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A METHOD FOR REMOVING TITANIUM DIOXIDE IMPURITIES FROM KAOLIN

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Abstract—The removal of titanium minerals from kaolin can be accomplished by treatment with dispersing agents in an amount in excess of that required to produce maximum deflocculation of the kaolinite particles. In this reflocculated state the kaolinite particles attain a high degree of suspensional stability, and the titanium mineral particles, primarily anatase, are liberated and can be separated by sedimentation. Substantial removal of anatase impurities can be achieved by this method.

INTRODUCTION

SEDIMENTARY kaolins generally are contaminated with titanium minerals to the extent of about 1·3–3·5 per cent expressed as TiO_2. This is in marked contrast to primary kaolins which contain much smaller amounts of TiO_2, usually less than 0·5 per cent.

Titanium minerals in the clay fraction of sedimentary kaolin have been identified primarily as anatase, although small amounts of other minerals such as leucoxene and brookite also have been detected (Weaver, 1968). These minerals are usually heavily stained by iron and as a result vary from yellow to dark brown in color. For purposes of discussion, these mineral impurities will be referred to as anatase or TiO_2.

Conventional methods of classification and leaching with salts of dithionous acid, while markedly enhancing clay whiteness, have little, if any, effect on the removal of anatase. In fact, finer clay fractions resulting from classification contain somewhat higher amounts of TiO_2 than the original whole clay and the coarser fractions.

Because of the strong commercial interest in upgrading brightness of kaolin, particularly in the paper industry, considerable effort has been expended for the development of processes to remove anatase impurities. Two methods, both employing flotation, have been developed in recent years. According to published descriptions (Green and Duke, 1962; Cundy, 1968), both methods reject titanium impurities as part of the overflow fraction and both are capable of removing substantial portions of the original TiO_2 content. This ability to separate anatase particles from kaolin establishes that at least a portion of the titanium impurities occur in kaolin as a discrete phase. In both cases, the improvement in clay brightness is some 2–4 points* over the best results obtainable with conventional processes. This constitutes a significant and important improvement in the quality of beneficiated sedimentary kaolin.

The purpose of this paper is to describe a new and simplified process for the removal of anatase impurities employing the principle of sedimentation, a concept opposite to that presently used in flotation processes. Briefly, the process involves treatment of an aqueous clay slurry with dispersant to impart a high degree of suspensional stability to the clay particles and at the same time free anatase impurities from clay surfaces. The settling of anatase particles then becomes possible due to their higher specific gravity and their strong inherent tendency to aggregate.

DEFLOCCULATION AND REFLOCCULATION

It is well known (H. Van Olphen, 1963; Riddick, 1968) that the deflocculation or dispersion of clays by polyanions relies on generation of an electrical charge on particles sufficient to achieve maximum fluidity in a clay–water system. The effectiveness of wet beneficiation, as well as the use of kaolins in various commercial applications, depends on the attainment of maximum fluidity or minimum viscosity. It is also well known that the addition of increasing amounts of dispersant to a clay slurry progressively reduces viscosity to a minimum value, beyond which continued additions cause the viscosity to rise. The addition of dis-

*All brightness data refer to measurements made according to the standard procedure T 646 m-54 of the Technical Association of Pulp and Paper Industry.

persant beyond the point of minimum viscosity causes a reflocculating effect. For obvious reasons, this state of "reflocculation" (Thompson, 1953; Robinson, Thompson 1963; Millman, 1964) has been scrupulously avoided in beneficiation and in the commercial handling of kaolin slurries.

Figure 1 illustrates this effect of dispersant concentration on viscosity. The tests were made on a suspension containing 60 per cent of a fine particle East Georgia kaolin. The dispersing agent in this case was sodium hexametaphosphate. Viscosity measurements were made with a Brookfield viscometer at a spindle speed of 10 rev/min. Note that the addition of dispersant in excess of the amount required for minimum viscosity causes a reverse effect, indicating the development of a reflocculated state.

