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ETHYL CORPORATION
Medical Department
Baton Rouge, Louisiana

INDUSTRIAL HYGIENE SURVEY

of

Baton Rouge Plant

Preliminary Survey of Materials and Processes

in

TEL OPERATIONS

I. General

The sector of the plant designated as "TEL Operations" utilizes sodium from the Sodium Area, ethyl chloride and methyl chloride from the Hydrocarbon Area, and purchased lead metal to produce the lead alkyls. Antiknock compounds are principally blends of these alkyls with ethylene dichloride (EDC) from the Hydrocarbon Area and ethylene dibromide (EDB) from the company's bromine plant in Arkansas.

The writer had the benefit of walk-through tours with Mr. Al Carville and Mr. R.H. Jones, along with a detailed briefing by Mr. Jones. An excellent condensed account by Mr. Jones of the way lead alkyls are produced is attached as Appendix B. I recommend this version on processing for those who have no need for detail.

Materials involved. The purpose of this report is to provide a general description of the operations in the TEL Area, and then identify the materials involved, both in the processes and the supportive operations. While these materials are normally mentioned in the text of the report, they are identified more completely in Appendix A.

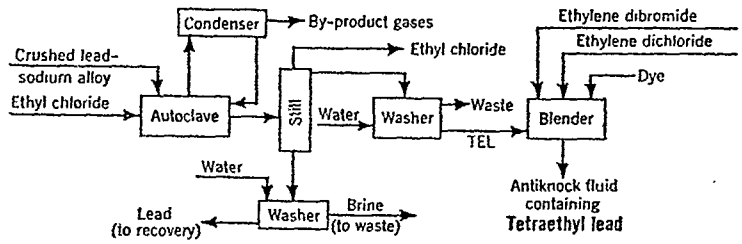
General Process Description. The following two pages from Faith, Keyes, and Clark ("Industrial Chemistry") give a thumbnail description of the TEL manufacturing process.

TETRAETHYL LEAD

(LEAD TETRAETHYL, TEL)

$Pb(C_2H_5)_4$

From Ethyl Chloride and Lead-Sodium Alloy



Reaction

$$4NaPb + 4C_2H_5Cl \rightarrow Pb(C_2H_5)_4 + 3Pb + 4NaCl$$

85–90% yield (based on sodium)

Material Requirements

Basis—1 ton tetraethyl lead (100%)

Sodium	650 lb
Lead (theo)	1,280 lb
Ethyl chloride (theo)	1,595 lb
Catalyst	15 to 50 lb
Ferric chloride	Small
Sodium thiosulfate	Small

Process

Tetraethyl lead is made by reacting a lead–sodium alloy with ethyl chloride in an autoclave. The crude product is purified by vacuum distillation

An alloy of 9 parts lead and 1 part sodium is prepared in an alloy pot, cast, crushed, and cooled. All operations are carried out in an atmosphere of nitrogen. The crushed alloy is charged to a horizontal autoclave fitted with a heavy-duty agitator. Ethyl chloride is then fed slowly into the autoclave until 70 per cent excess of theoretical has been added. Heat evolved by the reaction vaporizes part of the ethyl chloride, which is then condensed in a reflux condenser and returned to the autoclave. This vaporization, supplemented by circulation of a coolant in the autoclave jacket, keeps the reactants at 65 to 75°C (50 to 60 psi). Any gaseous by-products are vented through the reflux condenser. Various catalysts (aldehydes, acids, ketones, esters, etc.) in concentrations of 1 to 2 per cent are mentioned in the patent literature and may be used to speed the reaction.

When the reaction is completed, the autoclave is vented into batch-type steam stills partly filled with water. The last trace of ethyl chloride is vaporized and then the TEL is distilled from the spongy metallic mass. To prevent "balling" of the solid material a mixture of ferric chloride and sodium thiosulfate is added to the reaction mass fed to the still. After vaporization of the crude TEL, the remaining lead-salt sludge is washed free of sodium chloride, partially dried, and resmelted in a recovery furnace, since only about 25 per cent of the lead fed to the autoclave enters the reaction.

The crude TEL from the still is washed, settled, and then pumped to blending equipment where it is mixed with appropriate amounts of ethylene dibromide, ethylene dichloride, and a dye. The product, motor antiknock fluid, after filtration, is shipped to refineries for blending with gasoline. The current composition of motor fluid is 61 per cent TEL, 18 per cent ethylene dibromide, 19 per cent ethylene dichloride, and 2 per cent dye. Aviation fluid contains no ethylene dichloride, but the same amount of TEL.

Tetramethyl lead (TML) can also be made by a process similar to that described in which methyl chloride is used in place of ethyl chloride. If mixtures of ethyl and methyl chlorides are used, equilibrium conditions can be adjusted to put various amounts of methyl and ethyl radicals on the lead atom to give various mixed lead alkyls. The mixed compound may also be produced by redistribution or equilibration reactions of mixtures of TEL and TML.

– Faith, Keyes, Clark
(1965)

II. TEL Manufacture

Principal Operations. As will be apparent from the F-K-C process description, there are several basic operations involving in making an "Antiknock Compound" from the raw materials coming into the Area. For TEL antiknock these would be:

1) Alloy Manufacture. Lead and sodium metals are melted together, and the alloy broken up into small, reactive flakes.

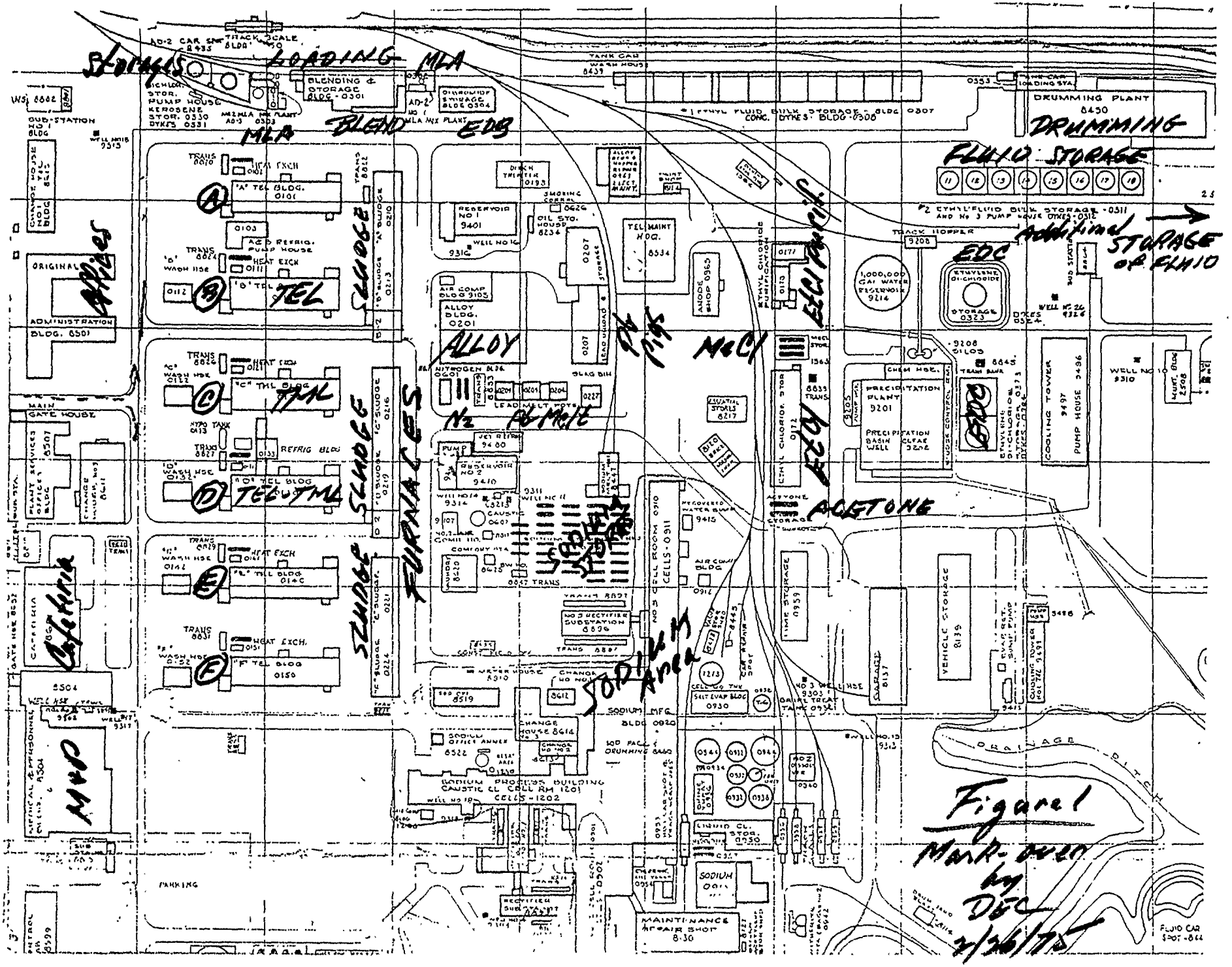
2) Tetraethyllead. The alloy flakes are reacted with ethyl chloride to form the TEL. A residue ("sludge") contains about 75% of the lead as recoverable metal.

3) TEL purification. An elaborate system of stills, condensers, washers, aerators, and filters are necessary to recover pure TEL from the crude reaction mass. The first stage uses a steam still to separate out the crude TEL, and drop out a sludge rich in lead metal.

