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ETHYL CORPORATION

RESEARCH AND DEVELOPMENT DEPARTMENT

PROCESS DESIGN SECTION

Baton Rouge, Louisiana

Problems Associated with Production of Volatile Lead Alkyls

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PROBLEMS ASSOCIATED WITH PRODUCTION OF VOLATILE LEAD ALKYLS

SUMMARY

Customer interest has given impetus to consideration of manufacture of mixed lead alkyls (mixtures of methylated and ethylated lead compounds) and tetramethyl lead. All of these compounds are more volatile than TEL and may be referred to as volatile lead alkyls.

Manufacture of volatile lead alkyls is more hazardous than manufacture of TEL because of their toxicity and explosivity. The volatile lead alkyls are as toxic as TEL or maybe more toxic. The higher volatility of these compounds increase the probability of contamination.

The temperature required to initiate spontaneous thermal decomposition of the pure volatile lead alkyls varies from slightly less than for TEL to somewhat more than for TEL. However, once initiated, decomposition of the volatile lead alkyls proceeds with much more violence than does decomposition of TEL.

Existing facilities can be converted to manufacture of some of the volatile lead alkyls. However, since both contamination and decomposition violence increase as the percentage of methylated compounds produced increases, a point would be reached where it would not be attractive to convert existing facilities. Thus development work and new facilities would be needed for production of TML and probably needed for production of mixtures containing a high percentage of methylated compounds.

Studies will be required to determine whether or not gasoline containing the volatile lead alkyls can be handled safely by refiners and the public.

INTRODUCTION

The possible commercial manufacture of volatile lead alkyls has become important to the Corporation because of increased customer interest. California Research recently requested timing and pricing for test and commercial quantities of tetramethyl lead (TML). Foreign refiners have been interested in mixed lead alkyls for some time.

Tests have indicated that production of these volatile lead alkyls is more hazardous than production of TEL, with TML being an extreme case. There are many problems involved in coping with the hazards. However, it may be attractive to solve these problems if customer interest is sufficient.

When sodium-lead alloy is reacted with ethyl chloride and methyl chloride, a mixture of lead alkyls results rather than one compound. These lead alkyls form a series from TEL to TML. The following five compounds form the series and each would be present in varing fractions in any mixed lead alkyl manufactured:

1. Tetramethyl lead
2. Triethylmethyl lead
3. Diethyldimethyl lead
4. Ethyltrimethyl lead
5. Tetramethyl lead.

The fraction of each compound present in a mixed lead alkyl is determined by the ratio of ethyl chloride to methyl chloride used in the reaction and can be found from the following equation:

$$(x + y)^{n-1} = 1.0$$

where x = the mole fraction of ethyl groups in the alkyl groups present
y = the mole fraction methyl groups in the alkyl groups present
n = the number of compounds in the series (5).

Distributions calculated from this equation are in agreement with experimental results.

Classification of the mixed lead alkyls can be made on the basis of percent of methyl groups present, since a certain percentage always gives the same distribution. An example of the method used to designate various mixtures is as follows:

MA-250 = Mixed lead alkyl in which 25 mole percent of the alkyl groups are methyl and 75 mole percent of the alkyl groups are ethyl.

Thus TEL would be MA-000 and TML would be MA-1000.

Two types of facilities could be provided for manufacture of volatile lead alkyls:

1. Converted existing plant
2. New plant.

It appears probable that conversion of existing facilities might provide an economically attractive route to manufacture of mixed lead alkyls containing a small percentage of methyl groups. Mixed alkyls up to MA-500 have been manufactured in conventional TEL-type facilities. However, since the production problems increase as the percentage of methyl groups increases, new facilities would probably be more attractive for manufacture of lead alkyls containing high percentages of methyl groups.

The production rate range of interest appears to be 15-25 MM pounds of lead alkyl per year. This amount could be produced in a converted Baton Rouge building. The Pittsburg plant, for example, could also be converted to mixed lead alkyl production.