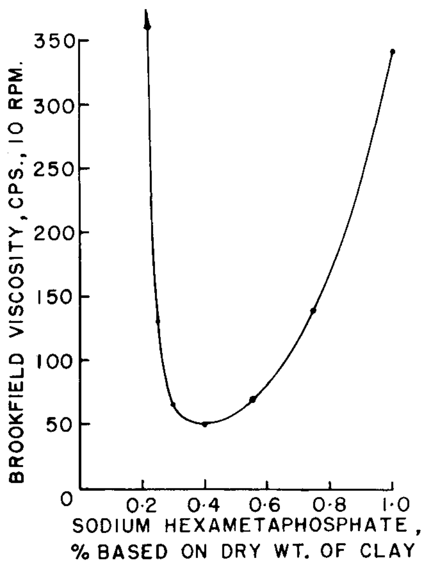

Fig. 1. The effect of sodium hexametaphosphate on the viscosity of clay–water suspensions.

DIFFERENTIAL SEDIMENTATION IN THE REFLOCCULATED STATE

Formation of a reflocculated fine particle kaolinite suspension by addition of excess dispersant to a deflocculated system reduces the mobility of kaolinite particles and creates a stabilized suspension because of the well known electrolyte effects (Lyons, 1961) on charged kaolinite particles. Reduced mobility of kaolinite imparts a stabilized structure of suspension compared with fully deflocculated and flocculated systems. This suspensional stability is evidenced by the greatly reduced settling rate of kaolinite in our reflocculated slurries. In this condition, adsorbed anatase impurities are released from the kaolinite surface and gradually form visually observable flocs which are capable of penetrating and settling from the clay system.

This process contrasts with ordinary classification in dispersed slurries, wherein the anatase impurities appear to remain attached to kaolin particles. Thus the distribution of TiO_2 impurities in conventionally classified kaolin substantially reflects the degree that various size fractions of kaolin adsorb titanium impurities. In such suspensions anatase impurities are not fully liberated and therefore are not free to settle in accordance with their size and mass.

The separation of anatase impurities from a reflocculated clay–water system is characterized by a clearly observed sequence of stages which may be described as follows:

1. Suspensional stabilization of the kaolinite particles (relative to sedimentation) accompanied by a release of adsorbed impurities and a darkening of the slurry.
2. Agglomeration of the impurities.
3. Formation of vertical tracks or streaks as the agglomerated TiO_2 impurities settle through the kaolinite suspension.
4. Whitening of the clay suspension from the top and the accumulation of a dark brown sediment.

These stages are illustrated in Fig. 2.

Four suspensions, approximately 54 in. in height, are shown. All suspensions contain about 26 per cent by weight of the same relatively fine crude clay from East Georgia.

Suspension 1, on the left, represents a normal deflocculation which has been allowed to settle for 24 hr. A typical coarse clay sediment has collected leaving a suspension of clay particles which, after treatment with conventional leaching chemicals, showed a brightness of about 87 per cent.

Suspension 2, on the extreme right, has been treated to produce a reflocculated state just before the photograph was taken, This suspension differs from No. 1 in that it has a higher viscosity and is somewhat darker. The latter is particularly noticeable when freshly prepared suspensions are compared.

Suspension 3 shows Suspension 2 after 24 hr of settling. It shows a much lower sediment collection than in Suspension 1, confirming that a marked increase existed in the suspensional stability of the clay particles. This suspension is now characterized by a separation of discolored flocs in the form of yellow-brown streaks.

Suspension 4, after 90 hr of settling, shows the final stage of this beneficiation as related to the particular treatment used in these illustrations. At this stage there is a complete disappearance of

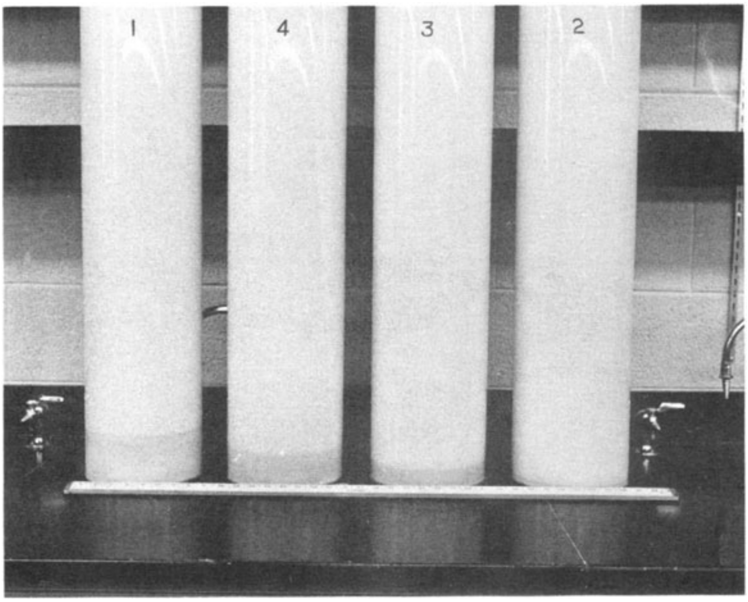

Fig. 2. Photograph of clay columns.

