Oct. 30, 1951 R. STANTON 2,572,887

SOLID-LIQUID REACTION PROCESSES

Filed May 29, 1948 3 Sheets-Sheet 1

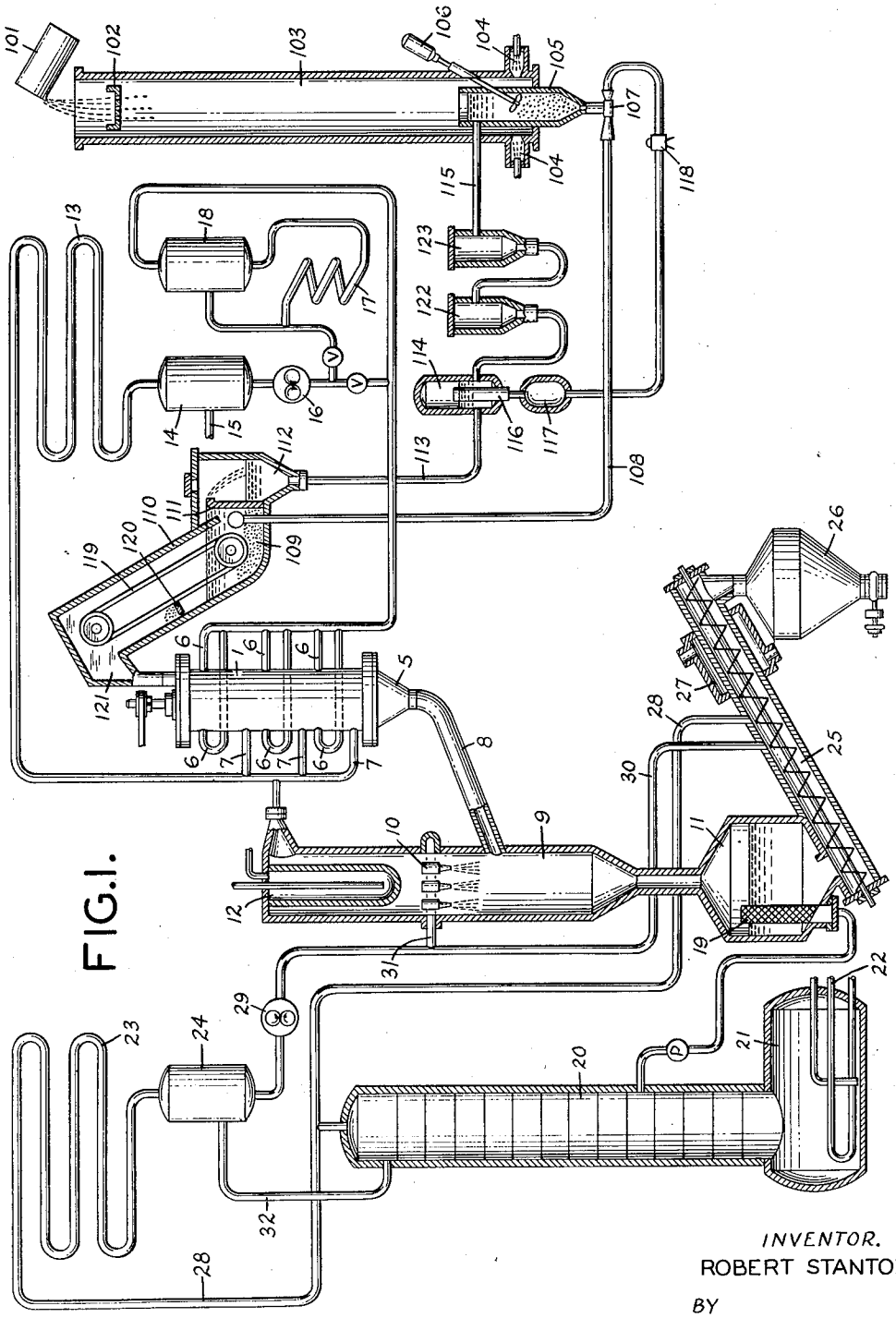


FIG. 1.

