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METHOD OF BLEACHING CLAY AND IMPROVED CLAY PRODUCT

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This invention relates to an improved method of bleaching clay and to the resulting improved clay product.

In particular, this invention relates to an improved process for bleaching clay which utilizes orthorhombic phosphorus pentoxide (hereinafter referred to as $O-P_2O_5$) as the acidulating and deflocculating agent. As a result of this invention it is now possible to effectively disperse clay particles in an acid medium for the purpose of bleaching.

It is well known in the manufacture and processing of clays that in utilizing many naturally occurring clay deposits the clay must be bleached before it will provide a marketable product. This is particularly true of clays which are intended for use in such fields as paper coating, certain rubber compounding, etc. It is also well known that the clays usually employed in such fields often contain colored impurities, generally iron compounds, which can be effectively destroyed by bleaching. Sodium hydrosulfite has generally been used in bleaching clays of this type, but other well-known bleaching agents may also be used.

In the typical prior art clay bleaching process the clay, after certain initial preparation such as degritting and removal of gross impurities, is dispersed in water and acidified. This acidification is generally considered necessary in order to solubilize the iron compounds for effective bleaching. To be successful in this respect a pH of 3.0 to 4.5 is usually necessary. Sulfuric acid has generally been used for this acidification.

It has often been difficult, however, to achieve a low enough pH for satisfactory bleaching without getting such a low pH that the clay crystal structure is attacked. This problem is particularly troublesome as the pH approaches about 2 to 3.

After acidification the hydrosulfite bleaching agent is thoroughly mixed into the clay slurry and allowed to react until maximum bleaching takes place. At this point, if the clay is to be filtered and dried, it is sometimes necessary to add further acid to completely flocculate the clay in order to make filtering easier. This step often acts as a disadvantage during subsequent use of the dried clay since the ultimate user may wish to completely deflocculate the clay to give a low viscosity, smooth clay suspension for final use. To do this generally requires the addition of an alkaline dispersing agent.

According to the improved process of this invention a number of these prior art difficulties are overcome and an improved clay product is produced. This new product is whiter, i.e. more effectively bleached, and is more readily dispersed by the ultimate user.

In particular we have found that the problem of needing a low pH for effective bleaching and a high pH for effective dispersion is more nearly resolved. It is well known that the usual dispersants or deflocculants such as tetrasodium pyrophosphate, sodium tripolyphosphate or sodium hexametaphosphate perform best in an alkaline medium. We have now found that by using $O-P_2O_5$ as the acidulent good dispersion is accomplished in slurries with a pH as low as 3 to 4 and that good bleaching may be accomplished with a pH as high as 6.5. Our preferred range is within a pH of 5 to 6, however.

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In the preferred method of practicing our invention a clay slurry is first made up to which is added the sodium hydrosulfite bleaching agent. The slurry is then mixed thoroughly and after a short time the dry $O-P_2O_5$ is added to the mixture. When bleaching is complete the slurry is filtered, washed and dried.

The filtering and drying steps are obviously not necessary to the practice of our improved bleaching process. Since the clay after bleaching is already in the form of a dispersed bleached slurry it may be used as such if convenient to the process of the anticipated end use.

We have found that for best results the $O-P_2O_5$ should be added as the dry solid material. This is apparently due to the relatively slow solubility of this product. At any rate, we do not get good results if the $O-P_2O_5$ is first dissolved in water or if the ordinary hexagonal P_2O_5 is used. By using $O-P_2O_5$ a good dispersing or deflocculating effect is produced which lowers the slurry viscosity and aids bleaching. An additional valuable result is that some of the $O-P_2O_5$ apparently remains undissolved and is therefore in the final clay product. This product, due to the $O-P_2O_5$ present, is easily dispersed into a relatively low viscosity slurry. Once again, if the ordinary hexagonal P_2O_5 is used, it all dissolves and is removed during filtration. Due to this rapid solution and resulting acidity the clay is more flocculated and bleaching is inhibited.

Thus, by the use of $O-P_2O_5$ a threefold improvement is obtained. First, and foremost, better bleaching is obtained. This is apparent in subsequent data concerning the whiteness of various samples.

Second, the viscosity of the bleaching slurry is reduced which aids handling and improves bleaching.

Third, the resulting filtered, dried clay product has improved marketability due to its easy dispersibility and lower viscosity when put into a slurry for commercial use. This combination of advantages is not present in any prior art process.

In order to demonstrate the superior bleaching obtained with our new process a series of tests was run in which the whiteness of the finished products was compared for three different processes.

Process A.—This process represents the common prior art procedure. A 40% clay slurry of crude Georgia kaolin was adjusted to a pH of 3.4 with sulfuric acid. Sodium hydrosulfite in an amount of 0.11% of the weight of the dry clay was then added and the slurry was allowed to stand for 40 minutes. A 100 gram portion was then diluted with 200 cc. of water, filtered, washed and dried.

