[illegible]

[illegible]

[illegible] of [illegible] been used in the lining of various [illegible] in the [illegible]. The [illegible] problem of the removal [illegible] gas [illegible] which formerly covered the lead linings in the [illegible]. Stainless steel has [illegible] placed lead in some cases. The many lead [illegible] pipes are also a [illegible] of trouble and some have been replaced by stainless [illegible]. (See Part 1)

Lead lined pyridine towers have not given adequate length of service under conditions involving rapid heat changes with alternate acid and basic washes. (See Part 2)

PLANT LOCATIONS

Part 1: refers to the United States Steel Corporation by-product coke plant at their Clairton Works near Pittsburgh. The Koppers Co. engineers supplied the information on their stainless replacements of lead in their coke plants near Pittsburgh.

Part 2: refers to the pyridine tower in the Clairton Works of the United States Steel Corporation.

PART 1. AMMONIUM SULPHATE IN LEAD LINED EQUIPMENT

a. INTRODUCTORY HISTORY

When coal is distilled by heating in absence of air it is converted into a number of solid, liquid and gaseous products. The principal product by weight is coke but equally important are the by-products such as the solids anthracene, naphthalene, ammonium salts and cyanogen compounds. Liquids produced are water, tar and various oils, while gases consist of hydrogen, methane, ethylene, hydrogen sulfide, ammonia, nitrogen, and the oxides of carbon.

The average oven holds about 17 tons of coal and is intermittent, but as there are usually 30 to 80 ovens, each is staggered so that there is continuous production of gas of good average composition. This gas is cooled and it is modern practice to remove most of the tar, leaving three-fourths of the ammonia and about 80% of the light oils.

b. PROCESS DESCRIPTION

The gas is next brought into lead lined saturators where a 5-10% sulfuric acid solution forms solid crystalline ammonium sulfate by absorbing the ammonia. The gas is fed in under the surface of the liquid through a serrated distributor called a cracker pipe. For makeup, 60° Bé sulfuric acid is added and the acid concentration may be as high as [illegible] at the start of a charge. The temperature is kept around 60° C by the heat of neutralization and a reheater. The ammonium sulfate crystals may be removed from the bottom of the saturator by a compressed air injector or centrifugal pump and the mother liquor is returned to the saturators after the crystals have dryed.

c. EQUIPMENT DESCRIPTION

In the by-product coke plant of the United States Steel Corporation at Clairton, Pa., the saturators and separators are closely connected in function and in location by a steel reducing pipe (30 to 36 in. diameter) lined with 3/8-in. lead. The separators are closed steel tanks 14-ft. deep with a 14-ft. diameter lined with 1/4-in. lead. Saturators are slightly smaller and are lined with 3/8-in. lead. There are 14 sets of these and each unit uses 77,770 lbs of lead, including the huge serrated cracker pipe of one-inch lead with slots cut in the sides to allow the vapors to bubble through the acid.

d. DETAIL DESCRIPTION OF LEAD

The saturator separator combinations are completely lead lined but the entry and exit conduits are of steel. There is a 3/8-in. lining in the saturators and 1/4-in. lead in the separators. The two are joined by a reducing lead lined pipe, 30 to 36-in. Some of these linings have lasted 15 years and have given trouble only on the bottom.

e. LEAD PERFORMANCE

The ammonium sulfate crystals formed in the bottom of the saturators cause some abrasion troubles and while the lead linings as a whole are satisfactory, relining has been done on the bottoms several times. In the old days the tar in the coke oven gas used to be sufficient to cover the bottom of the saturator and afford protection for the lead. However, the modernized process includes the use of tar separators and extractors which remove most of the tar before the gas enters the saturators. Cottrell tar precipitators may also be used.

The other source of dissatisfaction are the one inch thick lead cracker pipes. The vertical slits cut in the sides break open due to heating and abrasive action and repairs are difficult and time consuming. They complain of excessive sagging though straps in various combinations have been tried. There is one saturator at a Massilon plant that has served for 21 years using a 3/8-in. lead lining and a lead cracker pipe one inch thick.

In the Koppers Co. by-product coke plants in the Pittsburgh area they have used stainless 316 cracker tubes which have given very good service for six years. They have also had good service from stainless bottom linings in the saturators and separators. It was claimed by Koppers Co. engineers that higher yields under stiffer conditions could be obtained by using stainless. They use monel in their

12,000 gal. agitators where temperatures are high and washing is done in both acid and basic solutions. Stainless will not do the job where both acid and basic conditions prevail alternately.