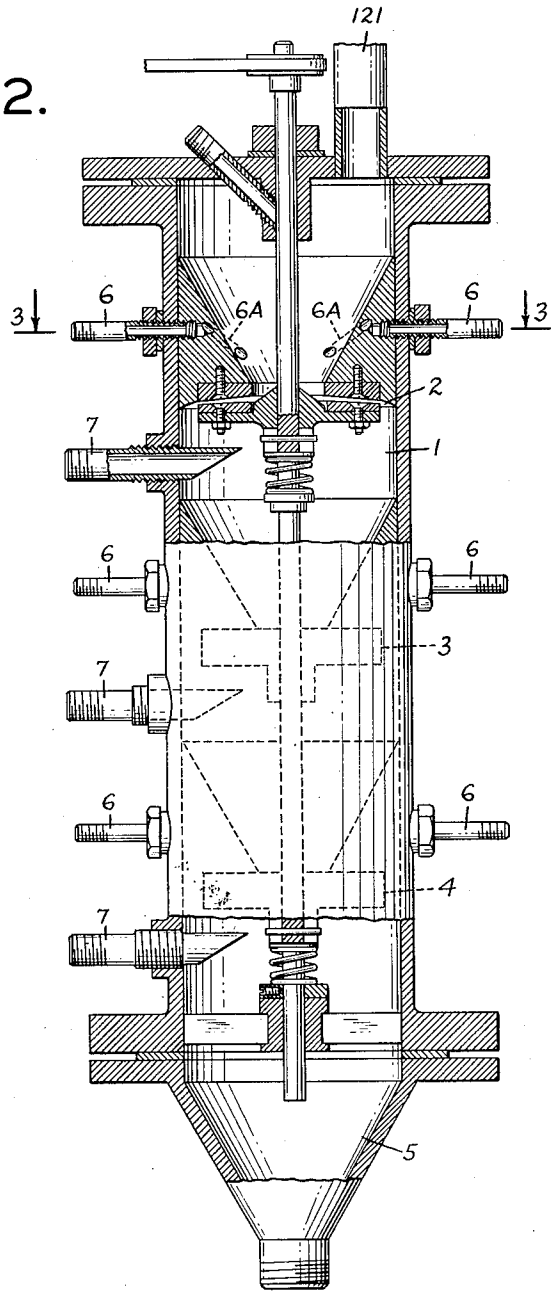
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SOLID-LIQUID REACTION PROCESSES

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FIG.2.



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SOLID-LIQUID REACTION PROCESSES

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FIG.4.

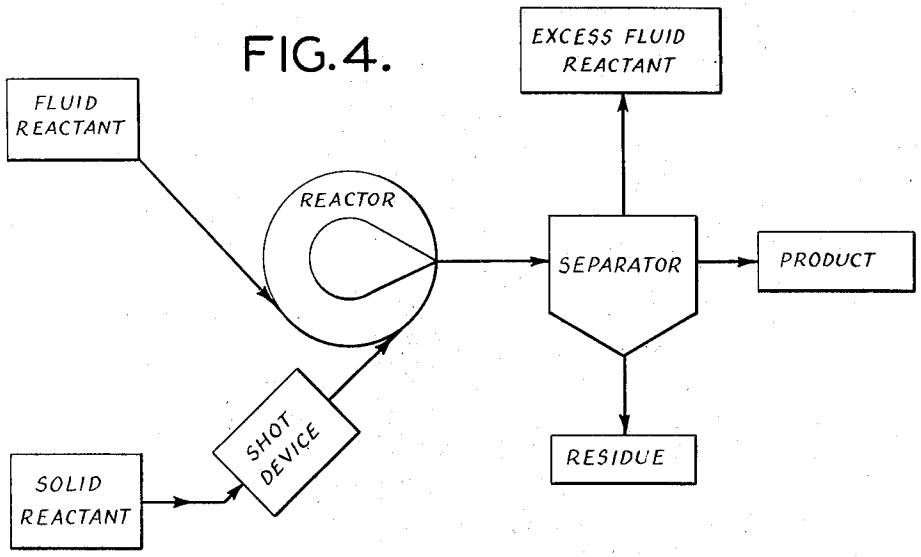
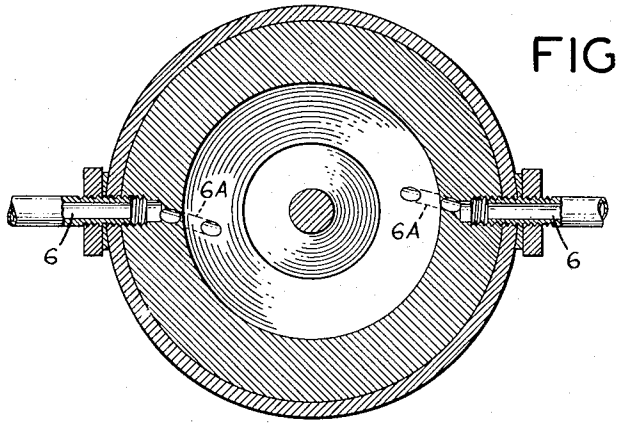


