

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station

PROJECT INITIATION

Date: October 10, 1974

Project Title: Fire Retardant Characteristics of Alumina Trihydrate Obtained from Kaolin

Project No.: A-1681

Project Director: Mr. W. H. Burrows

Sponsor: H & S Industries, Inc.

Effective 10/1/74 Estimated to run until 11/30/74

Project Agreement: Letter/Proposal dtd 9/23/74 Amount: \$ 1,974.00

Supports Required:

Sponsor Contact Person (s):

Mr. J. W. Hankins
H & S INDUSTRIES, INC.
P.O. Box 601
Dalton, Georgia 30720

Assigned to TAG Division

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GEORGIA INSTITUTE OF TECHNOLOGY
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Date: July 29, 1977

Project Title: Fire Retardant Characteristics of Alumina Trihydrate Obtained from Kaolin

Project No: A-1681

Project Director: W. H. Burrows

Sponsor: H&S Industries

Effective Termination Date: 3/31/76

Clearance of Accounting Charges: All Clear

Grant/Contract Closeout Actions Remaining: NONE

- Final Invoice and Closing Documents
- Final Fiscal Report
- Final Report of Inventions
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ENGINEERING EXPERIMENT STATION
GEORGIA INSTITUTE OF TECHNOLOGY • ATLANTA, GEORGIA 30332

March 25, 1975

H & S Industries, Inc.
P. O. Box 601
Dalton, Georgia 30720

Attention: Mr. J. W. Hankins

Subject: Interim Report, Project A-1681, "Fire Retardant Characteristics of Alumina Trihydrate Obtained from Kaolin"

Gentlemen:

At the beginning of the research, as stated in our proposal of September 23, 1974, it was our understanding that your company is interested in the possibilities of applying the ammonium bisulfate process to certain grades of kaolin for the purpose of obtaining an alumina trihydrate suitable for use as a fire retardant additive in carpet manufacture. For this application, the alumina trihydrate product would not be required to have as high a purity as that required in the electrolytic production of aluminum metal; consequently, a higher tolerance of such impurities as iron oxide, silica and titanium oxide would be allowable. In order to determine the susceptibility of kaolin to processing by this method and the degree of purity of the product alumina obtained, a laboratory bench-scale study was proposed.

Work to be Performed, as Stated in the Proposal of September 23, 1974:

1. Kaolin, supplied by H & S Industries, Inc., will be calcined by heating and stirring at 1,300° F for a period of time to be determined by experiment. The time will be that required to render the alumina readily soluble in hot ammonium bisulfate solution.
2. The calcined clay will be leached with hot ammonium bisulfate solution. The concentration of the solution, the temperature required, and the optimum pressure to be applied, if any, will be determined by experiment.
3. Ferric ion, if present in sufficient concentration to cause unacceptable discoloration of the product, will be reduced by addition of ammonium sulfite and separated as ferrous hydrate by fractional crystallization. If the level of iron is sufficiently low, no reduction or separation will be required.
4. The alum solution will be treated with aqueous ammonia to precipitate alumina trihydrate, which is the desired product. The trihydrate will be separated by filtration or centrifugation, and dried to the optimum water content.

The quality of the resultant alumina hydrate will be judged by compounding it with latex according to acceptable formulations of the carpet industry and testing the resultant compound for fire retardant characteristics.

Subsequent to September 23, 1974, it is our understanding, by verbal agreement with Mr. J. W. Hankins, that the testing of the quality and fire retardant characteristics will be performed by H & S Industries, Inc.

Experimental Process

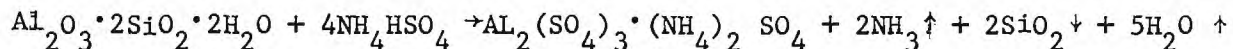
Very early in the research (See Work to be Performed, Parts 1 and 2), it became evident that calcination and leaching with hot ammonium bisulfate were undesirable processes, especially for a 1000 tons of alumina trihydrate per day plant. According to the Bureau of Mines Report 6573, 7.4 million BTU are required to dry and calcine sufficient kaolin to produce 1000 tons of anhydrous alumina. This value does not include the heat necessary to convert aluminatrihydrate to anhydrous alumina--a process not required in this study. The calcination process accounts for at least one half of the capital investment for a 1000 ton per day plant.

