

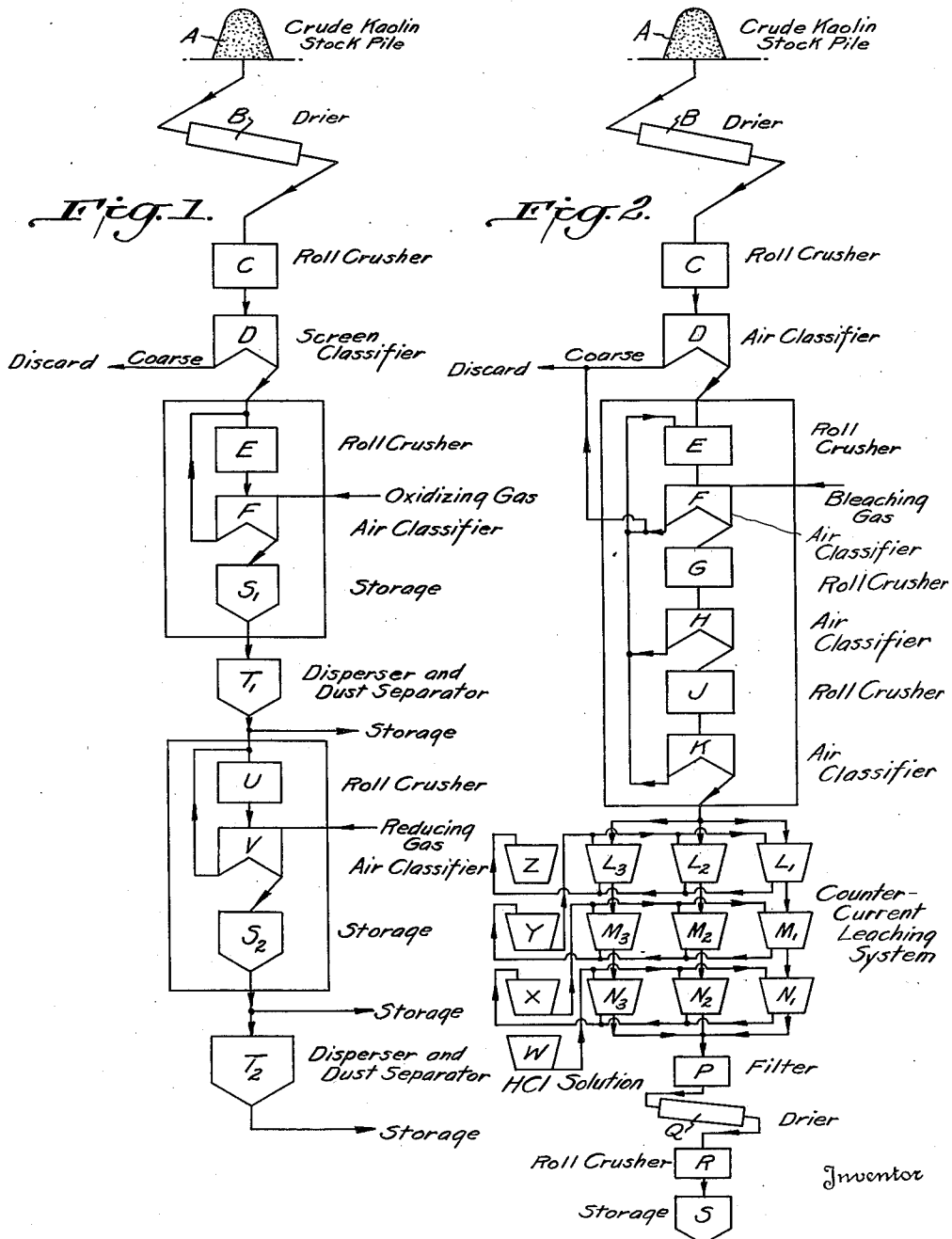
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TREATMENT OF ARGILLACEOUS MATERIAL

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TREATMENT OF ARGILLACEOUS MATERIAL

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This invention relates to the treatment of argillaceous material and particularly to the beneficiating of kaolin by comminution classification, bleaching, segregation of impurities and the like. The invention includes a new method and novel apparatus.

A principal object of the invention is the provision of a method and means for economically and efficiently converting run-of-deposit crude kaolin into a high grade material for technical use.

