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METHOD OF BLEACHING MINERAL MATTER

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This invention relates to a method of bleaching mineral substances, such as fine sand, clay, bauxite, or the like.

In the various arts in which mineral substances are employed, it is a matter of common observation that, as originally obtained, such materials usually contain an appreciable amount of coloring matter. This may be present in two forms: first as an ingredient of the mineral itself and hence contained within each (or a large proportion) of the particles of the material when reduced to comminuted condition; and secondly as a coating or deposit upon the exterior of each particle, resulting from weathering of constituents of the surface of the particle, for example, or from deposition thereon by percolating ground waters or like agencies. The finely divided mineral may also contain extraneous coloring matter, independent of the mineral particles, but so finely divided or of such properties, in relation to the mineral particles, that separation is not mechanically practicable. Such coloring matter may be composed of finely divided coloring agents such as iron oxide or may be composed of organic residues.

It is an object of the present invention to treat such discolored mineral matters to reduce or eliminate the discoloration thereof by a simple and inexpensive and yet effective procedure. It is a further object so to convert the coloring matter that it may be rendered soluble and thereby removable from the charge. It is also an object to leave the mineral matter, after treatment, with substantially the same physical properties as before treatment, (such, for example, as the tendency to settle slowly from aqueous suspension) except for the removal or conversion of the objectionable coloring matter.

In my copending application, which is referred to below, a procedure has been described for the bleaching and removal of such colored mineral matters. But I have found that some mineral materials, when subjected to bleaching action, as therein described, may not acquire as light or white a color as may be desired. It is accordingly an object of this invention to correct and overcome this occurrence. Other objects will appear from the following disclosure.

In accordance with the present invention, I have discovered that, contrary to what would be expected, certain mineral substances, when subjected to a very active or rapid bleaching treatment, present the anomaly not only of failing to be bleached out but of acquiring a dark coloration,

which sometimes has a somewhat bluish cast.

I attribute such occurrences to the presence of titanium in the mineral matter under treatment and to the excessive reduction of such titanium content to one of its sub-oxides, such as the sesquioxide, Ti_2O_3 , which is black, and TiO which is bluish black, or some of its reduced compounds with iron, etc., which take on dark colorations, depending upon the specific form in which they may occur or to which they may be transformed. Titanium dioxide, on the other hand, is white and of such brilliancy as to provide, in large quantities, a very effective white pigment for paint and like purposes. It is, therefore, desirable to convert the titanium component of the mineral substance under treatment to this form and to avoid the formation of the sub-oxide or colored titanium compounds.

The method of the present invention includes the treatment of comminuted mineral substances, typically containing coloring matter which is reducible to a substantially colorless or readily soluble condition and which may include the higher forms of titanium oxide compounds, with a separately (and preferably freshly prepared) solution of a hydrosulphite and with an acid. It is found that, especially when oxidized compounds of titanium are present in the material under treatment, a less vigorous chemical reducing action is to be preferred. This may be provided for, in accordance with the present invention, by employing a weaker (or less ionized) acid, in general, including certain of organic acids such as acetic acid.

Acetic acid, for example, has a dissociation constant of 1.86×10^{-5} and acids of such low dissociation values are characteristically suitable in the present process. Using such acids, the pH value of the treating solution is reduced below 5.5 as recommended in the parent application above referred to and more particularly designated below.

It is also found advantageous, except with mineral materials which are decidedly alkaline, to treat and mix the material first with the hydrosulphite solution and then to acidify the hydrosulphite-treated mass, gradually and with agitation, to impart to it the desired pH value for the whole, namely below 5.5 and preferably between 4 and 5, to develop and activate its bleaching action.

A typical instance of the practical application of the invention will be described with reference to the treatment of clay. While clays, as they naturally occur in nature, vary widely in prop-

erties and in the industrial uses which they may serve accordingly, those which may serve the more exacting purposes, such as for high grade ceramic products and for paper coating, are relatively limited in quantity and hence in availability. English china clay and certain high grade clays from Georgia are indicative of this type of clays. These may be sufficiently white for use, per se, although it will be clear that, even these products, if they become contaminated or run in veins which are discolored, may be unsatisfactory. There are other clays of high quality, however, as from certain beds of Vermont, Georgia, and South Carolina, which contain iron oxide and are rendered slightly brownish thereby. These may be used for certain ceramic purposes, or other uses, but would be much more valuable if the color were removed.

While some of these clays are adequately bleached by the procedure described in my parent application, other clays, or some of those which may contain minerals capable of reduction to dark colored compound by too rapid bleaching action, such as titanium oxide above mentioned, are especially susceptible to a highly satisfactory degree of whiteness by the procedure and reagents herein recommended.

Such clays may be generally alkaline, i. e., when mixed with fresh water, they will impart thereto a pH value of 7.0 to 7.6 or perhaps higher—or they may be substantially neutral. In this condition, the oxidized coloring matter which is present will not dissolve.

