THE EFFECT OF GLUCOISOSACCHARINATE ON THE

BAYER PRECIPITATION OF ALUMINA TRIHYDRATE

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SUMMARY

Bayer plant oxalate, which is generally defined to include degraded organic materials in Bayer liquor, has been blamed for inhibiting the precipitation of alumina trihydrate.

Our recent work has identified numerous organic compounds associated with plants' tray seed. Identified as some of the major fractions have been components of defoamer, sodium oxalate and an organic compound similar to glucoisosaccharinate. Glucoisosaccharinolactone has been synthesized in our laboratory and when added to a caustic solution this compound forms glucoisosaccharinates. Compared to the control test, this compound added in the minute amount of 0.8 g/L as organic carbon to synthetic green liquor lowered the precipitation yield by 17% and increased the quantity of particles finer than 20 μm by 23%. This study thus, has shown that unlike pure sodium oxalate, certain types of organic compounds similar to glucoisosaccharinate exist in Bayer liquor, which do have an adverse effect on the precipitation of alumina trihydrate.

INTRODUCTION

One of the important steps in the production of aluminum oxide by the Bayer process is the crystallization of alumina trihydrate. In this step, called precipitation, seeded, supersaturated sodium aluminate solution cools and decomposes to yield alumina trihydrate. The precipitation process is significantly affected by aluminate supersaturation, temperature, seed surface area, liquor impurities and the hydrodynamic conditions during precipitation. The economics of industrial production is controlled by the alumina yield and the generation of fine crystals. An uncontrolled process will lower the precipitation yield and accumulate fines, which is economically unattractive. In addition, fines will cause severe dusting and handling problems during the calcination and its subsequent electrolytic decomposition of alumina. There is evidence that certain types of organic compounds in the Bayer liquor stream are primarily responsible for the accumulation of fines and lowered yield, but definite identification is needed.

A variety of organic compounds with widely different properties exist in Bayer plant liquor. Some of them have been classified as the sodium salts of oxalate, formate, acetate, glycolate, humate and lignin compounds. Lever (1) classified them as the colored high molecular weight humic matter, "building blocks" which are compounds such as benzene carboxylic acids and phenolic acids, and low molecular degraded products such as oxalic acid. Generally plant oxalate which is defined to include degraded organic materials in Bayer liquor, has been blamed for inhibiting the precipitation of alumina trihydrate. However our work which is in good agreement with those reported in the literature (2,3), has shown that pure sodium oxalate in the usual concentrations of Bayer liquors, has little effect on precipitation.

In their studies of removing impurities from the precipitation system in Bayer process, Roberts et al (4,5), defined "sodium oxalate" to include degraded organic materials in solution. It was further reported (4), that in addition to oxalate, certain types of poisons were adsorbed on the surface of the seed hydrate. He referred to these as unknown ingredients in caustic aluminate liquor, which have a tendency to deactivate the seed surface. Yamada et al (6) reported the coprecipitation of humates with sodium oxalate during its crystallization process. Gnyra et al (7), reported that the high molecular weight colored humic compounds in Bayer liquor are responsible for the deactivation of Bayer hydrate and oxalate seeds, and increased the liquor stability with respect to alumina and oxalate solubilities. Pearson (2), briefly mentioned several organic impurities suspected of acting as crystallization "poisons" and referred to these as organic substances containing hydroxyl groups.

Several investigators (3,8), studied the effect of alcohol, sugar, glucose and starch on the hydrolysis of sodium aluminate solutions. Those compounds have not been positively identified to exist in Bayer liquor. Starch is added to the Bayer stream as flocculant to promote red mud settling. Starch consists of amylose and amylopection. It is postulated that the amylopectin fraction promotes flocculation by adsorbing onto the red mud particles and subsequently removed from the stream. Amylose, the labile fraction of starch, and cellulose compounds undergo degradation in hot sodium hydroxide solution, generating

saccharinates as the main degradation products (9). Solymar et al (10), investigated the effect of organics on alumina trihydrate crystallization. The organics used, were isolated from the Bayer stream and were claimed to be humate type compounds. Humic acid has been defined (11), as the fraction of soil alkaline extract precipitated by mineral acids and is insoluble in alcohol. It is a complex mixture consisting of numerous organic compounds such as phenolic and benzene carboxylic acids (12).