A further object of the invention is the provision of an effective method for increasing the reflective power of crude kaolin.

Further objects and advantages of the invention will appear from the following description:

Broadly the invention comprises subjecting finely divided argillaceous material in suspension in air, water, or other fluid medium to the action of bleaching agents, such as, for example, chlorine, hydrogen chloride, sulfur dioxide, and the like. This treatment of the kaolin or the like with gaseous agents while in suspension is advantageously associated with the sizing and classification of the material whereby, if desired, the same apparatus may serve for both the classification and the chemical treatment.

The principles of the invention may be embodied in a wide variety of systems of operation and apparatus layouts. For the purpose of illustration the invention will be more particularly described with reference to the accompanying drawing in which:

Fig. 1 is a flow sheet of one embodiment of the invention; and

Fig. 2 is a flow sheet of a modified embodiment of the invention.

The process is described as applied to the size classification and color beneficiation of natural, run-of-deposit kaolin, such as is found in the properties of Vermont Kaolin Company, Bennington, Vermont.

In Fig. 1, B represents a drier, for example as inclined rotary kiln drier.

After being thoroughly dried at about 95° C., a typical sample of this natural Vermont kaolin showed the following screen analysis:

U. S. standard sieve size	Percent by weight
+20	0.8
-20 +50	4.0
-50 +80	0.7
-80 +100	0.6
-100	93.9

This natural Vermont kaolin, after being dried at 95° C., had a relative apparent density of 1.215 and a relative total reflection factor of 83.7%, measured in terms of pure, precipitated mag-

nesium carbonate with an American Photoelectric Corporation reflection meter. Using identically the same methods and apparatus, a sample of high-grade, bolted English kaolin (paper clay) had a relative apparent density of 0.822 and a relative total reflection factor of 90.5%, these measurements being indicative of greater fluffiness or fineness, and of greater whiteness, than the natural, dried Vermont material.

After drying and preferably while still warm, say at a temperature in excess of 60° C., the natural kaolin is passed between rollers C spaced not more than 0.297 millimeter (0.0117 inch) apart, i. e. a spacing no greater than the opening in a U. S. standard No. 50 sieve, and is then passed through a rotary or vibrating screen D with openings no larger than those in a No. 50 U. S. standard sieve. The fraction that does not pass through the screen, i. e. the larger particles, are discarded. This relatively small fraction, the size of which varies with differences in the quality and composition of the natural kaolin that is processed, is discarded because it is largely comprised of particles of silica (quartz), mica, graphite, and other mineral matter, that were contained in the original feldspar of which the kaolin deposit is a metamorphic product.

The fine fraction, i. e. the -50 portion, is then passed between rollers E spaced not more than 0.149 millimeter (0.0059 inch) apart, i. e. a spacing approximately equal to the opening in a No. 100 U. S. standard sieve. The finely rolled material is then dispersed in an oxidizing atmosphere, as for example one containing chlorine gas, and the gas stream with its suspended particles passes through a dust classifier F preferably of the type described in copending applications of George H. Horne and Marcel Lissman now U. S. Patents 1,939,710, 1,978,801, 1,978,802, 1,990,943 and 1,996,076.

The setting or adjustment of this classifier is such that the suspended dust particles are separated into two fractions, (1) about 70% fine and (2) about 30% coarse. The coarse fraction is returned to the 0.149 millimeter rolls E for further partition and comminution, and the fine fraction is removed to suitable storage, as for example a hopper-bottom bin S₁ from which it is subsequently withdrawn for further processing.

The oxidizing atmosphere into which the rolled material is first dispersed and from which it is later classified as to size is kept wholly apart from the surrounding air in a closed gas circulating system which includes the rolls, dispersing fan, classifier, fine-fraction storage-bin, and the connecting conveyor system through which the material is moved. Only that portion of the oxidizing atmosphere, as for example chlorine, that is occluded among, or adsorbed by, the fine fraction can escape from the closed gas circu-

lating system as described. Substantially every part within the closed gas circulating system with which the oxidizing atmosphere may come into contact is preferably built of such material as to withstand attack by the oxidizing gas or gaseous mixture, even when appreciable quantities of moisture are also present therein.

