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# LEAD INDUSTRIES ASSOCIATION

420 LEXINGTON AVENUE
NEW YORK 17, N. Y.

METALLIC LEAD PRODUCTS DIVISION

re Chemical Bull. No. 5

December 5, 1952

LEAD CHEMICAL CONSTRUCTION
BULLETIN NO. 6

SUBJECT: MANUFACTURE OF
LIQUID SULPHUR DIOXIDE

Attached is the latest "Lead Chemical Construction Bulletin," describing the construction and performance details of the newest method for the manufacture of liquid sulphur dioxide.

Previous Bulletins issued by the Lead Industries Association are:

Lead Chemical Construction Bulletin No. 1 - "Corrosives Versus Lead as a Construction Material"
Lead Chemical Construction Bulletin No. 2 - "The Use of Lead in the Pulp and Paper Industry"
Lead Chemical Construction Bulletin No. 3 - "New Developments Expand Use of Lead Construction"
Lead Chemical Construction Bulletin No. 4 - "Lead Versus Sulphuric Acid"
Lead Chemical Construction Bulletin No. 5 - "Lead in Modern Chemical Construction"

As long as our supply lasts, we will be pleased to send you additional copies of this or any of our previous Bulletins. Meanwhile, we shall continue to send new Bulletins to you so that they may be added to the series.

Very truly yours,

Robert L. Ziegfeld

Robert L. Ziegfeld
Secretary

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[illegible] CONSTRUCTION

COPY

Liquid sulphur dioxide of 99.997 percent purity is now being manufactured on a commercial scale by the "Absorption-Desorption" process using by-product roaster gases as the sulphur dioxide source and dimethylaniline as the absorption medium.

First put into commercial operation in the Fall of 1947, this new process successfully utilizes chemical and antimonial lead as the chief materials of chemical construction. Lead is used in this instance for its excellent resistance to the corrosive characteristics of sulphur dioxide in combination with dimethylaniline. Of particular interest from the viewpoint of both design and performance are the lead heat exchanger coils.

PROCESS (See Flow Diagram)

There are two plants in existence for extracting pure sulphur dioxide from impure dilute roaster gases by dissolving the dust-freed gas in dimethylaniline: the Selby, California, plant of the American Smelting and Refining Company and the Coppermill, Tennessee, plant of the Tennessee Copper Company. The process was developed and patented by E. P. Fleming and T. C. Fitt both of American Smelting and Refining (Patents No. 2,295,587 and 2,399,013) and has been licensed to the Tennessee Copper Company.

In the course of partially converting sulphide ore concentrates by roasting prior to smelting, a considerable quantity of sulphur dioxide gas is produced. Part of this gas is conveyed to the sulphur dioxide plant. After cleaning to remove excess solid foreign material, the gas enters an absorbing tower consisting of a series of bubble caps which force the gas into intimate contact with dimethylaniline, a weak organic base capable of dissolving sulphur dioxide. The quantity of gas that may be dissolved in the DMA depends upon the temperature; the cooler the liquid, the greater the quantity of gas dissolved. Conversely, when the liquid is heated the gas is expelled. During absorption the DMA liquid changes color from yellow to ruby red, increases in temperature and so must be cooled at intervals by re-circulating through a water cooled lead pipe coil situated outside the tower.

After the dimethylaniline passes through the absorbing tower it is essentially saturated with sulphur dioxide.

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To raise the temperature of the 'pregnant' liquid before sending it to the stripping tower is economically advantageous. This is accomplished by passing it through heat exchanger coils which serve a dual purpose: one to preheat the liquid before going to the stripping tower, thus saving steam, and the other to cool the 'stripped' liquid from the stripping tower. The 'pregnant' liquid is thus preheated in the heat exchanger, then passes through the stripping tower, where it is heated by indirect [illegible] heat, and [illegible] of its sulphur dioxide content. The heated, stripped DMA liquid leaving the stripping tower passes back through the heat exchanger, where it is cooled before reentering the absorbing tower. The sulphur dioxide from the stripping tower passes through a third bubble cap tower where concentrated sulphuric acid reduces its water content to less than 25 parts per million.

The gas now 99.9975 percent pure passes to a compressor where it is liquified under pressures of 40 to 50 psi and stored in a large steel tank. Shipment from the plant is made in tank cars and in smaller containers.

