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(54) COMPOSITE SILICATE PIGMENT

(71) We, WESTVACO CORPORATION, of 299 Park Avenue, New York, New York 10017, USA, a corporation of the State of Delaware, USA, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates in general to inorganic composite pigments. More particularly, the invention relates to a composite pigment comprising clay and a metal silicate. The pigment is prepared according to a precipitation reaction wherein spherical, hydrous metal silicate particles are precipitated on the planar surfaces of clay particles having a platelet-type structure. Subsequently, when the composite pigment is incorporated in a sheet of paper or the like, the precipitated metal silicate particles act as spacers between individual clay particles to produce void volume or pigment-air interfaces and provide improved optical properties to the paper. The composite pigment so produced has an unexpectedly high light scattering power as compared with that of the base clay material alone, or as compared with that of a simple physical mixture of the two components. Moreover, with only a small amount of the metal silicate component precipitated on the base clay material, the optical efficiency of the composite pigment approaches that of the metal silicate component alone. Finally, based on the experimental data disclosed herein, the composite pigment of the present invention finds particularly good application in papermaking.

Clays are familiar components of the papermaking process and the term "clay" as used herein, refers to a class of earthly materials that are used as pigments in the papermaking process as filler materials, sizepress components and in coatings. For instance, as used in the paper industry, the term clay ordinarily refers to Kaolin or china clay, but it also includes attapulgite clay. In general, however, the clays useful in the present invention are only those which have a platelet-type structure. Ordinary kaolin clay or kaolinite meets most of the requirements of a good papermaking pigment except for its low index of refraction, 1.55. Therefore, clays are often used in the papermaking process in conjunction with more expensive and more optically efficient pigments in order to meet the optical requirements of the final product.

In addition, the patent literature contains several teachings for modifying clay to produce a more optically efficient pigment. For instance, U.S. Patent 2,296,637 discloses a process for acidifying a clay/sodium silicate mixture to increase the dry bulking value, oil absorption, and brightening and opacifying properties of clay. Moreover, U.S. Patent 3,690,907 discloses a clay base pigment comprising a mixture of clay with an alkaline earth metal hydroxide that has improved optical properties.

On the other hand, metal silicates are also well known pigments in the paper industry. For instance, calcium silicates are sometimes used as fillers in paper to improve the bulk, opacity and brightness of the final product. However, calcium silicate, like clay, has a fairly low refractive index, of 1.50.

Accordingly, like clay, calcium silicate is often modified or used in conjunction with other more optically efficient pigments to produce high quality papers.

Also, it is known to attach calcium silicate pigment to papermaking pulp to increase the pigment retention. For instance, in U.S. Patent 2,599,094 (among others issued to W. L. Craig), there is disclosed a process for precipitating calcium

silicate on cellulosic pulp fibers after pretreating the pulp with a chloride solution. In addition, U.S. Patent 2,296,618 discloses a silicate modified titanium pigment with improved stability against heat and light. And, U.S. Patent 2,296,639 discloses a zinc sulfide pigment coated with a metal silicate to produce increased oil absorption with what is said to be excellent surface hiding power. Meanwhile, in U.S. Patent 2,786,777 (among others assigned to Columbia-Southern Chemical Corporation), there is disclosed a method for preparing a composite pigment with calcium silicate and alumina.

However, none of the above noted patents discloses a composite pigment comprising a metal silicate and clay, and none of the patents known to applicant discloses a precipitation reaction for precipitating a silicate pigment onto the planar surface of a platelet-type clay particle to produce a composite pigment having an unexpectedly high optical efficiency.

According to one aspect of the present invention there is provided a composite silicate pigment comprising a clay component and a metal silicate component. The clay component is preferably obtained from a class of papermaking clays known generally as kaolin clay or kaolinite, and the metal silicate component is a water-soluble alkali metal silicate, such as sodium silicate. The preferred method for preparing the composite pigment comprises the steps of, (a) forming an aqueous suspension of a clay pigment, (b) blending into the clay slurry a quantity of a salt such as calcium chloride, (c) metering into the slurry of clay and salt at high shear a quantity of a silicate component such as sodium silicate, and, optionally, (d) adjusting the pH of the slurry with the addition of alum to a pH no lower than pH 4, before (e) filtering and washing the precipitated product to remove any soluble salts. The product obtained is then either used directly in the papermaking process or dried, such as by spray drying or the like, to form a powdered pigment for later use.