PURPOSE

The purpose of this memorandum is

1. To describe the general hazards associated with commercial production of mixed lead alkyls, and in particular TML.

2. To point out anticipated plant design problems in the various plant areas.

3. To suggest possible solutions to the problems and to suggest needed development work.

4. To discuss associated fluid handling problems.

BASIC REACTIONS

TML and the mixed lead alkyls can be formed by reaction of alkyl chlorides with sodium-lead alloy. It is necessary to use a catalyst for the methylation reaction. Alkyl aluminum chlorides are the best catalysts now known.

The reaction to form TML is as follows:

$$4\ MeCl + 4\ NaPb \xrightarrow[170°F,\ 300\ psi]{Me_3Al_2Cl_3} PbMe_4 + 3\ Pb + 4\ NaCl$$

To form the various mixed lead alkyls, methyl chloride and ethyl chloride are fed in about the same ratio as the desired ratio of alkyl groups in the product. Thus:

$$MeCl + 3\ EtCl + 4\ NaPb \xrightarrow[160°F,\ 200\ psi]{Me_3Al_2Cl_3} MA\text{-}250 + 3\ Pb + 4\ NaCl$$

$$3\ MeCl + EtCl + 4\ NaPb \xrightarrow[160°F,\ 250\ psi]{Me_3Al_2Cl_3} MA\text{-}750 + 3\ Pb + 4\ NaCl$$

These reactions while quite similar to the present TEL reaction, are more hazardous to carry out due to the properties of the reactants and the lead alkyl product.

Another method of obtaining the volatility desired would be to combine enough TEL with an MA mixture having a higher volatility than that desired to give the fluid having the proper volatility. In such a case proportionately less of the initial MA mixture would be required.

Other methods of manufacturing lead alkyls are:

1. Mixed lead alkyls by redistribution of TEL and TML with suitable catalyst.

2. Pure trimethylethyl lead, etc., by fractionation.

These routes may be more attractive than alkylation alone in some cases. However, the special problems associated with redistribution, fractionation, etc., are not considered in this report. Thus it is pointed toward the manufacture of more volatile lead alkyls by alkylation alone.

HAZARDS

General

The compounds to be worked with in a plant producing the more volatile lead alkyls would present increased hazards over those now experienced

in TEL facilities. There would be an increased hygenic problem because of the relatively high volatility of the materials handled (See Figure 1) and because of their increased toxicity. There would also be an increase in the explosion hazard. This can be seen in Table I where a comparison of the decomposition rates is made. It should be noted that as the percentage of methyl groups increases, the rate of decomposition also increases. These general hazards would be aggravated by the pyrophoric nature of an alkyl aluminum chloride catalyst.

Lead Alkyls

The hazards involved in manufacturing and handling lead alkyls are two fold. These materials are both toxic and explosive to varying degrees. In mixed lead alkyls the relative hazard increases as the percentage of methyl groups increases.

The toxicity of TEL is well established. It is safe to assume that the toxicity of mixed alkyls and TML is at least as great as that of TEL and probably greater. Thus the danger of exposure to the vapors increases as the relative volatility of these compounds compared to TEL increases. The relative volatility of these compounds shows a marked increase as the percentage of methyl groups gets high. This can be seen in Figure 1.

Spontaneous thermal decomposition of TML occurs at a much higher temperature than that required for TEL while some mixed lead alkyls require a slightly lower temperature (See Item 7a, Table I). The temperature required to ignite mixed lead alkyls and TML is higher in all cases than that for TEL (See Item 9, Table I). Under unusual conditions such as sparks in the vapor phase and hot spots greater than 300°C (See Items 7b, 7c and 8, Table I), the minimum temperature of the bulk liquid required to initiate decomposition is less for mixed alkyl leads and TML than for TEL. Thus under normal conditions TML and mixed lead alkyls are probably not as prone to decomposition as TEL.

However, as indicated by Item 10, Table I, the rate of decomposition of mixed lead alkyls and TML, once initiated, proceeds at a rate which is much greater than that of TEL. The decomposition rate and thus the destructive power increases as the percentage of methyl groups increases.

