Oct. 14, 1958 C. M. NEHER ET AL 2,856,419

MANUFACTURE OF TETRAETHYLLEAD

Filed April 15, 1953 3 Sheets-Sheet 1

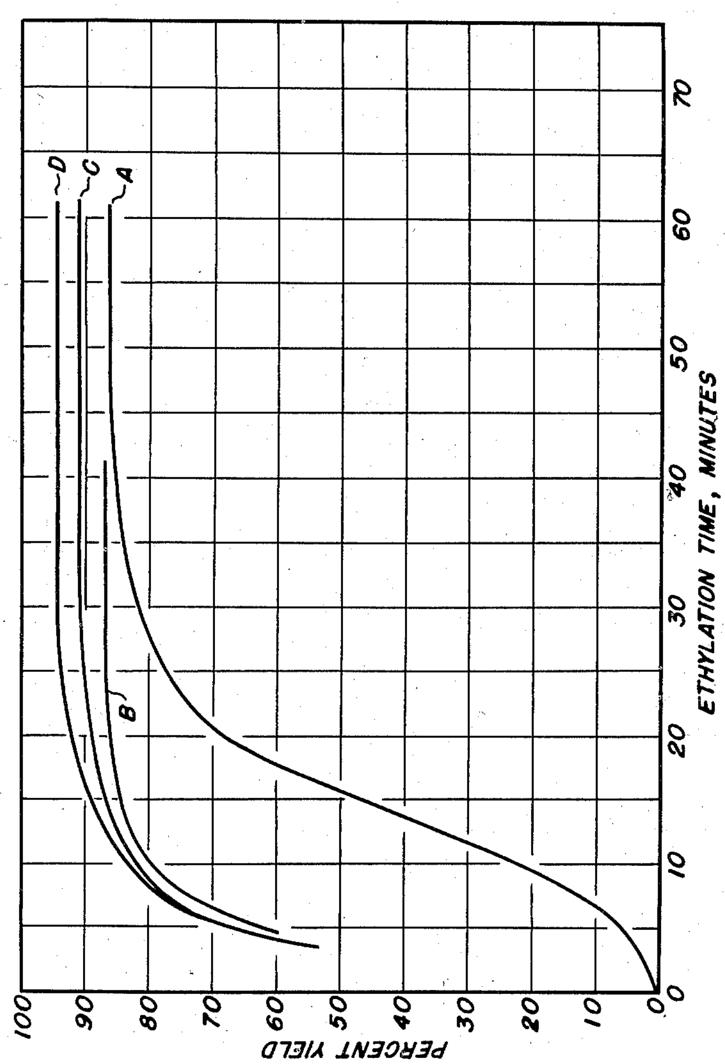

FIGURE I

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MANUFACTURE OF TETRAETHYLLEAD