Experimental quantities of kaolin were dried at 110° C, ground to powder and calcined at 705° C in a small simulated rotary kiln. This process changed the powdered kaolin into hard pellets which required very difficult grinding before leaching. Following the calcination and grinding, the samples were leached with hot 50 per cent ammonium bisulfate solution. It was experimentally evident that complete leaching had not occurred even after prolonged heating. Only with concentrated hydrochloric acid for at least five hours can total leaching be assured.

Through fortunate inspiration and extensions of basic principles, it was decided to fuse raw "as received" kaolin with molten ammonium bisulfate. Obviously, if this approach were successful, parts 1 and 2 of the "Work to be Performed" could be eliminated. Furthermore, great economic savings in energy and capital investment would result if the process were adopted.

A trial experiment was performed and the results were most encouraging. A careful series of experiments were then performed on "as received" kaolin and kaolin pre-dried at 110° C to determine the minimum ammonium bisulfate to kaolin ratio. The ratio was determined to be 4.5:1, with "as received" kaolin yielding the better result. This ratio may possibly be reduced by further research on fusion procedure. The fusion time is four hours. The temperature of the fusion is 625° F, a tremendous improvement when compared with the standard 1300° F calcination temperature process resulting in enormous savings.

The chemical equation is:



In the industrial process, the ammonia and water would be recovered for inclusion in the precipitation of aluminum trihydrate process.

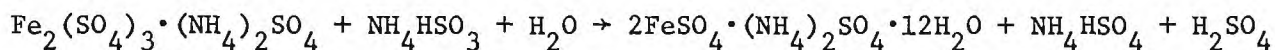
Following the fusion, the solidified melt was then dissolved in hot water with stirring. The amount of water needed is based on the original amount of ammonium bisulfate used in the fusion, ammonium bisulfate being the least soluble substance.

The remaining silica is removed by filtration, an easy process. However, the solution during filtration must be kept hot so as to prevent crystallization of the dissolved salts with its attendant mechanical difficulties.

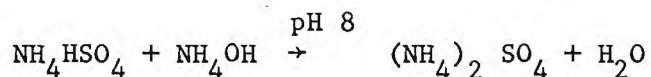
The silica is recovered as a fine white powder containing about 9% Al_2O_3 and less than 0.1% iron. Longer fusion times would further reduce the per cent Al_2O_3 , but the cost-benefit ratio consideration under large scale operation would determine the optimum fusion time. The silica may be an economic credit, as a filler for plastics, especially if the impurities were further reduced by leaching with concentrated hydrochloric acid, followed by washing and calcination to drive off any adsorbed hydrochloric acid.

Before aluminum trihydrate is precipitated from the hot solution, steps must be taken to prevent ferric hydroxide from precipitating before the precipitation of aluminum trihydrate to avoid iron contamination. Ferric salts precipitate at a pH of 3 to 4, aluminum salts precipitate at a pH of 7 to 8, and ferrous salts precipitate at a pH of 9 to 10.* Therefore, any ferric salts present must be converted to ferrous salts.

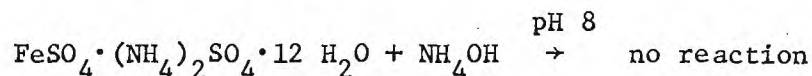
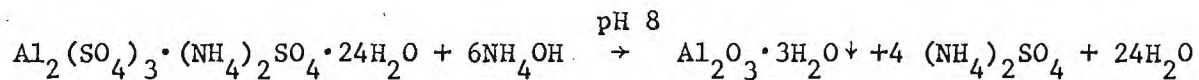
Experimentally, this conversion was accomplished by a small addition of sulfur dioxide in the form of ammonium bisulfite solution. The small amount of iron present did not present any major difficulties. The chemical equation is:



The solution is now ready for the precipitation of aluminum trihydrate with concentrated ammonium hydroxide. This solution now contains a large quantity of unreacted ammonium bisulfate, ammonium aluminum sulfate and some ammonium ferrous sulfate. It has a pH of 1 to 2. Concentrated ammonium hydroxide is added until the solution has a pH of approximately, but not exceeding, 8. The following reactions occur:



* PH is an inverse measure of the amount of acid present.



