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# ALIEN PROPERTY CUSTODIAN

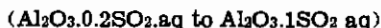
## PROCESS FOR PREPARING ALUMINA FROM ALUMINUM SULFITE

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No Drawing. Application filed April 18, 1941

This invention relates to a process for preparing alumina from aluminum sulfite.

The known decomposition of siliceous aluminum minerals with the aid of sulfurous acid yields aluminum sulfite solutions from which basic aluminum sulfites of different composition can be precipitated by driving out the sulfurous acid. Depending on the manner of conducting the precipitating process, either amorphous high-basic sulfites of changing composition



or the accurately defined crystalline monobasic aluminum sulfite ( $Al_2O_3 \cdot 2SO_2 \cdot 5H_2O$ ) is precipitated.

Various processes have been proposed for subsequently working these products to obtain alumina, which fundamentally consist in heating the products to drive out the sulfur dioxide and to obtain the remaining alumina. For example, it has been suggested to mix water or salt solutions with the precipitated high-basic aluminum sulfites and then to boil the mixture or to heat it to more than 100° C in a closed vessel while the sulfurous acid was slowly distilled off under pressure. It was found out later on that rapid distillation of the sulfurous acid represented a considerable improvement, since the easily occurring decomposition of the acid was avoided thereby.

The hydrates of alumina obtained in this manner from the high-basic sulfites are, however, open to the objection that they are rich in water, have a low content (10 to 15%  $Al_2O_3$ ), are extremely fine and partly even slimy, and therefore difficult to filter.

The treatment of the precipitated monobasic aluminum sulfite to obtain alumina consisted hitherto in separating it from the solution for instance by centrifuging and then subjecting it to calcination to drive acid and water out of the salt and to obtain a crude alumina as final product. Calcination has moreover been carried out in peculiar manner for the purpose of obtaining a highly reactive alumina of high content. The monobasic aluminum sulfite has for instance been heated to temperatures not exceeding approximately 600° C., or a two-step process was applied in which during the first step at indirect heating temperatures of about 200-300° C. prevailed and during the second step at direct or indirect heating higher temperatures were employed.

This treatment of the monobasic aluminum sulfite by calcination involved, however, certain difficulties, since it was necessary indirectly to heat the furnaces to prevent the reaction gases from coming into contact with the gases of combustion. Another requirement that had to be met consisted in always maintaining a slight excess pressure in the furnaces to prevent the ad-

mission of foreign air and further oxidation and rarefaction of the sulfur dioxide. In addition, it was a difficult task to precipitate the fine dust entrained by the reaction gases, so that the treatment required the use of highly sensitive and expensive apparatus.

However, as the monobasic aluminum sulfite was hitherto considered an extremely stable compound, it was generally believed that the only way to obtain alumina therefrom was that of thermal decomposition. It was known that high-basic aluminum sulfites could be freed to a large extent from the sulfurous acid by treating them at higher temperature in aqueous suspension, but such hydrothermal decomposition was assumed not to be possible with respect to monobasic aluminum sulfite in view of its high stability.

By systematic research the surprising fact has now been discovered that it is possible to decompose also monobasic aluminum sulfite in aqueous suspension at elevated temperature and under pressure practically down to alumina hydrate. According to the invention, finished and separated monobasic aluminum sulfite as obtained under one of the known processes may be used, or an aluminum sulfite solution may be heated in stages, in which case monobasic aluminum sulfite is formed in the lower stages and converted in the higher stages into crude alumina hydrate totally freed from sulfurous acid. For example, monobasic aluminum sulfite can be obtained in three stages from aluminum sulfite solutions and then suspended and hydrothermally decomposed in water or aqueous solutions, or crude alumina hydrate can be produced directly from aluminum sulfite solutions in four continuous stages by working in the first stages, through proper temperature control, towards the production of monobasic aluminum sulfite which, however, is not separated but jointly with the mother liquor converted in the following stages at elevated temperatures into crude alumina hydrate while the sulfurous acid is distilled off.

If the monobasic aluminum sulfite obtained in three stages were to be calcined in the known manner, a considerable quantity of fuel gas would have to be consumed. Hydrothermal decomposition, on the other hand, requires little steam, since in the first stages in which the monobasic aluminum sulfite is formed temperatures of approximately 100° C. prevail already and the subsequent stages in which the alumina hydrate is produced are carried out at temperatures of only about 150-170° C. The requisite amount of heat is therefore relatively slight and may be utilized again for the process by expansion or substitution.

