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CLAY BLEACHING

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This invention relates to the bleaching and refining of clays, and more particularly to a method of treating clays which increases their brightness and retains their desirable physical properties.

Clays, particularly refined kaolins, are employed in a variety of uses such as fillers and finishing agents for papers and paper-boards, as base ingredients and as fillers for the molding of electrical and other ceramic or plastic products, and as finishing agents for a variety of articles. To be suitable for these applications, it is important that a clay be highly reflective, that is, that it have a high degree of brightness as measured on the basis of percent of light reflectance. It is also important that the clay have a low and uniform shear viscosity to permit optimum and reproducible processing in utilization; the electrical charges on the clay particles affect viscosity, and must be retained to as great an extent as possible.

Since the clays as they are obtained from natural sources normally are discolored, it has been necessary to brighten them with bleaches, and the large volume of use of clays has been a great incentive to chemists who have expended considerable research effort in developing bleaching methods for them. Thus, the oxidizing bleaches, for example chlorine bleaching agents such as chlorine dioxide, hypochlorites and the like, and active oxygen bleaches such as hydrogen peroxide, sodium peroxide and the organic peroxides, have been applied to this problem, as have the reducing bleaches such as the oxalates and the low oxidation state sulfur compounds.

Quite surprisingly, these efforts have not provided a bleaching technique which provides as high a degree of brightness in clays as is desired and at the same time retains the desirable physical properties possessed by them. While it has been found that the reducing bleaches generally are superior to the oxidizing bleaches in this application, even the most desirable of these agents has not provided the looked-for characteristics in the final bleached clay. Furthermore, processing with these agents has been time-consuming and expensive.

It is a feature of this invention to provide a method of bleaching clays which is adapted to low-cost continuous processing and also provides a degree of brightness in the clays which is satisfactory to paper makers, molders of ceramic products, producers of finishing agents and the like.

It has now been found possible to bleach clay to a degree of brightness unexcelled by any prior method, by a new process which despite its effectiveness in bleaching does not substantially degrade the clay. These desirable ends are accomplished by providing an aqueous slurry containing a clay in the amount of about 5 to 75%, and preferably about 15 to 35%, adding to this slurry an alkali bisulfite in an amount to provide 0.7 to 5.6, and preferably 2 to 4.5, pounds of the bisulfite per ton of the clay, adding an alkali borohydride to this slurry in an amount to provide 0.125 to 1, and preferably about 0.36 to 0.82, pound of the borohydride per ton of the clay, stirring the slurry mildly for a time to effect bleaching of the clay and thereafter washing the clay to free it of residual bleaching reagents and reaction products. The processing is carried out at a pH of about 2.5 to 5, and preferably about 3 to 3.5. Where necessary mineral acids such as sulfuric acid or other acids are employed

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to provide this pH. The operating temperature used is between about 40° and 200° F., and preferably between 70° and 180° F.

In our process the bisulfite is used in the amount of about 5.6 times the amount of borohydride, within the above recited ranges. Use of substantially more than this amount does not improve bleaching, and use of less is apt to provide less bleaching than normally could be obtained with the given amount of borohydride.

This process provides a bleached clay having a higher degree of brightness than is provided by any other method known to us. The excellence of this bleach is quite unexpected; when the borohydride is employed in herein amounts alone in an attempt to bleach clay, substantially no brightness increase is obtained, and in some cases the brightness is reduced. This is despite the fact that sodium borohydride is known as a reducing bleaching agent for some materials. Likewise, the bisulfite alone provides no brightness improvement.

Furthermore, although it may be theorized that sodium borohydride and sodium bisulfite might react to form the known clay-bleaching agent sodium hydrosulfite, direct addition of sodium hydrosulfite to the clay as a bleach provides a noticeably lower degree of bleaching than is provided by the present process, even when substantially more of the hydrosulfite is employed than theoretically would be formed by reaction of the herein amounts of the borohydride and bisulfite. In fact, attempts to achieve the extent of clay brightening obtained by the herein process by addition of increasing amounts of hydrosulfite, actually reduce the brightness and result in an undesirable degradation of the clay. Furthermore, quite contrary to what would be expected if the bleaching mechanism were simply through hydrosulfite formation, the process of this invention achieves its bleaching effect more rapidly than does hydrosulfite. These factors are not susceptible to simple explanation.