FIG.3.



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UNITED STATES PATENT OFFICE

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SOLID-LIQUID REACTION PROCESSES

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Application May 29, 1948, Serial No. 30,090

8 Claims. (Cl. 260—437)

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This invention relates to processes for the production of organo-metallic compounds, which comprise impinging a jet of a fluid alkylating agent upon the stressed area of a metal while said metal is subjected to intense mechanical stress, such as shear, torsion, and the like; and it relates more specifically to a process of preparing tetraethyl lead by impinging a high speed jet of liquid ethyl chloride upon lead-sodium alloy while said alloy is being subjected to a grinding action between relatively moving surfaces, e. g., in a Buhr type mill.

In the usual processes of reacting lead-sodium alloy with an alkyl halide, the alloy is prepared in a coarsely divided form by grinding or crushing in a device of the ball-mill type. The milled alloy is then charged into a reactor through a suitable opening. Dangerous conditions may result from the exposure of the alloy to the atmosphere, or by leakage of tetraethyl lead vapor from the reactor. In addition, the usual processes employ large reaction vessels involving relatively large reaction mixtures, and the reactions are relatively slow and difficult to regulate.

In accordance with the invention, it has been found that such processes can be conducted in a rapid and relatively safe, readily regulated manner, with improved yields. Small reaction mixtures are suitable. The new processes may be conducted in a fully continuous manner and give a highly desirable product.

The objects achieved in accordance with the invention include the provision of processes whereby organometallic compounds may be prepared by impinging a jet of a fluid organo-reactant upon a stressed area of a metal while said metal is being subjected to mechanical stress; the provision of processes for the preparation of alkylated lead by impinging a jet of an alkyl halide upon lead alkali metal alloy particles while said particles are being subjected to mechanical stress in a Buhr type mill; the provision of a process for the preparation of tetraethyl lead by preparing coarsely divided lead-sodium alloy and then impinging upon said alloy particles a jet of liquid ethyl chloride while said particles are being subjected to mechanical stress in a Buhr type mill; and other objects which will be apparent as details and embodiments of the invention are set forth hereinafter.

In accordance with the invention, a high speed jet of a fluid organo-reactant is impinged upon a stressed area of a metal while said metal is being subjected to mechanical stress between

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two grinding surfaces; all under reaction temperature and pressure conditions.

In one embodiment of the invention, coarsely divided friable metal particles are passed between the grinding surfaces of a Buhr type mill, and a jet of a fluid alkylating agent is impinged upon the metal particles while they are being subjected to mechanical stress between the grinding surfaces. This favors chemical reaction, and there will also be a reduction in size of the larger particles. The stressed surfaces of the particles are in highly reactive form and are maintained clean. The reaction process takes place rapidly, and the final reaction products and residue are processed to recover reaction products, unconsumed reactants and by-products or residues.

The process may be conducted in a fully continuous manner, in a partially continuous or intermittent manner, or in a batch type process. The fully continuous process is preferred for commercial operation.

In order to facilitate a clear understanding of the invention, reference may be had to the accompanying drawings in which:

Figure 1 illustrates an arrangement of an apparatus, partially diagrammatical and partially in section, which may be employed for conducting a process in accordance with the invention, e. g., in the manufacture of tetraethyl lead.