DESCRIPTION OF EQUIPMENT (Tennessee Copper Company Installation)

A. Absorbing tower and cooling coils.

The absorbing tower is of lead cage-type construction consisting of 12-lb. chemical sheet lead supported within a steel framework of columns and ring angles. Inside the tower are 19 bubble cap trays made of 8½ percent antimonial lead 3/4 in. thick and supported on bonded lead steel spiders. The bubble caps each 4 in. in diameter are constructed of antimonial lead.

As the gas is absorbed in the tower, the DMA liquid becomes heated thereby reducing the absorption efficiency. To compensate for this the hot liquid is pumped off at various levels to be recirculated through coolers and then returned to the tower. These coolers are constructed of 6 percent antimonial lead pipe, 1 in. in diameter in the form of two concentric helical coils, one nested within the other. Cooling water is sprayed over the outer surface through a circular lead distributor.

After the maximum volume of sulphur dioxide has been absorbed, the 'pregnant' DMA liquid is pumped from the absorbing tower through a heat exchanger.

B. Heat Exchanger.

The heat exchanger consists of four coils connected in parallel with each coil made up of two lead pipes, one inserted within the other as illustrated in the drawing on the last page. The larger pipe has an inside diameter of 2 in. with a ¼-in. wall thickness. The inside pipe is 1 in. in diameter with a wall thickness a little less than ¼ in. at the thinnest section. The exterior of the inner pipe has been extruded in the shape of a six-pointed star to provide support and also retain concentricity. In addition, the pipes were designed so that the areas of the space between the two is approximately equal to the cross-sectional area of the inner pipe. After extrusion in 10 and 12 ft. lengths, the smaller pipe is inserted into the larger and both are then coiled into units 11 ft. in circumference.

The saturated DMA containing 15 percent by weight of sulphur dioxide enters the heat exchangers at a temperature of 86° F and is calculated to leave at about 175° F. The stripped DMA enters the exchangers at a temperature of 195° F and is calculated to leave at about 110° F.

C. Stripping Tower.

After leaving the heat exchanger, the 'pregnant' liquid is pumped to the stripping or desorption tower where it is stripped of gas by passing through stainless steel clad pipe calandrias surrounded by steam. The [illegible] is recovered and [illegible]. The stripping tower is somewhat smaller than the absorbing tower and also differs in construction being made [illegible] of steel with a bonded lead lining; the steel and lead each ½ in. [illegible]. A bonded lead lining is necessary here because of the higher temperatures involved. Supported on bonded lead covered steel bars welded to the tower shell are 29 antimonial trays holding the bubble caps. After leaving the stripping tower the "water phase" is separated from the DMA liquid. The former is charged to the regenerator for recovery of contained DMA and the anhydrous dimethylaniline returned to the absorber circuit.

D. Other Equipment.

Drying of the purified sulphur dioxide gas is effected in a steel bubble cap tower, the lower portion of which is lined with 16-lb. lead to serve as a sulphuric acid storage vessel. The first tray in the drying tower is subject to weaker acid and wet gas and therefore is constructed of lead as in the absorbing and stripping towers. The upper six trays and caps exposed to 98 percent acid are of steel.

Most of the auxiliary equipment is constructed of lead. Clean sulphur dioxide gas enters the system through a 12-in. lead duct. The weak sulphuric acid feed tank for the absorbing tower is a steel tank lined with 16-lb. chemical lead. The solution collector from the soda and acid scrubbers is a cage-type vessel made of 45-lb. chemical lead. The DMA separating tank is similarly constructed with 30-lb. chemical lead. Two other DMA separating tanks are of steel lined with 8-lb. chemical lead as is a stripper water tank. The acid dilution tank using spent sulphuric acid from the drying tower and supplying weak acid to the absorbing tower feed tank is a steel shell lined with 16-lb. chemical lead. Lead pipe, an antimonial lead pump and valves conduct the acid to the point of use.

PERFORMANCE

Operator's of the Tennessee Copper Company's plant state that, "Dimethylaniline saturated with sulphur dioxide is acidic and its corrosive action is entirely similar to that of weak sulphuric acid. There is no specific data on its corrosion rate available; suffice it to say that there is no corrosion of any of the lead equipment apparent after nearly two years service."

