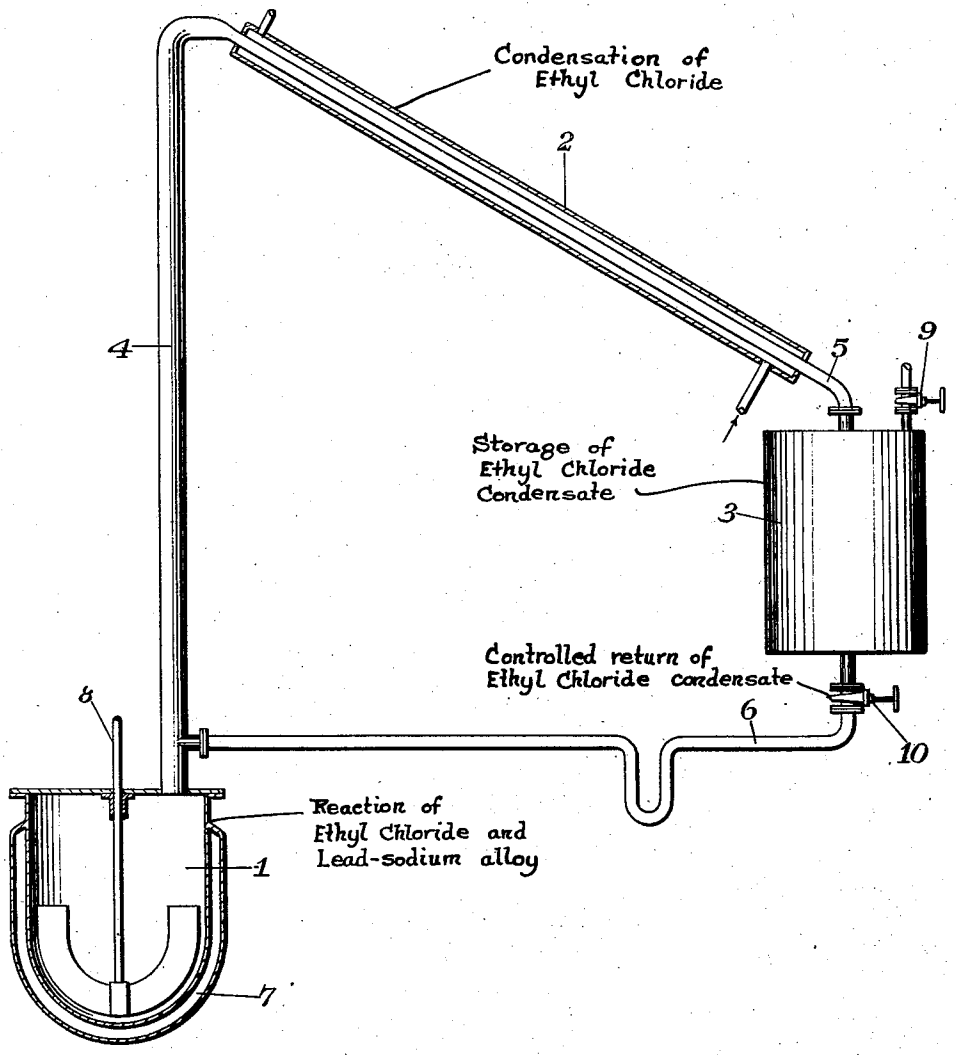
Aug. 24, 1937. H. W. DAUDT 2,091,114

PROCESS OF MAKING TETRA-ALKYL LEAD

Filed Oct. 27, 1934



INVENTOR.

Herbert W. Daudt

BY Charles A. Kingsbury

His ATTORNEY.