Filed April 15, 1953 3 Sheets-Sheet 2

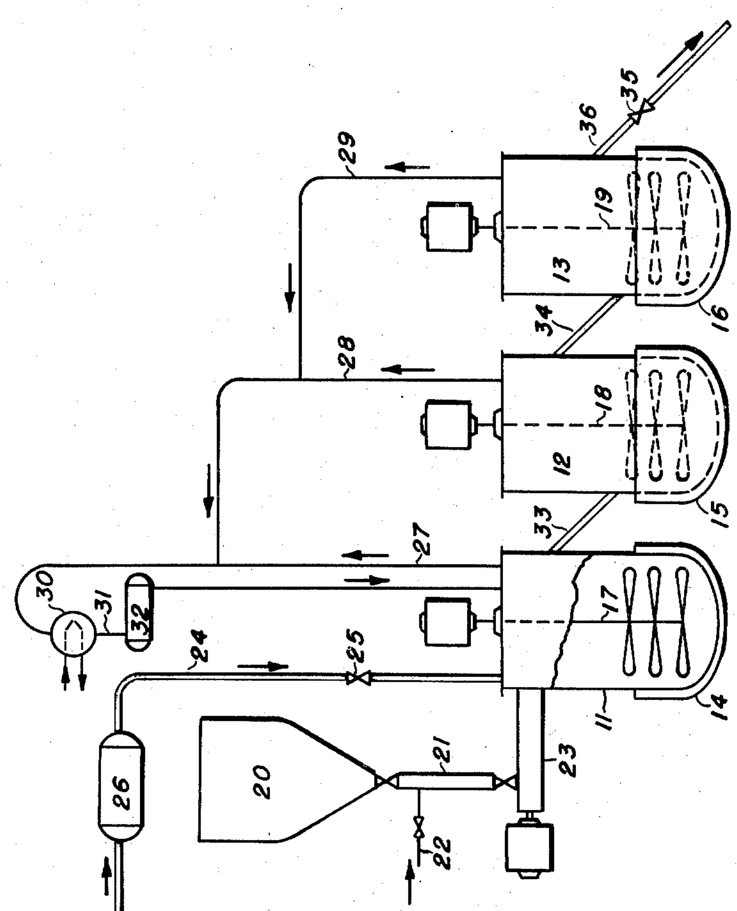

FIGURE 2

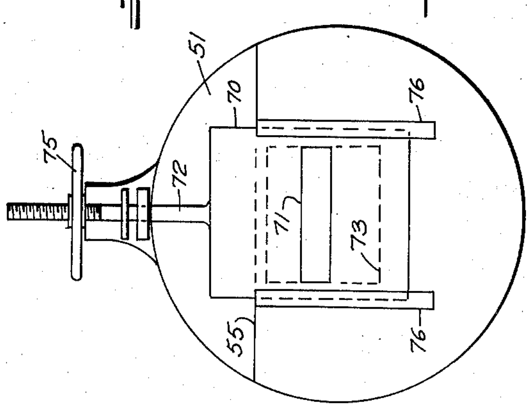

FIG. 4

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MANUFACTURE OF TETRAETHYLLEAD

