[redacted]

[redacted] LEAD PRODUCTS DIVISION

[redacted]

(See [redacted])

[redacted]:

In saturators and separators of [redacted] ammonium sulfate recovery units constructed by the Koppers Company in the Pittsburgh area lead linings have not given satisfactory service for two reasons. Highly corrosive gas has exposed lead linings to greater erosion from the hard ammonium sulfate crystals. Greatly increased (45 times) gas flow though the units has brought about much more severe operating conditions. Newer units handling 45,000,000 cu. ft. per day have used stainless steel with negligible corrosion or erosion for over four years.

Very heavy lead linings have given 17 years good service in the Pittsburgh Coke and Chemical Company saturator and separator units handling 100,000,000 cu. ft. of gas per day. Even these users of lead who should be satisfied are planning to go to stainless steel as lining material for saturators and separators in their by-product ammonium sulfate units.

Stainless steel provides a lining of greater hardness than the crystals formed, thus giving greater abrasion resistance and better service than lead linings which are in a hardness range lower than the crystals. Recent use of tar extractors have greatly increased the deterioration rate of lead linings as the layer of tar used to adhere to the lead forming a protective coating which prevented abrasion by the ammonium sulfate crystals.

Chemical Bulletin No. 3 was based on observations of the by-product coke plant of one of the larger steel companies. Since that time it has been learned that that company has instigated a broad program to determine where their own product, stainless steel, could be used in place of other materials. It may be expected that they will have full access to the stainless information obtained by the Koppers Company.

a. INTRODUCTORY HISTORY (See Chemical Bulletin No. 3, Part 1a)

This bulletin is supplementary to Bulletin No. 3 and presents newly obtained information on the same subject, i.e., the replacement of lead linings by stainless steel in saturators and separators. For years engineers have studied the problem of removing ammonia from coke oven gas and obtaining a better quality ammonium sulfate. It was found necessary to produce a moderately dry, about [redacted] with definite limits for size of [redacted] no crystal size grading had been done here as in Europe. To meet these conditions the dilute

acid bath was agitated by the use of air or gas, by mechanical mixers and the use of liquor circulation. Crystal size could thus be increased by bringing about better contact and longer time of contact of the supersaturated solution with the previously formed crystals.

During the late thirties when better quality competitive synthetic sulfate was produced in southwestern Canada, Koppers developed a mixing type saturator which gives better and longer time of contact of the supersaturated solution with the previously formed crystals. The salt produced meets high purity specifications for size and reduces the differential pressure loss. The first saturator of this type to use stainless steel linings and cracker pipe was built in 1941.

In addition to ammonium sulfate from coke plants large amounts are produced from synthetic ammonia which caused a decrease in nitrogen cost from $0.151 per pound in 1935 to $0.068 per pound in 1940 (Chemical Engineering, December, 1946). Since then the producing capacity for synthetic nitrogen compounds has been greatly expanded in both the United States and Canada. When European production is resumed further downward trends are probable.

In this highly competitive situation the coke oven operator is faced with the necessity of reducing costs to stay in the ammonium sulfate business or to find new products such as ammonium phosphate, ammonium nitrate or ammonium carbonate through carbon dioxide. These also may be produced from synthetic ammonia. There is apparently no good answer yet and his only recourse is to study recovery methods and make every possible effort to reduce costs. By using stainless 316 to replace lead linings in saturator-separator units their maintenance costs have been reduced from the level of excessive to negligible.

b. PROCESS AND EQUIPMENT DESCRIPTION

Coke oven gas, with or without reheat, enters the outer section of the saturator as shown on the drawing, passes through slots in the lower portion of the cracker pipe and bubbles through (theoretical seal depth, 4-3/4 in.) liquor containing 4 to 6% free acid. The gas leaving the bath level carries with it some sulphuric acid spray which removes additional ammonia. The gas passes through the acid separator, whirling around the inner section through which it finally leaves. The acid particles and the few droplets of tar that may still remain in the gas are thrown outward, impinge upon the walls and drain off through the bottom to the tar skimmer tank as shown.

The cracker pipe forms a ring around the liquid level of the saturator bath and the liquor is circulated as shown, being withdrawn through the top center of the bath from the area of ammonia absorption and supersaturation fast enough to limit its concentration of ammonium sulfate above the normal saturation and thus control the rate of new crystal formation. The circulating liquor passes up through the crystals which collect on the bottom of the saturator. Contact with the crystals desupersaturates the liquor in preparation for additional absorption and supersaturation when the liquor reaches the zone of contact with the gas at the top.