Process B.—This process is similar to the prior art procedure but uses our invention of substituting $O-P_2O_5$ for sulfuric acid. To a 40% clay slurry of crude kaolin was added 0.20% $O-P_2O_5$ and 0.11% sodium hydrosulfite both on the basis of the weight of the dry clay. The slurry was allowed to stand 40 minutes after which a 100 gm. sample was diluted, filtered, washed and dried as in Process A.

Process C.—This process represents the preferred process of the present invention. To a 40% slurry of crude kaolin was added 0.11% of sodium hydrosulfite based on the weight of the dry clay. After 20 minutes 0.20% of $O-P_2O_5$ (basis dry clay) was added and after another 20 minutes a 100 gm. sample was diluted, filtered, washed and dried as in Process A.

The above three processes were each carried out on separate clay samples on four successive days and each day's results were compared for whiteness by a panel of seven observers. The following results were obtained:

TABLE I
Procedures Compared

	A and B	A and C	B and C
1st day-----	(A whitest 1 B whitest 6)	A whitest 3 C whitest 4	B whitest 6 C whitest 1
2nd day-----	(A whitest 0 B whitest 7)	A whitest 0 C whitest 7	B whitest 2 C whitest 5
3rd day-----	(A whitest 1 B whitest 6)	A whitest 3 C whitest 4	B whitest 2 C whitest 5
4th day-----	(A whitest 0 B whitest 7)	A whitest 0 C whitest 7	B whitest 2 C whitest 5
Total-----	{ A-2 B-26	{ A-6 C-22	{ B-12 C-16

It can be clearly seen from the above data that both Processes B and C, which rely upon our invention of using $O-P_2O_5$, are superior to the prior art process using sulfuric acid as the acidulent. The data also show that procedure C, wherein the $O-P_2O_5$ is added after the sodium hydrosulfite, is better than Process B. This process of adding the hydrosulfite, followed after a period of time by the $O-P_2O_5$, is thus our preferred process.

In addition to the improved bleaching qualities noted above there is also an improvement in viscosity when using $O-P_2O_5$. This is evident both during the bleaching and during subsequent use of the finished clay product. The following data illustrate this point.

Sample A: Prepared according to Process A above except that a 50% slurry was used.

Sample C: Prepared according to Process C above except that a 50% slurry was used.

TABLE II

Sample	pH After 40 mins.	Apparent Viscosity in Centipoises ($\times 1,000$)
A-----	4.5	16
C-----	5.1	8

These same samples, after being diluted, filtered, washed and dried, were then made up into 50% slurries again and the following viscosities were noted:

TABLE III

Sample	Apparent Viscosity in Centipoises ($\times 1,000$)
A-----	23
C-----	2

The above viscosities were measured with a Model HAF Brookfield viscometer and Helipath stand using a TA spindle at 5 r.p.m.

It can readily be seen from these viscosity data that the use of $O-P_2O_5$ in the bleaching of clay not only provides a more workable slurry during the bleaching operation, but also provides a superior product to the ultimate consumer. These results are not possible using the prior art processes.

As a further illustration of the advantages of our new process the following tests were run on clay slurries containing sodium hexametaphosphate as a dispersant. It is a common practice in some mining operations to add a small amount of sodium hexametaphosphate at the mine in order to facilitate dispersion and thus aid in transporting the slurry to the point where the bleaching process is carried out.

Process D.—A 40% slurry of crude kaolin containing 0.2% by weight of the dry clay of sodium hexametaphosphate was adjusted to a pH of 3.4 with sulfuric acid. Sodium hydrosulfite in an amount of 0.75% of the weight of the dry clay was then added and the slurry was allowed

to stand for 40 minutes. A 100 gm. portion was then diluted with 200 cc. of water, filtered, washed and dried.

Process E.—The procedure of Process D was followed exactly except that the initial clay contained no sodium hexametaphosphate.

Process F.—To a 40% slurry of crude kaolin containing 0.2% by weight of the dry clay of sodium hexametaphosphate was added 0.2% $O-P_2O_5$ (same basis). Sodium hydrosulfite in an amount of 0.75% (basis dry clay) was then added and the slurry was allowed to stand for 40 minutes. A 100 gm. portion was then diluted with 200 cc. of water, filtered, washed and dried.

Process G.—The procedure of Process F was followed exactly except that the initial clay contained no sodium hexametaphosphate.

Process H.—To a 40% slurry of crude kaolin was added 0.75% of sodium hydrosulfite (basis dry clay). After 20 minutes 0.2% of $O-P_2O_5$ was added and after another 20 minutes a 100 gm. portion was diluted with 200 cc. of water, filtered, washed and dried.