The stainless grade 316, is one of the austenitic chromium nickel steels which possess great corrosion resistance, greater strength at elevated temperatures, can be hardened only by cold work, and are easily fabricated by welding. The 316 grade is not stabilized with titanium or columbium and the analysis is approximately:

C = 0.10% Max.
Mn = 2.0% Max.
Si = 1.0% Max.
S & P = 0.04% Max.
Cr = 16-18%
Ni = 10-14%
Mo = 1.75-2.0%

PART 2. LEAD LININGS IN PYRIDINE TOWERS

a. INTRODUCTORY HISTORY

Pyridine (C_5H_5N) is a liquid with a strong and unpleasant odor, density 0.982 and boiling point of 115.3°C. This product of the destructive distallation of coal is derived from the tar bases. It can be halogenated, nitrated, sulphonated, and with reducing agents piperdine is formed by the addition of six hydrogen atoms to this carbon-nitrogen ring compound. Picolines may be formed by the addition of methyl groups. It is quite stable and is unaffected by oxidizing agents.

In 1940 crude and refined pyridine was valued at $296,441. This was in comparison with the total market value of $77,258,333 for all coal tar products.

Until recently pyridine bases have not been recovered in this country, but have been allowed to remain in the heavy oil with the phenols. The separation is accomplished by agitating the light oil with dilute sulfuric acid in a lead lined conical bottom tank with a lead covered propeller on a long shaft extending down to the bottom of the tank.

Many organic compounds and their aqueous solutions are soluble in pyridine and it is widely used because it is an excellent nearly netrual solvent. In a competitive way pyridine is used to inhibit the attack of phosphoric acid on steel thus allowing concentrated crude acid to be shipped in steel tank cars and also make possible the use of steel in place of lead in apparatus where concentrated crude acid is handled in making various sodium salts. It is useful in making an asthma remedy and is encountered as a combustion product of your daily cigarettes.

b. PROCESS DESCRIPTION

To separate pyridine from the tar bases the liquor is boiled for two hours at 106° C (222.8°F) in dilute sulfuric acid. The solution is next made neutral or slightly basic and given a reboil for two hours at the same temperature before emptying the tank and recharging.

The tower operates on an 8-hour cycle with rapid temperature changes between outdoor temperature and 223° F. For much of the Pittsburgh winter this temperature change would be in the range of 223° F and over.

c. EQUIPMENT DESCRIPTION

The 7,000 gal. pyridine tanks are cylinders 14 ft. deep, 9 ft. in diameter with a conical bottom. The bottom and sides are lined with 3/8-in. chemical lead and the top is covered with 3/16-in. lead. Steel supporting straps, 8 in. wide, are used and these are 29-30 in. apart. A lead covered propeller on a long shaft mounted through the top of the tank agitates the solution while a 1-in. coil supported near the top of the tank furnishes heat. The coils are 34. in. in radius and are now of stainless though they were once of 1-in. lead pipe.

d. LEAD INSTALLATION AND PERFORMANCE

In March, 1940, 1/4-in. homogeneous lead was the first type lead lining tried, but it gave them trouble within three months and was kept in use for a total service of two years only with excessive maintenance. Homogeneous lining was abandoned in March, 1942, when 1/4-in. sheet lead with straps, 30 in. apart, was installed. By April, 1943, it was found necessary to install 3/8-in. lead on the bottom and sides up to 5 ft. However by October, 1944, failures along the seams and sagging had progressed to such an extent as to require replacement with 3/8-in. lead all-over. This has served to date, but it is claimed only with high maintenance.

An abandoned stainless steel heating coil was seen discarded on the ground near the pyridine tower with heavy encrustations of corrosion products. It had replaced a lead coil, served for over five years, and just recently been replaced by another stainless coil.

CONCLUSIONS

The Koppers Co. engineers claim increased yields under stiffer operating conditions through the use of stainless 316 in their cracker pipes and bottom linings of saturators and separators. By using their own stainless products the steel companies can probably use stainless steel at a lower cost than homogeneously lead lined products and seem willing to make the change to stainless if too much trouble is encountered with the cheaper chemical lead. Stronger lead sections could possibly be obtained by redesigning the cracker pipe slits to a pattern of round and half-oval exit holes.

Lead linings in the pyridine tower have given poor service under exposure to extremes in temperature and concentration variations. The wide and fairly rapid variations in temperature coupled with alternate acid and alkaline washings would suggest a lining combination of lead and brick as a possible solution rather than push lead alone too far until the dissatisfaction brings about a change to another material.