Our recent work has identified numerous organic compounds associated with Bayer plants' tray seed. Among which components of defoamer, sodium oxalate and an organic compound similar to glucoisosaccharinate were identified as the major fractions. Defoamer in the usual concentrations of Bayer liquor has been shown (13), to have little effect on precipitation. In order to carry out controlled experiments in the laboratory it was felt that glucoisosaccharinate should be produced synthetically. Glucoisosaccharinolactone has been successfully synthesized in our laboratory and this compound when added to a caustic solution forms glucoisosaccharinate. The effect of this organic compound on the Bayer precipitation of alumina trihydrate is presented in this report.
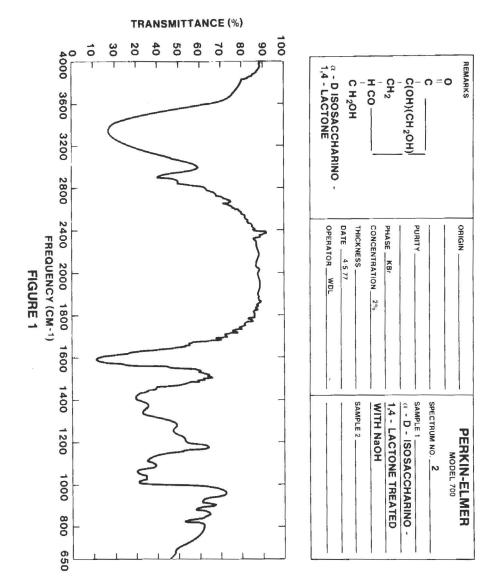
EXPERIMENTAL WORK

α-D-Isosaccharino-1,4-lactone was synthesized according to Kiliani's method (14). The melting point of the crystallized product is 93.5-$94^{\circ}C$ which agrees with that reported in the literature (14). The infrared spectrum of the glucoisosaccharinate is shown in Figure 1.
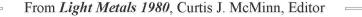
The synthetic and plant test tank liquors used in these experiments had the following composition:

	Synthetic	Plant Liquor
Al_2O_3	67.7 g/L	72.1 g/L
Caustic*	185.5 g/L	186.7 g/L
Total Alkali*	186.6 g/L	250.2 g/L
Organic Carbon	none	14.1 g/L

*expressed as gram per litre Na_2CO_3

Supersaturated sodium aluminate solutions were prepared by digesting pure alumina trihydrate with 3 litres of synthetic liquor in a nickel autoclave at $143^{\circ}C$ for 15 minutes. The composition of the solutions used was in the normal industrial range of about 185 g/L total caustic soda concentration TC, expressed as Na_2CO_3 equivalent and alumina to caustic soda weight ratio of about 0.66. Each litre of filtered green liquor was adjusted to the precipitation test temperature, the appropriate amount of glucoisosaccharinate in the concentration range of 0.2 to 0.8 g/L expressed as organic carbon was added, well mixed and the liquor was seeded with 50 grams of pure alumina trihydrate. All precipitations were performed using round polyethylene bottles, rotated at a constant temperature of $65.5^{\circ}C$. After 24 hours of precipitation, product alumina trihydrate was filtered using No. 42 Whatman paper, washed with 2 litres of hot distilled water, dried and weighed. Product size distribution was determined using the wet sieve and sedigraph analysis.

FIGURE 1

To determine the effect of glucoisosaccharinate on the precipitation of alumina trihydrate in green liquors obtained from bauxite test tank liquor digests, similar experiments were conducted by digesting bauxite containing 58.6% Al_2O_3, 1.09% SiO_2, 5.68% Fe_2O_3, 3.21% TiO_2 and 0.01% CaO using plant test tank liquor.
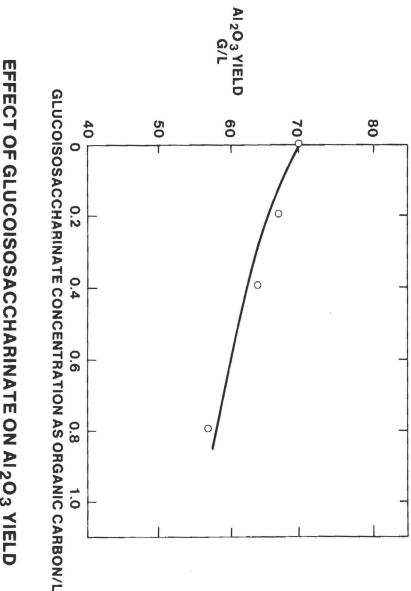
RESULTS AND DISCUSSION