During the reaction, the spherical, hydrous metal silicate pigment particles are precipitated on the planar surfaces of the clay particles. Later on, when incorporated in a sheet of paper or the like, the metal silicate particles act as spacers between individual clay particles, to create additional air interfaces on sheet drying. The result of the precipitation reaction is to produce a vast improvement in the optical efficiency of the clay component with as little as 10% by weight silicate precipitated on the clay. In addition, the scattering coefficient of the composite pigment is considerably higher than the scattering coefficient of a physical mixture of the two component pigments.

Examples of water-soluble salts of polyvalent metals that may be used in the process of the present invention include the water-soluble salts of calcium, barium, zinc and magnesium. however, from a purely economical point of view, the calcium salts are deemed most desirable. Then alkali metal silicate preferred for the invention is sodium silicate, although other alkali metal silicates, such as potassium silicate, may be employed. In addition, different grades of clays having properties similar to those of kaolin clays or kaolinite may be employed in preparing the composite pigments disclosed. Of the polyvalent alkaline earth metal salts useful for the present invention, calcium chloride is the preferred soluble calcium salt, although other salts such as calcium nitrate or calcium acetate could be used. Of course, as noted hereinbefore, other water-soluble chloride salts, such as salts of barium, zinc or magnesium, could also be used as a substitute for calcium chloride. The amount of alkaline earth metal salt added to the clay slurry should be proportioned so as to obtain an excess over the stoichiometric quantity required to react with the silicate component. The salt is added to the clay slurry under turbulent mixing conditions wherein the salt dissociates, permitting the earth metal to become chemically attached to the clay particles. In the case of calcium chloride, the calcium ions are adsorbed onto the clay and the chloride goes into solution. Generally, the preferred method is to add the alkaline earth metal salt to the clay slurry prior to adding the silicate component. However, reversing the order of addition still produces a precipitated product, albeit one having less optical efficiency.

The silicate component is preferably a water-soluble alkali metal silicate. More particularly, sodium silicate is preferred, but other water-soluble alkali metal silicates, such as sodium or potassium silicate, could be used. Sodium silicates containing between 2 and 5 moles (preferably 3 to 4 moles) SiO_2 per mole of Na_2O are preferred since they are commercially available and, as a rule, are the least expensive alkali metal silicates. The silicate component is added to the clay/salt slurry under high shear wherein an almost instantaneous precipitation reaction

occurs between the earth metal ions on the clay and the silicate ions from the alkali metal silicate. The temperature of the reaction is not particularly critical and may range from 20°C to 85°C. The concentration of the silicate solution is correlated with the remaining variables so as to produce a final pigment having from 10—90% by weight of the spherical silicate particles precipitated on the clay platelets for improved optical efficiency.

The reaction of the present invention, if carried out without pH adjustment, generally proceeds at a pH of pH 9—10. However, the optical efficiency of the final precipitated product and the yield of the reaction can both be increased with a pH adjustment down to a pH no lower than pH 4. The pH of the reaction is preferably adjusted with the addition of alum. However other additives could be used depending upon the ultimate use of the pigment. In general, for wet end addition of the pigment on the papermachine as a filler material the pH should be fairly low, down to pH 4.

However, for coatings and sizepress application the pH need not be adjusted to as low a level as pH 4 for satisfactory results. In the latter cases, the reaction may be carried out at a neutral pH or at least on the alkaline side (pH 7 or above) with satisfactory results.

In the final stages of the process, the precipitated pigment is filtered and washed to remove any unwanted by products of the reaction such as soluble salts or the like. After washing and collecting the pigment, it may be used directly in the intended application or be further dewatered and dried for storage and/or shipment to the intended user.

The present invention will now be described, by way of example, with reference to the accompanying drawings, in which:—

FIGURE 1 shows a schematic representation of a typical flow sheet for the process of the present invention;

FIGURE 2 is an electron micrograph showing the platelet structure of a typical kaolin clay;

FIGURE 3 is an electron micrograph showing the structure of a composite precipitated pigment according to the present invention consisting of 80% by weight of the clay of FIGURE 2 and 20% by weight calcium silicate;

FIGURE 4 is an electron micrograph showing the clay of FIGURE 2 incorporated in a handsheet, and

FIGURE 5 is an electron micrograph showing the composite precipitated pigment of FIGURE 3 incorporated in a handsheet.