4) Blending. The purified TEL is blended with EDB and also usually EDC, together with dyes and other additives to produce a finished Ethyl Antiknock Compound for shipment to refiners.

5) Lead Recovery. The sludge is dried and smelted in special furnaces to recover lead and separate the large fraction of unalkylated lead metal. A slag on top contains additional lead which is recovered for Ethyl by Schuylkill.

The Operations Area in Baton Rouge. Figure 1 shows the lay-out of the grounds of the TEL Area. The locations of the principal operations have been indicated. A schematic diagram (Figure 2) of the TEL process follows the Area map.


Storage
LOADING MLA
MLA BLEND EDC
DRUMMING
FLUID STORAGE
Additional STORAGE OF FLUID
Allies
SLUDGE
FURNACES
ALLOY
Hg
MeCl
EDC
N2
Melt
ACETONE
Cafeteria
MWD
Figure 1
Marked by DEC
2/26/79
ADMINISTRATION BLDG. 6501
MAIN GATE HOUSE
ORIGINAL
"A" TEL BLDG. 0101
"B" TEL BLDG.
"C" TEL BLDG.
"D" TEL BLDG.
"E" TEL BLDG. 0140
"F" TEL BLDG. 0150
ALLOY BLDG. 0201
BLENDING & STORAGE BLDG. 0301
PRECIPITATION PLANT 9201
COOLING TOWER 9497
PUMP HOUSE 9496
SODIUM MFG. BLDG. 0820
SODIUM Area
MAINTENANCE REPAIR SHOP 8-30
PARKING
DRAINAGE DITCH

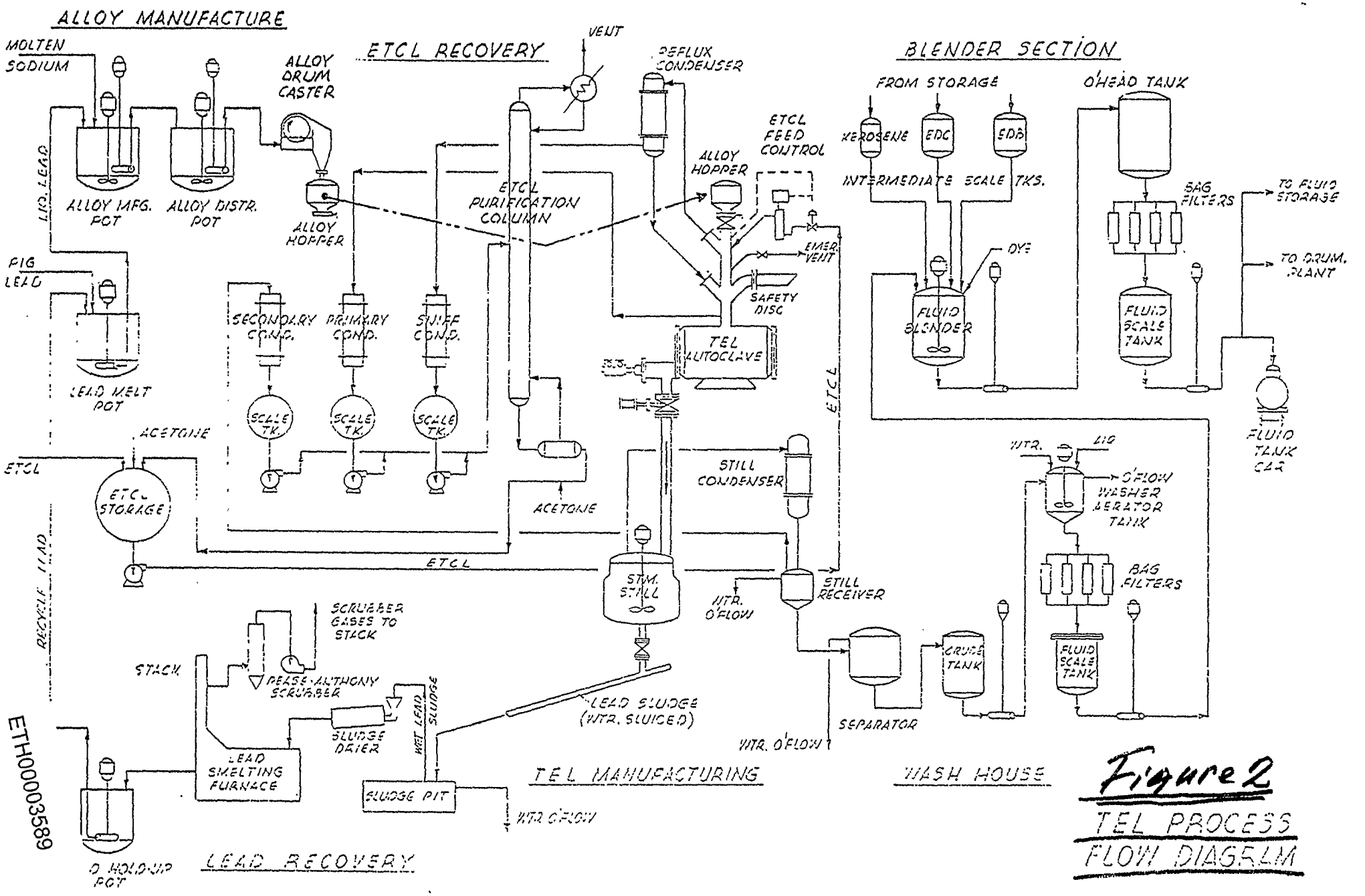


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Figure 2

TEL PROCESS FLOW DIAGRAM

Alloy Manufacture

Molten sodium is vacuum-pumped from one of the 34 tanks located on the east side of the Area, near Sodium Operations. These 160 M lb capacity tanks are heat-jacketed, and four are always kept molten by hot oil (Paralux-70 or Harmony-53). The sodium is supplied by the No. 2 and No. 3 Sodium shops. About 80% of these sodium stores are used to make alloy for TEL and TML, with most of the remainder going to Ethyl's plant in Greece in special containers. A smaller amount is shipped to U.S. buyers in tank cars.

Most of the liquid lead melt for alloying comes from the Lead Smelters where it is recovered from the autoclave sludge (See later). About 25% is made up by new pigs dropped into the Lead Melt Pots to supplement the lead recycled from the Smelters.

There are two Alloy Manufacturing Pots in use. A great many melts, of about fifty tons each, are produced daily. The temperature of the melts is brought down by Dowtherm A.

The molten alloy flows into one of the eight rotating drum casters ("flakers"). The inside of the drum is chilled by a mineral oil (Mentor-28), and the sheet of alloy which solidifies on the drums' outside surface is continuously scraped off as flakes by a doctor blade.

The flakes drop into a series of hoppers ("surge", "weigh", and finally "transport" hoppers on rail wheels) for haul to the charging floor of the autoclaves. Each sealed hopper carries several thousand pounds of alloy. The alloy contains a varying admixture of 2 to 20 lbs of graphite added through a screw feeder at the weigh hopper. This graphite serves as a lubricant for the plow agitators in the autoclaves.

(All of the operations involving either sodium or its alloy--from sodium storage to autoclave reaction--are protected by nitrogen blankets).

Ethyl Chloride Storage

The second basic reactant is stored in 16 tanks of 75 M lb capacities. A small amount of acetone is blended into the chloride to serve as an initiator for the alkylation reaction.

(In addition to the storage tanks, the plant maintains bulk storage of additional ethyl chloride in 5 Hortonspheres having capacities well over a million pounds each.)