Figure 2 represents a more detailed view of the Buhr mill type reactor shown in Figure 1.

Figure 3 illustrates a cross-sectional view along the lines **3—3** of Figure 2.

Figure 4 represents a sketch of the process steps.

In Figures 1, 2 and 3, a Buhr mill type reaction chamber is represented by **1**. This is in the form of a vertical cylindrical chamber enclosing three grinding and reaction zones **2**, **3** and **4**, arranged in series. Each grinding zone includes a stationary (upper) buhr plate, and a rotating (lower) buhr plate attached to the central shaft in the chamber. The grinding plates are preferably constructed of hardened steel, and preferably provided with a series of radially-disposed raised ridges on the milling surfaces and curving or raking slightly backward from a true radial position (so that the milled metal is urged from the inner area of the plate to the outer edges thereof as the lower plate revolves). Preferably, the upper stationary plate grinding surface is conical or concave, and the lower rotating plate grinding surface is conical or convex at a slightly greater angle or

curvature, so that the outer edges of the plates are closer together and provide a relatively wide clearance therebetween at the inner edges, for facilitating introduction of coarsely ground alloy at the inner edges. A splined shaft attachment and a spring tension member maintain each pair of plates in proper spaced relationship. The distance between the plates is progressively smaller from zone 2 to zone 3 to zone 4; and the coarse particles undergo a rough grinding and reaction in zone 2, a finer grinding and reaction in zone 3, and the finest grinding and reaction in zone 4. The clearance between the plates in the latter zone may be of colloid mill order.

A pair of fluid reactant inlet pipes 6 is provided for each grinding and reaction zone, and these communicate with the fluid inlet jets 6A, set at an angle so as to direct the jet of fluid into the space between the grinding plates. The lines 6 are in communication with the fluid reactant supply tank 14 through optional pump 16, or also optional heater 17, and chamber 18. Tank 14 is equipped with a feed line 15. Each grinding and reaction zone is also supplied with an excess fluid reactant outlet line 7, which lines are connected to the fluid reactant recovery condenser 13.

A molten alloy supply vessel 101 is positioned so that alloy may be poured therefrom onto a perforated member 102, from which it drops in the form of droplets within a stack 103 into a cooling liquid such as light mineral oil contained in vessel 105. The alloy particles partially solidify by cooling in contact with a rising current of gas, and are chilled in the mineral oil. The temperature of the melt, the distance of fall through gas, the character of the cooling medium, and the like variables are preferably adjusted to provide alloy particles coated with a thin carbonized oil-protective film. Burners 104 are provided at the lower end of the stack for supplying combustion gases (a non-oxidizing atmosphere) in the stack. Other gases, or even air, could be circulated therein; and passed out of the tap. The vessel 105 is provided with agitating means 106 for keeping the alloy particles suspended in the liquid. A hydraulic ejector 107, energized by a high-pressure stream of cooling fluid, is arranged to continuously feed portions of the slurry from vessel 105 into transfer pipe 108 which delivers it into compartment 109 of the elevated vessel 110. The liquid level in this compartment is maintained sufficiently high to constitute a seal against backward flow of toxic vapors from the reaction zone. This vessel is divided vertically by the weir plate 111. The alloy particles settle due to the relatively low velocity in the compartment, and fluid overflows the weir plate into the discharge compartment 112. From there, the fluid flows by gravity through pipe 113 into surge tank 114. Liquid from the surge tank constantly passes through the cooling vessel 105, under a constant level or pressure head, either directly through a pipe 115 (or preferably through pipe 115 and purification vessels 122 containing boiling aqueous hydrochloric acid or the like and 123 containing aqueous caustic or the like neutralizing agent, for removing alkylated lead, as shown). Excess fluid overflows through line 116 into receiver 117; from which it is delivered under elevated pressure through pump 118 to activate the hydraulic ejector 107.

The alloy may be made up and melted at ground level and then elevated to the top of the stack or shot tower, e. g., by hoisting and tilting, or by pumping, or by a gas-lift (in which hydrocarbon gas may be used and ignited at the discharge to maintain the alloy in molten condition).