The aluminum trihydrate precipitates as a gel and is recovered by filtration. This filtration has proven to be a slow process. The gel was dried to constant weight at 230° F for analytical purposes. The dried hydrate is easily ground. The analysis of the hydrate will be discussed in the "Results" section.

The filtered solution now contains ammonium sulfate and ferrous ammonium sulfate. This removal of ferrous salt is accomplished by oxidizing the ferrous salt back to the ferric salt with oxygen, experimentally in the form of a small quantity of 30 per cent hydrogen peroxide. As previously stated, ferric salts precipitate as ferric hydroxide if the solution has a pH greater than 3 to 4. The filtered solution has a pH of 8, ammonium hydroxide having been added, hence ferric hydroxide precipitates out as the ferrous salt is oxidized. The ferric hydroxide is recovered by filtration. This step was performed without any experimental difficulties.

The filtered solution now contains only ammonium sulfate which is recovered by evaporation, an experimentally and industrially simple step. Experimentally, of 100 grams of ammonium bisulfate used, 95 grams of ammonium sulfate were recovered. No attempts were made to recover any ammonia lost during the fusion.

The recovered ammonium sulfate is converted to ammonium bisulfate and ammonia at temperatures greater than 455° F. The ammonium bisulfate is returned to the fusion reactor for recycling and the ammonia recovered for use in the aluminum trihydrate precipitation step. This step was not experimentally performed since it is well documented in the cited Bureau of Mines report.

Results

The total system is a closed cycle in terms of the ammonia and ammonium bisulfate except for attendant mechanical losses which can be minimized by proper equipment design. The high cost of ammonium bisulfate is therefore offset by recycling. The number of recycles is dependent on the attendant mechanical losses. If the losses were 0.5 per cent, then 200 recycles are possible as a first approximation. The actual cost of ammonium bisulfate, having a hypothetical cost of \$300 per ton, would be \$1.50 per ton, more realistically \$10 per ton. This price is competitive with the hydrochloric acid recycling process. The total system requires "as received" kaolin, heat, small quantities of sulfur dioxide (the amount dependent on the iron impurity level), rinse water and air.

The research "break through" fusion step itself, which eliminates the standard calcination step with its attendant high energy and high capital investment costs and the additional leaching step, increases further the competitiveness of the process. The low "kitchen oven" temperature required greatly simplifies heat loss reduction. Energy losses could be further reduced with heat exchangers. Also, the cheapest fuel sources could be used for these low temperatures.

The analysis of the recovered aluminum hydrate is:

Al_2O_3	NH_4^+	Fe^{+2}	SO_4^-	SiO_2	H_2O
58.93	0.00738	0.26	14.02	0.91	25.87% (by balance) per cent

The aluminum hydrate composition is calculated to be $\text{Al}_2\text{O}_3 \cdot 2.49 \text{H}_2\text{O}$ at a drying temperature of 110°C (230°F). The yield of hydrate³ extracted was 77.1%.

The high sulfate content is unacceptable not only since it is dead shipping weight but is detrimental to the latex carpet industry. Even low concentrations of sulfate compounds coagulate the latex emulsion.

The high sulfate occurs in the hydrate precipitation step since the physical form of the hydrate is a gel. Occlusion and/or co-precipitation occurs during the formation of gel. If the hydrate were crystalline, then the sulfate contamination would have been "forced out" of the crystal structure as the crystals form. This "forcing out" of the sulfate contamination does not occur if colloidal gel forms. Also, gels are not easily washed on a filter bed. Unlike crystalline materials, channelling occurs with the result that wash water flows around the gel and not through it.

Attempts were made at reducing the sulfate contamination. The sulfate content on the first filtration was 30%. By recovering and re-dispersing the gel in water and filtering four times, the sulfate content was reduced to 14%. A second method of reducing the sulfate content was tried by diluting the aluminum ammonium sulfate solution to a 10 per cent concentration, and the ammonium hydroxide concentration to 5% before mixing. The hydrate still contained 9% sulfate. It is doubtful that greater dilutions and increasing the number of re-dispersion and filtration would reduce the sulfate content to less than 0.1%.