Each of Processes D through H was repeated three times and the following results were noted upon visual comparison of the final samples:

(1) Clay slurries containing sodium hexametaphosphate (processes D and F) did not bleach as well as slurries in which the metaphosphate was absent (Processes E, G, and H). There was also evidence of more settling out upon standing in the slurries containing sodium hexametaphosphate. This shows a further advantage of our process, namely that $O-P_2O_5$ may be used in place of the usual metaphosphate to aid in dispersion at the mine prior to bleaching. It then continues to aid in the subsequent bleaching process.

(2) Clay slurries using $O-P_2O_5$ (Processes F, G and H) in place of sulfuric acid (Processes D and E), regardless of the presence or absence of sodium hexametaphosphate, always bleached better.

(3) The addition of $O-P_2O_5$ after the addition of sodium hydrosulfite (Process H) gives slightly better bleaching than adding the $O-P_2O_5$ initially (Processes F and G).

(4) The presence of sodium hexametaphosphate in slurries containing $O-P_2O_5$ (Process F) causes a greater drop in pH during bleaching than when no metaphosphate is used (Processes G and H). This tends to cause deflocculation and causes settling as noted in (1) above.

The foregoing examples show the use of crude Georgia kaolin but this process applies generally to all clays of a similar nature wherein bleaching to remove iron discoloration is a problem. Typically in the United States these clays are found primarily in Georgia and South Carolina in a belt commonly known as the Fall Line.

Such clays may be handled as slurries with concentrations as high as 70% solids under certain circumstances. Generally, however, slurries of 30–50% concentration are most satisfactory.

In this respect the concentration of the slurry has an effect on the length of time required for bleaching due to the ease with which the bleaching agent may be distributed and thereby made available to the clay particles. Bleaching time may run from as low as 15 to 30 minutes to as long as a few hours in some cases. The precise length of time is not critical to this invention but must be determined in each case according to amount of impurities, slurry thickness, etc. as is well known in the art.

The amount of sodium hydrosulfite used may vary widely depending again upon the slurry thickness and allotted bleaching time. Generally, a considerable excess is used, often as much as 20 times the theoretical amount necessary to reduce the iron present. We find that the use of 0.05% to about 1% (basis dry clay) will generally give satisfactory results.

The $O-P_2O_5$ used in this invention is a well-known product and is described by Hill et al., Journal of the American Chemical Society, vol. 65, pages 794–802. The

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amount which must be used will vary depending upon the particular clay used and its relative requirements as to dispersion and bleaching acidity as discussed previously. Generally we find that good bleaching can be obtained by adding 0.05% to about 2% O-P₂O₅. Normally a concentration of 0.2% O-P₂O₅ is satisfactory.

All percentages of sodium hydrosulfite and O-P₂O₅ used in this patent are based upon the dry weight of the clay used.

The foregoing description is given for clearness of understanding only and no unnecessary limitations should be derived therefrom as various modifications will be obvious to one skilled in the art.

We claim:

1. In a process for bleaching clay slurries with sodium hydrosulfite the step which comprises dispersing about 0.05% to about 2% of orthorhombic P₂O₅ in the clay slurry prior to the completion of the bleaching.

2. In a process for bleaching 30-50% clay slurries with about 0.05% to about 1% sodium hydrosulfite the improvement which comprises dispersing about 0.05% to about 2% of orthorhombic P₂O₅ in the clay slurry prior to the completion of the bleaching.

3. In a process for bleaching clay slurries with sodium hydrosulfite the improvement which comprises dispersing about 0.05% to about 2% of orthorhombic P₂O₅ in the clay slurry after addition of the sodium hydrosulfite but prior to completion of the bleaching.

4. In a process for bleaching 30-50% clay slurries with about 0.05% to about 1% sodium hydrosulfite the improvement which comprises dispersing about 0.05% to about 2% of orthorhombic P₂O₅ in the clay slurry after addition of the sodium hydrosulfite but prior to completion of the bleaching.

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5. A process for producing an improved bleached clay product from a clay slurry comprising dispersing about 0.05% to about 2% of orthorhombic P₂O₅ in the clay slurry prior to the completion of the bleaching.

6. A process for producing an improved bleached clay product from a clay slurry comprising dispersing about 0.05% to about 1% sodium hydrosulfite and about 0.05% to about 2% of orthorhombic P₂O₅ therein, allowing a period of time for the bleaching action to reach completion, filtering to remove a major portion of the water and drying the resulting product.

7. A process for producing an improved bleached clay product from a clay slurry comprising dispersing about 0.05% to about 2% of orthorhombic P₂O₅ in the clay slurry after the addition of the bleaching agent but prior to completion of the bleaching.

8. A process for producing an improved bleached clay product from a clay slurry comprising first dispersing about 0.05% to about 1% sodium hydrosulfite therein and then after a period of time dispersing about 0.05% to about 2% of orthorhombic P₂O₅ therein, allowing a period of time for the bleaching action to reach completion, filtering to remove a major portion of the water and drying the resulting product.

9. The improved clay product produced by the process of claim 6.

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