The pigment of the present invention, because of its good dispersibility and excellent optical efficiency, is particularly suitable as a filler for use in the manufacture of paper. In addition, the pigment is also useful in the papermaking process as a component of the sizepress or in paper coatings. Moreover, the pigment could be used in the manufacture of paints or as a reinforcement in rubber compositions.

The pigment is preferably manufactured in a continuous manner according to a process as shown schematically in FIGURE 1. For this purpose, a feed tank 1 is provided where the clay and a polyvalent metal salt are premixed under constant agitation. This mixture is pumped by pump 2 to one or more in-line mixers 4,4' where the clay/salt slurry is mixed with the alkali metal silicate component from tank 6 *via* pump 7. The precipitation reaction in the in-line mixers 4,4' must be under high shear to achieve a prompt salt-induced precipitation of the siliceous material on the clay. Subsequently the pH of the precipitated pigment slurry may be adjusted to a pH no lower than pH 4, for instance, by the addition of alum or the like from tank 8 *via* pump 9 to in-line mixer 4'. After pH adjustment, the pigment is washed to remove any soluble salts and filtered for ultimate use.

The following examples are given in illustration and are not intended as a limitation on the scope of the invention.

EXAMPLE I.

The following procedure was used to prepare several composite pigments for an initial evaluation as a paper filler materal. In each case, 160 grams of water and from 10—40 grams of clay were slurried in a beaker under low shear agitation. A quantity of $CaCl_2.2H_2O$ was then added to the clay slurry in dry form and allowed to mix for 15 minutes. The clay/$CaCl_2$ slurry was then added to a Waring blender. Under high shear conditions, a 10% by weight solids sodium silicate solution was added slowly to the clay/$CaCl_2$ slurry to induce precipitation of calcium silicate on the clay, and the mixture was allowed to mix for a total

of 2 minutes. Subsequently, sufficient papermakers alum was added to the mixture to adjust the pH to pH 4—4.5. Mixing was continued for an additional 2 minutes. The reaction product of clay with calcium silicate precipitated thereon was then washed in a Buchner funnel to remove soluble salt by-products and the composite pigment was available for evaluation in handsheets.

Several sodium silicate grades were evaluated having molar ratios of SiO_2:Na_2O ranging from 2.50—3.75:1. However, for the experiment noted above, an "0" grade sodium silicate having a SiO_2:Na_2O molar ratio of 3.22:1 was selected for optimum optical efficiency of the final product and because of its lower price. Five commercially available Georgia Kaolin clays were used, ranging from a large particle size WP filler clay (60% by weight of particles finer than 2 microns) to a fine particle size Hydragloss 90 coating clay (97% by weight of particles finer than 2 microns). Additionally, a delaminated clay, Nuclay, was included in the experiments. In each case, the ratio of clay to sodium silicate in the composite pigment was varied at 20% intervals from 0 to 100%. The ratio of sodium silicate to $CaCl_2.2H_2O$ was held constant at 2.8 to 1. Table I shows typical additive concentrations for the clay-calcium silicate composite products.

TABLE I.
Additive Concentrations—Pigment Preparation

Pigment Composition %	Water gr.	Clay gr.	$CaCl_2$ $2H_2O$ gr.	Sodium Silicate gr.	Alum gr.
80 Clay 20 CaSil	160	40	3.57	10	8
60 Clay 40 CaSil	160	30	7.14	20	12
40 Clay 60 CaSil	160	20	10.71	30	18.5
20 Clay 80 CaSil	160	10	14.28	40	26.0
100 CaSil	160	0	17.85	50	27.7

Tables II—VI summarize the optical performance of the composite pigments prepared with the different base clays. The optical properties were determined from handsheets which contained about 5% by weight of the composite pigment. Handsheets incorporating physical mixtures of clay and TiO_2 were also prepared for comparison with the optical performance of the composite pigments. In each case, a standard pulp blend was used for the fiber furnish and handsheets were prepared according to standard TAPPI methods.