Recommendations

The question to be answered is whether the above outlined process, assuming that the sulfate problem is solved, would be more competitive at this time than the Bayer process, or other processes, to produce aluminum trihydrate. The cost data, per ton, that we have at present for the various

processes for alumina based on a 100 tons/day plant are:

	Nitric Acid	Hydrochloric Acid	Bisulfate	Bayer
Anhydrous, \$/ton*	126	123	--	110
Trihydrate, S/ton	110	90**	71.24***	90

* William C. Ward, Jr. and John E. Husted, "Alumina from Kaolin," Engineering Experiment Station Report on Project A-1458, Georgia Institute of Technology, Nov. 1974, pp. 23-28.

** The aluminum trihydrate from the hydrochloric acid process has not been developed to date. The cost arrived at is assumed that a trihydrate process could be developed.

*** See Appendix A.

The trihydrate costs are not firm. If confidentiality could be maintained, then we recommend that a third party be consulted. Should better data become available, we will keep you abreast, if you so desire. It should be remembered that Bayer process costs are expected to increase because of the international cartel. Acid processes lend themselves to a wide variety of alumina bearing ores rather than being restricted to high grade ore as is the Bayer process.

We do have a number of possible sulfate removal processes to research, should you decide to continue supporting research on the ammonium bisulfate process. We estimate a 50 per cent chance of success. Should the estimated costs prove accurate, then the "pay off" is well worth the additional research expenditure. The research effort would be directed primarily to the sulfate problem.

The bisulfate cost data was also based on "streamlined" closed cycle based on the ion-exchange method to eliminate impurities. This ion-exchange step is currently successfully used in the nitric and hydrochloric acid processes. Not only does this step simplify the experimental process used, but it should produce an aluminum-grade reduction alumina.

In conclusion, a closed acid system was developed to produce aluminum trihydrate for the latex carpet industry. As a first approximation, it is quite competitive when compared with other processes if a sulfate problem is solved. The success of solving the problem is given a 50 per cent chance. The possibility exists that this process would also produce a reduction grade alumina.

H & S Industries, Inc.

-7-

March 25, 1975

Should there be any questions, an interview could certainly be arranged.

Respectfully submitted,

A solid black rectangular redaction box covering the signature of Albert D. Poulin.

Albert D. Poulin
Assistant Research Scientist

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APPENDIX A

Direct Costs:

	<u>Cost per Ton Alumina</u>
Raw Materials	
Clay at \$2.50/ton 35 Al ₂ O ₃	\$ 7.14
Ammonium bisulfate at \$300/ton--3% make up	10.00
Reagents for sulfate and iron removal	11.01
Chemicals for steamplant water treatment	<u>.12</u>
Total	\$28.27
Utilities:	
Electric power at 1.4 cent/kW-hr.	\$ 2.28
Water, process at 10 cents/M gal.	.32
Water, raw at 1 cent/M gal.	.07
Energy (oil, coal)	<u>6.29</u>
Total	\$8.98
Direct Labor:	
Labor at \$4.50/hr.	\$5.08
Supervision, 15% of labor	<u>.76</u>
Total	\$5.84
Plant Maintenance:	
Labor	\$3.39
Supervision, 20% of maintenance labor	.68
Materials	<u>2.72</u>
Total	\$6.79
Payroll Overhead, 35% of above payroll	\$3.47
Operating supplies, 20% of plant maintenance	<u>1.36</u>
Total direct cost	\$4.83
Indirect cost, 40% of direct labor and maintenance	\$5.05

APPENDIX A (CONTINUED)

Fixed Cost	<u>Cost per Ton Alumina</u>
Taxes, 1.0% of total plant cost	0.86
Insurance, 1.0% of total plant cost	0.86
Depreciation, 20-year life	<u>4.30</u>
Total	6.02
TOTAL OPERATING COST	<u>\$65.76</u>
ADDING 10% TOTAL OPERATING COST FOR OVERSIGHT	<u>\$72.34</u>

This is based on the nitric acid process with appropriate modifications and elimination, e.g. expensive rotary kilns.