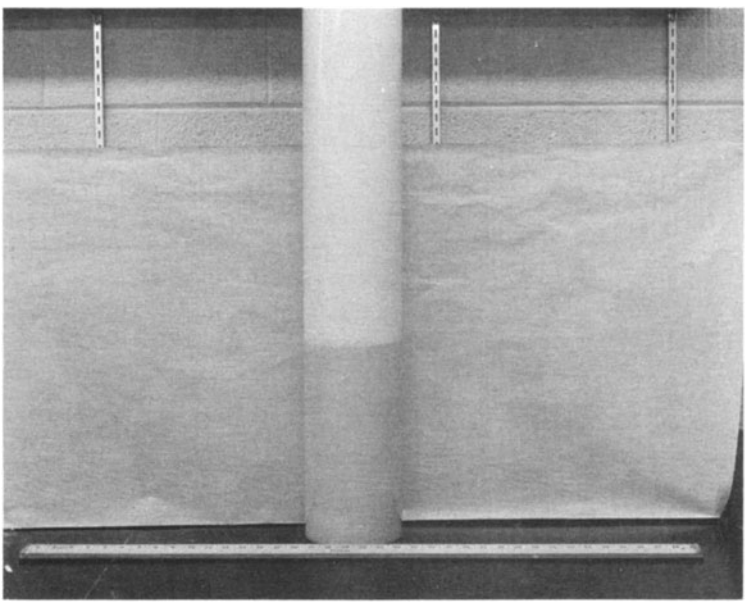

Fig. 4. Photograph of a clay column.

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the characteristic striations and the appearance of a substantial brown sediment. This sediment has been found to contain a 2–5 fold concentration of TiO_2 compared with the original clay. Here, again, the total volume of sediment is considerably less than in Suspension 1, indicating the much slower settling of kaolin particles in reflocculated systems. The recovered suspension, after substantial removal of soluble salts by washing, and subsequent treatment with conventional leaching agents, attains a brightness of about 91 per cent. Approximately 60 per cent of the anatase impurities were removed from the original material.

It should be observed that when kaolinite suspensions contain some coarse particles, as would be the case with crude clays, these are not stabilized in suspension but settle out with anatase flocs. The sediment from Suspension 4 contains some coarse kaolin and quartz particles along with TiO_2 impurities. However, when classified clays having a particle size of at least 80 per cent minus 2μ are used, this type of settling is not produced.

A practical application of the reflocculation process using a single dispersant, sodium hexametaphosphate, is shown in Fig. 3. In this case, the treatment was applied to a beneficiated, relatively fine fraction derived from a Central Georgia crude clay. The slurry, containing about 30 per cent clay by weight, was already treated with an amount of dispersant required to produce minimum viscosity, or about 0·3 per cent. Two separate curves are shown, one indicating the improvement in brightness with increasing dispersant, and the other, the corresponding removal of TiO_2 impurities. With the exception of the original slurry, the settling time for each treatment was about one hour per inch of depth. The brightness of each recovered clay was determined after appropriate treatment with zinc dithionite.

It can be seen that final brightness depends on the amount of anatase impurities removed which, in turn, depends on the chemical dosage. Even slight increments above that required for minimum viscosity are capable of minor reduction in TiO_2 impurities accompanied by some improvement in brightness. However, a treatment of about 1 per cent is required to obtain a removal of TiO_2 impurities sufficient to increase the brightness to about 90 per cent. Additions above this point yield a diminishing effect because of viscosity build-up within the suspension which tends to retard the descent of anatase flocs. This condition can generally be overcome by slight reduction in clay solids, or replacing a portion of the phosphate with an alkali such as sodium carbonate.

A laboratory procedure for attaining a high brightness clay from a Central Georgia crude is described below.

A dispersed clay suspension derived from a Central Georgia crude, containing 92 per cent, by weight, finer than 2μ diameter particles, and about 30 per cent clay solids was used. The clay of this suspension had a brightness of 81·8 per cent before leaching and 87·0 per cent after leaching.