The Alkylation Reaction

The autoclaves are charged on the 5th floors of the

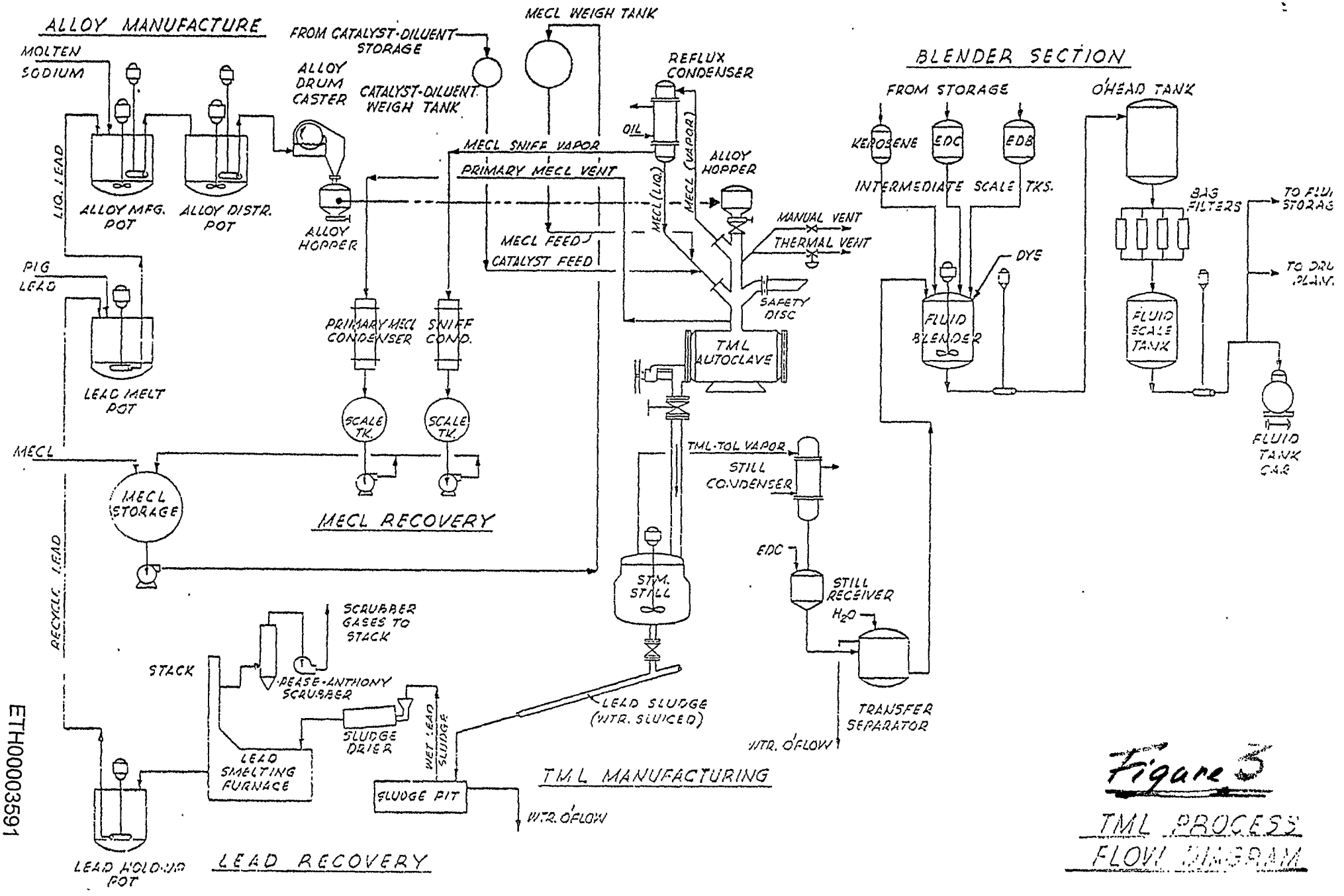

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Figure 5

TML PROCESS FLOW DIAGRAM

three of more of the TEL Manufacturing Buildings. The alloy flakes drop from hoppers into the charging heads of banks of horizontal claves located on the 4th floor. The ethyl chloride is then admitted to the alloy, the temperature is raised to start the reaction, cooling applied to absorb the reaction heat, and completion is signaled by autoclave pressure drop. All of the main instrument panel and process controls are located on the 5th floor.

The alkylation process is over in a matter of a few hours. At the conclusion the TEL product, mixed with a spongy mass consisting mainly of lead and sodium chloride, is dropped into a steam still located on the 3rd floor holding several hundred gallons of water. A number of "still aids" are added at this location. For the TEL stills these aids are ferrous sulfate, sodium sulfide, sodium thiosulfate solution, a thermal stabilizer for TEL (HB9700), and a soap solution. (The soap is made on the 2nd floor of "B" building, usin 25% caustic soda and a tall oil acid, followed by dilution).

TEL Recovery and Purification

Figure 2 showed the flows from the steam stills. The TEL falls from the Condenser into a Receiver and thence to a Separator. The diagram shows an elaborate ethyl chloride recovery and purification system from which the recovered halide is recycled. A feature not shown is two vents from the top of the Sniff and Primary Condensers. These condensers are at the left of the Purification Column which they feed. Gases escaping from the two vents contain ethylene, ethane, and a butane-ethyl chloride azeotrope. Because of the ethylene, in the future these gases will be piped to the furnace area, where they will be mixed and burned with natural gas fuel.

In the separator the lower phase TEL ("oil") is drawn off to the Crude Tanks and pumped to the washer-aerator tanks, where the TEL is washed with water and blown with compressed air. Some alkyl bismuth compounds (formed from the traces of natural bismuth metal present in the lead pigs), are oxidized to insoluble bismuth hydroxides. These are filtered off by fabric bag filters. The filtrate of purified TEL goes to the Fluid Scale Tank.

The upper aqueous phase from the receivers and separators goes to Wall Tanks (not shown) where more TEL drops out and is sent to recovery. The water above it overflows to a process ditch.

Sludge Processing and Lead Recovery

After each batch of TEL is steam-distilled off, the sludge from the Steam Still is water-sluiced to a Sludge Pit. A bucket crane scoops up this mass from the pit bottom, and feeds

it to a Drier where most of the water and residual TEL are evaporated. A condenser recovers some TEL (which is transferred back to the Separator) along with the water which is run back to the pit.

The dried sludge is fed into smelting furnaces heated by natural gas. These furnaces recover nearly 95% of the lead metal in the sludge. The other 5% is present as oxide or metal in a crude slag which floats above the molten lead. This slag is collected for hauling to Schuylkill, who recovers the lead in reverberatory and blast furnaces.

Figure 2 shows "Pease-Anthony" scrubbers on the furnace stacks. Since these scrubbers remove only 75% of the particulates, the company has recently replaced these with some high-energy venturi scrubbers, which remove about 95% of the particulates.

The recovered furnace lead flows to one of four Hold-up Pots, from which it is recycled to one of the two lead Melt Pots.

III. TML MANUFACTURE

The principal operations in TML Manufacture are shown in Figure 3. The process is basically the same as that for TEL. The alloy flakes are prepared as for TEL, although more graphite is screwed in at the alloy Weigh Hopper. The alloy is charged through the 5th floor charging heads of the claves in Building C. In addition, a catalyst (methyl aluminum sesquichloride ("MASC) dissolved in toluene) is added to each charge. No acetone is present in the methyl chloride.

TML Recovery and Purification. Although sodium thisulfate and ferrous sulfate are added as still aids, no soap, no sodium sulfide, and no thermal stabilizer are added to the Steam Stills on the 3rd floor. The condensate from the Still Condenser drops into a Separator, as with TEL.

The TML process features a special TML vapor recovery system designated AB-9. When a reaction mass is dropped into the steam still, a vent on its dome discharges the gases into two counter-current scrubbers which use chilled EDC. The EDC wash, containing TML and also toluene (from the MASC), flows to the still receivers. Both the toluene and EDC follow the TML into the finished product.

FLOW SHEET FOR MLA & TELMEL

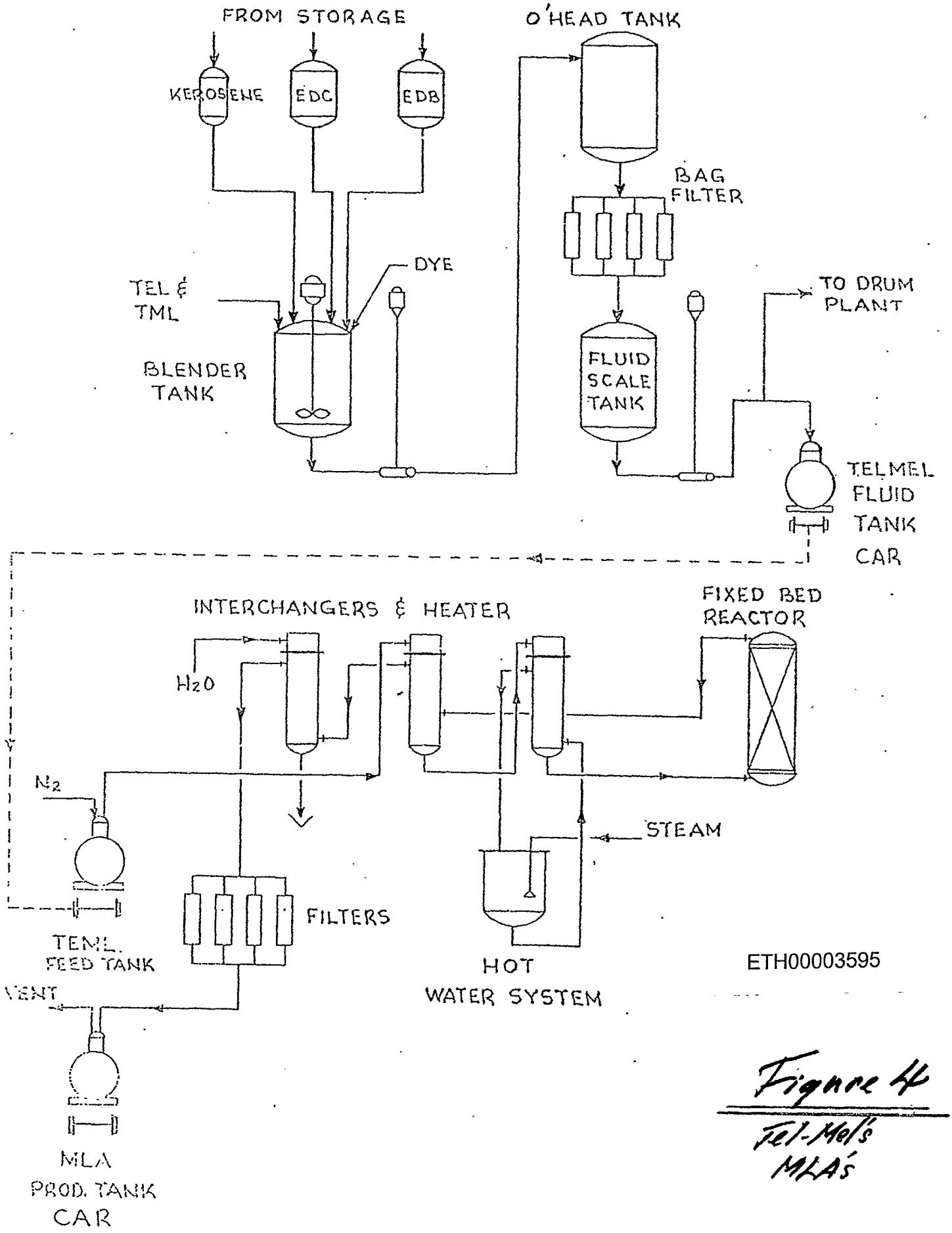

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Figure 4

Tel-Mel's MLA's

IV. Blending; MLA Manufacture

Figures 2 and 3 indicated the simple steps involved in regular antiknock blending. The finished TEL or TML, together with appropriate amounts of EDB, and usually EDC, are weighed and blended in a Fluid Blender tank. Kerosene is added whenever necessary to reduce the specific gravity to the refiners specifications. Appropriate dyes are added. AN-701, phosphate additives, AK-33-X, or other less common supplements also may be mixed in. The commonest Ethyl Antiknock Compound is TEL Motor Mix, consisting essentially of 61% TEL, 18% EDB, 19% EDC, and a trace of dye.