Dilution of any lead alkyl compound has been qualitatively shown to decrease decomposition rate. Further experimental work would be required to establish more quantitatively the effect of dilution on decomposition rate.

Alkyl Chlorides

In the forming of mixed alkyl lead compounds, both methyl chloride and ethyl chloride are used. The toxic effect associated with the breathing

of ethyl chloride vapors is well known. It has a narcotic effect on the body which is usually transient. It will give some warning of its presence because it is irritating but exposure can be tolerated to the point of unconsciousness.

Methyl chloride has a similar narcotic effect on the body which is more pronounced and may result in cronic aftereffects. In concentrations which are harmful it is almost odorless and thus dangerous exposure may go unnoticed. Even repeated exposure to low concentrations may cause damage to certain parts of the body.

Both methyl and ethyl chloride are explosive when mixed in the proper proportions with air. However, ethyl chloride is considered greater fire and explosion hazard than is methyl chloride.

Since both methyl and ethyl chloride have been safely handled in numerous plants throughout the country, it is reasonable to assume that any new plant could do the same.

Alkyl Aluminum Calorides

When a mixed alkyl or tetramethyl lead is formed, a catalyst is required to speed the reaction and also to improve the yield. The most satisfactory compounds found for use as catalysts are methyl and ethyl aluminum sesquichloride ($Me_3Al_2Cl_3$ and $Et_3Al_2Cl_3$). These compounds exhibit similar properties. They flame instantly when exposed to air. They react violently with water and other liquids. The combusion of these materials is difficult to extinguish. To date no satisfactory method has been found.

PROBLEMS BY PLANT AREA

Alloy

As now envisioned, the manufacturing of sodium-lead alloy will be the same for plants producing TEL, mixed alkyls or TML.

Reaction

The problems that would be encountered in operating a reactor for production of volatile lead alkyls are as follows:

1. The reactor would have to be free of vapor leaks and ventilation air flow would have to be high to avoid contamination.

2. The operating pressures would peak at 200-300 psig (compared to a peak of 90 psig in the TEL reaction) in making lead alkyls ranging from MA-250 to TML.

3. The higher operating pressure plus the higher explosivity of methylated leads would result in higher peak pressures if the reaction gets out of control.

TABLE I

Physical Properties of Various Alkyl Lead Compositions

Compound	Composition, Mole % Compound					
	TEL	MA-250	$PbEt_3Me$	MA-500	$PbEt_2Me_2$	MA-
Tetraethyl Lead	100	31.6	--	6.25	--	0.
Triethylmethyl Lead	--	42.2	100	25.00	--	4.
Diethyldimethyl Lead	--	21.1	--	37.50	100	21.
Ethyltrimethyl Lead	--	4.7	--	25.00	--	42.
Tetramethyl Lead	--	0.4	--	6.25	--	31.
1. Molecular weight	323.5	309.4	309.4	295.3	295.3	281.
2. Melting point, °C	M-136	--	--	--	--	--
3. Boiling point, °C	198	--	179	--	160	--
4. Density of liquid, 20°C						
g/ml	1.6528	1.712	1.7130	1.789	1.7906	1.
lb/gal	13.8	14.3	14.3	14.91	14.95	15.
5. Vapor pressure, mm Hg						
25°C	0.388	1.9	1.16	6.05	3.26	15.
100°C	28.4	65.3	51.2	142	108	278
6. Relative volatility to TEL						
25°C	1.0	4.9	3.0	15.6	8.4	39.
100°C	1.0	2.3	1.8	5.0	3.8	9.
7. Decomposition temperature for the Pure Liquids, °C. Method of initiating the decomposition--						
a. Increasing the temperature of the liquid	190	--	165	--	175	--
b. Sparking in an air-filled vapor space above the liquid	185	--	163	--	138	--
c. Sparking in a nitrogen-filled vapor space above the liquid	195	--	167	--	141	--