The clay bleached by the herein process is a hydrated alumina silicate, preferably kaolin. Other forms of hydrated alumina silicate clays, for example the bentonites, the montmorillonites and the like, can be treated by the present process, and such clays are intended to be included within the scope of this invention.

Normally the clay is prepared for bleaching by a wash, which is carried out by dispersing the clay in water, for example with the aid of caustic or a phosphate such as sodium hexametaphosphate, and washing it to remove siliceous impurities such as sand, mica and the like. This is a standard treatment employed in clay bleaching to reduce the amount of bleach needed and to cleanse the clay. The washed clay has a color depending on its grade, and this color will range anywhere from a blue-gray to tan up to a near white.

As the first step in the present process, the clay is slurried in water to provide a slurry having a clay concentration of about 5 to 75%, and preferably about 15 to 35%, by weight of clay in the water. This slurry is then treated by addition to it of an alkali bisulfite in an amount to provide about 0.7 to 5.6, and preferably 2 to 4.5, pounds of the bisulfite per ton of the clay. The bisulfite can be introduced in any physical form, although it is preferred to introduce it dry. When the metabisulfite— $\text{Na}_2\text{S}_2\text{O}_5$ —is used it converts in aqueous solution by addition of water to the normal bisulfite, NaHSO_3 . Thus, either of these bisulfites may be employed. It is important only that the bisulfite be in solution in the aqueous phase of the clay slurry, and it may be introduced in solid form, in slurry form or in solution, so long as it dissolves in the aqueous system. Likewise, additional agents useful in dispersing the clay, for example phosphates commonly used in clay processing, may be employed.

The bisulfites found to be particularly useful in this process are the alkali metal, alkaline earth metal and ammonium bisulfites, particularly the sodium, potassium, lithium, magnesium and ammonium bisulfites, and more particularly the alkali metal bisulfites. The bisulfites may have associated with them substantial amounts of sulfites of ammonia or one of these metals without detriment; at the pH of the present solutions the sulfite converts to bisulfite.

The alkali borohydride is a solid, and normally is introduced in this form, since in aqueous solutions it tends to decompose. It is possible, however, to introduce this reagent in its aqueous solution provided the pH of the solution is maintained slightly alkaline prior to use by addition of an inert alkaline material such as sodium hydroxide, sodium carbonate and the like. Preferred alkali borohydrides for use herein are the alkali metal borohydrides, particularly the sodium and potassium borohydrides, although any water soluble alkaline borohydride, for example magnesium and the like borohydrides can be used.

The alkali borohydride is employed in the amount of about 0.125 to 1, and preferably about 0.36 to 0.82, pound per ton of clay. Normally not more than about one part by weight of the borohydride is used for each 5.6 parts by weight of the bisulfite. It is important to note that use of these amounts of borohydride, or even more, in the absence of the bisulfite is ineffective to accomplish effective bleaching of clays.

The temperature employed in the course of this process ranges from about ambient temperatures to about 200° F., and preferably from about 70° to 180° F. When elevated temperatures within this range are employed, the bleaching and refining operation proceeds rapidly, so that it is especially suited to continuous operation. Operation at lower temperatures within the above range is particularly useful, however, in instances where it is not desired to install heating equipment or for other operating reasons. Operation above about 200° F. tends to decompose the active reagents in the system and therefore is undesirable economically. On the other hand, one of the principal advantages of the herein process is its ability to bleach and refine clay at temperatures encountered in water supplies even during the cold seasons. Thus it is possible to bleach clay by this process even with water as cold as about 40° F., water temperatures encountered in some areas.

The pH of the reaction system is maintained at about 2.5 to 5, and preferably at about 3 to 3.5. Operation below about pH 2.5 results in dissolution of substantial amounts of aluminum ion from the clay, whereas when the reaction is carried out above about pH 5 the brightness of the bleached clay is reduced. Where necessary, mineral acids, preferably sulfuric acid, are added to adjust the pH to the herein levels.

The concentration of the clay slurry during processing is not critical. It is desirable, however, to have as high a concentration of clay and bleaching agents as is possible consistent with efficient and uniform contact of reactants, and to this end concentrations of from 5 to 70%, and preferably 15 to 35%, by weight of clay are preferred.