Figure 4 shows the steps in MLA production. For this operation the TEL and TML are mixed in a Blender and scavengers and dyes are added. If marketed in this form the simple lead alkyl mixtures (in various proportions) are called Ethyl TEL-MEL Antiknock Compounds.

To produce lead alkyls with the ethyl and methyl alkyls randomly distributed on the Pb atoms, another step converts the TEL-MEL into an MLS (Mixed Lead Alkyls) Compound. The TEL-MEL mixture is preheated ina hot-water exchanger, and then through a fixed bed of Filtrol-25 to effect the redistribution.

A few MLA Compound formulations require certain dyes and also other additives which would be retained in the Filtrol redistribution bed to be added to the MLA Compound after the reaction.

(All Ethyl lead alkyl tanks of every type contain nitrogen blankets at all times.)

V. Drumming Plant

Most Antiknock Compound shipments overseas must be made in stell drums. The drumming plant is mainly housed in a well-ventilated building where drums are cleaned, repainted, filled, carefully inspected for leaks, and finally loaded for shipment. The following are the principal operations:

1. Portco Clean-up. In a ventilated enclosure, returned drums are flushed with hot water, and then dried by a blow of hot air. If inspection shows that a drum is still dirty, it goes to the:

2. Acid Wash Area. Diluted sulfuric acid is used to remove solids, after which the drums are returned to Portco.

3. Painting. Drums are sprayed as they move along on an enclosed conveyor, and are carried into a:

4. Drying zone, where a current of warm air evaporates virtually all of the paint vehicle.

5. Store for final maturing of finish

6. Filling. The drums, lying bung side up in a ventilated hood, are connected to a special filling apparatus, whose flow is automatically turned on and shut off. The drum lies on a scale which takes into account its tare weight. The flow is cut off when the fill reaches the proper weight-about 680-770 lbs, depending on the particular Fluid. The inside and topping bung stoppers are then screwed into place. The filled drums are stored, first upright, and later on-side with bung down, for:

7. Inspection as to possible leaks. Leaks are rarely seen around bungs, but occasionally at or near the chimes. Approved drums go to the:

8. Storage and loading area.

D.E. Cooper
February, 1975

Attachments: Appendix A
Appendix B

Appendix A

TEL AREA MATERIALS

Basic Raw Materials

Sodium metal
Lead metal
Ethyl chloride
Methyl chloride
Ethylene dichloride
Ethylene dibromide (Ethyl, Magnolia)

Special Additives for Products, NOT Dyes

AN-701 (DTBP) (O.B.)
AN-733 (O.B.)
Methyl diphenyl phosphate
Kerosene
AK-33-X (MTT)
(See Dyes at end)

Process Additives

Acetone (Ga. Pacific - Chevron)
Graphite (Southwestern Graphite)
Still Aids
- $Na_2S_2O_3$ (30% sol.) Grant Chemical
- Na_2S (Drums, PPG, CPC, Centerville)
- $FeSO_4$ (Cosmin, San Antonio)
- Soap (6% sol.) from
  - Caustic (25% sol.) (Allied)
  - Fatty Acid (Emersol, for example)
- HB-9700 (stabilizer) Exxon

MASC (11% toluene solution) (Ethyl-Houston)
Flaked Caustic (for recycle sodium in Melt Pots if high sulfide content) (McKesson)

Process Operating Materials

Freon refrigerants
Methylene dichloride (chilling liquid for EtCl and MeCl recovery systems)
Ultrasene (To cool TEL Reflux) (Atlantic-Richfield or low-odor kerosene
Filtrol 25 (Filtrol Corp., Los Angeles)

Dowtherm A (Dow)
Nitrogen (Cryogenic, from Big Three, through Exxon's supply lines)
Mentor-28 (cool alloy flaker) (Exxon)
Paralux-70 (Gulf) or
Harmony-53 (Gulf) to heat or cool sodium in tanks and cars
Autoclave (angle valve) grease (Exxon 4280)
Steam (Gulf States)
Water (Ethyl river water-treating plant, or Ethyl wells)

Miscellaneous Materials

Sulfuric Acid (98%). Dilute for drum clean-up (Stauffer)
Nitric Acid (for cleaning still condensers)
Paints, drum
- Ethyl Light green (Insl-X). Yonkers, NY
- Ethyl Motor Blue 54
- Ethyl Gray Drum Enamel (Mobil's 390-F-3)
- Light Gray Gloss Enamel No. 356 (Jones-Blair)
- Trisodium phosphate (cleaning)

Precautionary Supplies

Sulfuryl chloride (5% solution in kerosene) in case organic TEL spills (BASF-Wyandotte-W. Germany)
Potassium permanganate (5% solution in water) (TEL spills)

Antiknock Fluid Dyes

Orange (powder) American Color and Chemical
Bronze N (granular) American Color and Chemical
Orange (flake) American Cyanamid
Yellow DE (granular) American Cyanamid
Red 116 (beaded) Allied
Red 116 (powder) Allied
Red 115 (granular) Morton Chemical
Blue No. 2 (powder) Morton Chemical
Calco HS blue Calco Chemical and Dye

Appendix B

RHJ
11/17/74

II. Ethyl's Current Practices

A. Description of the Processes

Among the principal products produced at the Baton Rouge plant of Ethyl Corporation are lead alkyls fluids which are used extensively as octane improving ingredients in motor gasoline. Lead alkyls compounds produced at Baton Rouge are tetraethyl lead (TEL), tetramethyl lead (TML), and mixed lead alkyls (MLA's). These organic lead compounds are liquids at normal temperatures and, because of their toxic nature, require extreme care in handling during manufacture, purification, blending, and distribution. Minimizing personnel exposure to lead was a primary objective in design of the present plant at Baton Rouge, which began operation in 1937, and has continued to be of prime concern to Ethyl throughout the years.

TEL is manufactured by reaction of sodium-lead alloy with ethyl chloride. Lead is purchased commercially in the form of 2000 lb blocks and is melted in gas-fired melt pots. Sodium is produced at the Baton Rouge plant by electrolysis of molten sodium chloride in Downs electrolytic cells. Ethyl chloride is manufactured at the Baton Rouge plant by reaction of purchased ethylene with hydrogen chloride which is generated in other production areas on the plant.

Sodium-lead alloy, which consists of 90 wt % lead and 10 wt % sodium, is produced by mixing molten lead and sodium in agitated, temperature controlled mix pots. The reaction between sodium and lead is exothermic and the heat generated is removed by Dowtherm heat transfer fluid which is circulated through the jackets on the mix pots. From these mix pots, the sodium-lead alloy is pumped to distribution pots and then to rotary drum flakers where it is cooled and solidified into flakes. The alloy is then placed in hoppers and delivered to the TEL manufacturing buildings.

Each manufacturing building contains 18 autoclaves with related autoclave reflux condensers, steam stills, steam still condensers, and product receivers. TEL is produced by batch reaction of sodium-lead alloy and ethyl chloride according to the following chemical equation:

$$4NaPb + 4C_2H_5Cl \longrightarrow Pb(C_2H_5)_4 + 3Pb + 4NaCl$$

Alloy is charged by gravity from the hoppers into the autoclaves. Ethyl chloride is added to the reactors and the reaction is allowed to proceed to completion. Pressure in the autoclaves is 0 psig when alloy is charged and rises to 100 psig within a few minutes after start of the ethyl chloride feed. The reaction is exothermic and heat of reaction is removed by reflux condensers which condense and return excess ethyl chloride to the autoclaves in totally enclosed systems and by water jacketing on the autoclaves. The autoclaves are equipped with horizontal agitators to mix the alloy and ethyl chloride and to ensure efficient heat removal from the autoclave jackets.

After the reaction is completed, excess ethyl chloride is vented from the autoclaves to a central low-temperature brine (-40°C) recovery system where ethyl chloride is condensed and recovered for recycling. Reaction mass is discharged from the autoclaves to the steam stills by gravity for recovery of the TEL from the lead-salt residue. The TEL is steam distilled from the reaction mass, condensed in still condensers, and collected in product receivers.