Patented Aug. 24, 1937

2,091,114

UNITED STATES PATENT OFFICE

2,091,114

PROCESS OF MAKING TETRA-ALKYL LEAD

Herbert W. Daudt, Wilmington, Del., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

Application October 27, 1934, Serial No. 750,323

5 Claims. (Cl. 260—11)

This invention relates to the production of alkylated lead and in particular to a method, whereby the reaction between the alkyl halide, e. g. ethyl chloride, and the lead-alkali metal alloy, e. g. lead mono-sodium alloy, may be carried out continuously and with high percentage yields, making the process highly practicable commercially. Certain particular features of the process are that: although the process is, as is desirable, carried out at elevated temperatures, the temperatures and consequent pressures are readily controlled with the elimination of liability of extensive decomposition of the tetra ethyl lead; the operation is continuous, without interruption to from time to time reduce temperature and pressure, whereby the total time of treating a charge is held to a minimum; and the cooling of the reaction mass is such that large charges can be advantageously used. Other features will appear hereinafter.

One object of the invention is to provide a method for the production of alkylated lead whereby the reaction between the alkyl halide and the lead-alkali metal alloy may be carried on continuously at elevated temperatures with ready control of temperatures and consequent pressures, the feed of condensed alkyl halide to the autoclave being restricted and regulated and full advantage taken of the cooling possibilities of the alkyl halide. A further object is to provide an apparatus for the practice of such method. Further objects will appear hereinafter.

In my United States Patent 1,749,567 Daudt March 4, 1930, it is proposed to boil the ethyl chloride under reflux, with pressureless equipment and at or below the normal boiling point of ethyl chloride, and with uncontrolled and unrestricted return of the condensed ethyl chloride directly to the autoclave; but this does not readily permit of satisfactory commercial scale operations. In contrast to my previous method, in the present method operations are conducted at elevated temperature and pressure, the feed of condensed ethyl chloride to the autoclave is restricted and regulated, and full advantage is taken of the cooling possibilities of the ethyl chloride, giving highly superior results not obtainable with the process of my said patent.

Without restricting the invention thereto, reference is made to the apparatus illustrated in the accompanying drawing, wherein the figure is an elementary view of an apparatus for the practice of the method. The apparatus comprises a reaction vessel or autoclave 1, a condenser 2 for the controlled flow of cooling medium therethrough, and a storage vessel or tank 3, connected in closed circuit by the riser pipe 4, connector pipe 5, and return pipe 6. The autoclave is provided with a jacket 7 with suitable connections (not shown) for the controlled flow of a temperature controlling medium therethrough, and is also provided with an agitator 8. The tank 3 is provided with a pressure relief valve 9, and ethyl chloride return valve 10. The riser pipe 4 is of sufficiently large diameter to ensure that the proper rise of ethyl chloride vapors therethrough, and the passage of returning condensate from the tank 3 to the autoclave, will proceed without interruption or lock throughout the process.

The above objects of the invention are accomplished as follows, referring to the illustrated apparatus and to a specific example:—

1 kilo of lead mono-sodium alloy (lead 90%, sodium 10%) was used, and 750–800 cc. (740 g.) of ethyl chloride, the ethyl chloride being thus approximately 200% in excess of that theoretically necessary for combination with the alloy. The alloy was placed in the autoclave and all of the ethyl chloride was run into the autoclave. The mass was agitated by the agitator 8. With the autoclave and valve 9 closed there was established a closed circuit, autoclave 1, condenser 2, tank 3, and return to the autoclave. Cold (ice) water was circulated through the condenser jacket; and warm water was circulated through the autoclave jacket, heating the charge to 40° C., with evidence of reaction. By use of a flow of cold water through the autoclave jacket the rise in temperature was easily checked in the range 40–45° C. (43° C. and below). This temperature range was maintained for 2 hours, the temperature then raised to 55° C. in an hour, and then held at 55° C. for 2 hours, completing the reaction. No venting of pressure was required. Appearance normal. Reaction water the same. The charge was allowed to cool to below 40° C., drowned in water and steam distilled for the recovery of tetra ethyl lead.