Filed April 15, 1953 3 Sheets-Sheet 3

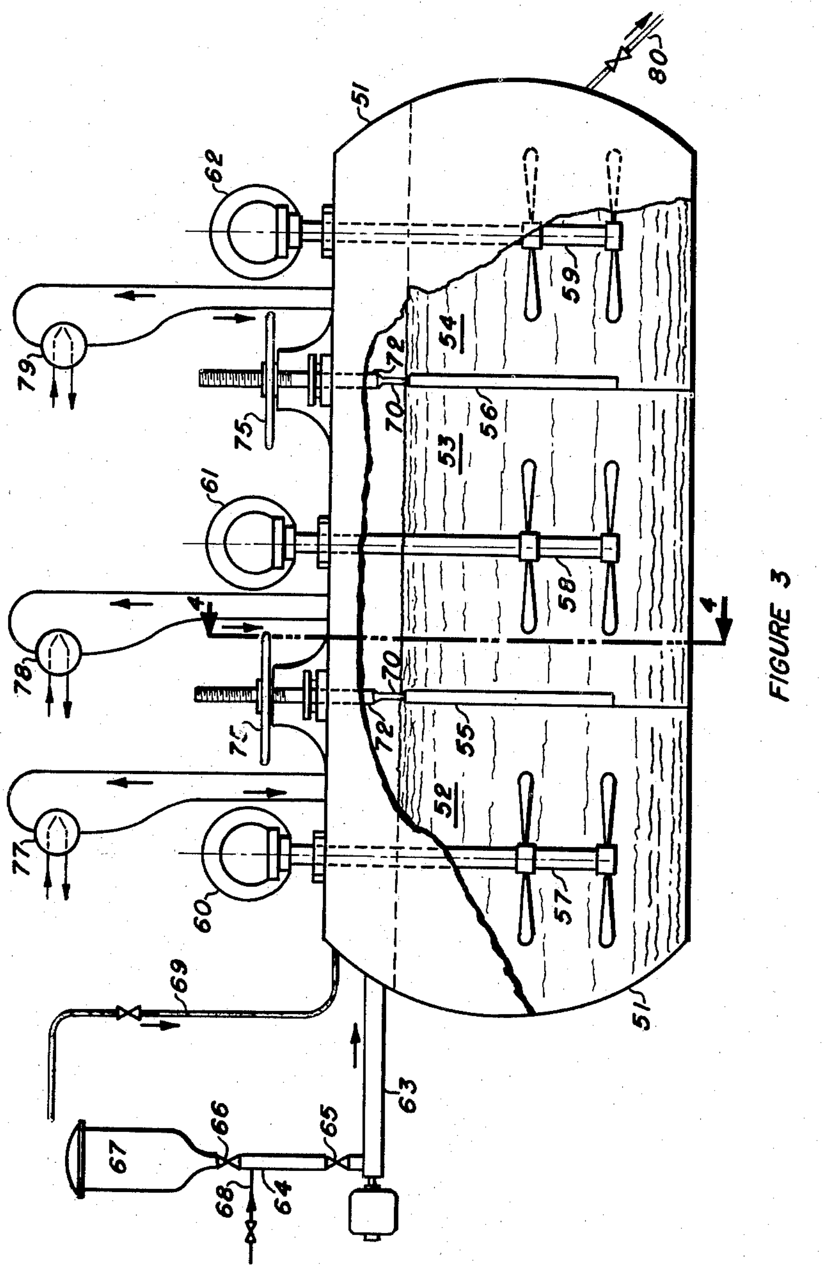

FIGURE 3

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2,856,419

MANUFACTURE OF TETRAETHYLLEAD

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Application April 15, 1953, Serial No. 348,946

6 Claims. (Cl. 260—437)

This invention relates to the manufacture of tetraethyllead. More particularly, the invention relates to a new and improved process whereby tetraethyllead is continuously produced by the ethylation of the lead of an alkali metal alloy of lead with an ethylation agent in a continuous manner.

Tetraethyllead, an important material employed extensively in the compounding of anti-knock mixtures, can be produced by a number of chemical processes. A proved reaction involves the ethylation of the lead in an alkali metal-lead alloy at an elevated temperature with a liquid ethylating agent. A typical reaction, representative of such a method, is

$$\underset{\text{Monosodium lead alloy}}{4NaPb} + \underset{\text{Ethyl chloride}}{4C_2H_5Cl} \longrightarrow \underset{\text{Tetraethyllead}}{Pb(C_2H_5)_4} + \underset{\text{Sodium chloride}}{4NaCl} + \underset{\text{Lead}}{3Pb}$$

The commercial operations employing the above reaction have consistently for many years been carried out by a batch technique. In such procedures, a substantial charge of commercial solid alloy is introduced to a horizontal cylindrical autoclave, then a charge of liquid ethylating agent is introduced as rapidly as permitted by the temperature-pressure relationships. The rate of addition of this liquid and the rate of carrying out the reaction is dictated by the pressure rise and heat evolution accompanying the reaction. The proportion of liquid employed is usually relatively low, that is, usually only a fraction of one part of liquid to one part of alloy by weight. Accordingly, in the progress of the reaction, the autoclave contents initially have only a minor proportion of liquid, and in the course of ethylation become a dry solid mass which from visual observation has virtually no liquid present. Upon completion of the ethylation, the excess pressure is released and the contents cooled by circulating a cooling medium in a jacket surrounding the vessel. The charge of reacted mass is then discharged into a pool of water in a steam distillation vessel. Live steam is then passed through this heterogeneous mixture with agitation and the tetraethyllead component is vaporized for subsequent solidification and decantation.

The major disadvantage of the above described operation is the large labor requirement involved and the nonsusceptibility of the process to continuous operation. Furthermore, it has been found that the distribution of the tetraethyllead product in the excess lead solids sometimes creates a rather hazardous condition in that there is no highly efficient means of uniformly reducing the temperature of the system. Accordingly, local decomposition of the tetraethyllead component may result in loss of materials and upon occasion exorbitant pressure rises. Thus, the prior process leaves much to be desired in the way of economics, capacity, and safety.

The object of the present invention is to provide a new and more efficient process for the continuous manufacture of tetraethyllead. An additional object of the invention is to provide a process wherein a substantial increase in a product capacity per unit of reaction space is provided.

A specific object is to provide as high or higher yields than has heretofore been commercially available. Yet another object is to minimize or reduce the formation of undesired co-products or by-products, for example hydrocarbons which must be vented from the system. Such hydrocarbons are accompanied by an irreducible amount of ethylating agent and they are thus released producing a dual loss. Still a further object is to allow a segregation of the reacting materials involved in a process into discrete stages or portions whereby the safety of operation is improved. Still further objects will appear hereafter.