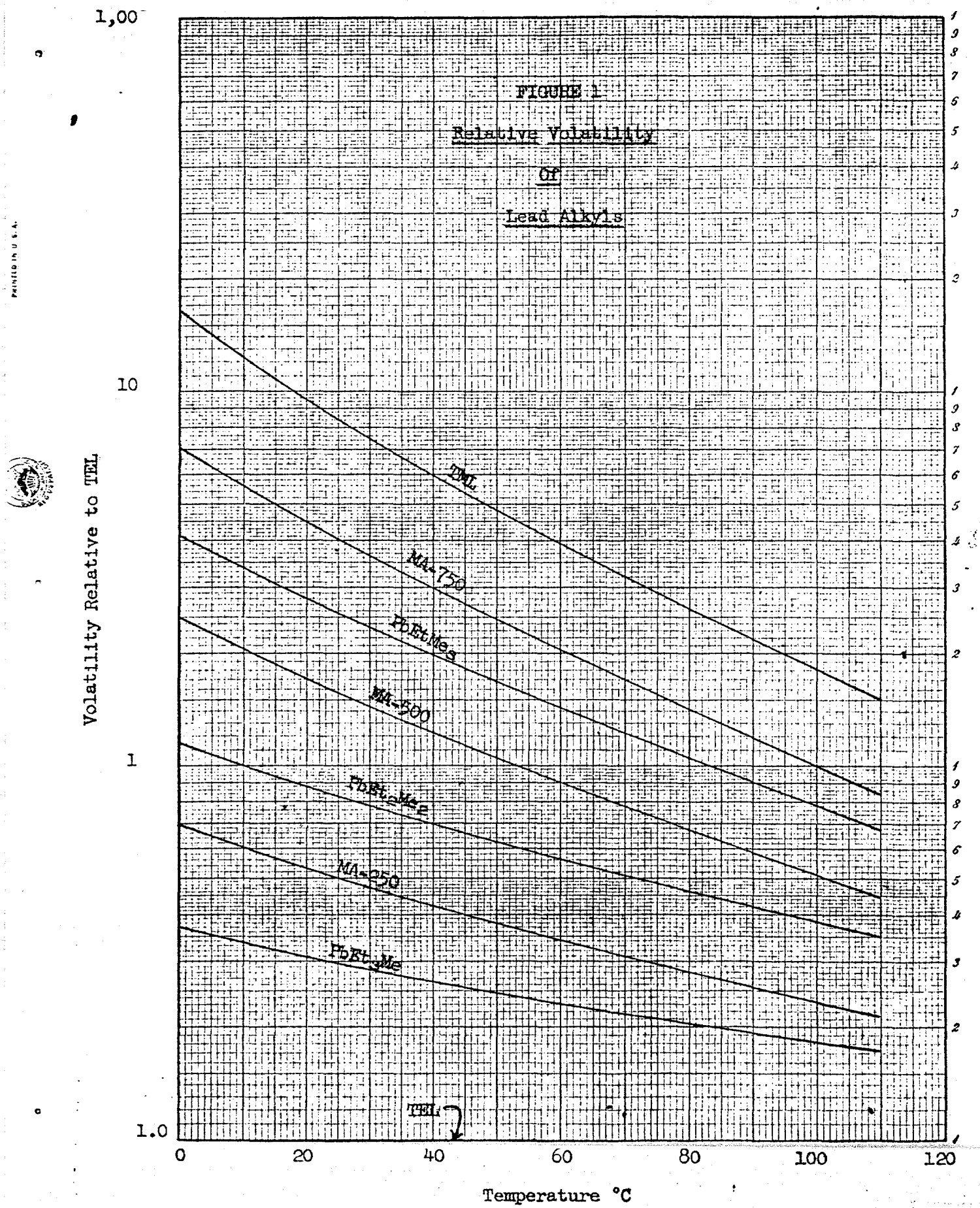
FIGURE 1
Relative Volatility
Of
Lead Alkyls
1,00
10
1
1.0
Volatility Relative to TEL
TML
MA-750
PbEtMe3
MA-500
PbEt2Me2
MA-250
PbEt3Me
TEL
0
20
40
60
80
100
120
Temperature °C