The effect of glucoisosaccharinate added to synthetic green liquor in the amount of 0.2 to 0.8 g/L as organic carbon on the precipitation yield is shown in Figure 2. Compared to the control test the addition of 0.8 g/L of this organic lowered the precipitation yield by 17%, i.e., from 69.4 to 57.1 grams Al_2O_3 per litre liquor. Figure 3 shows the effect on precipitation in terms of the alumina to total caustic soda finish ratio (Al_2O_3/TC). The addition of this amount of organic increased the alumina to caustic soda finish weight ratio from 0.318 to 0.355. Its effect on the particle size distribution is shown in Figures 4 and 5. 0.8 g/L glucoisosaccharinate added to synthetic green liquor increased the quantity of particles finer than 20 μm from 22 to 45%.

Figure 6 shows that the addition of glucoisosaccharinate in the amount of 0.8 g/L as organic carbon to green liquor produced from a bauxite test tank liquor digest, lowered the precipitation yield by 18%. Figure 7 indicates that the corresponding effect on the contribution of fines is less significant than with synthetic liquor.
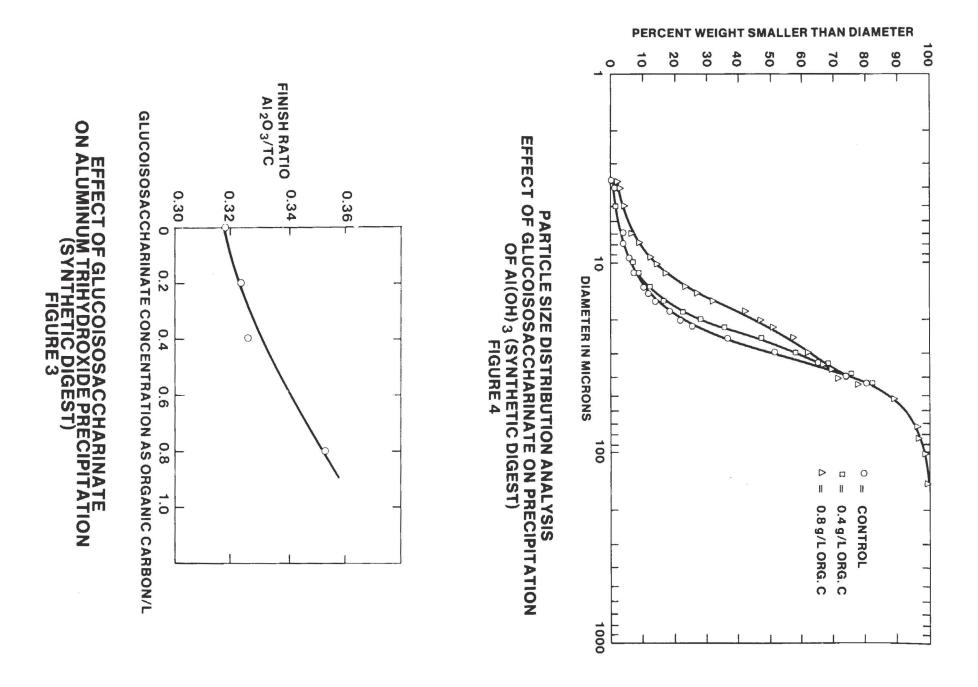
From these results, it may be postulated that glucoisosaccharinate, which has a molecular structure similar to glucose (or sugar), interacts with aluminate molecules on the surface of the hydrate to form soluble compounds, thereby stabilizing the aluminate liquor around the aluminum trihydroxide seed crystal surface. This results in a longer induction period in precipitation. It is known that when induction period precedes precipitation, outgrowths appear on the seed crystal surfaces. Interparticle collisions caused by mixing will dislodge and break them to form secondary nuclei, resulting in the generation of excessive fines and lower precipitation yield.
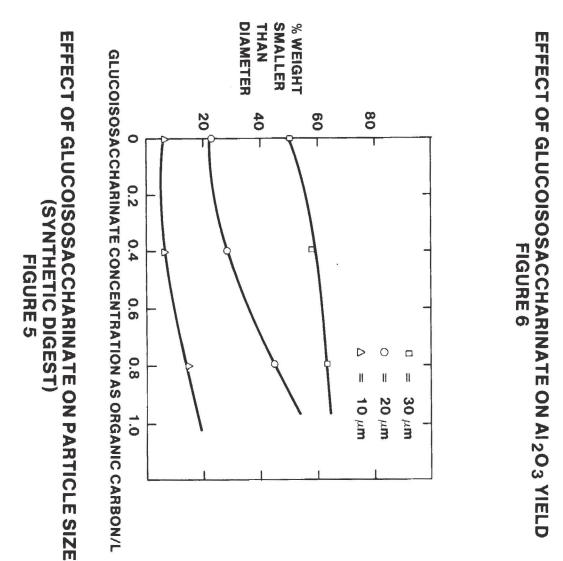
Significantly, this investigation has shown that, unlike sodium oxalate, certain other organic compounds similar to glucoisosaccharinate exist in Bayer liquor, which do have an adverse effect on the precipitation of alumina trihydrate.

