light scattering and opacifying properties when incorporated in paper by a process comprising the steps of

(a) forming a feed mixture of a fine particle size kaolin together with an aggregation enhancing agent selected from one or more members of the group consisting of an alkaline earth metal carbonate or hydroxide, and lithium carbonate, the enhancing agent being present in quantities to provide form about 5 to 120 millimoles of the enhancing agent metal ion species per 100 parts by weight of kaolin; and

(b) aggregating the kaolin particles to form the structured pigment, by combining said feed mixture in particulate form with a metal chloride having the general formula M Cl_x where M is Si, Al, or Ti; and x is 3 or 4 in accordance with M; and then adding ammonia to the combined feed mixture and metal chloride;

the moisture level present in the said feed mixture reacted in step (b) being sufficient to hydrolzye the metal chloride, but being insufficient to precipitate the corresponding metal oxide;

steps (a) and (b) being conducted under conditions such that the kaolinite structure is not impaired; and

(c) coating the paper with a coating composition containing said structured kaolin pigment.

24. A method as set forth in claims 20, 21, 22 or 23 wherein said metal chloride comprises silicon tetrachloride.

25. A method as set forth in claims 20, 21, 22 or 23 including the step of heating the reactants in step (b) to temperatures not higher than 150°C.

26. A method as set forth in claims 20, 21, 22 or 23 including the steps of aging the product of step (b) for a period of at least three days to enhance the scattering properties of the aggregated kaolin particles.

27. A method as set forth in claims 20, 21, 22 or 23 wherein said feed kaolin has a G.E. brightness in the range of from about 80 to 92.

28. A method as set forth in claims 20, 21, 22 or 23 wherein the feed mixture subjected to step (b) has a free moisture content of from about 0.4% to 1% by weight of the mixture.

29. A method as set forth in claims 20, 21, 22 or 23 wherein said kaolin utilized in step (a) is at least as fine as 94% by weight less than 2 micrometers E.S.D.

30. A method as set forth in claims 22 or 23, wherein said aggregation enhancing agent comprises from about 0.4 to about 12% by weight of the kaolin, of a particulate alkaline earth metal carbonate or hydroxide.

31. A method as set forth in claim 30, wherein said enhancing agent comprises calcium carbonate.

32. A method as set forth in claim 31 wherein the feed mixture of kaolin and calcium carbonate is dry-milled prior to step (b).

33. A method as set forth in claim 32, wherein the said feed mixture is dry-milled by repetitive passes through a micro-milling means.

34. A method as set forth in claims 21 or 23, wherein said ammonia is added at levels from about 8 to 16 lbs/ton of feed mix.

35. A method as set forth in claim 20 or 22, wherein the step of metal chloride addition is sequentially repeated.

36. A method as set forth in claim 20 or 22, wherein the step of metal chloride addition is sequentially repeated and ammonia is added only after the second addition of metal chloride.

37. A coated paper or paperboard coated with a struc-

tured kaolinitic pigment comprising porous aggregates of kaolin particles which are chemically bonded to one another, by the process of steps (a) and (b) of any of claims 20, 21, 22 or 23.

38. The coated paper coated with a structured kaolinitic pigment by the process of any of claims 20, 21, 22 or 23.

39. A coated paper or paperboard coated with a structured kaolinitic pigment being the reaction product of a fine particle size kaolin and a metal chloride having the general formula MCl_x in which M is Si, Al or Ti and x is 3 or 4 depending on the valence of M, and water for hydrolyzing said metal chloride.

40. A coated paper or paperboard as set forth in claim 39 in which said metal chloride comprises silicon tetrachloride.

41. A printing stock for use in an offset printing method comprising the coated paper of claim 39.

42. A printing stock for use in a gravure printing method comprising the coated paper of claim 39.

43. A method for improving the optical and printability properties of a paper or paperboard coated with a coating formulation of the type comprising a coating pigment component and an adhesive binder; said method comprising:

substituting into the said pigment component of the said coating formulation, from about 5 to 60% by weight of

said component, of a structured kaolinitic pigment comprising porous aggregates of kaolin particles which are chemically bonded to one another, by the process of steps (a) and (b) of any of claims 20, 21, 22 or 23.

44. A coated paper or paperboard, the coating of which comprises a coating pigment component and an adhesive binder, said pigment component including from 5 to 60% by weight of a structured kaolinitic pigment comprising porous aggregates of kaolin particles which are chemically bonded to one another by the process of steps (a) and (b) of any of claims 20, 21, 22 or 23.

45. A method for preparing an aqueous slurry of a pigment prepared by steps (a) and (b) of any of claims 20, 21, 22 or 23, comprising dispersing said pigment to form an aqueous slurry of up to 52% solids by weight, by intermixing said pigment with water and as dispersing agents a combination of from about .4 to 1% of medium viscosity carboxymethylcelulose, from about .1 to .5% of tetrasodium pyrophosphate, and from about 0 to .5% of sodium polyacrylate salts, said percentages being expressed as weight percent of the dry pigment present in said slurry.