It is now found, however, that if the pH value of the aqueous suspension of the clay be somewhat lowered, in the bleaching treatment, by the addition of a less rapidly reactive or less highly ionized acid or acids than the mineral acids, and treated with a solution of soluble hydrosulphite, such as an alkaline metal, alkaline earth metal, or zinc hydrosulphite solution, the oxidized coloring matter (including oxidized compounds of titanium) is both reduced and/or dissolved and hence may be readily and substantially completely overcome and/or separated from the residual particles of clay. The reagent materials also remain in solution and are readily removed from the clay along with the dissolved coloring matter. White titanium dioxide, on the other hand, will remain unaffected. The treated clay, as thus obtained, upon neutralizing, if necessary, and washing, retains its original desirable properties, such as fineness of subdivision, slow settling from suspension, plasticity, etc., and at the same time is substantially free from coloring matter.

It is now further found to be advantageous in some respects, in the course of the bleaching procedure, to add the hydrosulphite solution to the mineral matter first and subsequently to acidify and bring the reaction mass to the desired acidity or pH value. This procedure may sometimes be adopted to advantage whether a strong or weak acid is to be employed. However, this order of procedure would not be desirable with a very alkaline slag, for example, because the alkalinity would tend to decompose and precipitate the metallic content of some of the hydrosulphites, such as zinc hydrosulphite for example, and might also produce a decomposition of the hydrosulphite, rendering it less soluble or insufficiently reactive in the bleaching operation. In such event it might be desirable, first to counteract the alkalinity of the material to approximate neutrality (pH 7.0) as by removing the alkali or treating

with a suitable acidic reagent, then to add the hydrosulphite and then acidify, typically with a weakly ionized or organic acid, to a pH value below 5.5 or between 4 and 5. This order of treatment (that is, by treating the mineral first with hydrosulphite and then acidifying) seems to bring the bleaching into more intimate contact than when acidification is effected first, and to render its activity more uniform and more complete, and hence more economical.

If the mineral matter is not alkaline, and contains oxidizing coloring matter such as ferric oxide, etc., treatment with the soluble hydrosulphite solution alone may be sufficient. This, for the reason that the oxidizing coloring matter tends to oxidize the hydrosulphite and to convert the same into free acids which are effective, per se, to acidify the charge, to develop the required pH value and even to serve as an adequate solvent to dissolve the coloring matter itself, without further additions of acid reagents.

As an example, a separately and preferably freshly prepared solution of zinc hydrosulphite may be obtained by introducing approximately 8 lbs. of sulphur dioxide, preferably in liquid condition, into an aqueous suspension of a chemical excess of zinc dust, but without causing foaming. The resulting freshly prepared solution of zinc hydrosulphite is preferably used at once or within twenty-four hours, for the best results. Other soluble hydrosulphites may be prepared therefrom by metathesis.

Such preparation of the hydrosulphite separately from the charge to be treated is found to be necessary, not only for the efficient conversion of the zinc and sulphur dioxide to zinc hydrosulphite but also for the effective bleaching action of the latter upon the clay to be treated. In dilute aqueous medium, for example, the equation $\text{Zn} + 2\text{SO}_2 = \text{ZnS}_2\text{O}_4$ is retarded or may be reversed, by the presence of large amounts of water.

The preparation of the hydrosulphite solution may be conveniently carried out in the apparatus as described in United States Patent No. 1,472,828, dated November 6, 1923, to Frederic A. Eustis, and in accordance with the procedure described and claimed in my United States Patent No. 1,741,496, dated December 31, 1929.

The treated charge of clay or other mineral substance, after intimate contact with the hydrosulphite solution, and acidification may be allowed to settle, and at this stage the clay separates rapidly and completely. The supernatant reagent solution, containing excess of the original hydrosulphite, by-products of the reaction, and dissolved coloring matter or converted compounds of the same, may then be decanted or otherwise readily removed from the treated and purified solid matter. More complete removal may be accomplished by repeated mixing with similar quantities of fresh water (and/or mineral or organic acids), settling, and decanting, as before, and finally filtering and drying, if desired. Other modes of washing may be adopted, however, as by passing through a counter-current continuous washer, or by filtering, or by similar treatments which are well known.

If a slow settling clay is desired, which is often advantageous for use in the paper trade, the bleached and washed slip or slurry may be neutralized just before filtering. This would be done by the addition to the slip just before it reaches the filter of a suitable amount of soda ash or caustic soda or other alkali. For the slowest

settling, the pH of the slip may subsequently be brought to a value between 7 and 8. By this procedure I get the advantage of rapid settling during the washing step, which often is slow, and still retain the advantage of a slow settling final product.

By such procedure, it has been accomplished to produce either a flat, white or even a bluish white clay product, but without dulling or loss of brilliancy, even when titanium or like materials are present. Such a product may, for some purposes, be too white. In such event, a less amount of reagent or a shorter time of treatment may be employed. On the other hand, it may be desirable first to produce a high white product and then to modify the color by the addition of pigments, dyes, or the like, which will then not be altered as they would be by residual coloration of the clay.