TABLE I

Physical Properties of Various Alkyl Lead Compounds (Continued)

Compound	Composition, Mole % Compound					
	TEL	MA-250	$PbEt_3Me$	MA-500	$PbEt_2Me_2$	MA-7
8. Minimum temperature, °C, of the liquid bulk at which bulk decomposition is initiated by a hot spot.	180	--	120	--	100	--
9. Temperature, °C, of a hot surface which will cause ignition of a liquid drop in open air.	180	--	185	--	245	--
10. Maximum rate of decomposition at temperature T expressed as cubic feet of gas (latm, T)/ millisecond-gallon of liquid						
T = 190°C	3.7	--	--	84*	--	--
T = 112°C	0	--	--	5*	--	--
11. Lead alkyl in vapor space above gasoline at latm, 25°C, milligrams/cubic foot						
1.5 cc TEL/gal orequivalent lead	0.7					
2.5 cc TEL/gal or equivalent lead	1.1		All other lead alkyls: a x mg/cu.			
3 cc TEL/gal or equivalent lead	1.3					

* Compositions for these samples only approximate MA-500.

Two general types of reactors have been used commercially or experimentally for the production of lead alkyls. They are:

1. The conventional autoclave where alkyl chloride is fed to sodium-lead alloy

2. A slurry-type reactor where alloy is fed into a large excess of alkyl chloride.

In the 1938-1940 period, volatile lead alkyls were successfully produced in conventional autoclaves at the Jackson Laboratories. In these runs, it was found that reaction mass is more stable than the pure lead alkyls. However, the most volatile lead alkyl made was the MA-500 mixture. TML has been made in the 5-gallon autoclave at Baton Rouge. This is a conventional-type autoclave.

As pointed out in the Introduction, it may prove economically attractive to use existing equipment for production of volatile lead alkyls. "E" Building at Baton Rouge was designed with 12 in. disc lines in anticipation of future production of mixed lead alkyls. It is recognized that contamination and overpressure problems may limit use of existing equipment to a lead alkyl considerably less volatile than TML.

Reference to Table I and Figure 1 shows that methylated lead compounds are considerably more volatile than TML. This, of course, means that the probability of contamination of air around the autoclaves would be increased. Careful operation would be required to detect and stop any leaks that occurred. If it were necessary to increase building ventilation air flow in direct proportion to the relative volatility of the compound being made, it would seem that existing equipment would be limited to production of a compound with low MA number. Defining the required ventilation air flow rate and flow pattern is necessary before existing equipment could be used for production of volatile lead alkyls.

The existing autoclaves are designed for 300 psi. Volatile lead alkyls up to TML could be made in present autoclaves from operating pressure considerations alone. However, the maximum pressure that would be obtained in the reactor during uncontrollable reaction or decomposition has not been completely explored for volatile lead alkyls and especially with respect to TML.

Reactors for making lead alkyls are protected from overpressure by use of safety discs. If a reaction gets out of control or decomposition occurs from a hot spot, the pressure in the reactor will rise rapidly. The disc will blow. The contents of the reactor will vent through a line to the atmosphere. It is likely that the pressure in the reactor will continue to rise after the disc has blown. It is this maximum pressure that must be used for safe reactor selection.

In general, the maximum pressure that will occur after disc rupture is a function of four variables:

1. The pressure at which the disc blows

2. The size and shape of the vent line

3. The reactor free volume

4. The amount of lead alkyl forming or decomposing (this in turn is a function of the amount of alloy fed to the reactor).

Any or all of these variables may be changed to allow manufacture of volatile lead alkyls in existing equipment. One would certainly expect the optimum case to be for production of lead alkyls with much lower explosivity than TML. Thus, if it appears economically attractive to manufacture lead alkyls containing a high percentage of TML, modification of the present autoclave design or development of a new reactor would be indicated.