The vessel 110 is provided with a vertically inclined continuous chain-type conveyor 119, having one or more perforated blades 120 attached to the traveling chain in such a manner as to drag the alloy upward along the lower inclined surface housing, and permit fluid to drain back into the compartment 109. By this means, or other equivalent elevating means, substantially fluid-free coarsely divided alloy may be discharged continuously from the spout at the upper end of the conveyor into the top of reactor 1.

The bottom of the reactor 1 leads through throat portion 5 into line 8, which communicates substantially tangentially with the side of the low velocity cyclone separator 9. This separator is provided with an annular arrangement of downwardly directed spray nozzles 10, positioned above the point of communication of the exhaust line 8. The top of the cyclone separator is equipped with a partial condenser 12, and also communicates serially with the final condenser 13, which final condenser communicates with the fluid reactant feed tank 14.

The lower end of the cyclone separator 9 communicates with a closed chamber 11 which is equipped with a strainer 19. The strainer 19 communicates with the stripping column 20 (which may be of the multiple tray, or packed tower type). The column 20 communicates at its lower end with the reboiler 21. The reboiler 21 is equipped with a product removal seal pipe 22.

The chamber 11 communicates with an upwardly inclined helical ribbon-type conveyor 25, which conveyor in turn communicates with a storage vessel 26. The conveyor 25 is equipped with an annular heating jacket 27 at the upper end thereof. Conveyor 25 also communicates with a vapor line 28, at a point below the heating jacket 27, and it also communicates with a back-wash line 30, at a point below the vapor line 28.

A solvent supply tank 24, which is equipped with a feed inlet (not shown), communicates through pump 29 with line 30. Line 30 also communicates with the annular spray nozzles 10 through line 31. Tank 24 also communicates with the upper part of the stripping column 20 through line 32. The upper part of stripping column 20 communicates with condenser 23 through line 28, and this condenser in turn communicates with tank 24.

Figure 4 schematically illustrates the process. The metal reactant is preferably prepared in shot or the like coarsely divided form (desirably but not necessarily in a shotting device) and is brought together with the fluid reactant in the reactor, under reaction temperature and pressure conditions, wherein high speed jet and stress activated reaction occurs. Both reaction and attrition of solid particles occur in the reactor. Substantially completely reacted and finely divided reaction mixture is passed from the reactor to a separator, wherein the desired product is separated. In addition, unconsumed fluid reactant may be separately recovered, and unconsumed solid reactant recovered as or in a residue.

Other types of reaction chambers, in which the high speed jet of fluid organo-reactant may be directed onto stressed areas of metal while sub-

jected to grinding stress conditions, are suitable. The cross section need not be cylindrical; the grinding surfaces need not be disk-like, and other means than rotation may be used for imparting the relative or sliding movement of grinding surfaces.

If desired, additional fluid alkylating agent jets may be positioned so as to direct the reactant into the grinding space between the grinding plates.

In one embodiment, the process of the invention may be applied to the manufacture of tetraethyl lead by the reaction of lead-sodium alloy and ethyl chloride. Tetraethyl lead is of great commercial importance and it is consumed in large quantities as an ingredient in gasoline and the like internal combustion engine fuels.

Various methods have been proposed heretofore for the manufacture of tetraethyl lead, e. g., from lead-sodium alloy and ethyl chloride. One type involves charging a batch of the (about 90% lead–10% sodium) alloy into a reaction vessel and treating this with a batch or a continuous or intermittent stream of ethyl chloride. The reaction vessel may be in the form of an autoclave equipped with a rotary stirrer, or a rotating ball-mill, or similar batch type apparatus. These prior processes are subject to many drawbacks. They involve long reaction periods and leave much to be desired as to yields. The alloy particles and the sodium chloride by-products of the reaction tend to agglomerate into larger lumps, and thus a substantial amount of the alloy is shielded from contact with the ethyl chloride reactants. In addition, the agglomerated mass retains a substantial amount of the tetraethyl lead product, and the recovery of the product therefrom is tedious and wasteful.