Broadly, our invention comprises effecting the ethylation of the lead of a lead alkali metal alloy with a large excess of ethylating liquid and in a plurality of discrete stages in series. The proportions of liquid ethylating agent to alloy are in the ratio of at least 2:1, and in fact the preferred ratio is even higher, a preferred range being between the ratios of 3.5 to 4.5. Each of said stages is characterized by the agitation of this mixture of solids and liquid in a nonideal manner, whereby the solids distribution is nonuniform. Employing our process the solids remote from the bottom of each stage or reaction space are present in a lower weight proportion and also represent a higher degree of reaction than the average solids present in such a stage. The mixture of reaction liquid and solids is withdrawn from each stage at a point remote from the bottom thereof and transferred to the succeeding stage, or, in the case of the last stage, to operations for recovery of the tetraethyllead from the mixture.

A surprising feature of the process is that we obtain higher yields than are obtained by batch operations, both according to the prior art commercial practice, as heretofore described, and when employing similar operations in a batch-wise manner. A further benefit is that it is unnecessary to employ an accelerating catalyst, as is believed necessary for present commercial operations. These advantages will be evident from the examples appearing hereinafter.

In all embodiments of the process, a liquid ethylating agent and an alkali metal lead alloy are introduced in a continuous manner into the first of a plurality of reaction zones. The contents of the reaction zone are maintained at an elevated temperature, preferably of the order of 70 to 100° C., with a temperature of about 80 to 90° C. providing the best results especially when processing monosodium lead alloy. The feed of the ethyl chloride and alloy is usually as a continuous stream of each, although by continuous is also meant the intermittent charging of portions at such frequent intervals and in such small proportions, relative to the volume of the reacting mixture, that the practical equivalent of continuous flow is obtained.

The ethylation of the alloy is initiated almost immediately after feeding and proceeds rapidly. The reacting mixture is vigorously agitated, but sufficiently only to maintain the system with a nonuniform distribution of solids in the liquid phase. The agitation is however sufficiently vigorous so that the liquid phase is, as far as can be determined, virtually homogeneous throughout. A stream of liquid and solids is continuously withdrawn from the initial stage at a point remote from the lowermost portion of the reacting mixture and is passed to the next stage, where the same operation is repeated, differing, of course, in the chemical composition of the components therein. At least two stages are of course employed in the process, but the benefits are obtained, in varying degree, in even more stages. The optimum number of stages in three.

As will appear hereafter, the process is susceptible to numerous variations in degree without departing from the spirit and benefits thereof. The manner and benefits in carrying out the invention will be fully understood from the examples and the accompanying figures.

Figure 1 is a group of plots giving the yield of tetraethyllead as a function of time, in the ethylation of monosodium lead alloy with ethyl chloride, employing different processing techniques in each instance, but all being at the same temperature conditions.

Figure 2 is a schematic representation of a fully proven embodiment of the process wherein separate vessels are employed for the several stages, whereby certain auxiliary advantages are obtained, as is described hereafter.

Figure 3 is schematic representation of an embodiment wherein the several stages of the process are established in compartmental portions of a common reaction vessel. This embodiment also provides significant advantages for certain situations, as will appear later.

Figure 4 is a transverse view of a section 4—4 of the apparatus shown by Figure 3, for illustration of certain details therein.

Before illustrating the proces by a working example thereof, an understanding of the nature of an ethylation reaction will be of value. In a very large number of carefully observed ethylations, it has been shown that the progress of an ethylation follows a sigmoid curve. Thus, in a yield vs. time relationship at controlled conditions, the tetraethyllead is produced initially at a very slow rate, then at a high and relatively uniform rate, and finally at a steadily decreasing rate as an apparent ultimate yield is approached. A reaction time of two hours is sufficient to asymptotically approach that yield in all cases, except in lower temperature reactions.

Referring to Figure 1, the curves A, B, C, illustrate the foregoing remarks. Thus curve A shows the time yield relationship for a typical ethylation. Referring to curve A, it will be noted that the rate of formation initially is relatively low, but that in a period of about seven or eight minutes, a high and uniform rate of reaction is realized. In other words, the increase in yield per unit time is constant from about 10 minutes to about 18 minutes. For longer periods, the yield increases, but the rate of formation steadily decreases, and there is hardly any detectable yield increase after a reaction period of 60 minutes, even when the total ethylation time is increased to 120 minutes.

From the foregoing it is apparent that the efficiency of a particular process can be expressed most accurately by citing the yield in conjunction with the reaction time employed. It will be noted that all the curves in Figure 1 approach an asymptotic limit, that is a yield which further processing time is powerless to increase. In the interest of accuracy, this limiting yield is hereafter referred to as ultimate yield.