The process of this invention operates in either a continuous or a batch fashion, in either case rapidly. This speed of the reaction may be the reason for the excellent retention of physical properties of the clay, for example retention of its rheological properties. It has been found that overall the process will operate in about 30 minutes at 70° F., and in only about 20 minutes at 120° F., whereas the operation with prior processes often takes on the order of twice as long for full bleaching.

The various steps of the process are carried out with mild agitation in order to assure intimate contact of the reagents with each other and with the clay. The washing of the treated clay normally is carried out with water, although common aids such as soaps, detergents and the like may be added, and other washing media, for example alcohols, may be used. Separation of the clay from the

washing liquid is achieved by common means such as filtration, centrifugation, pressing and the like. The clay following separation from the aqueous or other washing may be dried, if desired, at a temperature and pressure which will remove essentially all of the water. In some cases it is desired to use the clay as a slurry, and in such cases the clay will not be dried.

The following examples are presented by way of illustration only, and are not intended to limit the scope of the present process in any way.

Example 1.—Preparation of clay samples for bleaching

Crude kaolin as obtained from a mine was dispersed in water containing about 0.1% by weight of sodium hexametaphosphate to provide an aqueous slurry containing about 30% by weight of the crude clay. This slurry was stirred in a high speed agitator for 30 minutes, following which it was transferred to a large beaker, the slurry was diluted to provide a 20% solids slurry, and the slurry was allowed to settle for 20 minutes. The suspension which formed was decanted and saved, while the settled material was discarded. The suspension was then allowed to settle for 48 hours, and the precipitated or settled material therefrom was retained for bleaching studies. This material was dried overnight at 80–100° C. to provide a standard sample of so-called classified clay for use in the following experiments.

This classified kaolin clay had a percent reflectance brightness of 83.1% at 458 microns on the GE brightness scale. The instrument employed for this measurement was a Bausch and Lomb 505 Spectronic Spectrophotometer; brightness values presented hereinafter were all determined on this instrument.

Example 2

One hundred grams of the classified clay from Example 1 was slurried in 400 g. of water with mild stirring. The pH of the slurry was adjusted to 3.3 with sulfuric acid, and the temperature of the slurry was raised to 120° F. This pH and temperature were maintained throughout the experiment. 0.138 g. of sodium metabisulfite (2.76 pounds per ton of clay) was added to the slurry and dissolved with stirring in a few seconds. 0.025 g. of sodium borohydride (0.50 pound per ton of clay) was then added to the slurry, and the resulting slurry of clay in a solution of the metabisulfite and borohydride was mildly stirred for 30 minutes. The clay was then separated from the bulk of the bleaching solution on a filter and washed with water at room temperature, after which it was dried at 100° C. in an oven.

The brightness of the clay prior to the bleaching operation was 83.1%, whereas following bleaching it was 87.9%. This improvement was very noticeable; the naked eye can detect a difference of 0.1% in brightness, and a 0.5% difference is significant in the clay trade. Likewise, the clay following the bleaching operation had a uniform and low shear viscosity making it highly suitable for use as a paper filler and finishing agent, and as a molding ingredient in the preparation of electrical and other ceramic and plastic products.

Example 3

The procedure described in Example 2 was carried out in a series of experiments in which the temperature of the bleach was varied between 70° and 180° F. The results of these experiments are shown in Table I which follows.

TABLE I

Temperature, ° F.:	Brightness—percent GE reflectance (unbleached clay 83.1%)	
70	-----	85.6
100	-----	85.9
120	-----	87.8
140	-----	87.0
160	-----	87.0
180	-----	85.9

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As demonstrated by this example, the brightness of the clay is dependent upon the temperature at which the bleaching operating is carried out, with optimum brightness being achieved at about 120° F. and the brightness dropping off slightly on either side of this temperature. Operation at 40° F. likewise bleaches the clay to a higher brightness than it was prior to bleaching, as does bleaching at temperatures of 200° F. However, the preferred range of bleaching is about 70° to 180° F.