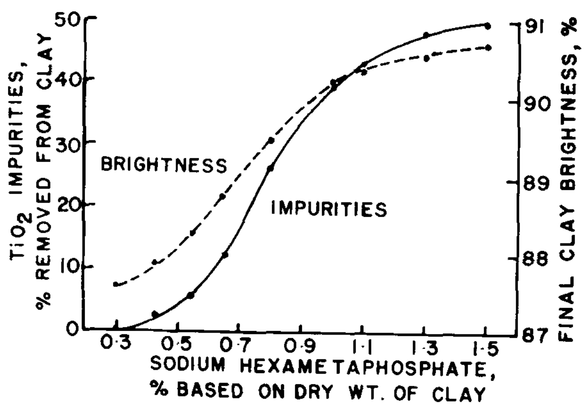

Fig. 3. Double graph showing relationship between chemical dosage and titanium removal and clay brightness.

800 ml of the original slurry was treated with 0·75 per cent sodium hexametaphosphate and 0·25 per cent sodium carbonate, based on the dry weight of clay, by mixing in a Waring Blendor for 30 min.

After treatment, the slurry was transferred to a 1000 ml capacity cylinder and allowed to settle at a slurry depth of 29 cm for a period of 14 hr.

After sedimentation, the whitened clay remaining in suspension was withdrawn from the sediment by siphoning, This suspension consisted of about 29 per cent clay solids and represented a yield of about 95 per cent of the original clay.

This beneficiated clay was then coagulated and filtered to remove excess soluble salts. The resulting filter cake was diluted with water and reslurried at about 30 per cent clay solids.

After washing, the clay was leached with 0·4 per cent zinc dithionite at 60°C for 30 min with mild agitation, After leaching, the clay was filtered and the filter cake was dried to about 1·0 per cent moisture content. This clay had a brightness of 91·0 per cent. The original starting clay contained 1·64 per cent, by weight, of anatase impurities, expressed as TiO_2 and 0·8 per cent after treatment.

The above examples demonstrate a TiO_2 extration sufficient to produce a clay brightness of 90–91 per cent. However, it is possible to produce nearly complete removal of TiO_2 impurities by the use of more complex dispersant systems. The preparation of such a clay from an East Georgia crude is shown in Fig. 4 which illustrates the extreme whiteness of the clay in suspension and the heavily discolored titanium rich sediment.

In conclusion, this differential sedimentation technique for TiO_2 is applicable to a wide range of clays in either the crude or beneficiated state. Its effectiveness depends on a suitable choice of processing parameters, including slurrying procedure, solids concentration, dispersant treatment (polyphosphates, silicates, alkalies, etc.) and settling times. The process can be used in gravity or centrifugal separations (Maynard, Skipper and Millman, 1968).

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Résumé—L'enlèvement des mineraux de titane du kaoline peut s'accomplir au moyen du traitement à l'aide d'une quantité d'agents de dispersion supérieure à celle nécessaire en vue de produire la déflocculation maximale des particules de kaolinite. A l'état reflocculé, les particules de kaolinite atteignent un degré élevé de stabilité en suspension, et les particules du mineral de titane, surout sous forme d'anatase, sont dégagées et peuvent être séparées par sédimentation. L'enlèvement important des impuretés d'anatase peut s'accomplir de cette façon.

Kurzreferat—Die Entfernung von Titanmineralen aus Kaolin kann durch Behandlung mit einer Menge von Dispergierstoffen, die einen Überschuss über die zur Erzielung einer maximalen Entflockung der Kaolinteilchen erforderlichen darstellt, erreicht werden. In diesem neu ausgeflockten Zustande zeigen die Kaolinitteilchen eine bedeutend erhöhte Suspensionsstabilität, und die Titanmineralteilchen, in erster Linie Anatas, werden frei gemacht und können durch Sedimentation abgeschieden werden. Auf diese Weise gelingt es beträchtliche Anatasverunreinigungen zu entfernen.

Резюме—Удаление титановых минералов из каолина достигается обработкой диспергирующим средством в количестве, превышающем количество требуемое для достижения максимальной дефлоккуляции частиц каолинита. В таком повторно флоккулированном состоянии частицы каолинита достигают более высокой степени взвешенной устойчивости, а частицы титановых минералов, преимущественно анатаз, освобождаются и отделимы седиментацией. Значительное удаление анатазовых загрязнений может быть достигнуто этим методом.