The ultimate result of the continuous return of the coarse fraction of this first classification to the 0.149 millimeter rolls for further partition is that substantially all the material fed into the rolls finally is recovered in the fine fraction, substantially every particle of which is smaller than the spacing between the rolls, in consequence of which relatively larger areas, i. e. the aggregate surfaces of the smaller particles, are exposed to the action of the oxidizing atmosphere.

The effect of this exposure of the fine fraction from the first classification to the action of the oxidizing atmosphere is to bleach impurities, particularly organic materials, and so to produce a whiter ultimate final commercial product. A further result, when chlorine is a component of the oxidizing atmosphere, is the conversion of iron, which may be present in various forms or combinations, as an impurity in the kaolin, to ferric chloride, a yellow compound, readily soluble in water, with which it may be leached from the substantially insoluble aluminum silicate (kaolin).

The fine fraction from the first classification is withdrawn from its storage bin and dispersed in a stream of air to effect the substantial removal of gases occluded or adsorbed during the oxidizing process. The stream of air, with its suspended, finely-divided kaolin particles, is then passed through suitable dust-recovery equipment T₁, as for example "Multiclones", or into a dust-collecting chamber wherein the kaolin is removed or settles out, and from which the air, now polluted with the oxidizing gases that had been occluded or adsorbed, is passed into the atmosphere, or if such disposal is unsuitable, into a medium in which the oxidizing gases are dissolved or absorbed. The kaolin obtained at this stage may be suitable for some uses without further treatment. In general, however, it is desirable to subject it to a further treatment.

For this purpose after the fine fraction from the first classification has been substantially freed from its occluded or adsorbed oxidizing gases by dispersal in air and subsequent recovery therefrom, the fine material is passed between rollers U spaced not more than 0.074 millimeter (0.0029 inch) apart, i. e. a spacing approximately equal to the opening in a No. 200 U. S. standard sieve. The finely rolled material is then dispersed in a reducing atmosphere, as for example one containing sulphur dioxide, and the gas stream with its suspended particles passes through a dust-classifier V similar to that employed for the first classification as previously described.

The setting or adjustment of this second classifier is such that the suspended dust particles are separated into two fractions, (1) about 65% fine and (2) about 35% coarse. The coarse fraction is returned to the 0.074 millimeter rolls U for further partition and comminution, and the fine fraction is removed to suitable storage.

The reducing atmosphere into which the rolled material is first dispersed, and from which it is later classified as to size, is kept wholly apart from the surrounding air in a closed gas circulating system, which includes the rolls, dispersing fan, classifier, fine-fractions storage-bin, and the

connecting conveyor system through which the material is moved. Only that portion of the reducing atmosphere, as for example sulphur dioxide, that is occluded among, or adsorbed by, the fine fraction in its storage-bin, can escape from the closed gas circulating system as described. Substantially every part within the closed gas circulating system with which the reducing atmosphere may come into contact is preferably built of such material as to withstand attack by the reducing gas or gaseous mixture, even when appreciable quantities of moisture are also present therein.

The ultimate result of the continuous return of the coarse fraction of this second classification to the 0.074 millimeter rolls for further partition is that substantially all the material fed into the rolls finally is recovered in the fine fraction, substantially every particle of which is smaller than the spacing between the rolls, in consequence of which relatively larger areas, i. e. the aggregate surfaces of the smaller particles, are exposed to the action of the reducing atmosphere.

The effect of this exposure of the fine fraction from the second classification to the action of a reducing atmosphere is to decrease its coloration and so to produce a whiter ultimate final commercial product. Thus when yellow ferric chloride is present in the fine fraction from the first classification, as the result of exposure in an oxidizing atmosphere containing chlorine, this compound is substantially converted during the second classification, during which it is simultaneously exposed to the action of a reducing atmosphere containing sulphur dioxide, to ferrous sulphate, a compound much more nearly white than the ferric chloride from which it is derived.

For many of the industrial uses of kaolin the presence of small amounts of occluded, or adsorbed, sulphur dioxide in the fine fraction resulting from the second classification is not considered deleterious. However, if it is considered desirable that the final commercial product shall be substantially freed from gases occluded or adsorbed during the final classification and the simultaneous exposure to a reacting gaseous atmosphere, this result can be attained in a manner similar to that previously described, in which the fine fraction from the first classification is substantially freed from occluded or adsorbed oxidizing gases by dispersal in a stream of air with subsequent recovery therefrom in separator T₂.