Throughout the run, the return of the condensed ethyl chloride, delivered to the tank 3 from the condenser 1, was controlled and restricted by adjustment of the valve 10 to deliver ethyl chloride to the autoclave at such rate that the reaction should proceed efficiently, and with adequate cooling effect by the ethyl chloride. That is, in the particular case, the valve 10 was opened so that it would deliver the ethyl chloride at the rate of 25 g. per minute (valve open one-sixth turn) and thus at a rate materially less than that at which it was being delivered to

the tank 3 during the period of marked reactivity between the alloy and the ethyl chloride. This restriction of flow was continued throughout the run. The pressures were but: 45 lbs. per sq. in. gauge at 41° C. in the autoclave; 50 lbs. at 50° C.; and 60 lbs. at 55° C. It will be noted that pressures correspond closely to the pressures of ethyl chloride alone at the stated temperatures, indicating that any gases, e. g. ethylene, ethane, butane and so forth, formed during the reaction and non-condensible under the cooling conditions, were dissolved in the ethyl chloride. The temperatures of the autoclave jacket corresponding to the mentioned autoclave temperatures were 50° C., 62° C., and 63° C. Just before the end of the 55° C. period the valve 10 was opened wide, but no evidence of further reaction was observed, showing that the reaction, and run, were completed. The temperature of the ethyl chloride condensate was approximately that of the condenser.

A procedure such as that exemplified by the above example provides for operation at elevated temperatures without the necessity of discontinuing the operation in order to cool the mass to avoid excessive pressures and consequent decompositions, since the combined cooling effects of the ethyl chloride and of the medium flowing through the autoclave jacket are entirely adequate to hold the mass at proper temperature and pressure. As a result, the operation can be continuous, with consequent high production speed. Furthermore, the cooling effect of the ethyl chloride evaporation is so great that, even in large scale operations the cooling water for the autoclave jacket need not be refrigerated and water at normal temperature may be used. This eliminates high refrigeration expense.

Also, the use of much larger charges than those previously useable, is made possible. While it would at first appear that to provide for larger charges it would be only necessary to correspondingly increase the size of the autoclave to accommodate the larger charges, such is not the fact. With small charges merely jacket cooling of the autoclave may be relied on. However, such cooling alone will not serve when it is attempted to use charges that are large. This is for various practical reasons, for instance, the mass is so large that the effects of the jacket cooling applied to the portions of the mass at the walls of the autoclave cannot penetrate adequately to the body thereof, even with the best design of autoclave. Further, the relative amount of cooling surface is reduced excessively. In consequence, when the use of large charges is attempted, it becomes necessary to interrupt the operation to permit cooling the mass, thus greatly prolonging the total time of operation—and frequently the attempted interruption will be too late, and consequent excessive decomposition of the tetra ethyl lead will occur. The present method eliminates these difficulties.

In the present method, although elevated temperatures and superatmospheric pressures are used, the temperatures and the pressures are under close control within the desired limits and excessive pressures are readily avoided without the necessity of venting. This is an operation that is usually required in order to avoid the excessively high pressures that would otherwise be created when the improvements of this invention are omitted. The control of temperature and pressure results in high yield, since the venting of gases and vapors in order to decrease pressure results in the loss of undue amounts of ethyl chloride, and consequent low yields.

With the pressure equalized between the feed tank and the autoclave there is no tendency for the pressure within the autoclave to interfere with the flow of ethyl chloride to the autoclave. This does away with the necessity of using an agent, e. g. nitrogen under pressure, to counterbalance the reaction pressures, when feeding ethyl chloride to the autoclave.

While the illustrated apparatus, for operating under pressure in closed system with control of flow of ethyl chloride to the autoclave, is shown as embodying an ordinary condenser, should it be desired to adapt a reflux condenser to the invention the insertion of the storage tank between the condenser and the autoclave may be accomplished by mounting the reflux condenser closed (e. g. valved) at the top on the storage tank, with the riser pipe from the autoclave connected with the top of the tank and the valved return pipe to the autoclave connected to the bottom of the tank.