FIG. 1

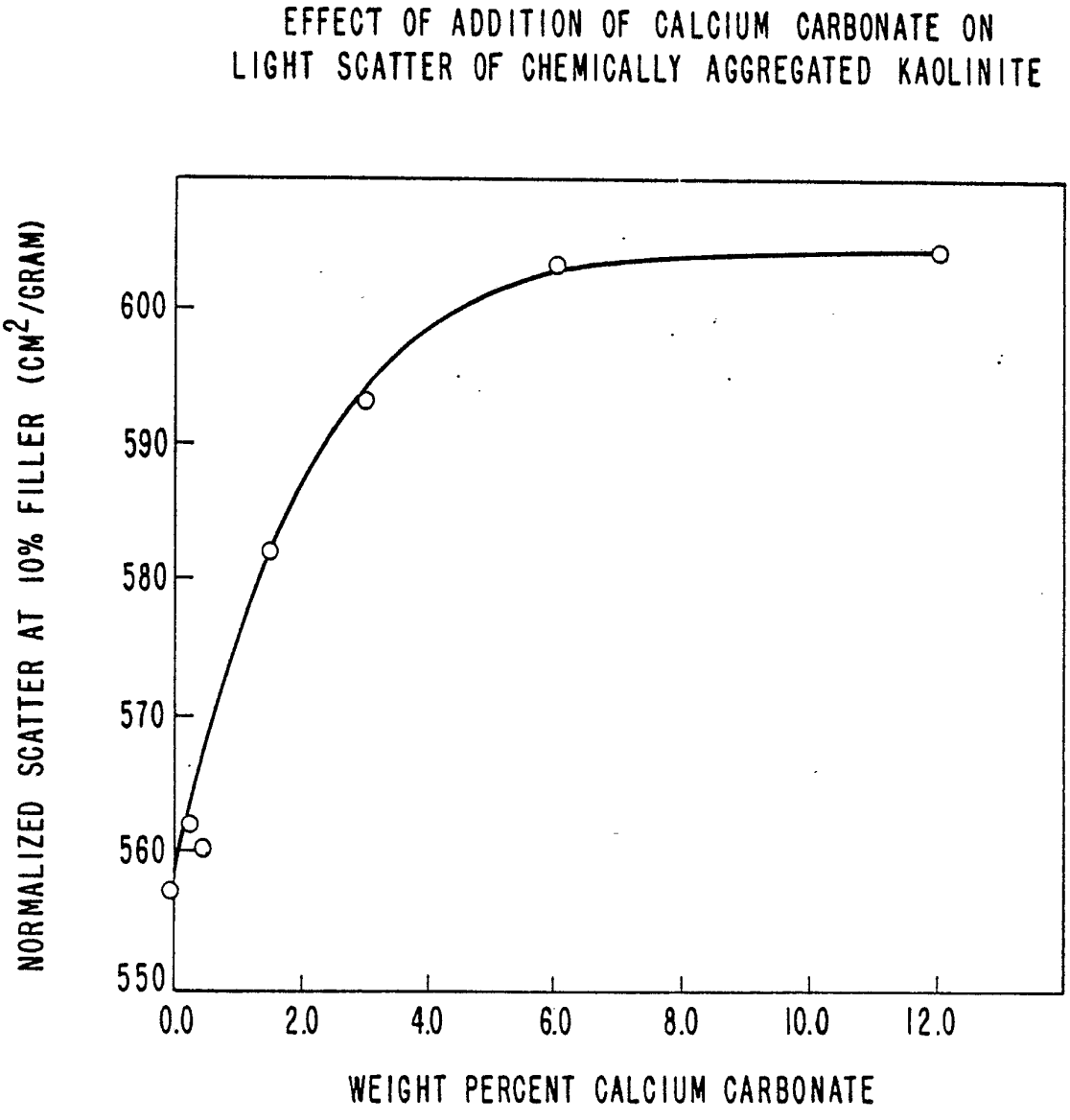

EFFECT OF ADDITION OF CALCIUM CARBONATE ON
LIGHT SCATTER OF CHEMICALLY AGGREGATED KAOLINITE
NORMALIZED SCATTER AT 10% FILLER (CM2/GRAM)
600
590
580
570
560
550
0.0
2.0
4.0
6.0
8.0
10.0
12.0
WEIGHT PERCENT CALCIUM CARBONATE