Where the natural run-of-deposit kaolin contains a negligible amount of organic material, and particularly where the presence of iron as ferrous sulphate in the commercial product is not considered deleterious, a material suitable for some industrial uses can be obtained by a modification of the process previously described, a simplification that omits the preliminary treatment in an oxidizing atmosphere during the first classification and retains only the exposure to the action of a reducing atmosphere during the second size classification; for example, by omitting the supply of oxidizing gas to F, or by passing the material directly from classifier D to rolls U.

The improved quality of final product obtainable by this dry chemical process carried out simultaneously with mechanical classification as to particle size is illustrated in the following tabulation. For purposes of comparison the relative apparent density and the relative total reflection factor, measured with an A. P. C. reflection meter, 75

of the material at each step in the process, is set forth, together with similar measurements of a high-grade bolted British paper clay, and of products obtained from the same natural raw materials by methods of treatment here employed.

Comparative measurements

No.	Material—all samples dry	Relative apparent density	Relative total reflection factor ¹
1	High-grade bolted British china clay	0.822	Per cent 90.5
2	Run-of-deposit Vermont kaolin	1.267	
3	Run-of-deposit Vermont kaolin	1.215	
4	Commercial washed kaolin from 2	0.991	79.1
5	Commercial washed kaolin from 3	1.043	75.8
6	Chemically treated product from 2	0.854	80.2
7	Chemically treated product from 3	1.001	80.8

Process of the invention

8	Fine from 2 after first classification in air	0.789	83.5
9	Fine from 2 after first classification in chlorine	0.789	85.0
10	Fine from 2 after first classification in sulphur dioxide	0.789	84.6
11	Fine from 8 after second classification in air	0.543	86.7
12	Fine from 8 after second classification in sulphur dioxide	0.543	88.2
13	Fine from 9 after second classification in sulphur dioxide	0.543	88.8

¹ Magnesium carbonate equals 100 per cent.

In Fig. 2, B represents a drier, C a roll crusher having a spacing between the rolls of, for example, about 0.25 mm., and D is a preliminary classifier in which all of the crushed material from C is dispersed in air and separated into two fractions, one relatively coarse and the other relatively fine, as described with reference to Fig. 1. The relatively coarse material is discarded and the relatively fine material is passed to roll crusher E having a spacing between the rolls of about 0.149 mm. F is the first reclassifier in which the fine fraction from D, after passing through roll crusher E, is dispersed in an atmosphere of reactive gases and separated into two unequal fractions, (1) fine, 70% to 80%, which goes to G, and (2) coarse, 30% to 20%, which is returned to roll crusher E along with the fine fraction coming from preliminary classifier D. Varying with the amount of impurities, particularly iron, contained in the original crude kaolin, the reactive gaseous atmosphere in which the finely divided particles are dispersed and suspended, may contain from 5% to 50% by volume of hydrochloric acid gas or chlorine, and advantageously from 0.05% to 1.0% by volume of bromine vapor or nitrogen dioxide, the presence of which accelerates the action of the hydrochloric acid gas or chlorine. G is a roll crusher having a spacing between the rolls of about 0.105 mm. H is a second reclassifier in which the fine fraction from F, after passing through roll crusher G, is dispersed and separated into two unequal fractions as in the first reclassifier F, the fine fraction going to J, and the coarse fraction being returned to roll crusher E.

J is a roll crusher having a spacing between the rolls of about 0.074 mm. K is a third reclassifier in which the fine fraction from H, after passing through roll crusher J, is dispersed and separated into two unequal fractions as in the first and second reclassifiers F and H, the fine fraction going to L₁, L₂ or L₃, and the coarse fraction being returned to roll crusher E.

It should be noted that many of the common

mineral impurities in natural crude run-of-deposit clays, such as micas, feldspar, talc and crystalline silicon dioxide, have specific gravities greater than that of pure kaolin ($\text{Al}_2\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$), so that as each component in any crude material is successively divided and subdivided until all are approximately equal in particle size, it becomes practicable to effect a separation of the kaolin from its accompanying mineral impurities through the differences in densities. Also, the common mineral impurities that contaminate natural kaolin are usually crystalline in form and tend to remain in larger aggregates during the process of disintegration than does the kaolin which is amorphous and so tends to disintegrate readily. This tendency of the crystalline impurities to cohere in larger particle sizes, and of the amorphous kaolin to disintegrate into its component particles, increases the facility with which separation can be effected through differences in density.