TABLE II.
Optical Comparison—WP Filler Clay

Pigment Composition %	Brightness	Opacity	Filler %	Scattering Coefficient S′
Control	78.4	72.5	—	——
100 WP clay	79.3	75.9	4.93	.158
80 Clay 20 CaSil	80.5	77.7	4.75	.241
60 Clay 40 CaSil	81.1	78.5	4.79	.273
40 Clay 60 CaSil	82.1	78.9	4.71	.304
20 Clay 80 CaSil	82.4	78.4	4.45	.317
80 Clay 20 TiO_2	81.1	79.3	5.23	.293
60 Clay 40 TiO_2	82.3	80.9	5.04	.405
40 Clay 60 TiO_2	83.0	82.0	4.99	.465
20 Clay 80 TiO_2	83.3	82.8	5.01	.521

TABLE III.
Optical Comparison—PDM Filler Clay

Pigment Composition %	Brightness	Opacity	Filler %	Scattering Coefficient S′
Control	78.9	71.5	—	—
100 PDM Clay	78.7	74.9	4.08	.156
80 Clay / 20 CaSil	81.1	78.7	5.01	.300
60 Clay / 40 CaSil	81.5	78.7	4.36	.330
40 Clay / 60 CaSil	82.1	79.6	4.64	.380
20 Clay / 80 CaSil	82.3	79.5	4.30	.400
80 Clay / 20 TiO_2	80.8	79.0	5.05	.300
60 Clay / 40 TiO_2	82.2	81.0	5.02	.410
40 Clay / 60 TiO_2	83.0	82.9	5.25	.500
20 Clay / 80 TiO_2	83.3	83.2	4.44	.620

TABLE IV.
Optical Comparison—Ultra White 90 Clay

Pigment Composition %	Brightness	Opacity	Filler %	Scattering Coefficient S′
Control	78.4	71.8	—	—
100 UW 90 Clay	79.0	75.1	5.36	.13
100 TiO_2	83.3	84.0	4.45	.66
100 CaSil	82.4	79.0	4.15	.37
80 Clay / 20 CaSil	80.9	77.2	4.28	.26
60 Clay / 40 CaSil	81.7	78.9	4.44	.37
40 Clay / 60 CaSil	81.3	78.6	3.74	.37
20 Clay / 80 CaSil	81.8	78.6	4.13	.34
80 Clay / 20 TiO_2	78.9	78.5	4.53	.27
60 Clay / 40 TiO_2	81.6	79.8	4.84	.34
40 Clay / 60 TiO_2	82.7	82.0	5.05	.46
20 Clay / 80 TiO_2	83.0	83.6	5.13	.55

TABLE V.
Optical Comparison—Hydragloss 90 Clay

Pigment Composition %	Brightness	Opacity	Filler %	Scattering Coefficient S'
Control	77.6	71.7	—	—
100 Hydragloss 90	78.2	73.7	5.49	.100
80 Clay 20 CaSil	81.2	78.7	5.11	.291
60 Clay 40 CaSil	81.6	79.4	5.06	.327
40 Clay 60 CaSil	82.2	80.1	5.06	.327
20 Clay 80 CaSil	82.5	79.3	4.88	.357
80 Clay 20 TiO_2	80.6	77.4	5.42	.220
60 Clay 40 TiO_2	82.1	80.1	5.32	.365
40 Clay 60 TiO_2	83.3	82.5	5.39	.471
20 Clay 80 TiO_2	83.9	83.5	5.41	.552

TABLE VI.
Optical Comparison—Nuclay Clay

Pigment Composition %	Brightness	Opacity	Filler %	Scattering Coefficient S'
Control	79.0	71.7	—	—
100 Nuclay	79.8	75.7	5.03	.164
80 Clay / 20 CaSil	81.5	78.3	5.17	.272
60 Clay / 40 CaSil	82.3	79.2	4.77	.346
40 Clay / 60 CaSil	82.5	79.5	4.93	.353
20 Clay / 80 CaSil	82.0	77.7	3.74	.344
80 Clay / 20 TiO_2	81.7	78.9	4.91	.296
60 Clay / 40 TiO_2	82.8	80.8	4.93	.397
40 Clay / 60 TiO_2	83.7	82.5	4.87	.531
20 Clay / 80 TiO_2	84.2	83.6	5.07	.586