Crystals are pumped from the bottom of the saturator through lead pipe to a lead lined slurry feed tank from which the liquor returns by gravity as shown. A constant level overflow in the saturator maintains the liquor level at 4-3/4 in. above the distributor slots in the cracker pipe and with this seal depth over 99.8% ammonia is removed. The overflow runs off into the tar skimmer

tank and then to the mother liquor tank. [illegible] the gas prior to entering the saturator that it need be [illegible] of the tar skimmer tank only once or twice a week. [illegible] at a rate of several gallons per minute [illegible] the tar [illegible] at the top and [illegible] through the gas coming from the [illegible] any circulation of mother liquor through the tar skimmer and [illegible] is also added at the top of the saturator.

c. [illegible]

Lead has given good service for lining saturators and separators until the introduction of tar extractor units which removed the tar from the coke oven gas before it entered the saturators. Previously tar collected on the lead linings and cracker pipes and took most of the abrasion of the ammonium sulfate crystals. The old type was known as the P & A tar extractor which was 60-75% efficient and removed tar particles by impingement on plates placed perpendicular to the gas flow. The newer units, the Elix and Cottrell types, are even more efficient, with an almost complete removal of tar. When this came about it was found that a 1/4-in. lead lining was torn out in a few months time by the hard crystals of ammonium sulfate. As much as 36 tons of crystals may be formed per day in one saturator.

It must be remembered that with the increased competition the coke makers have had from the synthetic ammonia producers they have been forced to use much larger quantities of gas per day. Where a small plant might not produce more than 1,000,000 cu. ft. of gas per day, the larger companies have been forced to send more gas per unit of time through their ammonia recovery units. In one of the new saturators built by the Koppers Co., 2,000,000 cu. ft. per hour are put through the stainless lined equipment first operated in January, 1945. This particular unit is apparently serving as a pilot plant for study of operations with stainless linings and cracker pipes.

One stainless steel (316) unit, installed in 1942 has served in excellent fashion since that time. They have used 3/16-in. stainless for bottom linings which are still in service though said to be wearing thin in spots. Stainless steel cracker pipes, 1/4-in. thick, have been miked every year since but no measurable difference has been found while the one inch thick lead cracker pipes failed in a few months. The teeth between slots for gas exit from lead cracker pipes broke off, which apparently caused irregularities in crystal formation.

Acid separators are of the tangential type wherein the acid particles are thrown against the outer wall by the rapidly moving stream of gas which flows downward and around the vertical exit shaft. Since tar removal has been perfected, erosion troubles have set in. With the increased flow of gas through the units the acid particles have been thrown against the lead lining with even greater [illegible], causing failure through erosion. This is a localized failure, occurring principally at the top in the area where the acid particles are first thrown against the lining. Stainless linings have served with no trouble since first installed 4 to 6 years ago.

The Koppers Company engineers have tried [illegible] and separators without success. [illegible] responsibility for mother liquor tanks and [illegible] Copilt was formerly used with the old [illegible] stone for gas piping is obtained with [illegible] reduction in tank depth (now 3-5 in.).

d. CHARLES PLANT OPERATIONS

The saturators of the Pittsburgh Coke and Chemical Company consist of three units, one of these always being kept in reserve. The saturators are of the same general design as shown in the accompanying drawing and were installed in 1939. After 17 years service they have passed for the first time recently and the 1-in. lead cracker pipe and the 3-in. lead bottom linings were in good condition and have been put back in service. The only replacement was a new 30-lb. lead lining for the vertical section. The saturator is a 10-ft. unit through which is generally handled about 1,000,000 cu. ft. of gas per day.

The General Superintendent of this plant anticipates a lowering of cost of stainless steel and plans to change to this material when the price suits him.

CONCLUSIONS

In general lead has not given satisfactory service in the saturators and separators which are the major portions of the unit for recovery of ammonia. Failure may be traced to tar removal from the coke oven gas and the greatly increased flow of gas in an effort to lower costs and meet competition from synthetic ammonia producers.

1. Lead linings (sides and bottoms) of saturators have failed from abrasion by hard ammonium sulfate crystals since the protective tar is now removed from the gas.

2. Teeth between gas exit slots in the sides of one-inch thick lead cracker pipes break off in a few months under accelerated processing now used in large plants.

3. Lead linings in acid separators have failed by erosion near the entry port where acid particles are thrown from the gas by centrifugal force.

4. Tile was tried for saturator linings and was not well liked.

The competition of synthetic ammonia has caused coke plant engineers to bend every effort to increase production of ammonium sulfate, cut the cost of production and to obtain maximum use from production equipment.

1. Stainless steel, 316, 1/4-in. thick has served since 1942 as cracker pipes with no measurable change in thickness.

2. Saturator bottom linings of 3/16-in. stainless have served since 1942 with no repairs required, though said to be wearing thin in spots.

