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ETHYL CORPORATION

Inter-Office
Correspondence

TO: Dr. R. C. A. Bock — Baton Rouge

FROM: K. F. Cast — Baton Rouge

SUBJECT: Tetramethyl Lead Production — December 8, 1959

Facilities are presently being designed for production of six million pounds per year of tetramethyl lead (TML) in idle TEL autoclaves at Baton Rouge. Customer requests for TML led to development of the manufacturing process and a contract for sale of the material is expected soon. Funds for construction of the facilities will be requested at the December board meeting. Plans to market TML for use in gasoline and results of field hygienic tests of its use will be discussed soon with the Surgeon General by Dr. Kehoe. Present plans, based on favorable results from the items above, would allow commercial production to begin in March, 1960.

This letter will advise you of (I) the materials used in the manufacture, (II) the planned method of operation, (III) the scope of the conversion and (IV) the precautions taken to insure safe operation when handling TML and its raw materials. The information included applies only to the manufacturing steps to be accomplished at Baton Rouge. Production and blending of alkyl aluminum catalyst at Orangeburg are not covered. No information is included on the blending and other handling of the product by customers.

I. Materials Used in TML Manufacture

The reaction to form TML is as follows:

$$4\ MeCl + 4\ NaPb \xrightarrow[120^\circ C,\ 200\ psig]{Me_3Al_2Cl_3 + Diluent} PbMe_4 + 3\ Pb + 4\ NaCl$$

Materials handled in the course of manufacture are:

A. Methyl chloride, CH_3Cl - properties similar to ethyl chloride, higher vapor pressure.

B. Sodium-lead alloy, NaPb - same alloy as used for TEL reaction.

C. Methyl aluminum sesquichloride, $Me_3Al_2Cl_3$ - catalyst necessary to make reaction take place. It will be handled at Baton Rouge only as a dilute solution in toluene as described below.

D. Toluene, $C_6H_5CH_3$ - used as a carrier for the catalyst and as a diluent in TML. It will be handled at Baton Rouge only as a solution with sesquichloride or TML as described below.

E. Catalyst-diluent solution - a solution containing 7.85% methyl aluminum sesquichloride in toluene. This solution is flammable but not pyrophoric. When exposed to air, the sesquichloride reacts to give off a white smoke and the solution foams vigorously when contacted with water. It will be stored and handled beneath an inert gas to protect the sesquichloride from decomposition.

F. Tetramethyl lead, $Pb(CH_3)_4$ - the product, which is a material similar to TEL. It will be produced as a 70% solution in toluene and will not be handled except in this diluted form. TML is much more volatile than TEL. However, during development testing in E-2 and E-4 autoclaves, lead-in-air analyzers located in positions most likely to detect airborne contamination, did not indicate excessive lead levels except during maintenance jobs requiring contaminated lines to be opened. Decomposition is much more difficult to initiate with undiluted TML than TEL, but once initiated the decomposition is much faster. When diluted with toluene, the rate of decomposition is greatly reduced. Small scale tests in vented bombs, which simulate geometrically the TEL autoclaves, showed that TML diluted with toluene can be heated above the temperatures normally expected in commercial operation, then ignited with thermite, and the resulting reaction vented with no further pressure rise after disk rupture.

All other materials encountered in the TML reaction are the same as used in TEL manufacture. Quantities are the same or are reduced in all cases except for graphite. Graphite is added to the TML methylation at the rate of 35 pounds per charge as compared to a rate of one pound of graphite per TEL charge.

II. Method of Operation

In most respects the TML operation is almost the same as the TEL operation. Methyl chloride will be received in tank cars and unloaded into storage tanks. The unloading will be accomplished by vaporizing a portion of the liquid from the car and using the gas thus formed to force the remainder of the liquid from the car.

Sesquichloride-toluene mixture will be blended at Orangeburg and shipped by tank car to Baton Rouge. The tank cars will be unloaded with a pump into inert blanketed storage. As the cars are unloaded they will be filled with nitrogen.

The methylations will be carried out on a 4-1/2 hour cycle using 3500 pound alloy charges. An alloy charge and its graphite will be fed to the autoclave as is presently done in the TEL reaction. Sesquichloride-toluene mixture will be pumped from storage into the existing ethyl chloride scale tanks on the fifth floor and then charged to the autoclaves. Methyl chloride is pumped from storage through automatic feed devices into the autoclaves. Autoclave operating pressure is 200 psi and the operating temperature ranges from 60°C to 120°C. Noncondensible gases are sniffed off during the reaction. Residual methyl chloride is vented to the recovery system after the reaction and the autoclave contents are discharged to the steam still.

Preparation of the steam still is the same as for TEL except that smaller quantities of still aids are used and no naphthalene is used. Distillation is accomplished by direct steam addition and it occurs quickly at about 87°C. The toluene and TML distill together and are not separated. There is no secondary distillation of methyl chloride. The residue in the steam still is discharged to the sludge pits for recovery of its lead in the sludge furnace.

The TML-toluene product is washed to remove any graphite and then blended. Aeration is not necessary since product sample analyses show only trace quantities or no bismuth. Blending is the same as with TEL except that no inhibitor is added to the fluid since laboratory tests indicate that decomposition is negligible.

Methyl chloride vented from the autoclave is condensed in the recovery system and recycled without purification. The relatively high volatility of TML results in about 10% TML in the recovered methyl chloride. This material is pumped to methyl chloride storage and diluted with fresh methyl chloride before recycling. Because of the recycle of recovered material, the methyl chloride fed to the autoclaves normally contains three to four percent TML.

III. Scope of the Conversion

TML production will be started at the rate of six million pounds per year in five autoclaves in "C" or "E" Building.

Tank car unloading facilities will be provided for methyl chloride and sesquichloride-toluene solution. Two methyl chloride storage tanks will be provided at the ethyl chloride intermediate storage area. One sesquichloride-toluene storage tank will be provided west of the ethyl chloride recovery columns. Feed and transfer pumps and necessary piping will be provided. All other major pieces of equipment will be converted TEL equipment.

Quantities of major materials handled at design production rates are shown in the following table.

Material	Pounds/Day
Methyl Chloride	37,700
Toluene-Sesquichloride Soln.	10,100
NaPb Alloy	93,500
TML-Toluene Product	29,500

IV. Precautions in Handling TML and Raw Materials

A. Methyl chloride in all cases except tank car unloading, will be contaminated with three to ten percent TML. It will, therefore, be treated as an organic lead contaminant. The precautions used to protect personnel from exposure to TEL will be applied to methyl chloride, except that lead-in-air monitors will not be used at the methyl chloride storage or unloading areas.

No monitor will be used at the unloading area because the material is not contaminated. The methyl chloride storage tanks are not under roof and a monitor is not necessary.

B. Toluene-sesquichloride solution is slightly toxic because of the toluene content and will produce chemical burns because of the sesquichloride content. Air and gas masks will be provided for maintenance or for use in event of spills or leaks where dangerous concentrations can occur. Protective clothing such as gloves, goggles, etc. will be required where contact with the material can occur.

C. TML-toluene product is an organic lead contaminant very similar to TEL, except that its volatility is much greater. The same precautions observed in handling TEL will be observed in handling the TML-toluene product.

All of the above materials are flammable and necessary fire prevention precautions must be taken such as restricting use of spark or flame producing devices, grounding pipe lines, etc.

Any suggestions from the Medical Department concerning TML manufacture will be welcomed.

J. H. Browning

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JHB:paa