A particular advantage afforded by alumina hydrate obtained in the manner described from crystalline monobasic aluminum sulfite is its

granular condition, so that it can be well filtered.

The following examples have been found to give satisfactory results:

*Example 1*

95 g. of monobasic salt composed of

	Per cent
Al <sub>2</sub> O <sub>3</sub> -----	28.83
SO <sub>2</sub> -----	32.60
SO <sub>3</sub> -----	2.06
H <sub>2</sub> O -----	Remainder

were mixed with 750 cu. cm. of so-called thin acid composed of

	grams
Al <sub>2</sub> O <sub>3</sub> -----	6.02
SO <sub>2</sub> -----	27.40
SO <sub>3</sub> -----	3.33
S <sub>2</sub> O <sub>3</sub> -----	0.44

per liter. The mixture was heated in a stirring autoclave to about 165° C. for four hours and kept at a constant pressure of 6.2 atmospheres excess pressure by blowing off sulfurous acid. The escaping sulfur dioxide was collected in soda lye and quantitatively determined. 94% could be recovered. This treatment was followed by filtration. The crude alumina obtained had the following composition:

	Per cent
Al <sub>2</sub> O <sub>3</sub> -----	30.88
SO <sub>2</sub> -----	1.50
SO <sub>3</sub> -----	2.78
H <sub>2</sub> O -----	Remainder

The waste acid contained only 2.67 g. sulfur per liter and 0.16 g. alumina.

*Example 2*

An equal amount of a suspension similar to the one mentioned in Example 1 was heated in a stirring autoclave to about 155° C. for two hours and then to about 165° C. for another two hours. The pressure amounted in the first stage to 4.5 atmospheres excess pressure and in the second stage to 6.4 atmospheres excess pressure. 92% of all the sulfurous acid was recovered. The crude alumina obtained has the following composition:

	Per cent
Al <sub>2</sub> O <sub>3</sub> -----	24.61
SO <sub>2</sub> -----	1.31
SO <sub>3</sub> -----	2.49
H <sub>2</sub> O -----	Remainder

The waste acid contained 2.34 g. sulfur and 0.19 g. alumina per liter.

These results have been confirmed by large-scale experiments made with suspensions of 25 cu. m. In treating sulfite solutions in plants the following operations are for instance involved:

*Example 3*

A sulfite solution containing 200 g. SO<sub>2</sub> and 40 g. Al<sub>2</sub>O<sub>3</sub> per liter is stirred at 100° C. for two hours and subjected to 4 atmospheres excess pressure to cause the escape of sulfurous acid. A large part of the alumina will then separate in the form of the monobasic salt. The suspension is then passed to a second stirring vessel in which it is stirred at 100° C. for two hours at approximately 2 atmospheres excess pressure, whereby the separation of the alumina in the form of monobasic sulfite is practically completed. Now the new working method commences. The suspension is heated in a third stirring vessel from 100° C. to about 155° C. and treated again for two hours at approximately 4.5 atmospheres excess pressure while the sulfurous acid escapes. In a fourth stirring vessel the suspension is heated to about 165° C. for two hours at 6.5 atmospheres excess pressure. To utilize the heat as much as possible the gaseous mixture of water vapor and SO<sub>2</sub> escaping from the third and fourth stages and chiefly comprising water vapor is introduced into the first two lower pressure stages and serves there for heating.

As a result of this treatment the originally produced monobasic aluminum sulfite has been converted into alumina hydrate and the mother liquor is practically free from alumina. The alumina hydrate can be separated by centrifuging, which operation is facilitated by the granular condition of the hydrate. The filtrate can be returned to the process or thrown out.

In order to prepare anhydrous alumina (Al<sub>2</sub>O<sub>3</sub>) the hydrate is calcined by direct heating in the usual manner.

Impurities are removed by dissolving the crude alumina hydrate in alkali liquor and precipitating it afterwards according to the known method. Investigation has shown that the solubility of the crude alumina hydrate obtained under the new process is just as good as that of crude alumina obtainable by calcination from monobasic sulfite.

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