FIG. 2

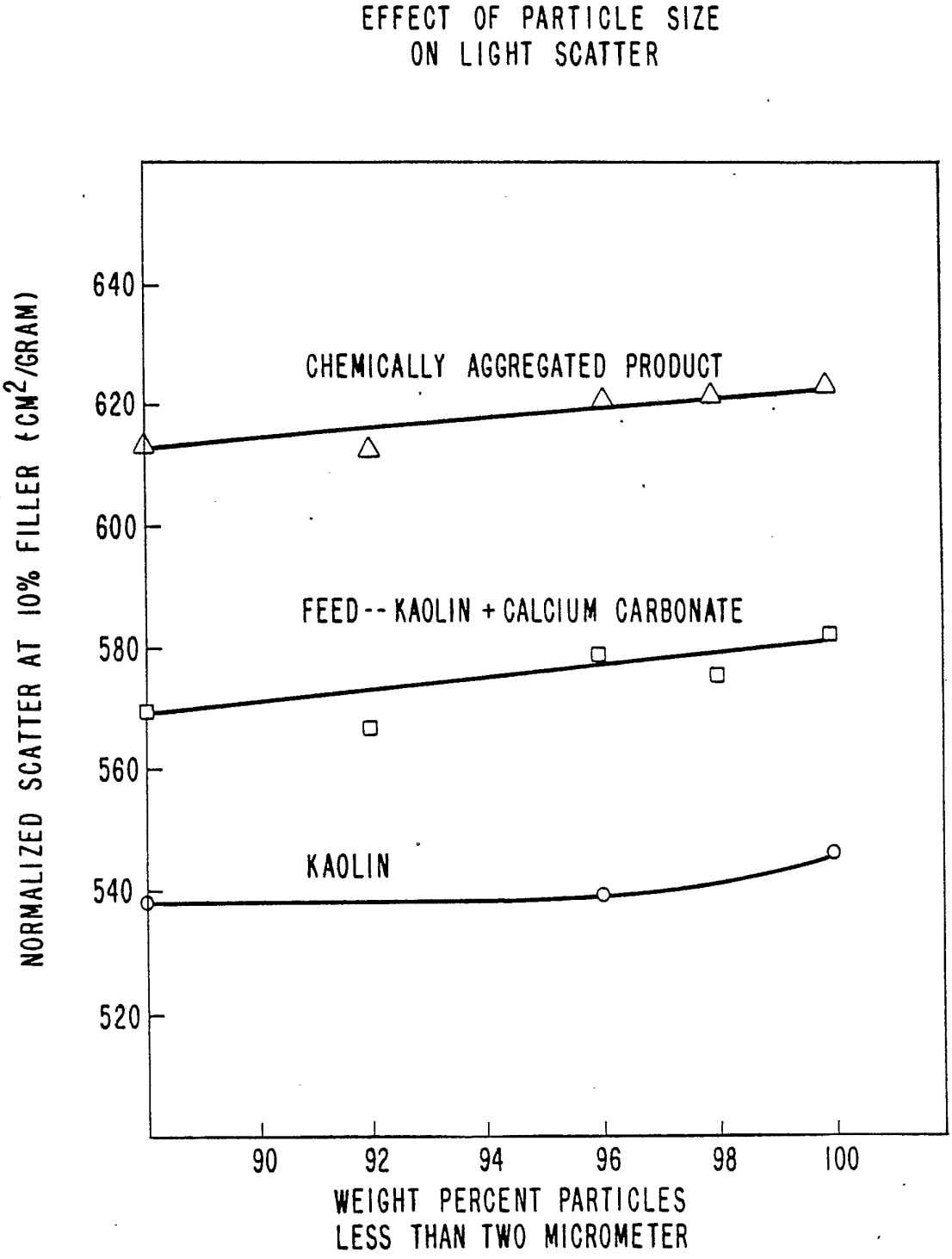

EFFECT OF PARTICLE SIZE
ON LIGHT SCATTER
NORMALIZED SCATTER AT 10% FILLER (CM²/GRAM)
640
620
600
580
560
540
520
CHEMICALLY AGGREGATED PRODUCT
FEED -- KAOLIN + CALCIUM CARBONATE
KAOLIN
90
92
94
96
98
100
WEIGHT PERCENT PARTICLES
LESS THAN TWO MICROMETER