If there were no bleed on the line through which the coarse fraction from the first reclassifier F is withdrawn, then through the continued return of the coarse fractions from the three reclassifiers F, H and K to roll crusher E, and their repeated re-rollings and reclassifications, the ultimate result would be that every part of the fine fraction from the preliminary classifier D would finally be reduced to such a state of subdivision that its small particle size, would bring it into the fine fraction from the final reclassifier K, and thus into the final product of the process. Such a result is not desirable, for three reasons, as follows:

(1) The proportion of materials other than pure kaolin in the final product should be as small as is commercially practicable;

(2) The series of roll crushers and reclassifiers E to K, inclusive, should be relieved so far as is practicable of the burden of subdividing and reclassifying the relatively refractory impurities, and utilized so far as possible only for the disintegration and reclassification of amorphous kaolin, the only material desired in the final product;

(3) The proportion of materials other than pure kaolin in the fine fraction from the final reclassifier K should be as small as is commercially practicable so that the consumption of chemicals in the subsequent counter-current leaching system L M N is kept at a minimum.

If there were no continuous bleed into the discard from the coarse fraction separated in the first reclassifier F, then starting with any uniform body of crude clay, the relative apparent density of this fraction would begin to increase, just as soon as the effect of the return of the coarse fractions from all three reclassifiers F, H and K became influential, and would continue to increase until equilibrium was established with all of the fine fractions from the preliminary classifier D contained in the fine fraction from the final reclassifier K.

However, by gradually increasing the rate of bleeding into the discard from the line through which the coarse fraction from the first reclassifier F is fed back into the roll crusher E until the relative apparent density of this coarse fraction is reduced to its minimum, then the condition is established whereby the maximum proportion of mineral impurities, heavier than pure kaolin, are removed from the process. Instead of bleeding continuously from the line through which the coarse fraction from the first reclassi-

fier F is fed back to roll crusher E, as indicated on the accompanying sketch and explained in preceding note 1, an alternative method may be employed for the elimination from the process of 5 impurities heavier than kaolin. Thus all of the coarse fractions from the three reclassifiers F, H and K may be consolidated, dispersed in a supplementary reclassifier F₁ and separated into two fractions, (1) fine, which goes to roll crusher E, 10 and (2) coarse, which goes into the discard along with the coarse fraction from preliminary classifier D.

The series of roll crushers and reclassifiers E to K, inclusive, all are advantageously included in 15 the closed circulating system of reactive gases.

The reactive gas to be employed for any particular crude clay, whether chlorine, hydrochloric acid, or a mixture thereof, and its degree of concentration in the circulating system, the 20 gaseous accelerator to be used, whether bromine vapor or nitrogen dioxide, and its degree of concentration, the velocities of the gas streams in the several reclassifiers; all these factors are subject to wide variation, being dependent upon 25 the nature and quality of the clay to be processed, the kinds and quantities of impurities with which it is contaminated, and finally upon local economic conditions.

Loss of reactive gases from the closed circulating system may occur in three ways, as follows:

(1) By chemical combination with impurities admixed with the kaolin and subsequent removal during leaching, filtering, washing and drying;

(2) By occlusion among, or adsorption by, the 35 particles in that portion bled continuously into the discard from the line through which the coarse fraction from the first reclassifier F is fed back to roll crusher E;

(3) By occlusion among, or adsorption by, the 40 particles in the fine fraction from the final reclassifier K, which goes into leaching tanks L₁, L₂ or L₃.

All losses of reactive gases from the closed circulating system may be made up continuously so 45 that the necessary degree of concentration is maintained at all times.