Surface areas of the clays used in Example I ranged from 8 m^2/gr. for the Georgia Kaolin WP filler grade to 22 m^2/gr. for the Hydragloss 90 coating grade clay from Huber Corporation. Table II summarizes the optical comparisons of the composite pigment manufactured with the WP filler grade clay. The composite pigment containing 80% by weight WP clay with 20% by weight CaSil precipitated thereon had an unexpected improvement in optical efficiency as compared with the WP clay alone. However, the same pigment was slightly poorer in opacity development than a physical mixture of 80% by weight WP clay and 20% by weight TiO_2. In a similar manner, as shown in Table III, the composite pigment containing 80% by weight PDM clay with 20% by weight CaSil precipitated thereon had a drastic and unexpected increase in optical efficiency as compared with the PDM clay alone. Moreover, the same pigment was equivalent in opacity development to a physical mixture of 80% by weight PDM clay and 20% by weight TiO_2. Similar trends were found for the other clays used, as demonstrated by the data in Tables IV—VI. In addition, the data showed that the scattering coefficient of the base clay materials generally increased as the amount of CaSil precipitated thereon increased.

Table VII shows some relationships between the surface areas of the base clay materials; the surface areas of the composite pigments prepared from the base clays, and general relationships between the particle size distribution of the clays and the percent increase in scattering coefficient achieved with the composite pigments. In each case, the particle size distribution of the composite pigments were found to be substantially the same as the particle size distribution of the base clay materials used in each case. As shown in the drawings (FIGURES 2—5), the relatively small spherical particles of calcium silicate that are precipitated onto the clay platelets do not significantly alter the overall particle size distribution of the base material.

TABLE VII.
Scattering Coefficient (s') vs. Particle Size Distribution

Pigment Composition %	Surface Area $m^2/gr.$	Scattering Coefficient S'	Scattering Coefficient % increase
Ultra White 90 Clay—90% Finer than 2 microns			
100 Clay	12.6	.13	—
80 Clay / 20 CaSil	16.4	.26	100
60 Clay / 40 CaSil	20.5	.37	169
Nuclay clay—80% Finer than 2 microns			
100 Clay	11.7	.164	—
80 Clay / 20 CaSil	23.1	.272	65.8
60 Clay / 40 CaSil	28.5	.346	111
PDM Filler Clay—67% Finer than 2 microns			
100 Clay	12.1	.156	—
80 Clay / 20 CaSil	23.7	.241	54.5
60 Clay / 40 CaSil	21.5	.273	75

The data in Table VII demonstrate the importance of the selection of the commercially available base clay material in optimizing the contribution of the silicate component. As the partricle size distribution of the base clay material in the composite pigment increases in fineness, the contribution of the silicate component is enhanced. Further, with increasing clay particle fineness, and at higher levels of substitution of the silicate component, the composite pigments provide equivalent optics when compared to the same level of TiO_2 addition. With the finer particle size coating clays, equivalent optical efficiency was obtained up to and including the 60% clay—40% CaSil or 40% TiO_2 filler systems (all percentages being in weight). Accordingly, the data demonstrate that it is possible to duplicate the optical contribution of TiO_2 in a paper substrate with the composite pigment of the present invention where from 20—40% of the total wet end filler would be TiO_2.

EXAMPLE II.

Samples of the composite pigment were prepared with a pilot plant apparatus substantially as disclosed in FIGURE 1 except that only one in-line mixer was used. The pH adjustment with papermakers' alum was made in small batches prior to filtering and washing of the composite product. PDM premium filler clay supplied by Georgia Kaolin was used in one set of experiments (Table VIII) and Ultra White 90 coating grade clay was used in a second set of experiments (Table IX). "0" grade sodium silicate supplied by Philadelphia Quartz Company was selected as the silicate component and calcium chloride as the salt component of the process. The sodium silicate solution concentration was varied from 0.42—1.68 lbs/gal. at flow rates of from 0.60—1.14 gal./min. into a clay/salt slurry containing 1.9—3.07 lbs/gal. of clay and from 0.17 to 0.27 lbs/gal. of salt. From these reactions, several composite pigments were obtained, filtered and washed. The composite pigment prepared in the first experiment (Table VIII) consisted of 80% PDM clay and 20% calcium silicate. In the second experiment (Table IX), the Ultra White 90 clay

component was varied from 60—90% and the calcium silicate component from 40—10%. The pigments were incorporated into standard TAPPI handsheets as a filler material and the optical properties were measured. (All percentages are by weight.)