In regard to the overpressure problem, it should be noted that pressure rise from decomposition of lead alkyls in reaction mass is not nearly as rapid as pressure rise from decomposition of pure lead alkyls. Data from Jackson Laboratories indicate that decomposition of MA-400 in reaction mass proceeds only four times as fast as decomposition of TEL in reaction mass. Whereas Table I shows that pure MA-500 decomposes about 30 times as fast as pure TEL.

A development program would be necessary to define a new reactor design. Perhaps a diluted system would be the answer to the explosivity problem. A few laboratory tests have indicated that hydrocarbons might be used as diluents. Ethyl has developmental experience with slurry reactors that could be brought to bear here.

Lead Alkyl Recovery

The problems associated with alkyl lead recovery are:

1. Contamination of air in the area

2. Possible overpressure from decomposition of lead alkyl.

Commercial and experimental units of the following types have been operated for lead alkyl recovery:

1. Steam distillation

2. Water displacement of lead alkyl in extract phase which is less dense than water

3. Reaction mass slurrying and lead extrusion.

The comments made in the Reactor section on area contamination and ventilation air flow are generally applicable to the lead alkyl recovery section.

If a hydrocarbon diluent or a stabilizer such as naphthalene were used, past experience indicates that lead alkyl recovery by steam distillation would be safe for compounds up to MA-500. This should also be true for compounds containing more methyl groups than MA-500. Diluents present at the lead alkyl recovery step would go through the remainder of the process and appear in the product.

Recovery of lead alkyl by the reaction mass slurrying technique now being developed might find good application in a process to produce the volatile lead alkyls. One big advantage is that this would be a low temperature operation. In the process as now designed, the lead alkyl would form a separate phase under a layer of water. Stabilizers could be added if necessary.

Alkyl Lead Cleanup

The major problems in alkyl lead cleanup are:

1. Contamination of air in the area from vessels containing lead alkyls and from aeration

2. Danger of overpressure if pure lead alkyls are handled by present procedures.

Washing and aeration of TEL has been accomplished batchwise and continuously (at Houston). Properly designed continuous aeration could reduce the lead alkyl hold-up and thus reduce the explosion hazard somewhat.

Aeration of a volatile lead alkyl, TEL for example, by present practice would involve exhausting the air used for aeration to the atmosphere. This might result in dangerous area contamination. It would be more desirable to operate in a closed system. In such a case the air would be continuously recycled with some oxygen make-up.

TML is more stable toward oxidation than TEL so there is no problem of product loss during aeration.

One way around the aeration problem might be to use debismuthized lead.

The problems associated with aeration would have to be solved before commercial manufacture could be undertaken.

In the TEL process, several tanks containing TEL are employed in clean-up. The explosivity of methylated lead compounds may preclude this practice. Again a diluent may be the answer.

Blending

The problems encountered in blending volatile lead alkyls would be similar to those encountered in the cleanup area.

The particular problem which stands out is area contamination from the dye chute. This could be prevented by pumping in the dye in solution.

Of course, the composition of the volatile lead alkyl blends would have to be established.

Alkyl Chloride Recovery

The principal problem encountered in alkyl chloride recovery in a plant making volatile lead alkyls would be condensation of methyl chloride vented to the recovery system.

In all prior experience, excess alkyl chlorides are recovered by vaporization and subsequent low temperature condensation. Three vents are now employed:

1. A sniff vent which removes products of side reactions and some ethyl chloride from the autoclave

2. A primary vent in which unreacted ethyl chloride is vaporized by hot water in the autoclave jacket

3. A secondary vent in which ethyl chloride retained in the reaction mass is vented from the steam still.

Methyl chloride boils at -10°F. When mixed with light hydrocarbons this presents a difficult condensation problem. Methyl chloride vented to the atmosphere would create an area contamination problem. Adequate refrigeration and condensers would have to be supplied.

Lead Recovery

The following problems would be associated with lead recovery:

1. If volatile lead alkyls were manufactured at the Baton Rouge plant, the necessity of occasionally breaking the long sludge lines would create a contamination problem.