3. Even in small plants where operating conditions are relatively light and lead has given good service, plans are to change to stainless.

Lead will continue to be used without or less satisfactory service in the following units. The amount of lead used in these auxiliary units would be negligible to the heavy lead covered pipes and linings formerly used in the scrubbers and exhausters.

1. As plates and linings for valves and pumps for handling ammonia liquor and sulfuric acid.

2. Lead linings for the slurry feed tanks suffer very little abrasion and will probably continue in use.

3. In small plant operations, where gas flow is not high, lead has given good length of service for cracker pipes and linings for esturaters and separators but will probably be replaced if the plant capacity is increased.

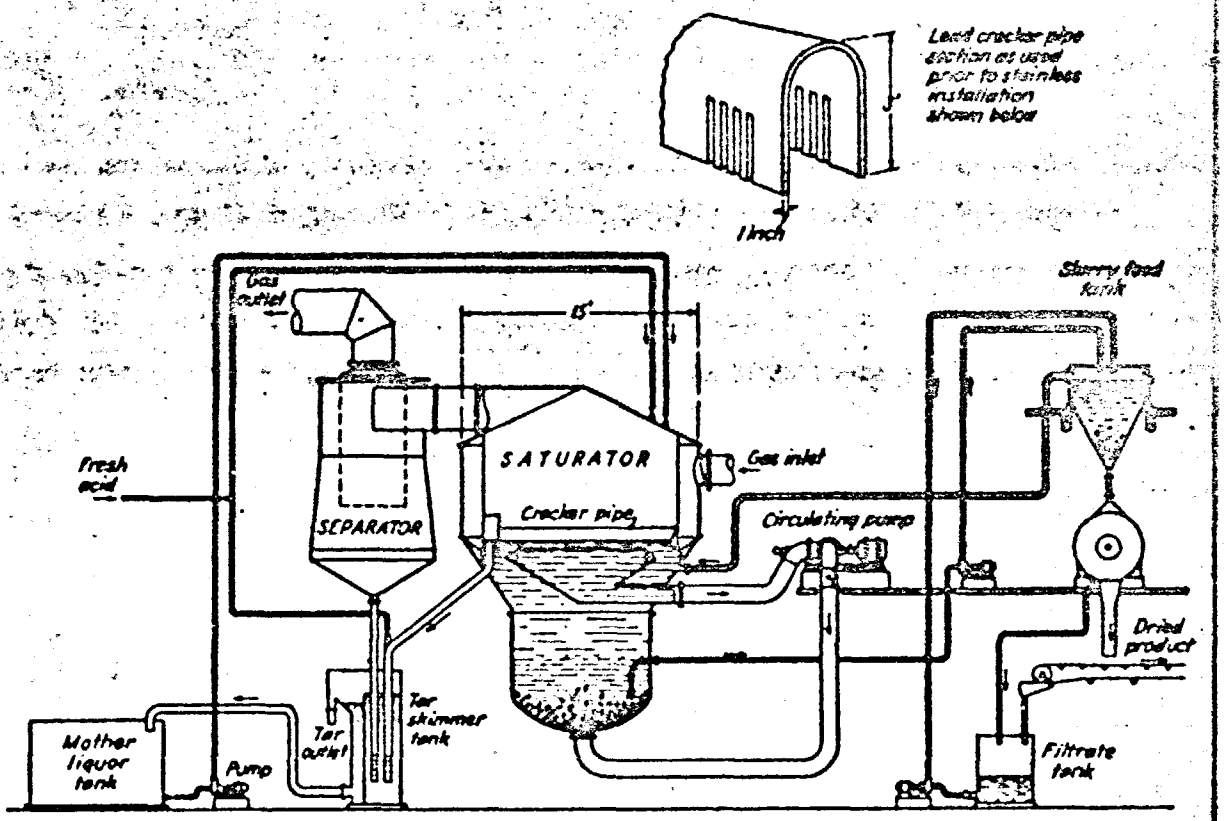
4. Filtrate tanks and tar skimmer tanks will probably continue to use lead linings.

5. Brick linings without lead have been used with success in mother liquor tanks and price will probably be the deciding factor.

JANUARY 17, 1947
By H. M. CHURCH, JR.

LEAD INDUSTRIES ASSOCIATION
420 LEXINGTON AVE. NEW YORK 17, N.Y.

CHEMICAL BULLETIN No. 8
BY-PRODUCT COKE PLANTS



Saturator and separator shown above with stainless steel linings - Type 316 For pipe, pumps and other units lead serves satisfactorily. Brick and steel linings have been used for Mother liquor tanks