As may be seen from the foregoing chemical reaction, only about one-fourth of the lead charged to the autoclaves is converted to TEL in each cycle. The remainder of the lead in the form of lead sludge and salt solution remaining in the stills after distillation is sluiced into sludge settling pits. The lead sludge is then fed to reverberatory furnaces for recovery and recycle of metallic lead.

Crude TEL from the product receivers is collected in tanks where it is purified and then pumped to the blending plant to be combined with the other components of "Ethyl" antiknock compounds. These components consist of ethylene dichloride, ethylene dibromide, dyes, stabilizers, kerosene, and various other additives.

Tetramethyl lead (TML) is manufactured by essentially the same process used for TEL production, except that methyl chloride is used instead of ethyl chloride. Methyl chloride is produced at the Baton Rouge plant by reaction of methyl alcohol and hydrogen chloride.

Mixed lead alkyls (MLA's) are mixtures of tetraethyl lead, triethyl methyl lead, diethyl dimethyl lead, ethyl trimethyl lead, and tetramethyl lead. MLA's are produced by reacting TEL and TML in a catalytic reactor where redistribution of the alkyl groups occurs according to the following equation:

$$TEL + TML \xrightarrow{\text{catalyst}} TEL + Et_3MePb + Et_2Me_3Pb + EtMe_3Pb + TML$$

Blended antiknock fluids are shipped from the Baton Rouge plant by rail tank cars, tank trucks, portable containers, and drums to markets throughout the world.

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11/15/74

TEL

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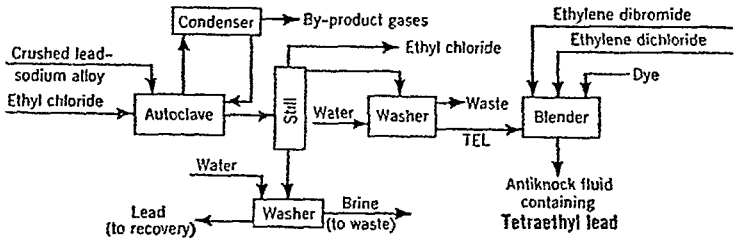

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85–90% yield (based on sodium)

Material Requirements

Basis—1 ton tetraethyl lead (100%)

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Ethyl chloride (theo)	1,595 lb
Catalyst	15 to 50 lb
Ferric chloride	Small
Sodium thiosulfate	Small

Process

Tetraethyl lead is made by reacting a lead–sodium alloy with ethyl chloride in an autoclave. The crude product is purified by vacuum distillation

An alloy of 9 parts lead and 1 part sodium is prepared in an alloy pot, cast, crushed, and cooled. All operations are carried out in an atmosphere of nitrogen. The crushed alloy is charged to a horizontal autoclave fitted with a heavy-duty agitator. Ethyl chloride is then fed slowly into the autoclave until 70 per cent excess of theoretical has been added. Heat evolved by the reaction vaporizes part of the ethyl chloride, which is then condensed in a reflux condenser and returned to the autoclave. This vaporization, supplemented by circulation of a coolant in the autoclave jacket, keeps the reactants at 65 to 75°C (50 to 60 psi). Any gaseous by-products are vented through the reflux condenser. Various catalysts (aldehydes, acids, ketones, esters, etc.) in concentrations of 1 to 2 per cent are mentioned in the patent literature and may be used to speed the reaction.

When the reaction is completed, the autoclave is vented into batch-type steam stills partly filled with water. The last trace of ethyl chloride is vaporized and then the TEL is distilled from the spongy metallic mass. To prevent "balling" of the solid material a mixture of ferric chloride and sodium thiosulfate is added to the reaction mass fed to the still. After vaporization of the crude TEL, the remaining lead-salt sludge is washed free of sodium chloride, partially dried, and resmelted in a recovery furnace, since only about 25 per cent of the lead fed to the autoclave enters the reaction.

The crude TEL from the still is washed, settled, and then pumped to blending equipment where it is mixed with appropriate amounts of ethylene dibromide, ethylene dichloride, and a dye. The product, motor antiknock fluid, after filtration, is shipped to refineries for blending with gasoline. The current composition of motor fluid is 61 per cent TEL, 18 per cent ethylene dibromide, 19 per cent ethylene dichloride, and 2 per cent dye. Aviation fluid contains no ethylene dichloride, but the same amount of TEL.

Tetramethyl lead (TML) can also be made by a process similar to that described in which methyl chloride is used in place of ethyl chloride. If mixtures of ethyl and methyl chlorides are used, equilibrium conditions can be adjusted to put various amounts of methyl and ethyl radicals on the lead atom to give various mixed lead alkyls. The mixed compound may also be produced by redistribution or equilibration reactions of mixtures of TEL and TML.

– Faith, Keyes, Clark (1965)

II. TEL Manufacture

Principal Operations. As will be apparent from the F-K-C process description, there are several basic operations involving in making an "Antiknock Compound" from the raw materials coming into the Area. For TEL antiknock these would be:

1) Alloy Manufacture. Lead and sodium metals are melted together, and the alloy broken up into small, reactive flakes.

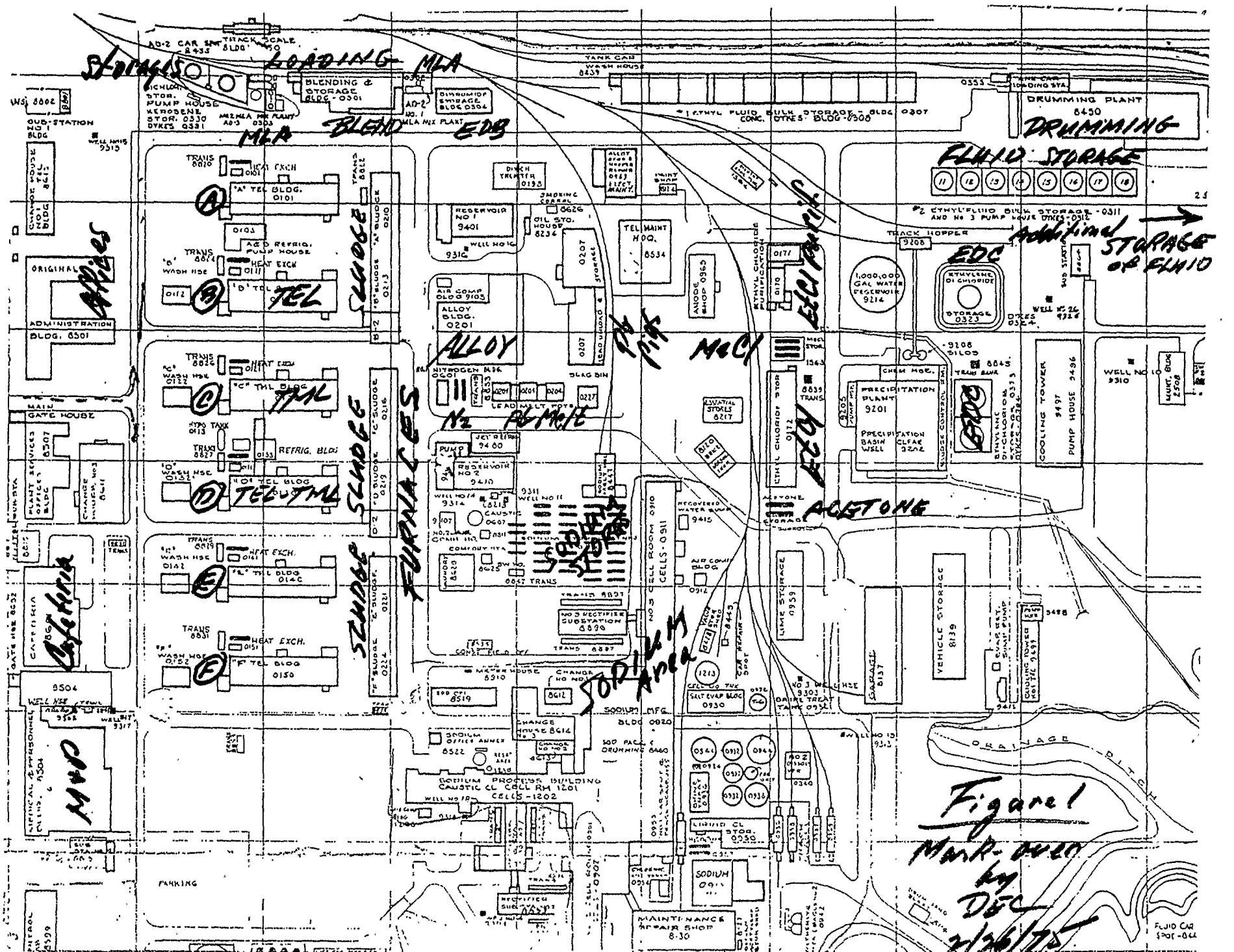
2) Tetraethyllead. The alloy flakes are reacted with ethyl chloride to form the TEL. A residue ("sludge") contains about 75% of the lead as recoverable metal.

3) TEL purification. An elaborate system of stills, condensers, washers, aerators, and filters are necessary to recover pure TEL from the crude reaction mass. The first stage uses a steam still to separate out the crude TEL, and drop out a sludge rich in lead metal.

4) Blending. The purified TEL is blended with EDB and also usually EDC, together with dyes and other additives to produce a finished Ethyl Antiknock Compound for shipment to refiners.

5) Lead Recovery. The sludge is dried and smelted in special furnaces to recover lead and separate the large fraction of unalkylated lead metal. A slag on top contains additional lead which is recovered for Ethyl by Schuylkill.