The Selby plant of A.S.&R. was put into operation in October, 1947 with essentially the above equipment, excepting the heat exchanger coil which was first constructed of type 316 stainless steel. In the middle of 1948 the stainless steel coil failed and was replaced by the lead coil described above. The stainless steel apparently was unable to withstand the corrosive

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attack of the solution at the temperatures involved. The balance of the equipment constructed largely of lead is still functioning as originally anticipated including the heat exchanger coil now made of lead.

It is interesting to note that the stainless steel installation did not last a full year. Contrary to many popular conceptions stainless steel is not a cure-all for corrosion problems. It has its particular applications for which it is well-suited just as has lead but where corrosion resistance to sulphuric acid (below 96 percent) and corrosive sulphates is the chief concern then lead by all means should be considered first. When strength plus corrosion resistance is demanded then it is a comparatively simple matter to combine the strength of steel with the anticorrosive properties of lead in a properly strapped lead lined vessel or a bonded lead lined vessel. In this manner lead's superior corrosion resistance can be successfully adapted to a variety of conditions encountered in modern chemical manufacture.

OTHER REFERENCES

Chemical Bulletin No. 14 - "$SO_2$ Purification Plant" describes in detail the uses of lead as a material of construction at the St. Joseph Lead Company's Josephtown Zinc Smelter where by-product $SO_2$ is handled.

Chemical Bulletin No. 20 - contains a reprint of an article which appeared in "Chemical Engineering" entitled "Sulphur Dioxide Versus Construction Materials." This article describes in detail the performance of lead with sulphur dioxide in a variety of installations.

"Lead" (Vol. 18, No. 3, 1950) - Lead Heat Exchangers: pure sulphur dioxide production utilizes unusual design. Photos and drawings.

"Lead" (Vol. 19, No. 2, 1952) - Modern Lead Construction in Newest Liquid Sulphur Dioxide Plant. Photos and flow diagram.

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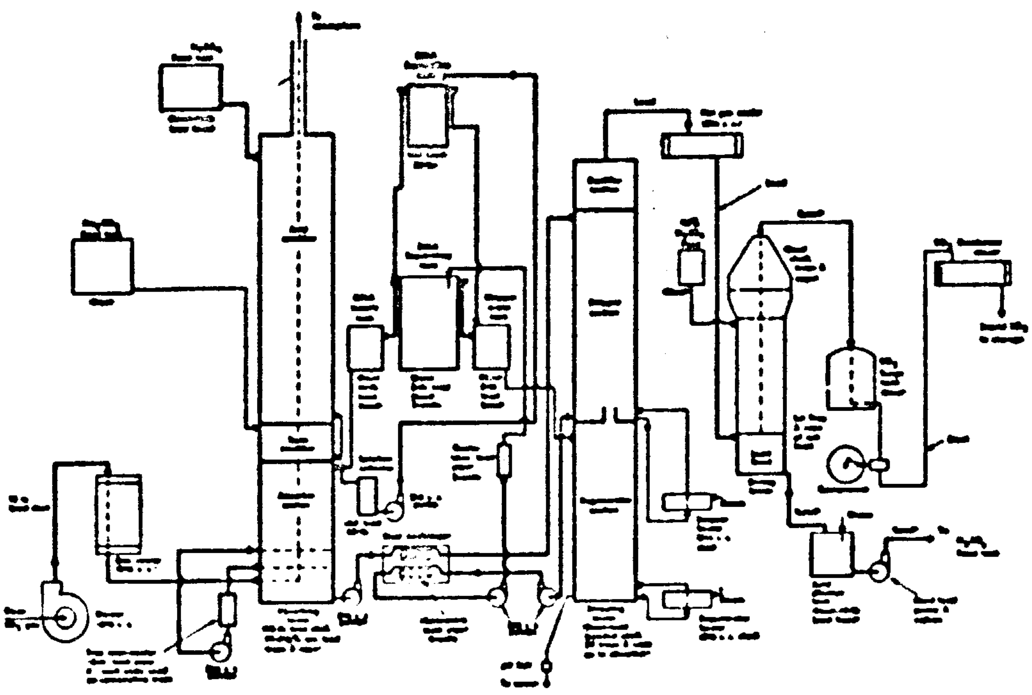

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| LIQUID SULPHUR DIOXIDE MANUFACTURE FLOW SHEET (DIMETHYLANILINE SOLVENT PROCESS)<br>R H ROLL NOVEMBER 1952 | LEAD INDUSTRIES ASSOCIATION<br>420 LEXINGTON AVE N. Y. 17, N. Y. | TENNESSEE COPPER COMPANY COPPERHILL, TENN. |