Example 4

The procedure of Example 2 was carried out employing varying concentrations of sodium bisulfite and sodium borohydride. The results of these experiments are shown in Table II which follows:

TABLE II

Chemical Concentrations (Expressed as Pounds Per Ton)		Brightness— Percent GE Reflectance (Unbleached Clay 83.1)
Sodium Bisulfite	Sodium Borohydride	
0.7	0.125	84.0
1.38	0.25	85.5
2.0	0.36	86.3
2.76	0.5	87.8
3.6	0.64	87.1
4.5	0.82	86.6
5.6	1.0	85.9

As demonstrated by this example the amounts of bisulfite and borohydride employed can be varied considerably without destroying the ability of the system to bleach clay effectively.

Example 5.—Comparative example, reducing bleach, not within this invention

A comparative bleaching operation was carried out with sodium hydrosulfite serving as the bleaching agent. It was employed under the conditions of Example 2 above, with the exception that in place of the sodium metabisulfite and sodium borohydride employed therein, 0.136 g. (2.7 pounds per ton) of sodium hydrosulfite was dissolved in the bleaching liquor. The bleached clay provided by this operation had a brightness 1.5% below that of the bleached clay from Example 2; the clay of this Example 5 had a brightness of 86.3%. This difference was very noticeable, and was considered by a clay manufacturer to be important in the production of clay for paper finishing and filling agents. Extension of the bleaching time with sodium hydrosulfite as the bleaching agent did not result in any increase in brightness, rather resulting in a drop off in brightness and adversely affecting the viscosity of the clay. Likewise, either increasing or decreasing the amount of hydrosulfite resulted in a drop off in brightness rather than in an increase in this desirable property.

Example 6

Substitution of potassium borohydride, lithium borohydride, and magnesium borohydride for the sodium borohydride employed in Example 2 results in the production of bleached clay likewise having excellent brightnesses. The same result is achieved when the sodium metabisulfite and sodium bisulfite of the above examples is replaced with any of the potassium, magnesium or ammonium bisulfites.

It is evident from the above examples that the process of this invention operates in a short time to provide an excellent brightening of clay. Furthermore, it operates

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with a readily observable advantage in degree of brightening over a comparative method employing sodium hydrosulfite as the bleaching agent. The improvement in brightness provided by the process of this invention is highly significant to clay producers and users; it represents an improvement readily discernible to the eye, and one which is in the area of the best bleach results obtainable heretofore.

This combination of characteristics is of great value to the clay industry, since it makes possible upgrading of clay to an extent which makes previously unsatisfactory clays useable in many applications. This is of particular importance since deposits of high quality clays are gradually being depleted, and it is becoming increasingly important to employ clays of a lower quality.

Pursuant to the requirements of the patent statutes, the principle of this invention has been explained and exemplified in a manner so that it can be readily practiced by those skilled in the art, such exemplification including what is considered to represent the best embodiment of the invention. However, it should be clearly understood that, within the scope of the appended claims, the invention may be practiced by those skilled in the art, and having the benefit of this disclosure, otherwise than as specifically described and exemplified herein.

We claim:

1. Method of brightening clay in which the clay is slurried in an aqueous medium, an alkali bisulfite is added to the slurry with stirring in the amount of about 0.7 to 5.6 pounds per ton of said clay, an alkali borohydride is added to the resulting slurry in the amount of 0.125 to 1 pound per ton of said clay, the temperature of the reaction system being held at about 40° to 200° F., and the pH being maintained at 2.5 to 5, and the clay is washed free of residual bleaching agents and reaction products.

2. Method of claim 1 in which the alkali bisulfite is an alkali metal bisulfite and the alkali borohydride is an alkali metal borohydride.

3. Method of claim 1 in which the alkali bisulfite is sodium bisulfite and the alkali borohydride is sodium borohydride.

4. Method of claim 1 in which the alkali bisulfite is potassium bisulfite and the alkali borohydride is potassium borohydride.

5. Method of brightening clay in which the clay is slurried in an aqueous medium, an alkali bisulfite is added to the slurry with stirring in the amount of about 2 to 4.5 pounds per ton of said clay, and alkali borohydride is added to the resulting slurry in the amount of 0.36 to 0.82 pound per ton of said clay, the temperature of the reaction system being held at about 70° to 180° F., and the pH being maintained at 3 to 3.5, and the clay is washed free of residual bleaching agents and reaction products.

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