TABLE VIII.
Composite Pigment—Optical Comparisons
PDM Filler Clay—Continuous Process

Pigment Composition %	Brightness	Opacity	Filler %	Scattering Coefficient S'
Control	79.0	71.5	0.50	—
100 PDM Clay	79.3	75.3	5.02	.155
100 PDM Clay	80.0	79.5	9.86	.179
80 Clay } 20 CaSil }	80.8	77.6	4.67	.257
80 Clay } 20 CaSil }	81.8	82.1	8.90	.277
80 Clay } 20 CaSil }	81.1	77.2	4.94	.236
80 Clay } 20 CaSil }	82.1	82.4	10.11	.259

TABLE IX.
Composite Pigment—Optical Comparisons
Ultra White 90 Clay—Continuous Process

Pigment Composition %	Brightness	Opacity	Filler %	Scattering Coefficient S'
Control	78.5	70.3	—	—
100 UW 90 Clay	79.2	74.4	5.30	.157
80 Clay } 20 CaSil }	81.0	77.5	5.25	.278
90 Clay } 10 CaSil }	81.0	78.0	5.23	.300
60 Clay } 40 CaSil }	82.2	80.3	5.42	.396

Each of the composite pigments observed in Tables VIII and IX were prepared with an agitation rate in the in-line mixer of 1700 rpm and incorporated in handsheets at the levels shown. Samples collected at lower speeds did not show any significant changes in optical performance. Two washes of the filter cake were performed on each batch using 1.6 parts water per 1 part pigment to remove up to 93% by weight of the sodium salt by-product produced during the reaction. A comparison of the data obtained from the pigments prepared in Example II with the data obtained from the pigments prepared in Example I shows that the product prepared in the continuous process apparatus produced about the same

results as the product produced with the bench scale Waring blender apparatus.

EXAMPLE III.

Composite pigments using as base clay materials Ultra White 90 clay and Nuclay were produced according to the continuous process described in Example II except that no pH adjustment was made. The pigments produced were incorporated in size press formulations and applied to a Westvaco Corporation basestock in web form. A gate roll size press apparatus was used to apply the formulations to produce a 61 lb/ream envelope paper and a 48 lb/ream Clear Spring offset grade, both of which are commercial products of Westvaco Corporation. For the purpose of this Example, a ream is defined as 500 sheets of paper measuring 25 x 38 inches. The sizepress formulations were prepared with composite pigments containing 80% UW 90 clay and 20% CaSil, 80% Nuclay and 20% CaSil and 90% UW 90 clay and 10% CaSil. The formulations containing the 80/20 composite pigments each comprised by weight about 40 parts starch and 60 parts pigment, while the formulations containing the 90/10 composite pigment contained by weight about 35 parts starch and 65 parts pigment. The component parts were slurried in water to a solids content of from 22—28%. The gate roll size press apparatus was operated with an applicator roll speed of 400 fpm and adjusted to give a pick up of less than 5 lb/ream. After sizing, the web was dried and sheeted, with sample sheets being analyzed to determine their optical properties and printability. The results are set forth in Table X.

TABLE X.
Optical and Strength Comparisons
Sizepressed Envelope Grade

Pigment Composition %	Coat Weight (lbs/ream)	Brightness	Opacity	Wax Pick Wire
Basestock	—	80.4	92.2	9
100 UW 90 Clay	4.3	79.5	92.0	14+
100 Nuclay	4.7	79.9	92.5	14+
80 UW 90 / 20 CaSil	4.8	81.5	93.6	12
80 Nuclay / 20 CaSil	5.5	81.0	93.6	13
90 UW 90 / 10 CaSil	4.8	80.9	93.1	14+
Clear Spring Offset Grade				
Basestock	—	81.4	89.0	12
80 UW 90 / 20 CaSil	2.7	82.2	90.1	13
80 Nuclay / 20 CaSil	2.7	81.6	90.2	14+
90 UW 90 / 10 CaSil	2.1	82.2	89.7	13