The fine fraction from the final reclassifier K enters the counter-current leaching system where it is successively agitated in a dilute solution of hydrochloric acid, which may contain a trace of bromine or nitrogen oxides, allowed to settle, and separated from the wash liquor by decantation, pumping, or any other convenient method. 50 The fine fraction from the final reclassifier K is run continuously into the leaching vat L₁ until a batch of the desired size has been accumulated therein. Then the fine fraction is run into L₂ and so on. The contents of all leaching vats may be heated, either by means of steam coils 60 or by the introduction of free steam. The dilute hydrochloric acid wash solution employed to wash the preceding batch in leaching vat M₁ is now stored in tank Y. This is transferred to leaching vat L₁ where it is agitated with the accumulated batch from the fine fraction from reclassifier K, allowed to settle, and separated. 65 The spent dilute hydrochloric acid wash solution is transferred to waste storage tank Z, whence it is disposed of in any convenient manner, as for example by drainage over broken limestone. The slurry in leaching vat L₁ is transferred to leaching vat M₁. The dilute hydrochloric acid wash solution, employed to wash the preceding batch in leaching vat N₁, is now stored in tank X. This 70 is transferred to leaching vat M₁ where it is

agitated with the batch just transferred from leaching vat L₁, allowed to settle, and separated. The partially spent dilute hydrochloric acid wash solution is transferred to storage tank Y, from 5 which it will be subsequently removed to leaching tank L₁ to wash the next following batch. The slurry in leaching vat M₁ is transferred to leaching vat N₁. A dilute hydrochloric acid wash solution, made up to the necessary degree of concentration in storage tank W, is transferred 10 thence to leaching vat N₁, where it is agitated with the batch just transferred from leaching vat M₁, allowed to settle, and separated. The slightly spent dilute hydrochloric acid wash solution is transferred to storage tank X, from which 15 it will be subsequently removed to leaching vat M₁ to wash the next following batch.

The slurry in leaching vat N₁, or in N₂ or N₃, as the case may be, is now transferred to filter unit P, with subsequent washing with clean fresh 20 water, if required. After filtration the cake is dried in unit Q, rolled in unit R to break up any lumps that might occur, and is then transferred into S, the storage bin for the finished product. The degree of concentration of the dilute hydrochloric acid solution made up in storage tank W 25 is determined by the quantity of acid soluble compounds present in the original crude kaolin or formed during the successive reclassifications and simultaneous exposures to reactive gases; that is, contained in the fine fraction from the final classifier K, and also by the volume of occluded or adsorbed reactive gases contained in this fine fraction as it accumulates in leaching 30 vat L.

The treatment of the kaolin with a gaseous bleaching agent in F may be substituted by a treatment in a special dispersing and separating device, such as T₁ in Fig. 1.

It has been found that in the chemical treatment of fine fractions of certain natural kaolins, 40 which are substantially free from organic matter, or which have been substantially freed from organic matter during the mechanical process of classification according to particle size, that 45 the removal of iron, the salts or compounds of which tend to impart a red or reddish-brown color to the material, can be accomplished by means of hydrochloric acid.

With certain kaolins, the fine fractions of 50 which contain such substantial amounts of iron that they are deeply discolored thereby, the formation of soluble iron compounds, which can be leached out subsequently, is accelerated when the necessary classifications according to particle 55 size are carried out in an atmosphere containing hydrochloric acid gas to which a small percentage by volume of either sulphur dioxide gas or nitrogen oxides has been added.

It has been found further in the chemical 60 treatment of fine fractions of certain natural kaolins, which are substantially free from organic matter, that final products suitable for some industrial uses can be secured even though the necessary classification according to particle 65 size is carried out under normal atmospheric conditions instead of in an atmosphere containing reactive gases, for example, by omitting the supply of bleaching gas to F of Fig. 2, and the chemical treatment is limited to digestion of the fine 70 fraction from the final classification in a hydrochloric acid solution of such volume, concentration and temperature, as to insure conversion of substantially all iron present into soluble compounds that can be removed by subsequent wash- 75

ing, preferably by a repeated series of stirrings, settlings and decantations with successive portions of fresh water. It has been found further that in the digestion of the fine fraction from the final classification in a hydrochloric acid solution, the conversion of the iron present into soluble compounds is accelerated if a small quantity of a water-soluble salt of an alkali, e. g. sodium chloride, sodium nitrate, or sodium bisulphite, is dissolved in the hydrochloric acid solution.

