TRAINING PROGRAM

METHYL CHLORIDE PLANT

WESTLAKE, LOUISIANA

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along with some HCl from the oxychlorination section of the Conoco VCM plant.

A new second oyster shell pit to neutralize the waste HCl solution (unreacted HCl in methanol recovery unit bottoms) was designed by LCCP in 1971 and installed early 1973.

Other minor debottlenecking steps were taken by LCCP between 1971 and 1973 which increased the plant capacity to the present 100 MM pounds per year.

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HISTORY

METHYL CHLORIDE PLANT

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The methyl chloride plant was built at Westlake in 1961 as a joint 50/50 venture of Conoco and Ansul Chemical. Conoco operated the plant and Ansul marketed the product. Design capacity of the reactor was 20 MM pounds per year with plans to add a second reactor later. Design capacity of downstream equipment was 40 MM pounds per year. Conoco and Ansul did the process design based on pilot plant data from Ansul. Blaw-Knox built the plant. Shortly after startup, the plant operated at 28 MM pounds per year.

Soon after the original plant was built, a steam distillation packed column was built to recover unreacted methanol to improve yield and reduce water pollution. The column was inadequate to handle the large volume of low concentration methanol solution, and its performance was at best erratic.

Several changes and additions were completed prior to 1966 based on a design by PED which increased the capacity to 55 MM pounds per year. A second reactor, methyl chloride compressor, methyl chloride condenser, and water scrubber were added. Higher capacity packings (polypropylene pall rings replacing ceramic berl saddles) and internals were installed in the scrubber train. Higher capacity packing was also installed in the methanol recovery column, but its performance was still poor at these higher rates.

Near the end of 1966, a design was issued by PED to expand the plant capacity to 78 MM pounds per year and revise the methanol recovery column. A third reactor was added, partial condensers were added to replace the water scrubbers, the methanol recovery column was repacked with a high efficiency packing (Goodloe), and numerous minor changes and instrumentation were added. Construction was completed January of 1968, and the plant was tested for full capacity in October of 1968 after PPG were able to supply Conoco with enough HCl feed. The plant and methanol recovery unit performed adequately at 78 MM pounds per year and was able to attain 90 MM pounds per year when adequate HCl feed was available.

History (Continued)

In January of 1970, a debottlenecking design to 98 MM pounds per year was issued by PED. A second compressor aftercooler, third methyl chloride condenser, and a new larger vent gas chiller were added. Also the scrubber train was repacked again with still higher capacity packing (polypropylene Intalox saddles replacing pall rings) and higher capacity distributors and support plates.

In May of 1970, a major expansion design to 170 MM was issued by PED. Major items were a new separate scrubber and reaction train and a third methyl chloride compressor. Three contractors bid on the job; and while contractor selection was in progress, the decision was made not to build the expansion. Since tetramethyl lead (gasoline additive) was the main end use of methyl chloride at the time and the government had started to consider "getting the lead out," the sales projections changed considerably. Although the silicones portion of the business was increasing, it was determined that it was not increasing fast enough to justify the expansion alone.

In 1971, an opportunity to buy HCl at approximately half the then existing price from PPG became available. Olin were starting up a TDI plant which produced a by-product HCl stream with CO_2 as an impurity. Since CO_2 ends up in methyl chloride product, a design was prepared by LCCP to strip the CO_2 from the methyl chloride. The economics for this project were overwhelmingly favorable since the HCl feed was essentially "half price." The CO_2 removal facilities were started up in May 1973. The plant continues to use PPG as a backup HCl source along with some HCl from the oxychlorination section of the Conoco VCM plant.

A new second oyster shell pit to neutralize the waste HCl solution (unreacted HCl in methanol recovery unit bottoms) was designed by LCCP in 1971 and installed early 1973.

Other minor debottlenecking steps were taken by LCCP between 1971 and 1973 which increased the plant capacity to the present 100 MM pounds per year.

In 1972, Conoco acquired full ownership of the methyl chloride plant in return for some concessions to Ansul.

History (Continued)

An expansion design to 112 MM pounds per year was completed by LCCP early 1973, the equipment is on order, and the project is scheduled for completion in late 1973.

A capital budget design was prepared by LCCP in July 1973 which would increase capacity from 112 to 184 MM pounds per year. This design was basically the PED design of 1970 with some revisions to account for recent expansions. The old PED design would have increased capacity from the then current 98 to 170 MM pounds per year. However, the 184 MM pound per year expansion was dropped from this year's capital budget due to concern over raw material availability. This may come up again in the future, but firm plans do not include any expansion beyond 112 MM pounds per year at this time.

Future plans do include some emissions control equipment to be installed by May 1975. One proposed design by LCCP utilizes a carbon adsorption bed to remove methyl chloride product from the chiller vent gas and CO_2 stripper overhead gas. The adsorption beds would be regenerated under vacuum, and the methyl chloride would be compressed and recycled to the methyl chloride condensers. The other design would take the effluent vapor (containing methyl chloride and methanol) from the methanol recovery unit condenser vent, compress it, and recycle it to the scrubber train. Presently these three streams are vented to the atmosphere.