There is considerable hazard involved in large reaction batch operations containing a large charge of the alloy. The reaction may occur with explosive violence. If moisture should happen to come in contact with the alloy, an explosion may occur. Where the process is conducted under pressure, there is considerable health hazard from any of the highly toxic tetraethyl lead vapors which might escape from the various valves, stuffing boxes and mechanical closures involved in batch type reaction vessels.

In accordance with the invention, it has been found that the above drawbacks may be overcome and the tetraethyl lead produced in a commercially more advantageous manner.

For the preparation of tetraethyl lead, using the apparatus illustrated in Figure 1, lead metal and sodium metal may be introduced and molten in vessel **101**. The molten alloy may be passed through the perforated member **102**, to form droplets which are substantially solidified by passing through substantially inert gases and then quickly chilled or cooled by passing into kerosene or the like light petroleum oil cooling fluid in vessel **105**, to give very brittle particles in the form of shot having a protective film coating; which particles are especially reactive when processed in the reaction chamber as discussed below. The shot is continuously transferred to compartment **109** of vessel **110** and then to the reactor **1**. The fluid supply tank **14** is filled with ethyl chloride. Ethyl chloride is maintained in the chamber **18** at a pressure of about 100 pounds per square inch gauge and a temperature of about 180° F. The alloy is fed into the reaction chamber **1** by means of the feeder mechanism, and ethyl chloride is injected by means of the jets **6A**. Optionally, heater **17** and chamber **18** may be by-passed.

Ethyl chloride pressures in the range of 100 to 1500 pounds per square inch gauge may be used; and the optimum pressure to be used is related to the composition of the alloy, intensity of grinding stress, and the other variables.

Both the amount of the ethyl chloride and the amount of lead used are in excess of the stoichiometric requirements. Preferably, an excess of ethyl chloride is chosen, and introduced under high pressure so as to flush the alloy particles into the entrance space of each grinding and reaction zone, and to sluice the milled material from between the grinding plates, in addition to combining chemically to form tetraethyl lead.

The reaction temperature is preferably maintained at about 120° to 140° F. The reaction of the ethyl chloride and the alloy occurs rapidly at the effective (stressed) contact surface. This surface is maintained in most reactive form by the mechanical stress of the grinding action, and also by the removal of any shielding coating. The by-product sodium chloride does not lump up or occlude any unreacted alloy or finished product, and is maintained in a finely divided state.

Substantially completely reacted and finely divided reaction mixture is withdrawn through exhaust line **8**. This withdrawn portion is then processed to recover tetraethyl lead, unconsumed ethyl chloride, and a residue which may contain recoverable lead. In one embodiment, the withdrawn reaction mixture is passed to the low pressure cyclone separator **9** and sprayed with acetone (from tank **24** through the spray nozzles **10**). The ethyl chloride vapor undergoes a scrubbing due to the effect of the partial condenser **12**, and then passes upward to the condenser **13**, where it is condensed and returned to the ethyl chloride tank **14**. Additional make-up ethyl chloride may be introduced through line **15**, if necessary.

The acetone solution of tetraethyl lead plus the solid residue passes to chamber **11**. The acetone solution, removed therefrom through strainer **19**, passes to the stripping column **20**. The acetone is vaporized, and the vapor passes to condenser **23**, is condensed, and then passes to acetone solvent tank **24**. Finished tetraethyl lead is removed through line **22**.

The solid residue passes from chamber **11** to the conveyor **25** wherein it is back-washed with acetone, supplied through line **30**. It is then heated at a temperature of about 200° F. to expel acetone vapors and impart a final drying effect to the spent alloy. The acetone vapor passes up to the condenser **23**, is liquefied, and then passes to tank **24**. The spent alloy passes to chamber **26**. It may be removed and processed to recover any lead therein, in accordance with known procedures.

The reaction chamber **1** may be supplied with a temperature regulating jacket, or set in a temperature regulating bath, in order to maintain the temperature thereof. The expansion of the ethyl chloride leaving the jets is accompanied by a refrigerating effect, and this will absorb heat evolved by the exothermic chemical reaction in the formation of the tetraethyl lead.