2. Ventilation of the sludge pit.

The long sludge lines in use at the Baton Rouge plant require breaking and cleaning occasionally. This could create an area contamination problem. An improved sluicing method for moving the sludge from the stills to the sludge pit would be in order.

Use of a hydrocarbon diluant in the stills may help reduce the lead alkyl in the sludge. Also more of the volatile lead alkyl would be removed in the sludge dryer. Thus less lead alkyl would be present in the dry sludge to cause contamination or overpressure in the furnaces.

It is likely that the lead extruder now being developed would prove attractive for lead recovery in a volatile lead alkyls plant. This, of course, would be the best method of lead separation if reaction mass slurrying were used for lead alkyl recovery.

Effluent Treating

No unusual problems are foreseen in treating effluent water from a volatile lead alkyls plant.

Laboratory

Safe procedures would have to be worked out for handling blender samples and recovered alkyl chloride samples for a more volatile lead alkyl plant.

Plant Layout

Two major hazards would guide the layout of a new plant to produce the more volatile lead alkyls. Those hazards are:

1. Contamination of working areas with organo lead compounds

2. Danger of equipment rupture due to overpressure.

Perhaps experience with plants making highly toxic materials such as nerve gas could be used as a guide to the plant layout and ventilation requirements. The nerve gas plant at Rocky Mountain Arsenal employed the following:

1. Three continuous processing trains each in separate concrete bays that are six stories high

2. Bays separated by halls where personnel traveled

3. All operations conducted by remote control from a control room on the first floor

4. Ventilation air entered halls, flowed to bays and was exhausted through scrubbers underground

5. Air turn-over every minute.

The danger of equipment rupture could be greatly minimized by careful vent line sizing. In the case of TML, however, it might be practically impossible to size vents due to the high rate of decomposition. If this proves to be the case, blow-out walls would have to be provided.

FLUID HANDLING

The handling of mixed alkyl lead fluids will present problems similar to those encountered with TEL but greatly magnified by their increased volatility and explosibility. Major considerations in fluid handling are tank car loading and drumming, shipping, and customer storage and handling.

Tank Car Loading and Drumming

While methods of loading tank cars or drumming mixed alkyl fluids will be similar to those used with TEL, extreme care will be required to prevent even the most minor leaks and spills. The hygenic danger increases at least as fast as the relative volatility of the compound being loaded. Care will also be required to prevent ignition of the material from sparks and other sources.

Shipping

Distribution problems on fluid containing diluent would have to be reconciled before process design bases could be firmly set.

The shipping of mixed alkyl lead fluids will fall under the jurisdiction of the Interstate Commerce Commission. A thorough investigation will have to be made to determine the regulations which will affect the shipping. Inasmuch as the fluid will probably be diluted to the point where it is no more dangerous than TEL, no changes in tank car design should be required.

Customer Storage and Handling

Customers purchasing these high volatility mixed alkyl lead fluids will be required to use considerably more caution in storing and handling them. It is probable that special storage facilities and transferring methods beyond those already supplied will not be required.

Continued emphasis on the customer's maintaining safe handling procedures will be required. He should fully understand and appreciate the dangers involved in the use of these compounds and to take necessary precautions to protect his personnel against possible exposure.

The use of gasoline containing mixed lead alkyls or TML by the public must be considered. As in the case of TEL the absorption of the more volatile lead alkyls through the skin from handling leaded gasoline will be of no practical consequence. However, the increased volatility of these mixed lead alkyls and TML increase the danger of exposure from vaporized material.

As shown in Table I, Item 11, TML is 70 times as volatile as TEL. Thus greater dilution of gasoline vapors containing the TML is required. Service station personnel would probably experience the greatest exposure. Gasoline leaks which totally evaporate over short periods of time present a similar contamination problem for all alkyl lead compounds including TEL. A study would be required to determine the seriousness of the problem relative to the existing exposure to TEL.

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