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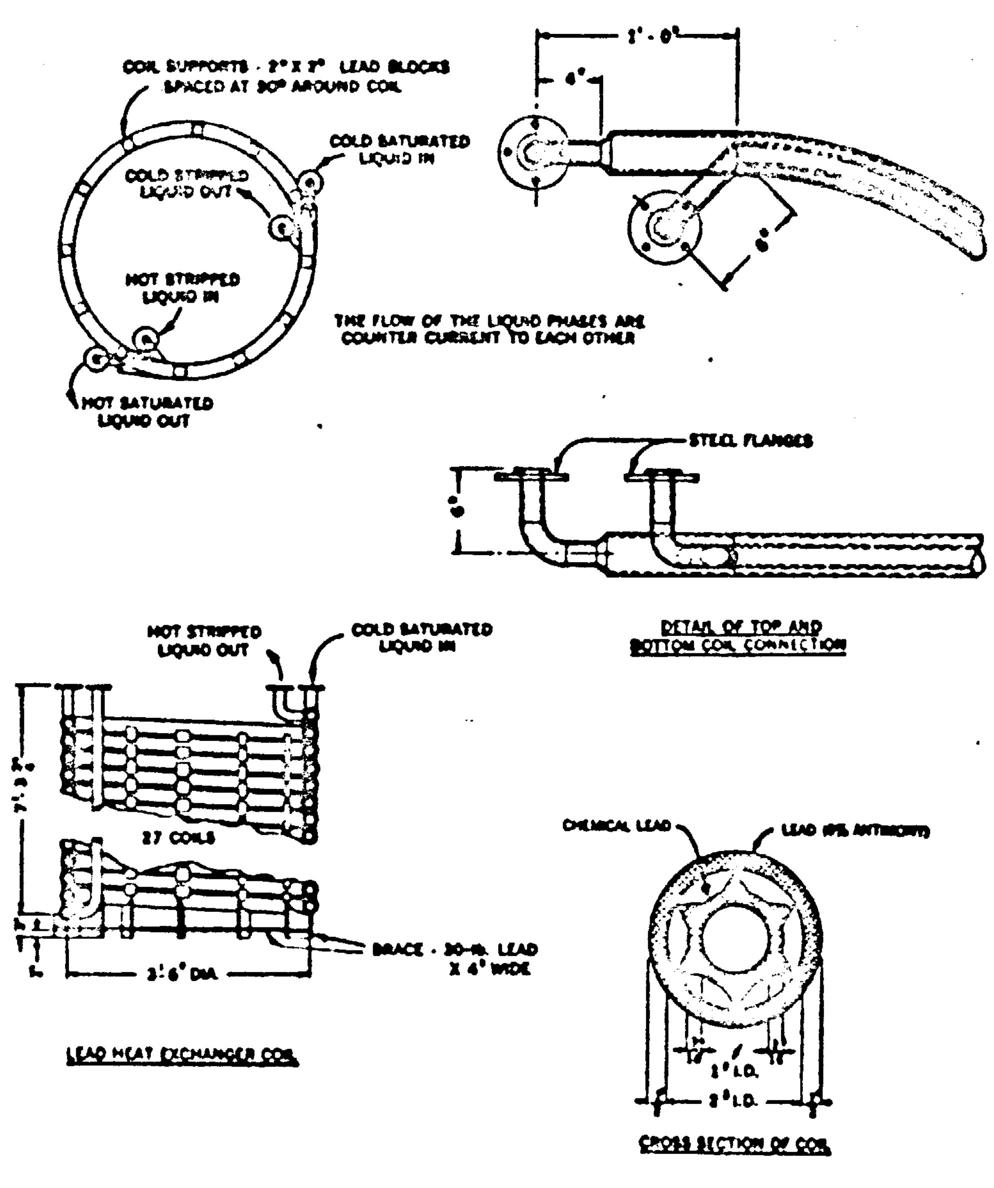


| LEAD HEAT EXCHANGER SYSTEM IN LIQUID $SO_2$ MANUFACTURE<br>K. H. ROLL   NOVEMBER, 1953 | LEAD INDUSTRIES ASSOCIATION<br>420 LEXINGTON AVE.   N. Y. 17, N. Y. | AMER. SMELTING AND REFINING CO.<br>SELBY, CAL. |
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