EFFECT OF GLUCOISOSACCHARINATE ON Al₂O₃ YIELD (SYNTHETIC DIGEST)
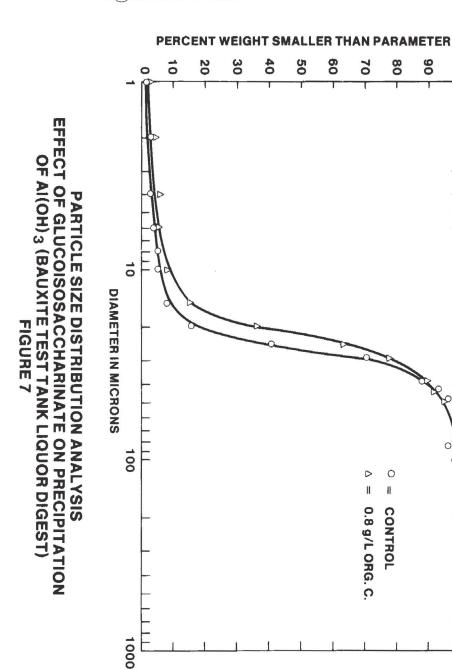FIGURE 2

EFFECT OF GLUCOISOSACCHARINATE
ON ALUMINUM TRIHYDROXIDE PRECIPITATION
(SYNTHETIC DIGEST)
FIGURE 3

PARTICLE SIZE DISTRIBUTION ANALYSIS
EFFECT OF GLUCOISOSACCHARINATE ON PRECIPITATION
OF Al(OH)₃ (SYNTHETIC DIGEST)
FIGURE 4

EFFECT OF GLUCOISOSACCHARINATE ON AI₂O₃ YIELD
FIGURE 6

Al_2O_3 YIELD g/L

GLUCOISOSACCHARINATE CONCENTRATION AS ORGANIC CARBON/L

O = SYN. DIG.

□ = BAUXITE
T.T. LIG.
DIGEST

EFFECT OF GLUCOISOSACCHARINATE ON PARTICLE SIZE
(SYNTHETIC DIGEST)
FIGURE 5

% WEIGHT
SMALLER
THAN
DIAMETER

GLUCOISOSACCHARINATE CONCENTRATION AS ORGANIC CARBON/L

□ = 30 μm
O = 20 μm
△ = 10 μm

PARTICLE SIZE DISTRIBUTION ANALYSIS
EFFECT OF GLUCOISOSACCHARINATE ON PRECIPITATION
OF Al(OH)₃ (BAUXITE TEST TANK LIQUOR DIGEST)
FIGURE 7

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