While the final products obtained from certain American clays by this process as previously and above described are finer in texture than high-grade English paper-coating clays, and their total reflection factors measured with an A. P. C. reflection meter are substantially equal to those of high-grade English paper-coating clays, it was found that for some commercial uses they were not considered as desirable as the English products, because their reflection factors throughout the upper ranges of the visible spectrum were higher than in the lower, so that, when examined visually, they appeared slightly yellow or reddish-yellow instead of slightly green or bluish-green, as does the highest grade English paper-coating clay. This deficiency of blue, or alternatively expressed, excess of red in the reflection characteristics of the final products made from certain American clays by this process, as previously described, may be compensated for either (1) by thorough admixture with the kaolin of any inert green, bluish-green, or blue material, e. g. Prussian blue, that is not deleterious in the commercial application for which the clay is intended, or (2) by the addition of a small quantity of a dilute solution of potassium ferrocyanide to the mass while the kaolin is being washed and the suspension still contains some ferric chloride in solution, with consequent formation of Prussian blue. Neither of these alternative methods is desirable, the first because the addition of any colored material decreases the total reflection factor of the product, and the second because it increases the iron content of the final product.

Following is a description of the preferred and novel method employed whereby the deficiency of blue in the reflection characteristics of the final product is compensated for without the addition of any colored material to the product, without the addition of iron or of any compound containing iron thereto, and with the elimination of some fraction of the iron originally contained in the natural kaolin which would not normally be removed during the commercial application of the process as previously described. After the fine fraction from the final classification has been leached with a solution of hydrochloric acid of the preferred concentration at the preferred temperature and pressure, in the presence of a dissolved salt of an alkali, if desired, and subsequently agitated, allowed to settle and decanted from successive portions of fresh water until substantially all the soluble iron compounds, alkaline salts, and hydrochloric acid have been removed therefrom, there is added to the mass with agitation a dilute solution of potassium or sodium cyanide, and the whole allowed to stand, with occasional stirring, if required, for a period of several hours and as much longer as there is any indication of additional formation of a blue, bluish-green, or green color. Usually no additional reaction, as indicated by the formation of more color, occurs after forty-eight hours of standing. After decantation of the super-

natant clear solution, the residual mass is then agitated and filtered. During the filtration part of the colloidal Prussian blue, formed during the digestion with the dilute solution of potassium or sodium cyanide, passes into the filtrate, thereby decreasing the amount of iron contained in the final product, but a sufficient amount is retained, dispersed throughout the kaolin, to compensate for the deficiency of blue in the reflection characteristics of the final product that would otherwise obtain.

The term "bleaching agent" as used in the foregoing specification and appended claims is intended to include substances adapted to decrease the color or increase the brightness of argillaceous materials, such as kaolin and the like, by oxidation, reduction, solution, neutralization, or other reaction with the coloring matter thereof.

I claim:

1. A method of treating argillaceous material such as kaolin which comprises suspending finely disintegrated argillaceous material in air and subjecting the material in suspension to the action of a bleaching agent of the group consisting of chlorine, hydrogen chloride and sulphur dioxide.

2. A method of treating argillaceous material such as kaolin which comprises suspending finely disintegrated argillaceous material in a fluid medium and subjecting the material in suspension to the action of a bleaching agent of the group consisting of chlorine, hydrogen chloride and sulphur dioxide in the presence of an auxiliary agent of the group consisting of bromine and oxides of nitrogen.

3. A method of treating argillaceous material such as kaolin which comprises disintegrating the argillaceous material, separating the disintegrated material into a relatively fine and a relatively coarse fraction, and subjecting the relatively fine fraction while in suspension in air to the action of a bleaching agent of the group consisting of chlorine, hydrogen chloride and sulphur dioxide and thereafter subjecting it while in suspension in an aqueous medium to the action of hydrochloric acid.

4. A method of treating argillaceous material such as kaolin which comprises disintegrating the argillaceous material, separating the disintegrated material into a relatively fine and a relatively coarse fraction, and subjecting the relatively fine fraction while in suspension in air to the action of a bleaching agent of the group consisting of chlorine, hydrogen chloride, and sulphur dioxide.

5. A method of treating argillaceous material such as kaolin which comprises disintegrating the argillaceous material, separating the disintegrated material into a relatively fine and a relatively coarse fraction, and subjecting the relatively fine fraction while in suspension in air to the action of a bleaching agent and thereafter subjecting it while in suspension in an aqueous medium to the action of a dilute acid.