It will be evident to those skilled in the art that the feature, exemplified by the present apparatus, of equalizing the pressure between the autoclave and the receptacle from which it is receiving ethyl chloride, has the advantage that it eliminates the necessity of applying pressure of an extraneous agent, e. g. nitrogen under pressure, to the receptacle in order to force the ethyl chloride into the autoclave. It will be further evident that this principle of operation is of general application in that it may be used to advantage whether or not the equalizing connection from the autoclave to the supply container includes a condenser or is merely connecting piping.

While particular reference has been made to lead tetra ethyl, it will be understood that the invention is applicable in connection with any of the analogous compounds of lead with alkyl radicals, or analogous metals, such as tin, etc. with corresponding alkyl radicals. It is particularly applicable to such compounds in which each alkyl group contains from one to four carbon atoms. Also, while the invention is more particularly described in connection with ethyl chloride, it is of course applicable with other hydrocarbon halides.

It is apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof and, therefore, it is not intended to be limited except as indicated in the appended claims.

What is claimed is:

1. In the art of making alkylated lead by reaction upon a lead-alkali metal alloy with an alkyl halide under pressure and at a temperature above the normal boiling point of the alkyl halide: providing a body of alkyl halide separate from the reaction mass and supplying the halide to the reaction mass therefrom, vaporizing a portion of the halide from the reaction mass, condensing the vapors, adding the condensate to the said body of alkyl halide, and feeding the alkyl halide mixture to the reaction mass at a restricted rate so controlled as to produce the cooling effect required to constantly hold the reaction at optimum reaction temperature.

2. A process as recited in claim 1, wherein the alkyl halide is fed at the controlled rate to the reaction mass continuously during at least the major portion of the reaction period.

3. In the art of making tetra ethyl lead by reaction upon a lead-sodium alloy with ethyl chloride, the process which comprises: reacting lead-mono-sodium alloy with ethyl chloride under pressure and at a temperature above the normal boiling point of ethyl chloride, condensing ethyl chloride vapors evolved from the reacting mass, storing the ethyl chloride condensate, and feeding ethyl chloride from storage to the reaction mass, thereby to control the reaction temperature and pressure, while so controlling and restricting said feed of ethyl chloride as to produce the cooling effect required to constantly hold the reaction at optimum reaction temperature, said reaction, condensation, storage and feeding being performed in closed circuit with the circuit under substantial pressure equilibrium throughout.

4. In the art of making tetra ethyl lead by reaction upon a lead-sodium alloy with ethyl chloride, the process which comprises: reacting a lead-sodium alloy with ethyl chloride under pressure and at a temperature above the normal boiling point of ethyl chloride, condensing ethyl chloride vapors evolved from the reaction mass, storing the ethyl chloride condensate, and feeding ethyl chloride from storage to the reaction mass, thereby to control the reaction temperature and pressure, while so controlling the cooling effected in the condenser and also so controlling and restricting said feed as to produce the cooling effect required to constantly hold the reaction at optimum reaction temperature, said reaction, condensation, storage and feeding being performed in closed circuit.

5. In the art of making tetra ethyl lead by reaction upon a lead-sodium alloy with ethyl chloride, the process which comprises: reacting a lead-sodium alloy with ethyl chloride under pressure and at a temperature above the normal boiling point of ethyl chloride, condensing ethyl chloride vapors evolved from the reaction mass, storing the ethyl chloride condensate, and feeding ethyl chloride from storage to the reaction mass, thereby to control the reaction temperature and pressure, while subjecting the reaction mass to supplemental cooling and so controlling the supplemental cooling and also so controlling and restricting said feed of ethyl chloride as to produce the cooling effect required to constantly hold the reaction at optimum reaction temperature, said reaction, condensation, storage and feeding being performed in closed circuit.

HERBERT W. DAUDT.