FIG. 3

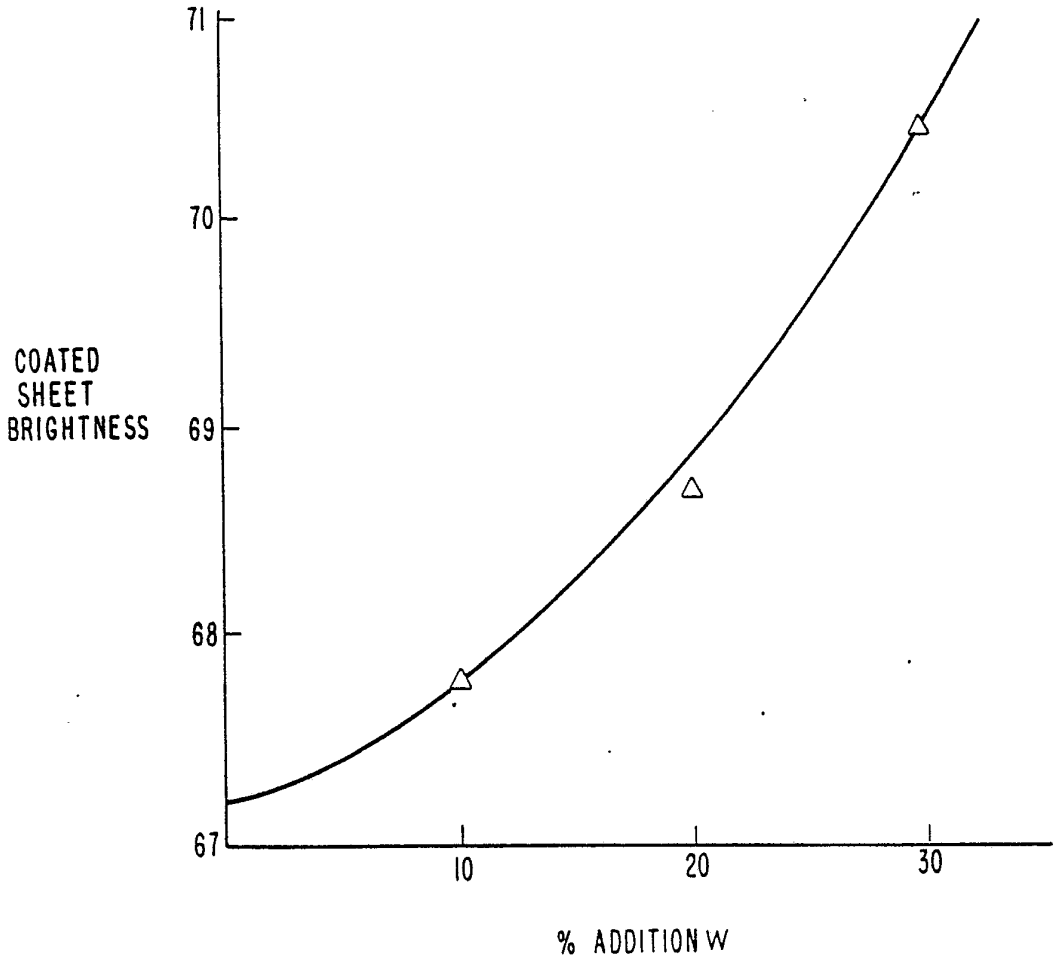

71
70
69
68
67
COATED SHEET BRIGHTNESS
10
20
30
% ADDITION W

FIG. 4

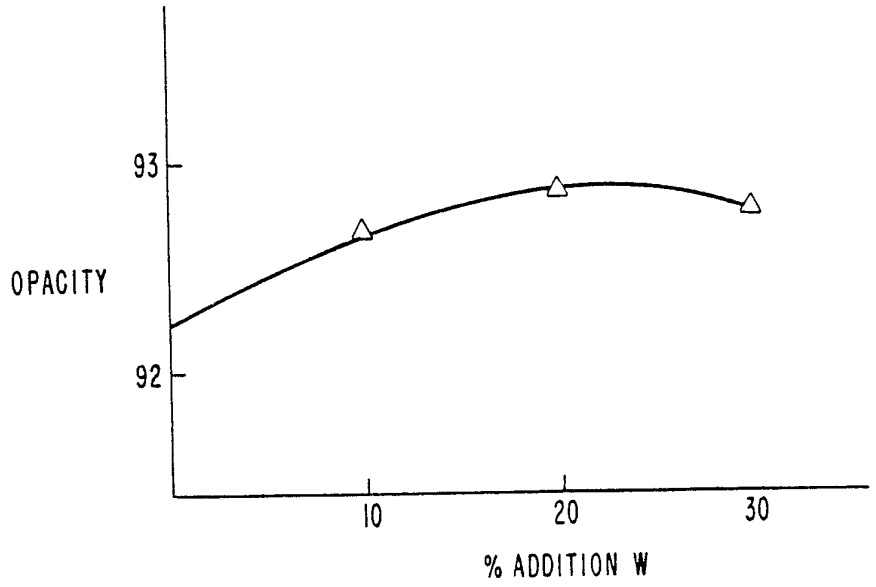

93
92
OPACITY
10
20
30
% ADDITION W

FIG. 5

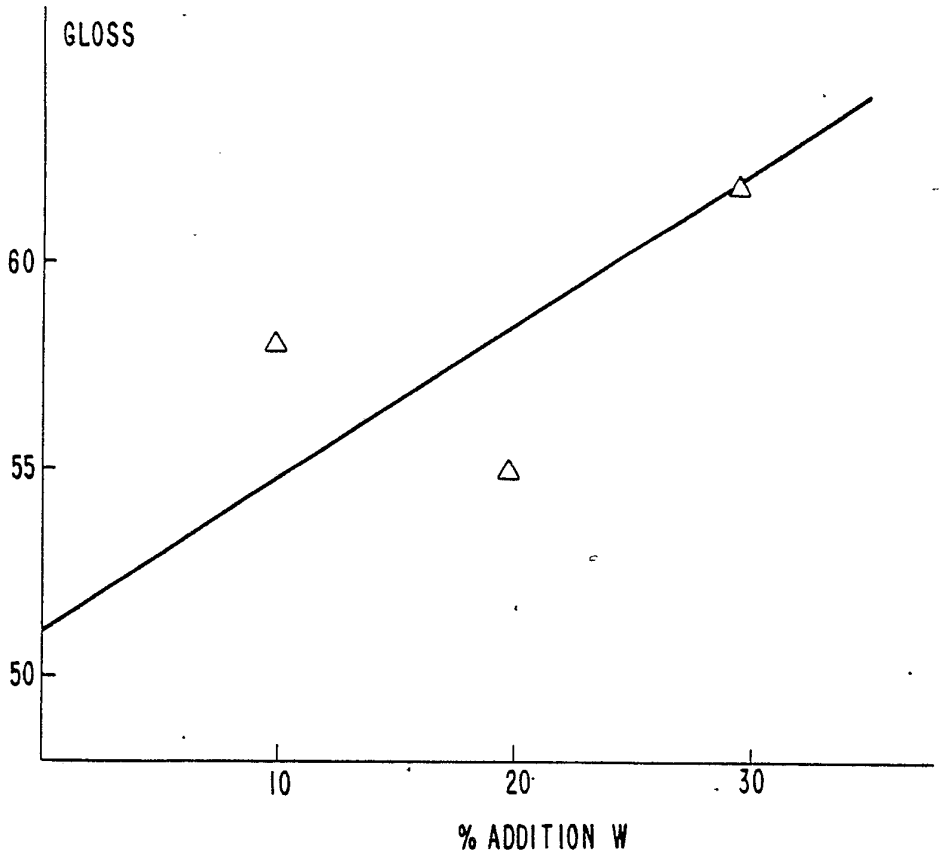


FIG. 6

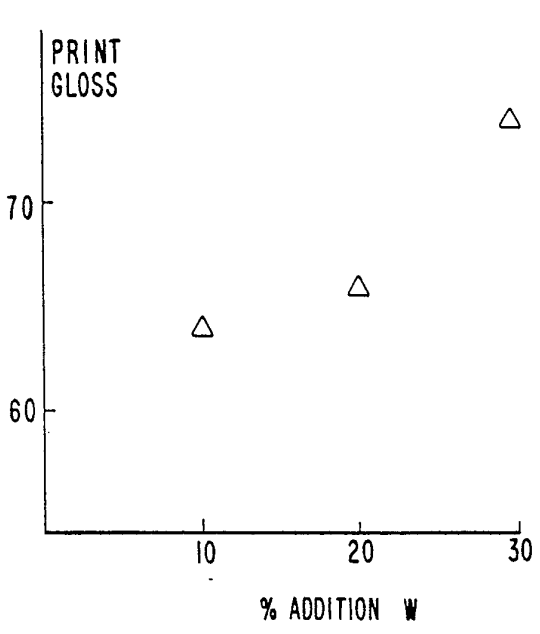


FIG. 7

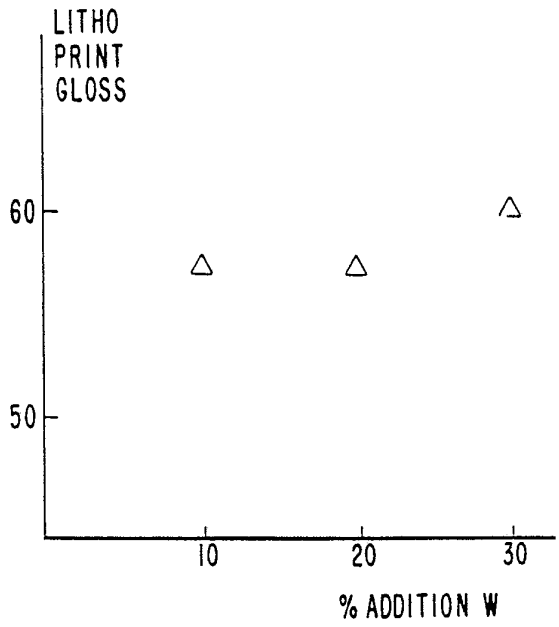


FIG. 8

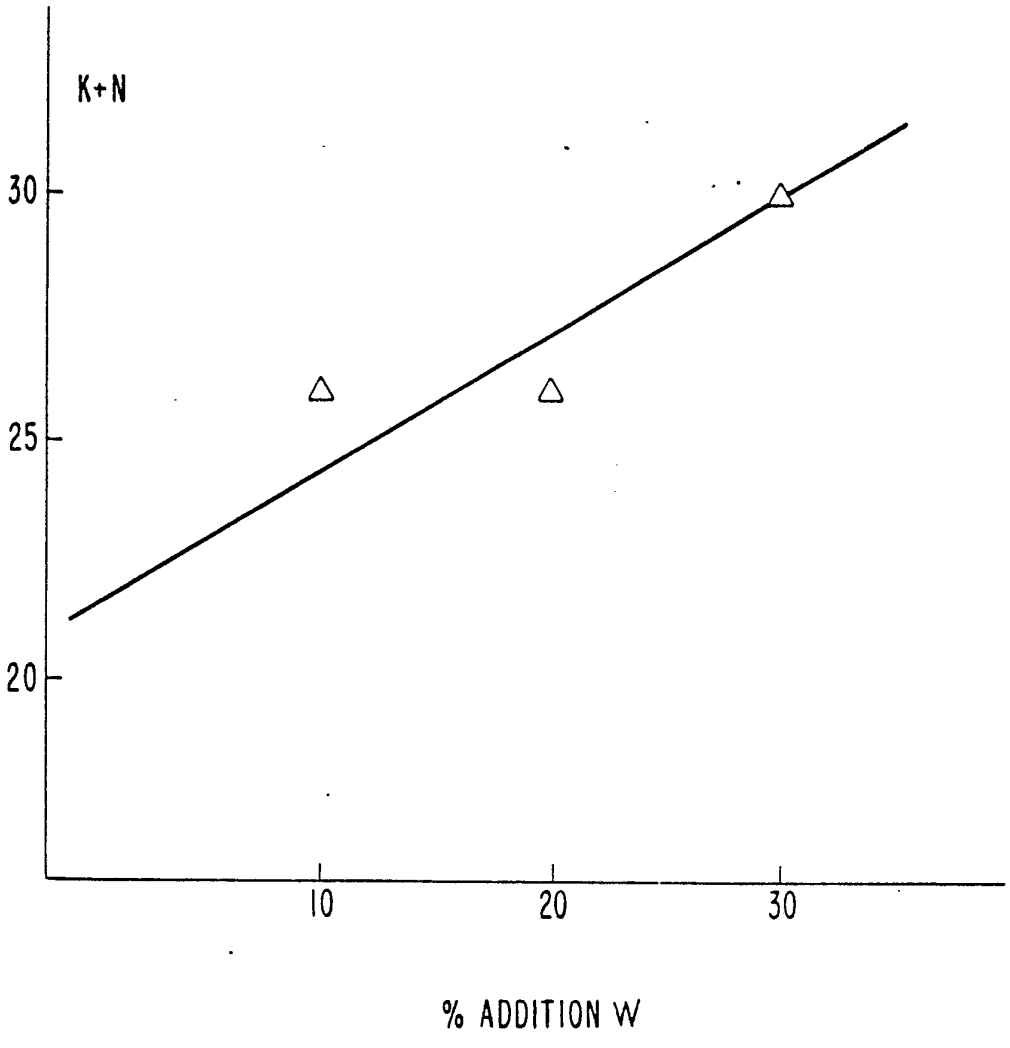


FIG. 9

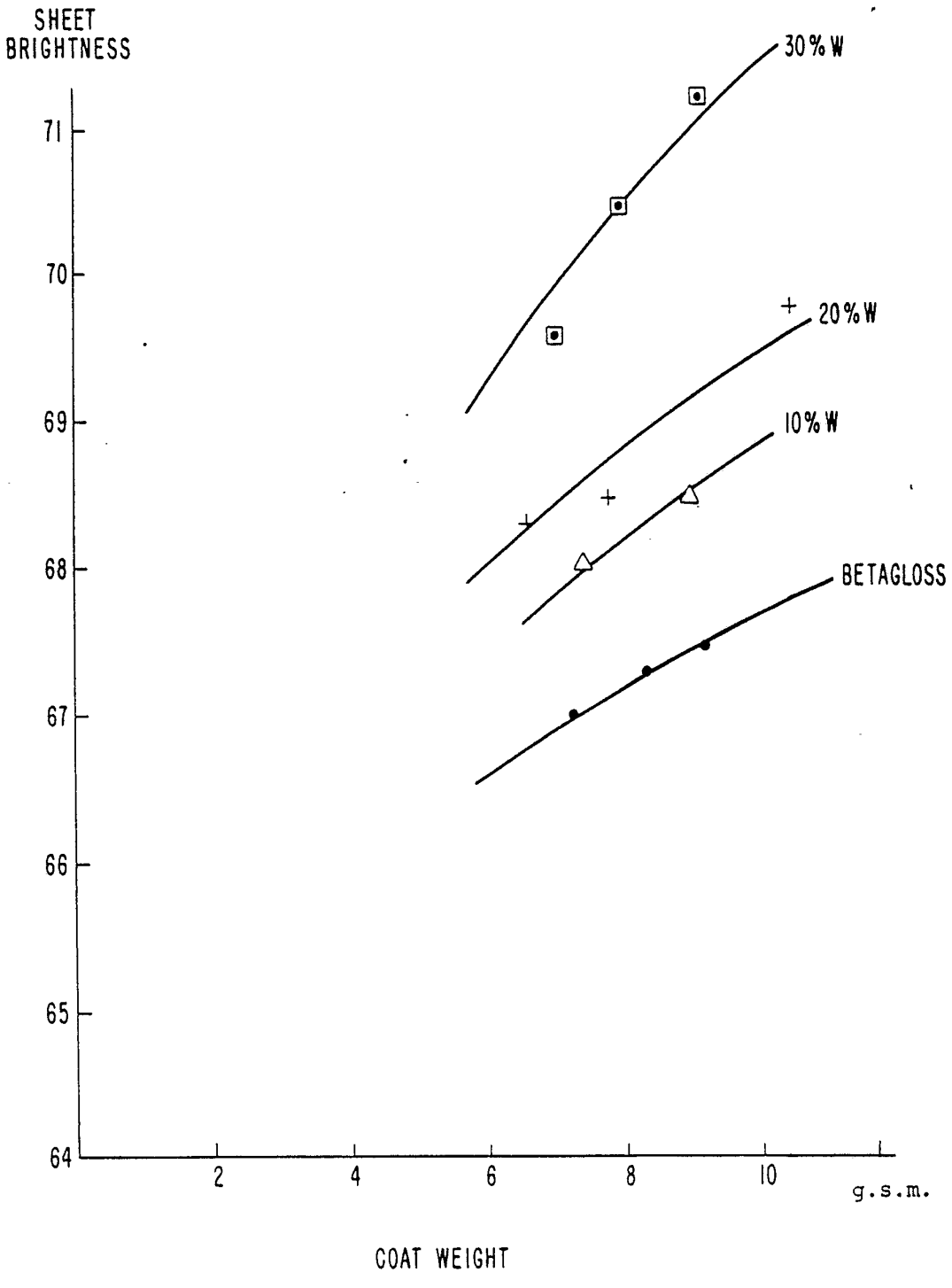

SHEET BRIGHTNESS
71
70
69
68
67
66
65