Long experience has shown that the ultimate yield level of tetraethyllead is primarily a function of the reaction employed. To a lesser extent, the ultimate yield is effected by the temperature of the process. However, when ethylating monosodium lead alloy with ethyl chloride, for example, at a carefully controlled temperature of 85° C., the ultimate yield obtained is substantially independent of such factors as the ratio of ethyl chloride to alloy, and of the physical character of the alloy. Thus, although alloy in different forms exhibits appreciably different reactivity, such reactivity does not affect the ultimate yields, but primarily the time required to attain that yield.

In view of the foregoing, an alternative processing technique would be expected to provide only advantages of convenience or ease of operation. While the present process does exhibit these benefits, it is found that unanticipated benefits are provided in several respects. Firstly, it is found that the processing method appears to affect the rate of reaction, so that, for example, a reaction period for attaining ultimate yield can be appreciably reduced. Secondly, it is found that the ultimate yield level itself is increased appreciably without benefit of catalyst. While it is not intended to limit the scope of this invention by any theory, it is believed that the increase in reaction rate (decrease in processing time) is a result primarily of intensive, but less than ideal agitation employed with a large excess of liquid ethylating agent. The increase in ultimate yields, however, is attributed primarily to the fact that the ethylation is conducted in a plurality of separate series stages.

Referring to Figure 1, the yield-time curves A, B, C, D, given therein illustrate the foregoing. Curve A presents the yield-time curve for the ethylation of monosodium lead alloy at 85° C. The method of carrying out this series of ethylations involved a batch-wise ethylation, employing an ethyl chloride: alloy weight ratio of 2:1, and mixing the reacting materials by end over end tumbling of the ethylation vessel. The results obtained, being the statistically firmed results of a large number of ethylations, shows that approximately 50 to 60 minutes are required to approach the ultimate yield of 87–88 percent. The alloy used in this series of ethylations was selected from commercial production, but had dusts screened out, inasmuch as fine particles are particularly susceptible to degradation by even trace amounts of moisture or oxygen.

Curve B, of Figure 1, is a similar yield-time plot of the results obtained when monosodium alloy is reacted at the same temperature (85° C.), but with an appreciably larger excess of ethyl chloride and with nonideal agitation during a large portion of the ethylation. The significant results of this series of ethylations is that the reaction rate, particularly in the initial phases of the reaction, was very much higher than in the series represented by the curve A. However, no significant difference in ultimate yield was noted. Accordingly, the sole benefit of the technique employed is a reduction in the processing time required.

Curves C and D present the yield time relationships in continuous operations. The results in the curve C represent single stage operation, whereas the yield curve D shows the results obtained with the present process employing two stage operation. It will be noted that, not only is the rate of reaction increased, particularly in the initial stages of the reaction, but in addition, when two stages are employed, the ultimate yield is also increased approximately 5 percent. This benefit is not realized when the same reaction is carried out in a batch manner, as shown by curve B, and only partially obtained when the ethylation is carried out in a single stage operation, as shown by curve C.

From the results above described, it is concluded that the ethylation of an alkali metal lead alloy is a sequence of reactions, and that an unknown intermediate may react to give either the desired product, tetraethyllead, or undesired by-products including hydrocarbons. It is believed that the present process provides a shift in the equilibrium of the reaction of this postulated intermediate to form by-products, so that the desired reaction has an opportunity to continue giving the higher yields encountered.

The examples given hereafter provide a fuller understanding of the benefits of the process and comparison with prior methods. The initial example below illustrates a typical ethylation such as was used in establishing the yield-time curve A.

Example I

This example illustrates the results obtained when an ethylation is carried out in a batch-wise manner and under such conditions that relatively uniform distribution and mixing of all components in the reaction space is obtained.

Ethyl chloride and comminuted monosodium lead alloy were charged to a cylindrical steel autoclave, previously cleaned and dried, in the weight proportions of two parts of ethyl chloride to one part of alloy. The alloy was charged while sealed in a thin glass envelope, to prevent reaction occurring prematurely. After charging, no catalyst or other additive being used, the autoclave was tightly sealed.

The autoclave and contents were then shaken briskly, to cause breakage of the glass envelope preventing contact of the reactant, by means of a steel ball previously inserted in the autoclave and contents were then immediately reinserted in a bath maintained at 85° C. and end-over-end agitation started. The reaction was continued for a period of 30 minutes, and the autoclave removed and immediately inserted in a chilling bath and cooled to a temperature of 0° C. at which temperature it has been established that no reaction occurs.