The Operations Area in Baton Rouge. Figure 1 shows the lay-out of the grounds of the TEL Area. The locations of the principal operations have been indicated. A schematic diagram (Figure 2) of the TEL process follows the Area map.



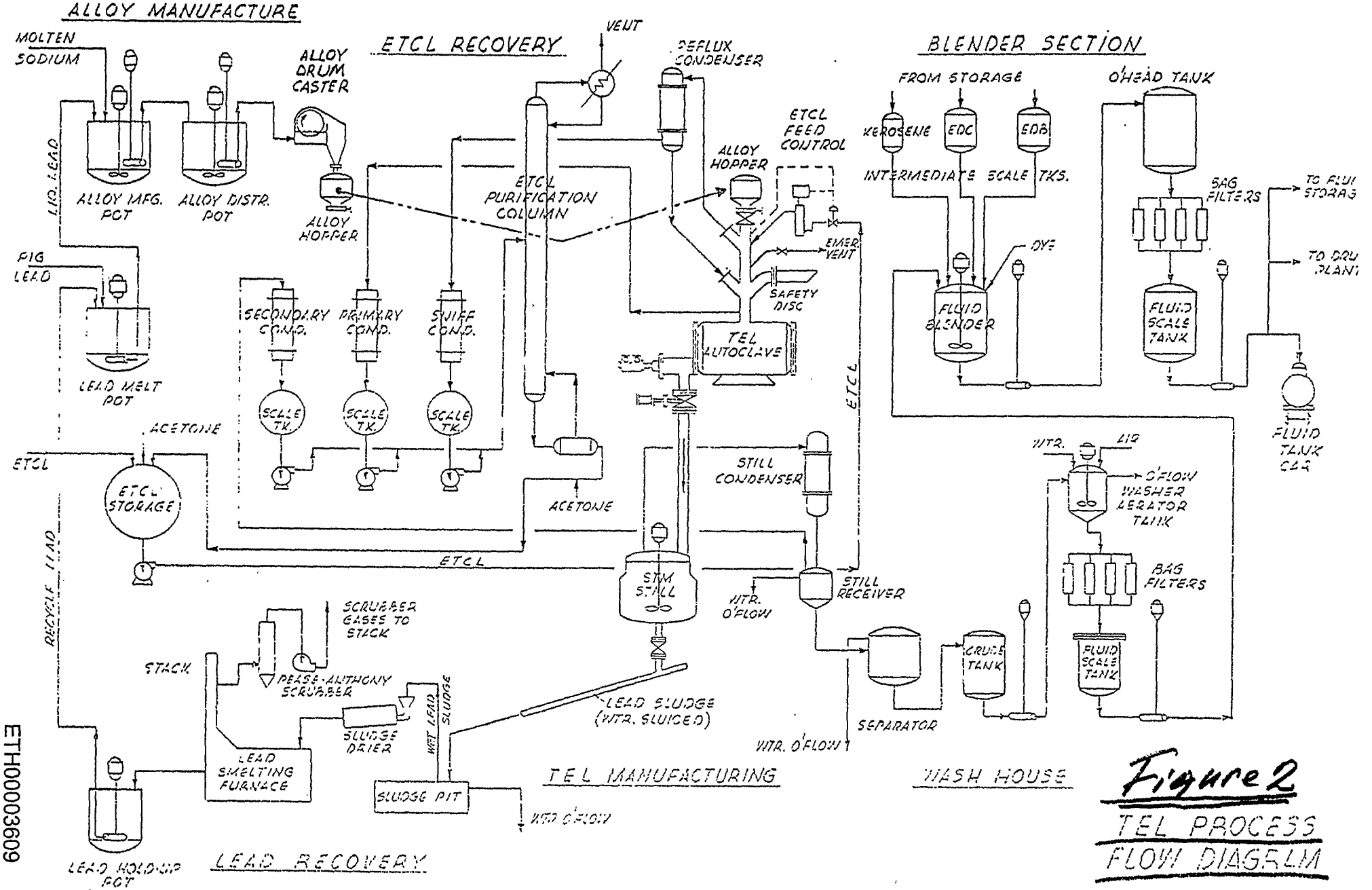


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Figure 2

TEL PROCESS FLOW DIAGRAM

Alloy Manufacture

Molten sodium is vacuum-pumped from one of the 34 tanks located on the east side of the Area, near Sodium Operations. These 160 M lb capacity tanks are heat-jacketed, and four are always kept molten by hot oil (Paralux-70 or Harmony-53). The sodium is supplied by the No. 2 and No. 3 Sodium shops. About 80% of these sodium stores are used to make alloy for TEL and TML, with most of the remainder going to Ethyl's plant in Greece in special containers. A smaller amount is shipped to U.S. buyers in tank cars.

Most of the liquid lead melt for alloying comes from the Lead Smelters where it is recovered from the autoclave sludge (See later). About 25% is made up by new pigs dropped into the Lead Melt Pots to supplement the lead recycled from the Smelters.

There are two Alloy Manufacturing Pots in use. A great many melts, of about fifty tons each, are produced daily. The temperature of the melts is brought down by Dowtherm A.

The molten alloy flows into one of the eight rotating drum casters ("flakers"). The inside of the drum is chilled by a mineral oil (Mentor-28), and the sheet of alloy which solidifies on the drums' outside surface is continuously scraped off as flakes by a doctor blade.

The flakes drop into a series of hoppers ("surge", "weigh", and finally "transport" hoppers on rail wheels) for haul to the charging floor of the autoclaves. Each sealed hopper carries several thousand pounds of alloy. The alloy contains a varying admixture of 2 to 20 lbs of graphite added through a screw feeder at the weigh hopper. This graphite serves as a lubricant for the plow agitators in the autoclaves.

(All of the operations involving either sodium or its alloy--from sodium storage to autoclave reaction--are protected by nitrogen blankets).

Ethyl Chloride Storage

The second basic reactant is stored in 16 tanks of 75 M lb capacities. A small amount of acetone is blended into the chloride to serve as an initiator for the alkylation reaction.

(In addition to the storage tanks, the plant maintains bulk storage of additional ethyl chloride in 5 Hortonspheres having capacities well over a million pounds each.)

The Alkylation Reaction

The autoclaves are charged on the 5th floors of the

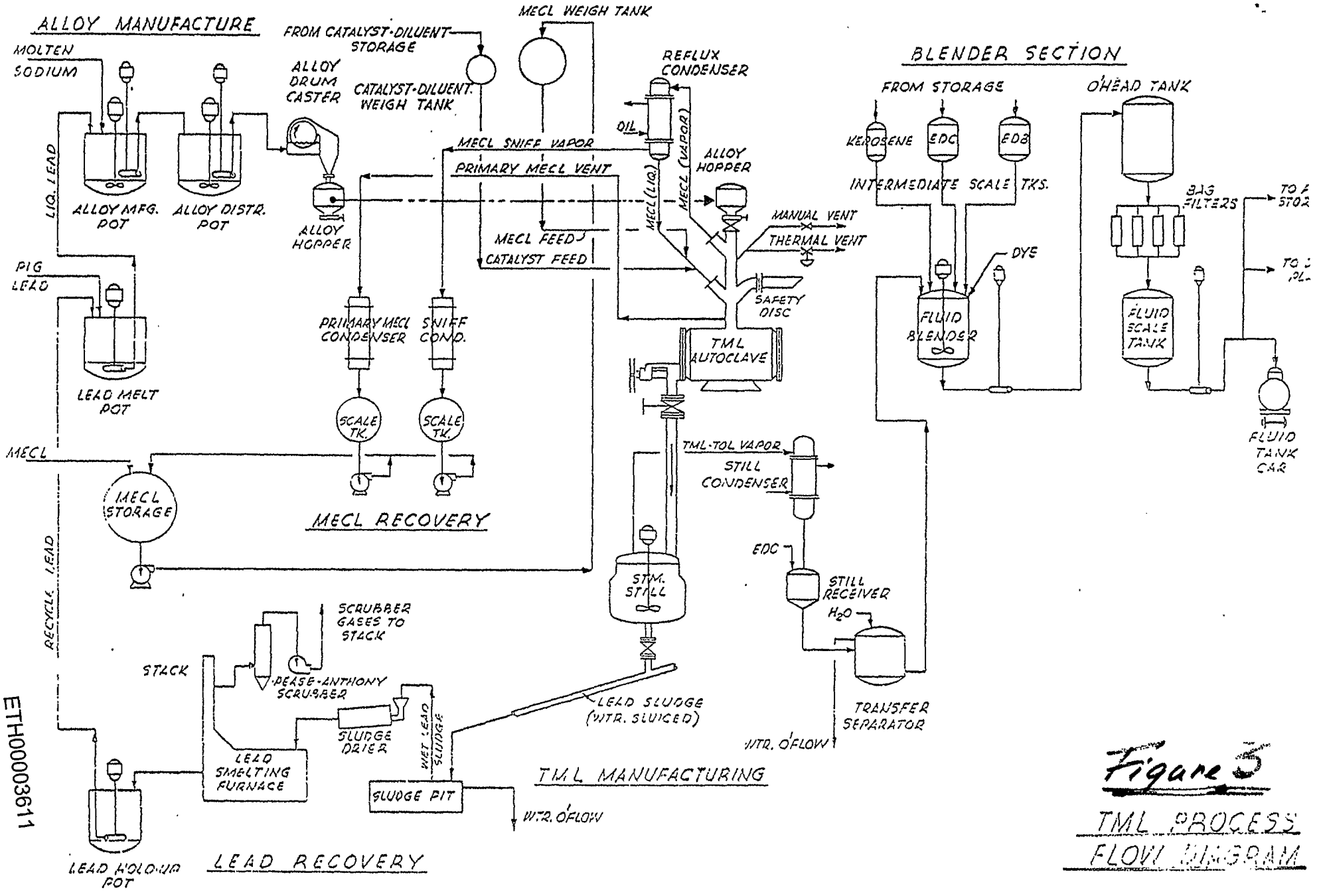

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Figure 3

TML PROCESS FLOW DIAGRAM

three of more of the TEL Manufacturing Buildings. The alloy flakes drop from hoppers into the charging heads of banks of horizontal claves located on the 4th floor. The ethyl chloride is then admitted to the alloy, the temperature is raised to start the reaction, cooling applied to absorb the reaction heat, and completion is signaled by autoclave pressure drop. All of the main instrument panel and process controls are located on the 5th floor.