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PRODUCTION AND USES OF METHYL CHLORIDE

METHYL CHLORIDE PLANT

WESTLAKE, LOUISIANA

Approximately 500 MM pounds of methyl chloride are produced per year in the U.S. However, 300 MM pounds are for captive requirements and the other 200 MM pounds are marketed. Conoco market all of their methyl chloride making it the supplier of 50 percent of all methyl chloride available for sale in the U.S. Conoco are the only true marketer since the other 100 MM pounds sold are excess production from companies with captive uses.

The main uses of methyl chloride are as follows:

1. Silicones
2. Tetramethyl lead
3. Additive in synthetic rubber
4. Propellant gas in aerosol spray bombs
5. Weed killers

Silicones and tetramethyl lead combined account for approximately 75 percent of the methyl chloride end use. At present, usage for each product is about the same, but usage for silicones will increase while tetramethyl lead will decrease due to environmental regulations concerning lead content in gasoline. If the EPA delays the regulations, the drop in tetramethyl lead will be gradual; but if regulations remain the same, the drop will be rapid in 1975.

The third important use for methyl chloride is in synthetic rubber production. All other uses of methyl chloride such as weed killers and propellant in aerosol spray bombs are minor.

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CHEMISTRY

METHYL CHLORIDE PLANT

WESTLAKE, LOUISIANA

Methanol and HCl are reacted at approximately 320°F and 22 psig in the presence of 60-70 percent ZnCl solution catalyst to yield methyl chloride and water as shown in the following reaction:

$$CH_3OH + HCl \xrightarrow[320°F]{ZnCl} CH_3Cl + H_2O$$

Theoretical conversion for CH_3OH and HCl is approximately 97-98 percent at these conditions. Actual reaction conversions typically run above 94 percent for HCl and approximately 89 percent for methanol. Overall plant yields for both HCl and methanol are 94 percent. The methanol recovery unit recycle raises the overall methanol yield above reaction conversion.

An undesirable side reaction also occurs which produces dimethyl ether. This tends to reduce methanol conversion to methyl chloride.

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$

Operating experience has shown that this reaction can be minimized by limiting the reaction temperature to under 350°F and feeding a slight excess of HCl. Typical mol feed ratios are 1.05-1.10 HCl to methanol.

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PROCESS DESCRIPTION

METHYL CHLORIDE PLANT

WESTLAKE, LOUISIANA

Methanol is partially vaporized in the preheaters and mixes with anhydrous HCl vapor as the reactor feed. The HCl-methanol mixture is sparged through the zinc chloride catalyst solution in the reactor and reacts exothermically to form methyl chloride and water at approximately 320°F and 22 psig. Some dimethyl ether is also produced in a side reaction.

The reactor effluent vapor enters the partial condensers where most of the water vapor and unreacted HCl and methanol are condensed at 85°F. The vapor liquid mixture is separated in the vapor-liquid separator. The liquid HCl-methanol solution is fed to the methanol recovery column and the impure methyl chloride vapor enters the brine scrubbers.

Methanol in the feed to the methanol recovery column (approximately 8%) is separated by steam distillation from the HCl solution and taken overhead at a concentration of approximately 80%. The recovered methanol is recycled to the reactors. The HCl solution bottoms is used to preheat the column feed and is then neutralized in an oyster shell pit or with waste caustic before discharging to settling ponds.

The vapor mixture to the brine-caustic scrubbers is mostly methyl chloride with about 2% dimethyl ether and small amounts of water and HCl vapor. Inerts such as nitrogen and CO_2 are also present. The brine-caustic scrubbers neutralize all of the HCl. Small amounts of methyl chloride product liquid are flashed into the scrubbers as a direct contact refrigerant to counteract the heat of reaction between HCl and NaOH. Brine-caustic is circulated from the brine-caustic receivers to the scrubbers which are packed with polypropylene intalox saddles. Fresh brine-caustic is metered into the second brine-caustic receiver and spent brine-caustic is discarded from the first brine-caustic receiver.

The vapor flows through a knockout pot before entering the sulfuric acid scrubbers. This prevents entraining caustic solution into the acid scrubbers during upset operation.

Process Description (Continued)

The sulfuric acid scrubbers remove the dimethyl ether and water from the methyl chloride stream. Methyl chloride refrigerant is flashed into each scrubber to compensate for the heats of solution and lower the temperature to 50°F out the last scrubber. Acid is circulated from the acid receivers to the scrubbers which are also packed with polypropylene intalox saddles. Fresh 93% H_2SO_4 is metered into the last acid receiver and spent acid is removed from the first acid receiver and goes to storage. The spent acid (approximately 75% H_2SO_4) is shipped to another processor where it is processed to remove water and dimethyl ether.

The methyl chloride flows through a knockout pot to prevent any sulfuric acid from entering the carbon bed or compressor suction. The carbon bed removes impurities which would foul the compressor cylinders.

The methyl chloride is compressed from 10 to 165 psig in the two-stage reciprocating lubricated compressors and is cooled to 120°F in the aftercoolers. The oil from the compressor cylinders, along with a small amount of condensed methyl chloride, is separated from the main process vapor stream in the oil knockout pot. This material goes to slop storage and is recycled to the process.