The autoclave was then opened and the contents flushed out with dry benzene for analysis and determination of the tetraethyllead found. A large series of ethylations in this manner provided an average yield of 80 to 82 percent, for the 30 minute reaction period employed.

In a further series of ethylations, in which the ethylation time was controlled as above described, the full yield-time relationship was developed and is shown as curve A in Figure 1. An ultimate yield of 87 percent is thus seen as being developed in approximately 60 minutes' ethylation time.

In this example better results were provided than hitherto obtained commercially. However, it is of course, impractical to operate a large scale process involving end over end tumbling of a massive autoclave. An approach to the above results was obtained, as already described, by providing continuous agitation in horizontal cylindrical autoclaves, as for example, those described in Stecher et al. Patent 2,170,353. However, it was desirable heretofore to utilize a much lower ethyl chloride:alloy ratio, of the order of 1:2 by weight. As a result, the commercial practice necessitated an appreciably more extended time to obtain a yield of 80 percent.

Example II

The following example illustrates results obtained when employing a large excess of ethyl chloride and ethylating in a batch-wise manner, but employing nonideal agitation.

A charge of ethyl chloride was introduced into a cylindrical steel reactor fitted with an efficient agitator. Solid comminuted monosodium lead alloy was introduced by a double valve lock chamber after the ethyl chloride was raised to an operating temperature of 85° C.

The ethylation was continued for an extended period, and the distribution of solid components within the reactor was followed. Samples were periodically withdrawn from the charge into a steel sampling bomb precooled at a temperature of about −78° C. These samples were used to determine both the amount of tetraethyllead formed and the distribution of solids. It was found that the average yield of tetraethyllead, with a reaction time of 30 minutes, was 85 to 87 percent, with ethyl chloride: alloy charge ratios of 6.6:1 and 25:1. During the formation of a major fraction—of about two-thirds—of the tetraethyllead so produced, the agitation applied was only adequate to provide a nonuniform distribution of the solids present. In other words, there was both a chemical and weight disproportionation of the solids. Thus, the solids present were less reacted toward the lower portion of the reaction mixture and also there was a higher proportion of solids by weight. The liquid phase was, however, homogeneous throughout.

A series of ethylations were carried out in this manner and the time-yield curve B of Figure 1 was so established. As will be apparent from curve B, the rate of reaction when employing the above described procedure was appreciably higher in the initial phases of the process. However, it was found that no appreciable change in the ultimate yield level was provided. Rather, the ultimate yield of about 87 percent was obtained in the relatively short period of about 30 minutes.

The results of ethylations carried out as above, and represented graphically by curve B of Figure 1 confirmed the expected invariant nature of the ultimate yield of the process. The following examples illustrate the results obtained when continuous operation is provided.

Example III

The apparatus used in Example II was also operated in a continuous manner as follows. Comminuted monosodium lead alloy was continuously fed through a gas pressurized screw conveyor to the reaction space. Liquid ethyl chloride was also fed, in a ratio maintained well above 2:1, usually over 4:1. A product stream was continuously withdrawn at a point remote from the bottom of the reaction, specifically, somewhat above the midpoint of the depth of the reacting mixture. Samples were immediately cooled on withdrawal from the discharge of stream to a temperature of 0° C. or below, prior to analysis.

A series of ethylations were made in the foregoing manner, with the residence or reaction time being varied by means of variation in the feed rates. The results obtained in this series, carried out at 85° C. is shown by curve C of Figure 1. This series of ethylations showed that a high initial reaction rate was obtained and in addition the ultimate yield was raised to an average of 91 percent.

The benefits of multi-stage operation are shown by Example IV below.

Example IV

Two cylindrical ethylation vessels connected in series were employed, the reaction space employed in the second vessel was approximately one-fourth the space provided in the first stage vessel. Each vessel was fitted with a plurality of agitators mounted on a common drive shaft and positioned at several levels in the mixture. A transfer line was provided, taking off at a point in the top 10 percent zone of the first stage. The discharge from the second stage was from a point about one-third of the vertical distance from the bottom.

In operation, alloy in several different forms was fed continuously or semi-continuously to the first stage. Liquid ethyl chloride was also continuously fed, in the proportions of as low as 2:1 and as high as 6:1, ethyl chloride to alloy.