The data in Table X show that optical improvements achieved with the composite pigment were significant as compared with the control formulations containing only Nuclay or Ultra White 90 clay. Examination of the sizepressed paper samples also showed that the formulations containing the composite

pigments produced a more uniform surface. The composite pigment formulations also appeared to wet more uniformly than the control when a drop of water was applied. Wax pick, a measure of the pick strength of the paper in offset printing, did not decrease any significant amount with the application of the composite pigment formulation. These results were confirmed with laboratory print tests where no differences in picking tendency were observed between the paper sized with the composite pigment formulations and the paper sized with the control formulations. In addition, ink show-through was greatly reduced with the composite pigment formulations while the sheet appearance was greatly improved.

The composite pigment of the present invention is also useful in coating formulations for paper. TiO_2 pigment is generally used in paper coatings to produce sheets having high opacity and brightness and because of the good hiding power of the pigment.

However, TiO_2 is a fairly abrasive material (typical Valley abrasion of about 25 mg.) and it is expensive. Thus, replacements for TiO_2 in paper coatings are constantly being sought.

EXAMPLE IV.

Coating formulations were prepared in which the conventionally used TiO_2 was replaced with an equal weight amount of the composite pigment of the present invention. For this purpose, a composite pigment consisting of 90% Ultra White 90 clay and 10% calcium silicate was produced according to the continuous process disclosed in Example II. Three coating formulations were prepared including a control coating containing no TiO_2, a second coating comprising 5% TiO_2 and a third experimental coating color comprising 5% of the 90/10 composite pigment, all percentages by weight. Each coating formulation also contained clay, chalk, starch and a latex prepared according to a standard formula. The control coating had a Brookfield viscosity of 14,000 cps at 60.4% solids while the composite pigment coating had a Brookfield of 20,000 cps at 59.8% solids. The coatings were applied by trailing blade to a 38 lb/ream Field Web Offset basestock (Westvaco Corporation product) at six different blade loadings to produce coat weights ranging from 5 to 13 lbs/ream. The coated basestocks were dried, calendered 3 nips at 600 pli and 150°F. and then sheeted to obtain samples from which the data in Table XI were obtained.

TABLE XI.
Composite Pigment/TiO_2 Coating Formulations Optical and Printability Comparisons

Coat Weight #/ream	Bulk Smoothness	Gloss	Opacity	Birghtness	Wax Pick
		5% TiO_2			
5.2	928	51	87.1	74.3	7
6.6	1088	57	87.7	74.8	7
7.9	1224	59	88.7	75.5	7
9.1	1296	61	89.1	75.8	7
9.9	1335	62	89.5	76.1	7
12.0	1467	66	90.5	76.4	7
		Composite Pigment 5%			
5.0	1057	48	86.5	73.6	7
6.1	1329	54	87.1	73.8	7
7.6	1330	57	87.7	74.4	7

TABLE XI — contd.
Composite Pigment/TiO_2 Coating Formulations Optical and Printability Comparisons

Coat Weight #/ream	Bulk Smoothness	Gloss	Opacity	Birghtness	Wax Pick
		Composite Pigment 5%			
9.4	1253	58	88.7	74.7	7
10.8	1561	58	89.6	74.9	6
12.8	1174	55	90.4	75.8	6
		Control			
5.5	867	47	86.2	73.3	8
7.0	1082	55	87.3	73.7	8
8.0	1182	56	87.8	74.0	7
9.4	1357	58	88.3	74.3	7
9.9	1381	59	88.9	74.4	7
13.1	1312	58	89.8	74.7	7

As may be observed from the data in Table XI, a coating formulation in which TiO_2 was replaced with an equal weight amount of a 90/10 composite pigment produced coated paper having optical properties (opacity and brightness) that fell about midway between those of the paper coated with the standard formulation containing TiO_2 and the control formulation without TiO_2. Gloss measurements for the composite pigment formulation were slightly lower than those obtained with the standard formulation while the smoothness increased. Based on other data (not disclosed), the Valley abrasion of the composite pigment used in Example IV would range from 8—12 mg., or lower than that of TiO_2, while the cost advantage of using the composite pigment would be substantial, i.e., less than the cost of TiO_2. Accordingly it may be seen that the composite pigment of the present invention offers a good choice for the replacement of TiO_2 in paper coating formulations.