The methyl chloride vapor is condensed at 100°F and 160 psig. Most of the CO_2 also condenses in the methyl chloride stream.

The condenser vent gas containing methyl chloride, nitrogen, and some CO_2 goes to a vent gas chiller which uses methyl chloride as a refrigerant to condense most of the remaining methyl chloride before venting the gas to the atmosphere at 20°F. The refrigerant methyl chloride is recycled to the compressors.

The methyl chloride product containing CO_2 goes to intermediate storage where it is pumped to the CO_2 stripper. Heat for stripping is furnished by a steam reboiler. The CO_2 rich vapor is taken overhead and goes to an overhead condenser similar to the vent gas chiller. Most of the methyl chloride in the gas stream is condensed and recovered

Process Description (Continued)

before venting the CO_2 stream at 40°F. As in the vent chiller, methyl chloride is used as a refrigerant and is recycled to the compressors.

The purified methyl chloride product (stripper bottoms) is cooled to 100°F in the product cooler and flows to product storage where it is loaded into tank cars.

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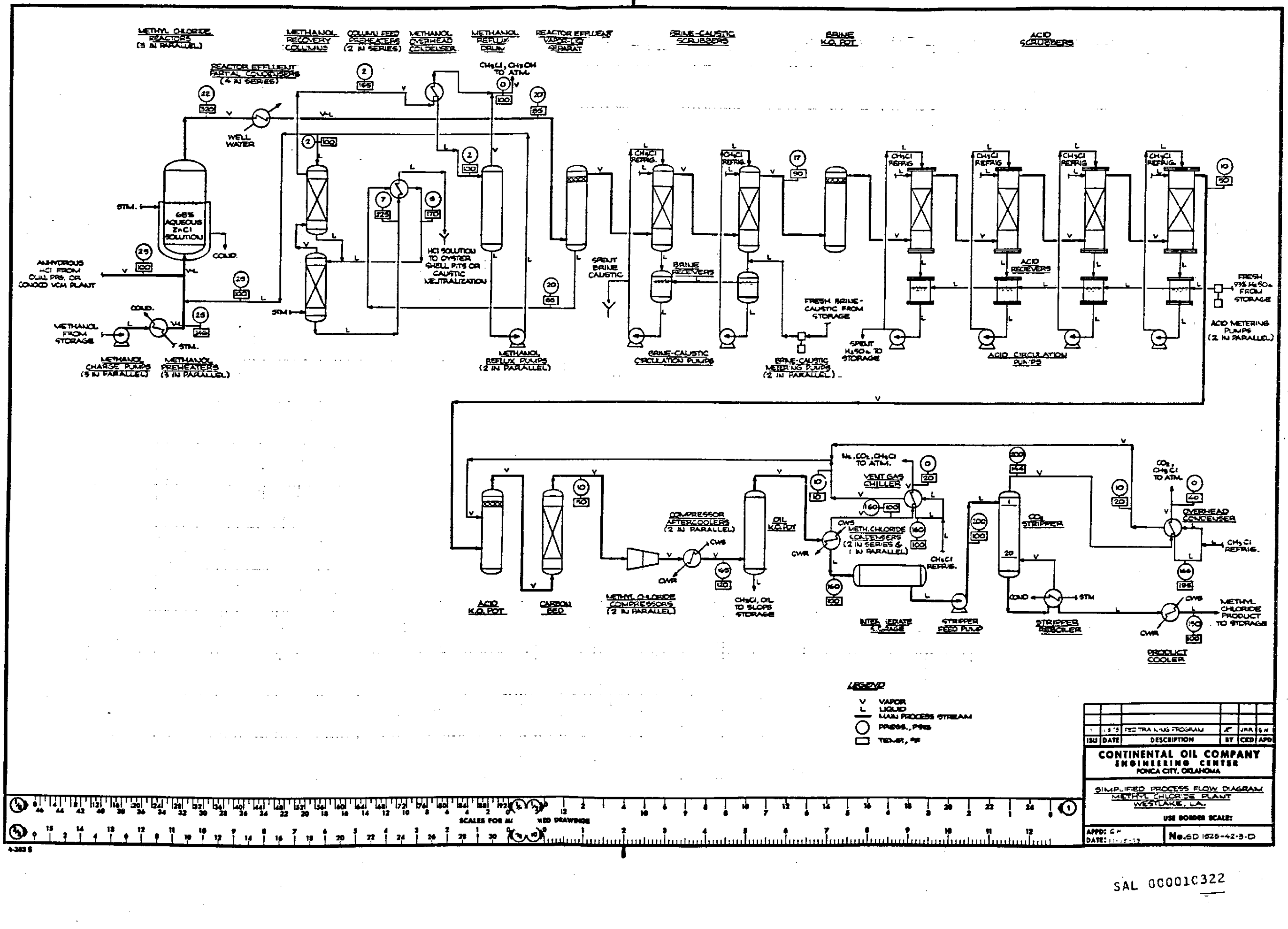

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