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ACID TREATMENT OF CALCINED KAOLIN

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This application is a continuation-in-part of our abandoned application Ser. No. 93,434, filed Mar. 6, 1961. This latter application is a continuation-in-part application of our prior application Ser. No. 676,711, filed Aug. 7, 1957, now Patent No. 2,974,054.

This invention relates to improvements in the treatment of clay for the production of improved silica residues, and includes improved processes of treating clay and improved silica residues produced by such treatment.

The invention includes an improved silica residue produced from kaolin clay, from which the greater portion of the alumina has been extracted, but which retains a substantial amount of alumina, and which also has combined therewith a substantial amount of phosphoric acid, and which is a valuable product as a paper coating composition, and for other purposes, and which retains the characteristic platelet or booklet appearance of the clay from which it is produced. This product will hereafter be referred to as product "A."

The invention also includes a silica product in a highly purified form, freed from most or all of the alumina and phosphate of product "A," but retaining the hexagonal platelet appearance of kaolin clay, even though X-ray diffraction shows the material to be amorphous. This product will hereafter be referred to as product "B."

The clay which is treated to produce the new silica residues is clay such as Georgia kaolin clay, of the kind commonly known as coating clays or filling clays, or run-of-mine clays, which are obtained after first separating the sand and grit and coarser particles from the mined and kilned clay. In the production of domestic coating clays, used extensively in the paper industry, the Georgia kaolin clays are subjected to settling and separation treatments to produce coarser and finer fractions, and the coating clay will contain around 80% to 90% of particles less than 2 microns in size, which are largely in the form of platelets, together with varying amounts of particles of larger size in the form of aggregates or booklets. The coarser or filling clay fractions of clay so separated are made up principally or largely of booklets or aggregates of fine clay platelets, with varying amounts of clay platelets of less than 2 microns in particle size. These coarser or filling clays may thus be made up largely or mainly of larger particles in the form of aggregates or booklets of over 5 microns in size and may, to some extent, contain particles exceeding 10 microns in size, and may contain, for example, 54% below 5 microns and 100% below 20 microns, and 25% below 2 microns.

In the treatment of clay according to the present invention, the clay, which may be run-of-mine clay or clay which has been produced by fractionation, such as coating clay or filling clay, is first subjected to calcining within the temperature range of 930°–1650° F. (about 500°–900° C.) and the calcined clay is then treated with dilute phosphoric acid, or with a mixture of dilute phosphoric and sulphuric acids, to extract the greater part of the alumina as aluminum phosphate, or a mixture of aluminum phosphate and aluminum sulfate, and to produce a silica residue in platelet or booklet or mixed platelet and booklet form, which still contains a substantial portion of the alumina and a substantial amount of phosphoric acid in combined form, this product being the product referred to as product "A."

The solution of aluminum phosphate, or of aluminum phosphate and aluminum sulfate, so produced, is largely separated from the silica residue and can advantageously be used for the production of composite phosphate, or phosphate-sulfate, pigments, as described and claimed in our application Ser. No. 676,711, filed Aug. 7, 1957, now Patent No. 2,974,054.

We have found that clays which have been previously calcined, within the range above indicated, can readily be treated with dilute phosphoric acid, or a mixture of dilute phosphoric acid and dilute sulfuric acid, to extract the greater part of the alumina therefrom and to produce an improved silica residue, made up mainly of silica, but still containing substantial amounts of alumina and phosphate, or of aluminum and phosphorous compounds, therein; and that the use of such dilute acids has advantages over the use of concentrated acids for such extraction and for the production of such silica residues. An excess, but not a large excess, of the dilute acid is required to keep the dissolved aluminum salts in solution to the desired extent, and the excess acid is recovered directly as a part of the solution except for such amount as remains combined in the silica residue.

When dilute phosphoric acid is used to extract the greater portion of the alumina from the calcined clay, the silica residue will be separated from the solution of aluminum phosphate but will retain substantial amounts of both aluminum and phosphate in combined form as aluminum phosphate or other aluminum-phosphorus compounds. When a mixture of dilute phosphoric and sulfuric acids is used, the amount of dilute phosphoric acid is equal to or approximately equal to the amount theoretically required to produce aluminum phosphate with the alumina of the clay, and the sulfuric acid is used as the excess amount of acid required for keeping the desired amount of the aluminum phosphate in solution, while leaving some of the aluminum phosphate in the silica residue.

The strength of the dilute phosphoric acid, or of the dilute phosphoric and sulfuric acids, used for extracting the greater portion of the alumina from the calcined clay, can vary somewhat, e.g., between about 20% and about 50% and more advantageously about 25%–30%. One advantage of the use of dilute acids for the extraction of the greater portion of the alumina from the clay is that the resulting acid solution containing dissolved aluminum can be readily separated from the silica residue and the silica residue can then be further washed to free it to the desired extent from adhering soluble aluminum salts while nevertheless leaving in the silica residue a substantial amount of alumina and phosphoric acid in a combined form.

The extraction of the clay with dilute acid is advantageously carried out at an elevated temperature and by the use of apparatus which is resistant to the action of the dilute acid at elevated temperatures, such as a glass-lined reactor.

The silica residue remaining after the extraction of the greater portion of the alumina from the calcined clay by the dilute acid treatment is a valuable silica residue. It retains the hexagonal platelet appearance, or the booklet appearance, or mixed platelet and booklet appearance, of the kaolin clay from which it is produced, even though X-ray diffraction shows the material to be amorphous. It still retains a small but substantial part of the original alumina content of the clay, together with phosphate which is present in the residue in an adsorbed or combined form, as an aluminum phosphate or a more complex form.

Where the silica residue "A" is produced by the treatment of coating clay fractions which contain the clay