6. A method of treating argillaceous material such as kaolin which comprises disintegrating the argillaceous material, separating the disintegrated material into a relatively fine and a relatively coarse fraction, and subjecting the relatively fine fraction while in suspension in air to the action of a bleaching agent and thereafter subjecting it while in suspension in an aqueous medium to the action of hydrochloric acid.

7. A method of treating argillaceous material such as kaolin which comprises disintegrating the

argillaceous material, separating the disintegrated material into a relatively fine and a relatively coarse fraction, and subjecting the relatively fine fraction while in suspension in air to the action of a bleaching agent and thereafter subjecting it while in suspension in an aqueous medium to the action of hydrochloric acid in the presence of an alkali metal salt.

8. A method of treating argillaceous material such as kaolin which comprises disintegrating the argillaceous material, separating the disintegrated material into a relatively fine and a relatively coarse fraction, and subjecting the relatively fine fraction while in suspension in air to the action of chlorine.

9. A method of treating argillaceous material such as kaolin which comprises disintegrating the argillaceous material, separating the disintegrated material into a relatively fine and a relatively coarse fraction, subjecting the relatively fine fraction while in suspension in air to the action of chlorine and thereafter subjecting the said fraction while in suspension in air to the action of sulphur dioxide.

10. A method of treating argillaceous material such as kaolin which comprises disintegrating the argillaceous material, separating the disintegrated material into a relatively fine and a relatively coarse fraction, and subjecting the relatively fine fraction while in suspension in air to the action of a bleaching agent of the group consisting of chlorine and hydrogen chloride in the presence of an auxiliary agent of the group consisting of bromine and oxides of nitrogen.

11. A method of treating argillaceous material such as kaolin which comprises disintegrating the argillaceous material, separating the disintegrated material into a relatively fine and a relatively coarse fraction, subjecting the relatively fine fraction while in suspension in an aqueous medium to the action of hydrochloric acid in the presence of an alkali metal salt and thereafter treating the material with a soluble cyanide.

12. A method of treating argillaceous material such as kaolin which comprises disintegrating the argillaceous material, separating the disintegrated material into a relatively fine and a relatively coarse fraction, and subjecting the relatively fine fraction while in suspension in air to the action of sulphur dioxide.

13. A method of treating argillaceous material such as kaolin which comprises disintegrating the material, dispersing the disintegrated material in a gaseous medium, and separating a relatively

fine and a relatively coarse fraction from said dispersion, and treating the material while dispersed in a gaseous medium successively with a gaseous oxidizing and a gaseous reducing agent.

14. A method of treating argillaceous materials such as clay, which comprises suspending finely disintegrated argillaceous material in a gaseous medium and subjecting the material in suspension to the action of an agent in gaseous phase effective to convert iron compounds contained in the argillaceous material into more soluble form and removing the resultant water-soluble compounds from the argillaceous material.

15. A method of treating argillaceous material such as kaolin which comprises disintegrating the material, dispersing the disintegrated material in a gaseous medium, and separating a relatively fine and a relatively coarse fraction from said dispersion, and treating the material while dispersed in a gaseous medium with a bleaching agent in gaseous phase effective to convert iron compounds contained in the argillaceous material into more soluble form and removing the resultant water-soluble compounds from the argillaceous material.

16. A method of treating argillaceous material such as kaolin which comprises suspending finely disintegrated argillaceous material in a gaseous medium, subjecting the material in suspension to the action of a bleaching agent of the group consisting of chlorine, hydrogen chloride and sulphur dioxide in gaseous phase, separating the argillaceous material from the gaseous medium and returning the gaseous medium in a closed cycle for the dispersion of a further quantity of argillaceous material therein.

17. A method of treating argillaceous material such as kaolin which comprises suspending finely divided argillaceous material in a gaseous medium, subjecting the material in suspension to the action of a bleaching agent in gaseous phase, thereafter subjecting the material in suspension in an aqueous medium to the action of a dilute acid and thereafter treating the material with a soluble cyanide.

18. A method of treating argillaceous material such as kaolin which comprises disintegrating the argillaceous material, separating the disintegrated material into a relatively fine and a relatively coarse fraction, subjecting the relatively fine fraction while in suspension in an aqueous medium to the action of hydrochloric acid and thereafter treating the material with a soluble cyanide.

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