64
30% W
20% W
10% W
BETAGLOSS
2
4
6
8
10
g.s.m.
COAT WEIGHT

FIG. 10

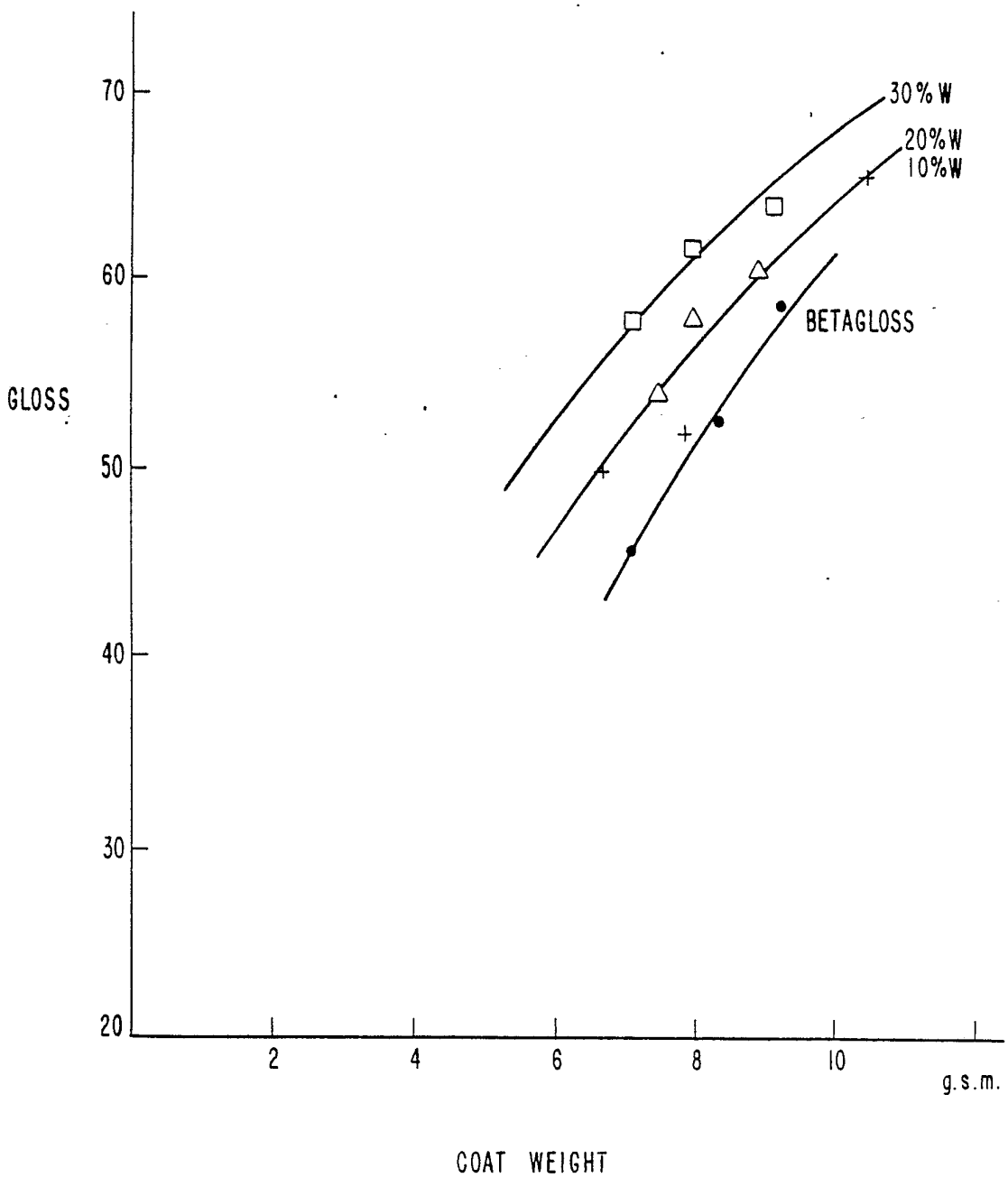

GLOSS
70
60
50
40
30
20
2
4
6
8
10
g.s.m.
30% W
20% W
10% W
BETAGLOSS
COAT WEIGHT

FIG. 11

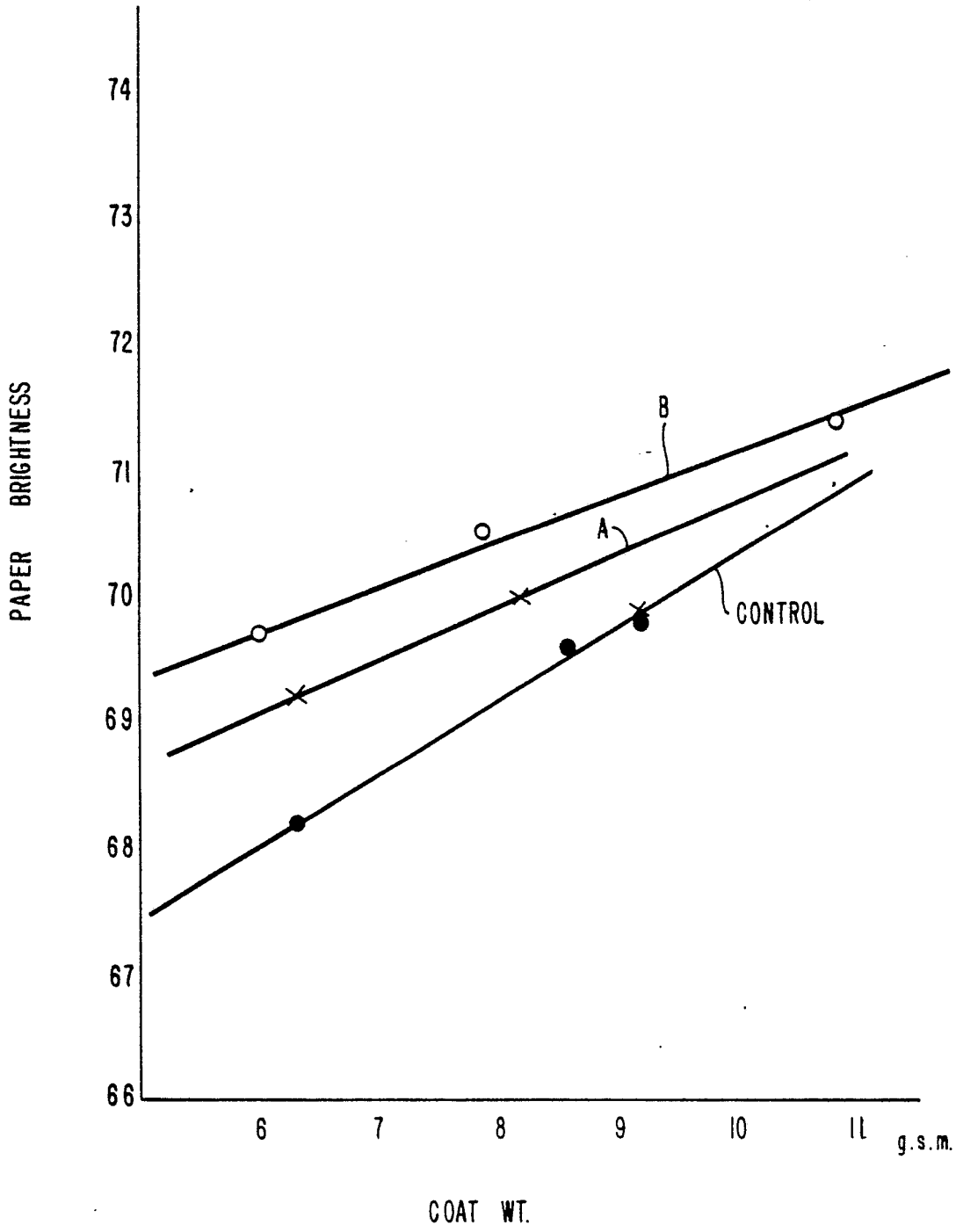
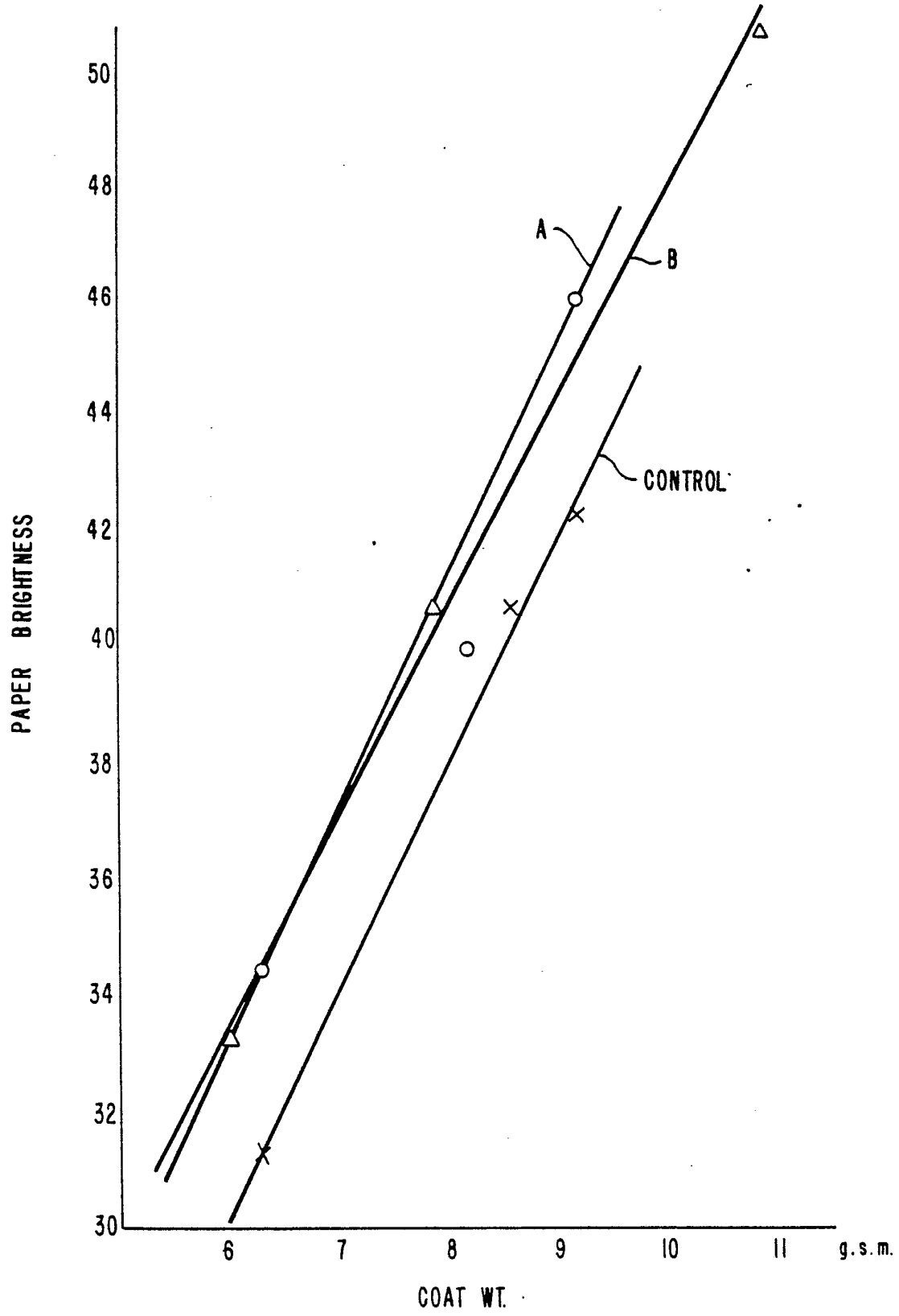

PAPER BRIGHTNESS
74
73
72
71
70
69
68
67
66
B
A
CONTROL
6
7
8
9
10
11
g.s.m.
COAT WT.

FIG. 12


PAPER BRIGHTNESS
50
48
46
44
42
40
38
36
34
32
30
A
B
CONTROL
6
7
8
9
10
11
g.s.m.