WHAT WE CLAIM IS:—

1. A method of preparing a composite white pigment of improved optical efficiency consisting of a clay component and a metal silicate component, said method comprising the steps of:
   (a) forming an aqueous slurry of a clay having platelet-type structure;
   (b) blending into the clay slurry a water-soluble salt of a polyvalent metal;
   (c) metering into the clay/salt slurry at high shear a water-soluble alkali metal silicate, thereby precipitating the silica in the form of spherical particles on the planar surfaces of the clay platelets, to form a composite pigment;
   (d) filtering the composite pigment from the slurry, and
   (e) washing the product.
2. The method of claim 1, wherein the clay component is a kaolin clay.
3. The method of claim 1 or 2, wherein the water-soluble salt is of calcium, barium, zinc or magnesium.
4. The method as claimed in claim 3, wherein the water-soluble salt is a calcium salt.
5. The method of claim 4, wherein the calcium salt is calcium chloride.
6. The method as claimed in any of claims 1—5, wherein the water-soluble alkali metal silicate is of sodium, potassium, or lithium.

7. The method of claim 6, wherein the water-soluble alkali metal silicate is sodium silicate.

8. The method as claimed in any of claims 1—7, wherein the amount of water-soluble salt added in step (b) is proportioned to obtain an excess over the stoichiometric quantity required to react with alkali metal silicate, and wherein the amount of alkali metal silicate added in step (c) is proportioned to obtain the desired weight ratio of clay to silicate in the final product.

9. The method as claimed in any of claims 1—8, wherein the precipitation reaction takes place at a temperature ranging between 20 and 85°C.

10. The method as claimed in any of claims 1—9, wherein the pH of the slurry containing the composite pigment is adjusted after step (c) to a value no lower than 4.

11. The method as claimed in any of claims 1—10, wherein at least 10% by weight of the metal silicate component is precipitated on the clay platelets.

12. The method as claimed in any of claims 1—11, including the further step of drying the filtered and washed pigment.

13. The pigment obtained as a product of carrying out the method claimed in any preceding claim.

14. Paper including the pigment claimed in claim 13.

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2 SHEETS This drawing is a reproduction of the Original on a reduced scale
Sheet 1

FIG. 1

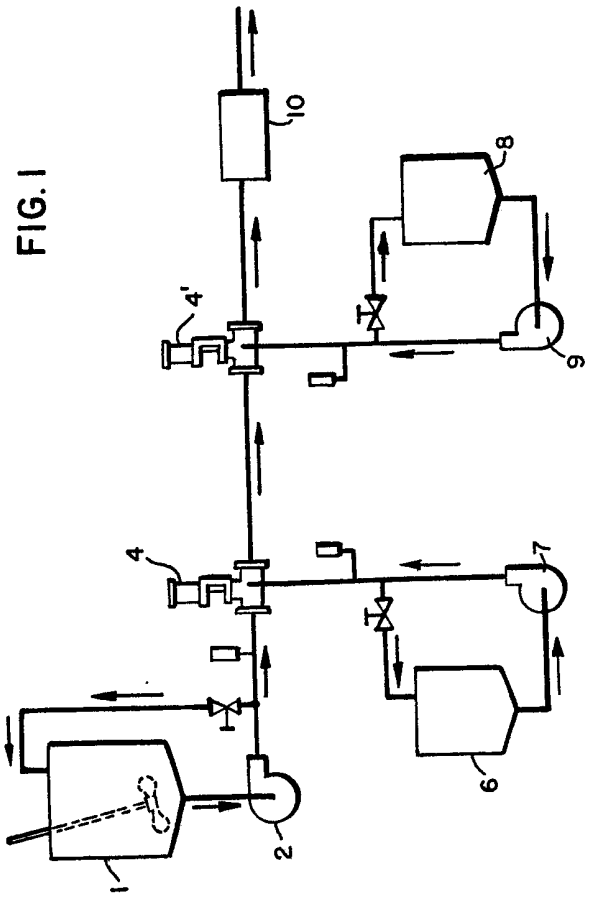

FIG. 3

FIG. 5

FIG. 2

FIG. 4