The acetone spray in the separator serves to strip tetraethyl lead from the vapors as well as to help settle the spent alloy particles and by-product, sodium chloride. The effect of the

partial condenser 12 is to further strip tetraethyl lead from the vapors of ethyl chloride.

It has been found that the recovered and recirculated ethyl chloride tends to give a higher yield of tetraethyl lead, than does fresh ethyl chloride. It is thought that some material carried over in the recovered ethyl chloride has a beneficial effect on the reaction.

The process may be carried out in apparatus which includes heat exchange devices; e. g., to use the heat contained in the ethyl chloride vapor to preheat fresh ethyl chloride liquid.

In an illustrative operation, a Figure 1 type of apparatus is used, the cylindrical reaction chamber being of about 6 inches inner diameter and about 2 feet high. The grinding plates in the first grinding zone 2 are set at a distance of 0.375 inch inner edge and 0.188 inch outer edge; the plates in the second grinding zone 3 are set at a distance of 0.250 inch inner edge and 0.125 inch outer edge; and the plates in the third grinding zone 4 are set at a distance of 0.156 inch inner edge and 0.016 inch outer edge. Two ⅛ inch fluid jets are used for each zone. The following are representative operation conditions:

Duration of run	2 hours
Weight of alloy charged	60 lbs.
Composition of alloy	10% Na, 90% Pb
Reactor temperature	138° F.
Pressure at inlet jets	500 to 1500 p. s. i. g.[1]
Pressure at reactor outlet	8 p. s. i. g.
Total ethyl chloride charged	60 lbs.
Rate-ethyl chloride feed	0.5 lbs./min.
Tetraethyl lead produced	16.2 lbs.
Yield based on sodium consumed	77%
Ethyl chloride consumed	14 lbs.
Yield efficiency based on ethyl chloride	92%
Average size of alloy feed	4 mesh
Average size of lead residue	64 mesh

[1] Pounds per square inch gauge.

In this procedure, the liquid is under a very high pressure gradient, e. g., the pressure difference between the inlet pressure and the outlet pressure is in the range of about 62- to about 188-fold. This is associated with a very rapid flow of the liquid between and around the alloy particles which are subjected to pressure between the annular milling surfaces, thus removing any shielding coating from the alloy and maintaining effective contact between both reactants while the alloy particles are subjected to intense mechanical stress. The reaction progresses very rapidly, and a high yield of the desired product is obtained in a very convenient manner.

It is indeed surprising that this reaction can be carried out so readily in accordance with the above-described procedure, and in such unexpectedly high yields. In the case of a process of preparing tetraethyl lead from the lead-sodium alloy and ethyl chloride in a ball-mill, the alloy tends to clinker up into lumps which contain unreacted alloy particles and by-product sodium chloride and also occlude some tetraethyl lead. There is also a tendency for a caking or coating of the balls (to form lumps) in the mill, and this will similarly isolate the two reactants from each other and occlude the reaction product so as to make recovery thereof difficult.

In the normal operation of the above-described process, there will be no appreciable health hazards from the escape of tetraethyl lead vapors. The high pressure part of the reaction system, wherein tetraethyl lead occurs, is completely closed. If desired, the pumping units may be completely submerged within the corresponding tanks, in order to avoid possible leakage of liquid from any stuffing boxes or rotary shaft seals. If desired, the condensing units and tanks may be set at a suitable height relative to the remainder of the apparatus, so that the static pressure of the liquid will be sufficient for movement of the liquid without the use of pumps.

Other proportions of lead to alkali may be used in the alloy, e. g., containing more than about 12.5% sodium. The alloy may be made up from one or more alkali metals, e. g., mixtures of alkali metals may be used. Other organic halides may be used, e. g., ethyl bromide, and other solvents than acetone may be used; as the art will readily appreciate in view of the above descriptions. A higher boiling fraction of gasoline may be used as a solvent; and the solvent solution of the tetraethyl lead could be directly blended with gasoline to give a desired motor fuel.

If desired, known promoters or catalysts may be included in the reaction mixture. Ferric chloride or anhydrous aluminum chloride may be suspended in an inert vehicle, such as a petroleum distillate, and introduced in controlled amounts into the reaction chamber at a convenient point.