COAT WT.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US86/00158

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. Cl.[4] C09C 1/40, 1/42, 3/00; B32B 19/00; D21H 1/10

U.S. 106/288B,309; 501/146; 427/391; 428/537.5; 162/135

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	106/288B, 309; 501/146, 147, 150; 162/135, 181.6, 181.8 427/391, 361; 428/537.5, 688, 446

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
A	US, A, 2,307,239 (Rowland) Published 05 January 1943	1-14
A	US, A, 2,347,496 (Muskat et al) Published 25 April 1949	1-14
Y	US, A, 4,030,941 (Kunkle et al) Published 21 June 1977	1-14
Y	US, A, 4,128,263 (Traxler et al) Published 05 December 1978	1-44
A	US, A, 4,117,191 (Kurrle) Published 26 September 1978	1-45
A	JP, 0,106,596, Published 20 June 1984	1-45

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
07 April 1986	14 APR 1986
International Searching Authority [1]	**Signature of Authorized Officer [20]**
ISA/US	Garnette D. Draper

Form PCT/ISA/210 (second sheet) (October 1981)

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers ...., because they relate to subject matter [12] not required to be searched by this Authority, namely:

2. ☐ Claim numbers ....., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

Group I, Claims 1-19
Group II, Claims 20-36 and 43
Group III, Claims 37-42 and 44
Group IV, Claim 45

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☒ No protest accompanied the payment of additional search fees.