The hydrosulphite solution may have the clay stirred into it, with gradual additions and continued agitation, or the clay may be first mixed with water to form a suspension or slip of any desired consistency, to which the hydrosulphite solution may be added, with constant agitation of the charge. The mixture is then acidified to the desired pH value, by adding a weak acid, typically an organic acid such as acetic, to lower the pH value of the charge at least below 5.5 and preferably to between 4.0 and 5.0. For example, 8 to 12 pounds of acetic acid or 5 to 8 lbs. of formic acid (which has a dissociation constant of 2.14×10^{-4}) have been found satisfactory, per ton, in the treatment of clay. Such acidification of the mixture is likewise effected with continued intimate agitation of the mix.

The bleached or decolorized materials, such as clay, obtained as above described (and in accordance with the following claims) is rendered suitable not only for producing ceramic objects in which color is a most important desideratum, but for incorporation in paper fillers and paper coating compositions in which a high degree of whiteness and duplication of such degree of whiteness is essential. At the same time, other desirable physical characteristics of the clay are not altered or are improved, such as fineness of subdivision, wettability by water, specific gravity and density (except possibly to be somewhat lighter), plasticity, friability when dry, softening range (except for removal of fluxing oxides), and in general the same or better suitability for the intended purpose than the untreated clay.

Moreover, if the mineral matter contains organic coloring matter, other than wholly inert substances, such as asphalt or elementary carbon, these coloring matters will likewise ordinarily be decreased or eliminated therefrom.

In connection with the above described procedure, raw materials to be subjected to treatment may contain ingredients which impart color to the material but are present in reduced condition and hence not susceptible to reducing bleaching action. In such cases, the material may be subjected to an oxidizing treatment, either before or after the hydrosulphite bleaching treatment above described, depending upon whether the coloring material may be reduced or removed satisfactorily from a higher degree or stage of oxidation, or whether, by converting to a higher degree of oxidation per se, the coloring matter is rendered of satisfactory color or susceptible to convenient removal.

It should be understood that the present disclosure is for the purpose of illustration only and

that this invention includes all modifications and equivalents which fall within the scope of the appended claims.

This application constitutes a continuation in part of application Serial No. 587,607, filed January 19, 1932.

While the term "hydrosulphite" has been employed herein as referring specifically to the neutral or completely substituted salts of hydrosulphurous acid, it is to be understood that acid hydrosulphite and/or hydrosulphurous acid are contemplated as being present in the subsequently acidified reagent solutions employed, and may be the intermediate reactive agent or agents derived therefrom, under and by virtue of the conditions of use.

I claim:

1. Method of treating mineral substances containing reducible coloring matter, comprising the steps of treating the same with a solution of a soluble hydrosulphite, and with a (weakly ionized) solution of an acid having a dissociation constant of approximately 2×10^{-4} or less.

2. Method of treating mineral substances containing reducible coloring matter, comprising the steps of treating the same, first with a solution of a soluble hydrosulphite, and then with a (weakly ionized) solution of an acid having a dissociation constant of approximately 2×10^{-4} or less.

3. Method of treating mineral substances containing reducible coloring matter, comprising the steps of treating the same with a solution of a soluble hydrosulphite, and then acidifying the material with a (weakly ionized) solution of an acid having a dissociation constant of approximately 2×10^{-4} or less and finally neutralizing the treated charge.

4. Method of treating mineral substances containing reducible coloring matter, comprising the steps of treating the same with a solution of a soluble hydrosulphite, and then acidifying the material with a (weakly ionized) solution of an acid having a dissociation constant of approximately 2×10^{-4} or less, to a pH value between 4 and 5.

5. Method of treating mineral substances containing reducible coloring matter, comprising the steps of treating the same with a solution of a soluble hydrosulphite, and acidifying the hydrosulphite-treated material with a (weakly ionized) solution of an organic acid having a dissociation constant of approximately 2×10^{-4} or less.

6. Method of treating mineral substances containing reducible coloring matter, comprising the steps of treating the same with a solution of zinc hydrosulphite and gradually acidifying with a weakly ionized solution of an organic acid having a dissociation constant of 2×10^{-4} or less.

7. Method of treating mineral substances containing reducible coloring matter, comprising the steps of treating the same with a solution of zinc hydrosulphite and gradually acidifying with a weakly ionized solution of an acid having a dissociation constant of approximately 2×10^{-4} or less.

8. Method of bleaching mineral substances containing reducible coloring matter, comprising the step of treating the same with a weakly ionized solution of an organic acid having a dissociation constant of approximately 2×10^{-4} or less and a solution of zinc hydrosulphite.

9. Method of bleaching mineral substances containing reducible coloring matter, comprising the step of treating the same in aqueous suspension,