If desired, the above-described product separation and recovery system may be replaced by conventional quenching and steam distillation methods. For instance, the mixture of tetraethyl lead and spent alloy can be discharged from the lower end of the cyclone separator 9 into a chamber containing a plurality of steam jets and then to a second cyclone separator, wherein the spent alloy particles are separated by a gravity effect, while the steam and tetraethyl lead vapor are removed, condensed, and the two immiscible liquids separately removed from the condensate.

The process may be used for the preparation of organo-compounds of other metals which give stable metalloorganic compounds. The metal reactant should be in brittle or frangible form. A suitable fluid organo-reactant is used for introducing the organo-group and the metal is subjected to the stress for presenting a very reactive surface. Instead of an alloy of lead with an alkali metal, a less expensive alloy agent may be used, such as silicon, which forms a friable reactive by-product slag. Where the metal is sufficiently hard and resistant, it need not be alloyed; e. g., with such metals as zinc (e. g., reacted with ethyl bromide in an atmosphere of carbon dioxide or similar non-oxidizable gas, to form diethyl zinc), magnesium, and the like. Mercury compounds may be formed by using a brittle or frangible amalgam (e. g., reacted with ethyl chloride, to form diethyl mercury).

Instead of an alkyl halide, another alkylating agent may be used, e. g., ethylene or an organic ester such as ethyl acetate dissolved in acetone or similar solvent.

In view of the foregoing disclosures, variations and modifications of applications of the invention will be apparent to those skilled in the art; and the invention contemplates all such other methods, variations and modifications except as do not come within the appended claims.

I claim:

1. A process for the preparation of organo-metallic compounds which comprises contacting a liquid organo-reactant with a friable solid metal reactant in coarsely divided form, the mixture of said reactants tending to form a shielding coating on said solid interfering with efficient reactive contact of the reactants, while subjecting said solid reactant to intense mechanical stress between relatively moving solid surfaces and maintaining the liquid reactant under a very high pressure gradient between said solid surfaces, under reaction temperature and pressure conditions, whereby the chemical reaction is intensified and fresh reactant surfaces are maintained, and separating organo-metallic compound product from unreacted organo-reactant and from the residue.

2. A process of claim 1 wherein alkylated lead is prepared by reacting solid lead alkali metal alloy with a liquid alkylating agent.

3. A process of claim 2 which is conducted in a continuous manner and wherein the alloy is in the form of solidified about 4 mesh particles and the alkylating agent is ethyl chloride.

4. A process of claim 3 wherein the pressure gradient is in the range of 62- to 188-fold between the relatively moving solid surfaces.

5. A process of claim 4 wherein the particles are subjected to intense mechanical stress between the first set of relatively moving solid surfaces set at a spacing of 0.375 inch at the alloy particle feed region and at a spacing of 0.188 inch at the region of discharge of reduced size particles therefrom, passing the reduced size particles from said first set of solid surfaces between a second set of relatively moving solid surfaces maintained at a spacing of 0.250 inch at the region of introducing the particles therebetween and 0.125 inch at the region of discharging reduced size particles therefrom and directing at least one high speed jet of liquid ethyl chloride upon said particles while they are being subjected to intense mechanical stress between said second set of solid surfaces, and passing the reduced size particles from said second set of solid surfaces between a third set of relatively moving solid surfaces maintained at a spacing of 0.156 inch at the region of introducing the particles therebetween and 0.016 inch at the region of discharging reduced size particles therefrom and directing at least one high speed jet of liquid ethyl chloride upon said particles while they are being subjected to intense mechanical stress between said third set of solid surfaces.

6. A process of claim 4 wherein the reaction mixture contains a catalyst.

7. A process of claim 6 which includes forming molten lead alkali metal alloy into substantially solidified coarsely divided hot particles in substantially round form and quickly cooling said particles in light petroleum oil whereby a protective film coating is formed on said particles and the metal therein is very brittle, whereby there is obtained an increased efficiency of attrition and reaction of said particles.

8. A process of claim 7 wherein the reaction mixture is contacted with a solvent for tetraethyl lead, and a solution of tetraethyl lead in said solvent is separated from unreacted ethyl chloride and from the residue.

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