The alkylation process is over in a matter of a few hours. At the conclusion the TEL product, mixed with a spongy mass consisting mainly of lead and sodium chloride, is dropped into a steam still located on the 3rd floor holding several hundred gallons of water. A number of "still aids" are added at this location. For the TEL stills these aids are ferrous sulfate, sodium sulfide, sodium thiosulfate solution, a thermal stabilizer for TEL (HB9700), and a soap solution. (The soap is made on the 2nd floor of "B" building, usin 25% caustic soda and a tall oil acid, followed by dilution).

TEL Recovery and Purification

Figure 2 showed the flows from the steam stills. The TEL falls from the Condenser into a Receiver and thence to a Separator. The diagram shows an elaborate ethyl chloride recovery and purification system from which the recovered halide is recycled. A feature not shown is two vents from the top of the Sniff and Primary Condensers. These condensers are at the left of the Purification Column which they feed. Gases escaping from the two vents contain ethylene, ethane, and a butane-ethyl chloride azeotrope. Because of the ethylene, in the future these gases will be piped to the furnace area, where they will be mixed and burned with natural gas fuel.

In the separator the lower phase TEL ("oil") is drawn off to the Crude Tanks and pumped to the washer-aerator tanks, where the TEL is washed with water and blown with compressed air. Some alkyl bismuth compounds (formed from the traces of natural bismuth metal present in the lead pigs), are oxidized to insoluble bismuth hydroxides. These are filtered off by fabric bag filters. The filtrate of purified TEL goes to the Fluid Scale Tank.

The upper aqueous phase from the receivers and separators goes to Wall Tanks (not shown) where more TEL drops out and is sent to recovery. The water above it overflows to a process ditch.

Sludge Processing and Lead Recovery

After each batch of TEL is steam-distilled off, the sludge from the Steam Still is water-sluiced to a Sludge Pit. A bucket crane scoops up this mass from the pit bottom, and feeds

it to a Drier where most of the water and residual TEL are evaporated. A condenser recovers some TEL (which is transferred back to the Separator) along with the water which is run back to the pit.

The dried sludge is fed into smelting furnaces heated by natural gas. These furnaces recover nearly 95% of the lead metal in the sludge. The other 5% is present as oxide or metal in a crude slag which floats above the molten lead. This slag is collected for hauling to Schuylkill, who recovers the lead in reverberatory and blast furnaces.

Figure 2 shows "Pease-Anthony" scrubbers on the furnace stacks. Since these scrubbers remove only 75% of the particulates, the company has recently replaced these with some high-energy venturi scrubbers, which remove about 95% of the particulates.

The recovered furnace lead flows to one of four Hold-up Pots, from which it is recycled to one of the two lead Melt Pots.

III. TML MANUFACTURE

The principal operations in TML Manufacture are shown in Figure 3. The process is basically the same as that for TEL. The alloy flakes are prepared as for TEL, although more graphite is screwed in at the alloy Weigh Hopper. The alloy is charged through the 5th floor charging heads of the claves in Building C. In addition, a catalyst (methyl aluminum sesquichloride ("MASC) dissolved in toluene) is added to each charge. No acetone is present in the methyl chloride.

TML Recovery and Purification. Although sodium thisulfate and ferrous sulfate are added as still aids, no soap, no sodium sulfide, and no thermal stabilizer are added to the Steam Stills on the 3rd floor. The condensate from the Still Condenser drops into a Separator, as with TEL.

The TML process features a special TML vapor recovery system designated AB-9. When a reaction mass is dropped into the steam still, a vent on its dome discharges the gases into two counter-current scrubbers which use chilled EDC. The EDC wash, containing TML and also toluene (from the MASC), flows to the still receivers. Both the toluene and EDC follow the TML into the finished product.

FLOW SHEET FOR MLA & TELMEL

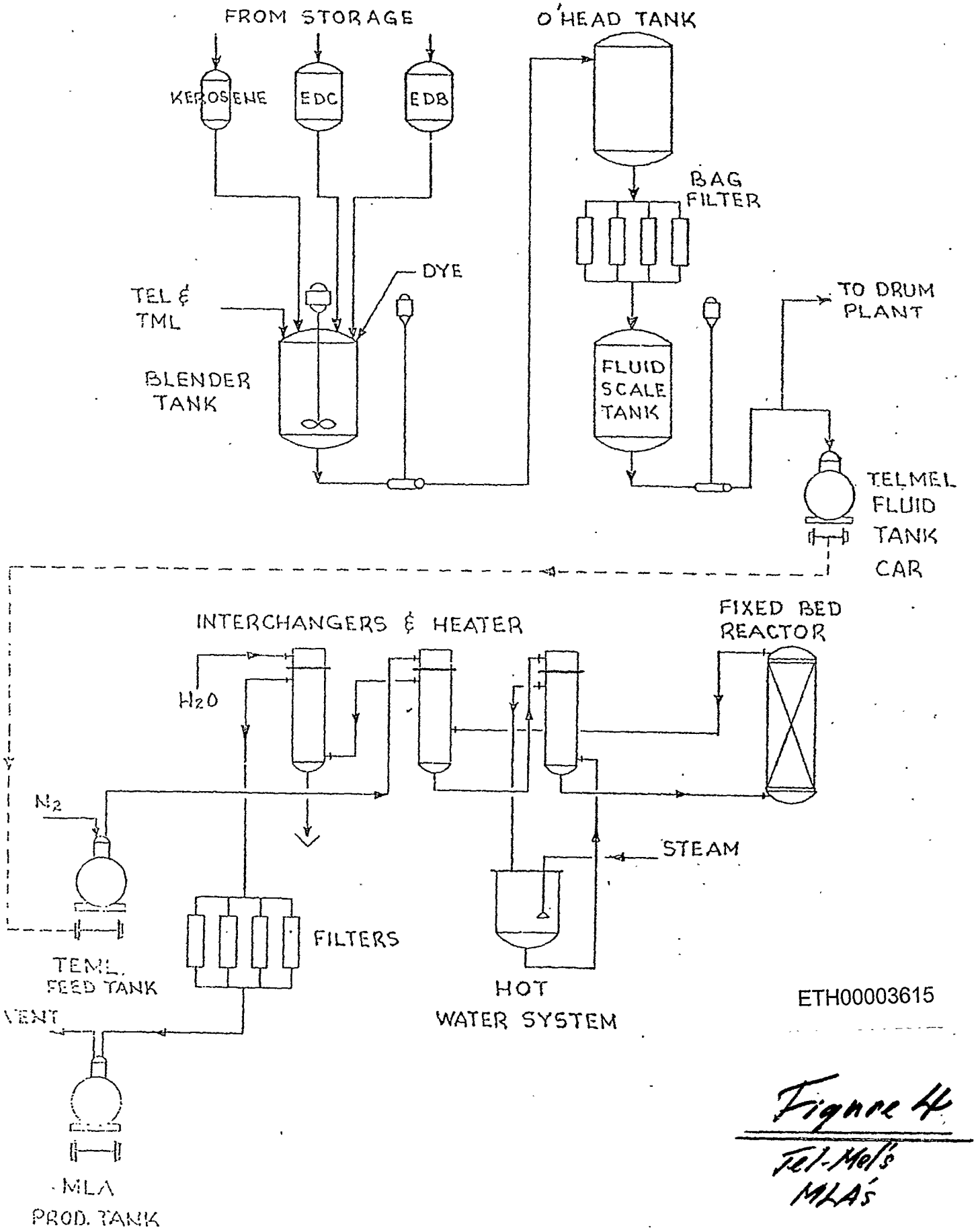

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Figure 4

Tel-Mel's MLA's

IV. Blending; MLA Manufacture

Figures 2 and 3 indicated the simple steps involved in regular antiknock blending. The finished TEL or TML, together with appropriate amounts of EDB, and usually EDC, are weighed and blended in a Fluid Blender tank. Kerosene is added whenever necessary to reduce the specific gravity to the refiners specifications. Appropriate dyes are added. AN-701, phosphate additives, AK-33-X, or other less common supplements also may be mixed in. The commonest Ethyl Antiknock Compound is TEL Motor Mix, consisting essentially of 61% TEL, 18% EDB, 19% EDC, and a trace of dye.

Figure 4 shows the steps in MLA production. For this operation the TEL and TML are mixed in a Blender and scavengers and dyes are added. If marketed in this form the simple lead alkyl mixtures (in various proportions) are called Ethyl TEL-MEL Antiknock Compounds.

To produce lead alkyls with the ethyl and methyl alkyls randomly distributed on the Pb atoms, another step converts the TEL-MEL into an MLS (Mixed Lead Alkyls) Compound. The TEL-MEL mixture is preheated ina hot-water exchanger, and then through a fixed bed of Filtrol-25 to effect the redistribution.

A few MLA Compound formulations require certain dyes and also other additives which would be retained in the Filtrol redistribution bed to be added to the MLA Compound after the reaction.

(All Ethyl lead alkyl tanks of every type contain nitrogen blankets at all times.)

V. Drumming Plant

Most Antiknock Compound shipments overseas must be made in stell drums. The drumming plant is mainly housed in a well-ventilated building where drums are cleaned, repainted, filled, carefully inspected for leaks, and finally loaded for shipment. The following are the principal operations:

1. Portco Clean-up. In a ventilated enclosure, returned drums are flushed with hot water, and then dried by a blow of hot air. If inspection shows that a drum is still dirty, it goes to the:

2. Acid Wash Area. Diluted sulfuric acid is used to remove solids, after which the drums are returned to Portco.

3. Painting. Drums are sprayed as they move along on an enclosed conveyor, and are carried into a:

4. Drying zone, where a current of warm air evaporates virtually all of the paint vehicle.

5. Store for final maturing of finish

6. Filling. The drums, lying bung side up in a ventilated hood, are connected to a special filling apparatus, whose flow is automatically turned on and shut off. The drum lies on a scale which takes into account its tare weight. The flow is cut off when the fill reaches the proper weight-about 680-770 lbs, depending on the particular Fluid. The inside and topping bung stoppers are then screwed into place. The filled drums are stored, first upright, and later on-side with bung down, for:

7. Inspection as to possible leaks. Leaks are rarely seen around bungs, but occasionally at or near the chimes. Approved drums go to the:

8. Storage and loading area.

D.E. Cooper
February, 1975

Attachments: Appendix A
Appendix B

Appendix A

TEL AREA MATERIALS

Basic Raw Materials

Sodium metal
Lead metal
Ethyl chloride
Methyl chloride
Ethylene dichloride
Ethylene dibromide (Ethyl, Magnolia)

Special Additives for Products, NOT Dyes

AN-701 (DTBP) (O.B.)
AN-733 (O.B.)
Methyl diphenyl phosphate
Kerosene
AK-33-X (MTT)
(See Dyes at end)

Process Additives

Acetone (Ga. Pacific - Chevron)
Graphite (Southwestern Graphite)
Still Aids
- $Na_2S_2O_3$ (30% sol.) Grant Chemical
- Na_2S (Drums, PPG, CPC, Centerville)
- $FeSO_4$ (Cosmin, San Antonio)
- Soap (6% sol.) from
  - Caustic (25% sol.) (Allied)
  - Fatty Acid (Emersol, for example)
- HB-9700 (stabilizer) Exxon

MASC (11% toluene solution) (Ethyl-Houston)
Flaked Caustic (for recycle sodium in Melt Pots if high sulfide content) (McKesson)

Process Operating Materials

Freon refrigerants
Methylene dichloride (chilling liquid for EtCl and MeCl recovery systems)
Ultrasene (To cool TEL Reflux) (Atlantic-Richfield) or low-odor kerosene
Filtrol 25 (Filtrol Corp., Los Angeles)

Dowtherm A (Dow)
Nitrogen (Cryogenic, from Big Three, through Exxon's supply lines)
Mentor-28 (cool alloy flaker) (Exxon)
Paralux-70 (Gulf) or
Harmony-53 (Gulf) to heat or cool sodium in tanks and cars
Autoclave (angle valve) grease (Exxon 4280)
Steam (Gulf States)
Water (Ethyl river water-treating plant, or Ethyl wells)

Miscellaneous Materials

Sulfuric Acid (98%). Dilute for drum clean-up (Stauffer)
Nitric Acid (for cleaning still condensers)
Paints, drum
- Ethyl Light green (Insl-X). Yonkers, NY
- Ethyl Motor Blue 54
- Ethyl Gray Drum Enamel (Mobil's 390-F-3)
- Light Gray Gloss Enamel No. 356 (Jones-Blair)
- Trisodium phosphate (cleaning)

Precautionary Supplies

Sulfuryl chloride (5% solution in kerosene) in case organic TEL spills (BASF-Wyandotte-W. Germany)
Potassium permanganate (5% solution in water) (TEL spills)

Antiknock Fluid Dyes

Orange (powder) American Color and Chemical
Bronze N (granular) American Color and Chemical
Orange (flake) American Cyanamid
Yellow DE (granular) American Cyanamid
Red 116 (beaded) Allied
Red 116 (powder) Allied
Red 115 (granular) Morton Chemical
Blue No. 2 (powder) Morton Chemical
Calco HS blue Calco Chemical and Dye

Appendix B

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II. Ethyl's Current Practices

A. Description of the Processes

Among the principal products produced at the Baton Rouge plant of Ethyl Corporation are lead alkyls fluids which are used extensively as octane improving ingredients in motor gasoline. Lead alkyls compounds produced at Baton Rouge are tetraethyl lead (TEL), tetramethyl lead (TML), and mixed lead alkyls (MLA's). These organic lead compounds are liquids at normal temperatures and, because of their toxic nature, require extreme care in handling during manufacture, purification, blending, and distribution. Minimizing personnel exposure to lead was a primary objective in design of the present plant at Baton Rouge, which began operation in 1937, and has continued to be of prime concern to Ethyl throughout the years.

TEL is manufactured by reaction of sodium-lead alloy with ethyl chloride. Lead is purchased commercially in the form of 2000 lb blocks and is melted in gas-fired melt pots. Sodium is produced at the Baton Rouge plant by electrolysis of molten sodium chloride in Downs electrolytic cells. Ethyl chloride is manufactured at the Baton Rouge plant by reaction of purchased ethylene with hydrogen chloride which is generated in other production areas on the plant.

Sodium-lead alloy, which consists of 90 wt % lead and 10 wt % sodium, is produced by mixing molten lead and sodium in agitated, temperature controlled mix pots. The reaction between sodium and lead is exothermic and the heat generated is removed by Dowtherm heat transfer fluid which is circulated through the jackets on the mix pots. From these mix pots, the sodium-lead alloy is pumped to distribution pots and then to rotary drum flakers where it is cooled and solidified into flakes. The alloy is then placed in hoppers and delivered to the TEL manufacturing buildings.

Each manufacturing building contains 18 autoclaves with related autoclave reflux condensers, steam stills, steam still condensers, and product receivers. TEL is produced by batch reaction of sodium-lead alloy and ethyl chloride according to the following chemical equation:

$$4NaPb + 4C_2H_5Cl \longrightarrow Pb(C_2H_5)_4 + 3Pb + 4NaCl$$

Alloy is charged by gravity from the hoppers into the autoclaves. Ethyl chloride is added to the reactors and the reaction is allowed to proceed to completion. Pressure in the autoclaves is 0 psig when alloy is charged and rises to 100 psig within a few minutes after start of the ethyl chloride feed. The reaction is exothermic and heat of reaction is removed by reflux condensers which condense and return excess ethyl chloride to the autoclaves in totally enclosed systems and by water jacketing on the autoclaves. The autoclaves are equipped with horizontal agitators to mix the alloy and ethyl chloride and to ensure efficient heat removal from the autoclave jackets.

After the reaction is completed, excess ethyl chloride is vented from the autoclaves to a central low-temperature brine (-40°C) recovery system where ethyl chloride is condensed and recovered for recycling. Reaction mass is discharged from the autoclaves to the steam stills by gravity for recovery of the TEL from the lead-salt residue. The TEL is steam distilled from the reaction mass, condensed in still condensers, and collected in product receivers.

As may be seen from the foregoing chemical reaction, only about one-fourth of the lead charged to the autoclaves is converted to TEL in each cycle. The remainder of the lead in the form of lead sludge and salt solution remaining in the stills after distillation is sluiced into sludge settling pits. The lead sludge is then fed to reverberatory furnaces for recovery and recycle of metallic lead.

Crude TEL from the product receivers is collected in tanks where it is purified and then pumped to the blending plant to be combined with the other components of "Ethyl" antiknock compounds. These components consist of ethylene dichloride, ethylene dibromide, dyes, stabilizers, kerosene, and various other additives.

Tetramethyl lead (TML) is manufactured by essentially the same process used for TEL production, except that methyl chloride is used instead of ethyl chloride. Methyl chloride is produced at the Baton Rouge plant by reaction of methyl alcohol and hydrogen chloride.

Mixed lead alkyls (MLA's) are mixtures of tetraethyl lead, triethyl methyl lead, diethyl dimethyl lead, ethyl trimethyl lead, and tetramethyl lead. MLA's are produced by reacting TEL and TML in a catalytic reactor where redistribution of the alkyl groups occurs according to the following equation:

$$TEL + TML \xrightarrow{\text{catalyst}} TEL + Et_3MePb + Et_2Me_3Pb + EtMe_3Pb + TML$$

Blended antiknock fluids are shipped from the Baton Rouge plant by rail tank cars, tank trucks, portable containers, and drums to markets throughout the world.

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