The residence time in the system was varied by appropriate changes in the feed rates, the yields obtained in such a series thereby supporting the time yield curve D of Figure 1. It will be seen that not only is the rate of reaction provided higher than in the time tested ethylation method (represented by curve A), but, in addition a substantial increase—of the order of 7 to 9 percent—is obtained over the prior batch method (curve A) and also over batch operations.

It will be understood that the process can assume a wide variety of forms for given situations. A description of a working example of a preferred embodiment follows, employing apparatus schematically illustrated in Figure 2. Referring to Figure 2, three equal size reaction vessels **11**, **12**, **13** are employed. Each vessel is fitted with a jacket **14**, **15**, **16** for conducting a heat transfer medium about the lower portions of the vessels **11**, **12**, **13**. Each vessel is fitted with an externally driven agitator assembly **17**, **18**, **19**. It is preferred that the drive motors be variable speed so that the agitation power input can be varied.

In operation, comminuted solid monosodium lead alloy is fed to the initial stage **11** from a supply hopper **20**. The supply hopper **20** feeds through a stand pipe **21** which is pressurized by an inert gas supply applied through line **22**. From the stand pipe **21** the comminuted alloy is dropped into a screw conveyor **23** which continuously feeds the alloy above the level of the reaction liquid in the first zone **11**. Liquid ethyl chloride is forced into the first zone through a line **24**, the flow rate being controlled by valve **25**.

Typical operating conditions employed are 80 to 85°

C. at a pressure of 95 pounds per square inch. The ethyl chloride supply is obtained from a tank 26 through a feed line 25. The supply of this ethylating liquid includes both fresh ethyl chloride and ethyl chloride which has been recovered from final product mixture.

During operation, considerable amounts of ethyl chloride are vaporized from the three reaction zones and are bled off through vent lines 27, 28, and 29. These lines conduct the vapors to a common condenser 30 which condenses the ethyl chloride component and delivers it to line 31 to a condensate hold up tank 32. This recovered ethyl chloride and fresh ethyl chloride are all fed to the first zone 11 and in the proportion preferably of 3:1 to 4:1.

The reaction product mixture is transferred from the first stage 11 to the second stage by an inclined transfer line 33 and from the second stage 12 to the third stage 13 by an equivalent line 34. A take off valve 35 in the discharge line 36 from the final stage 13 is employed to control the discharge of the fully reacted solids liquid mixture to subsequent recovery operations.

In a typical operation, monosodium lead alloy in the form of comminuted highly reactive flakes is introduced into the unit at a rate of one pound per hour per cubic foot of reaction space in the first stage 11. Concurrently, liquid ethyl chloride is fed in the proportions of 3.8:1. Agitation mechanical power input is applied to each of the three stages at the rate of 0.1 horsepower per cubic foot or less. These reaction conditions provide a residence time total of about thirty-five minutes. The discharge stream from the final stage 13 has the following approximate composition:

	Weight percent
Tetraethyllead	7
Ethyl chloride	75
Sodium chloride	5
Lead	13

this stream therefore representing a yield of over 90 percent.

The foregoing embodiment is particularly suited for large operations in that separate vessels are employed for the several stages. An additional advantage of such an embodiment is that provisions can be made for adjustment of the total proportion of the ethylation carried out in each discreet stage accompanied by the possibility of return of individual feed of liquid to a specific stage. Thus, if it is desired to provide for apportionment of the actual reaction, and hence of the heat evolution uniformly within the several stages, then a more vigorous agitation can be applied in the first stage so that a larger proportion of less reacted material is forwarded to the following stage for further reaction. Alternative means of accomplishing this desirable flexibility in distribution of the reaction involves the variance of the point of withdrawal of the discharge stream to the succeeding stage. Thus, although we frequently prefer to discharge at the top of the reacting mixture or near the top, it is quite feasible to take off at a point closer to the mid point when desired. Such variation in the take off point allows control of the average composition of the liquid-solid system within the reaction stage, and hence of the overall degree of completion of reaction provided therein. A still further mode of accomplishing such adjustment would involve the return of condensed ethyl chloride to a single stage. Thus, it is usually preferred, as in the foregoing working example, to incorporate all the ethyl chloride condensed in with the liquid feed to the first stage. When desired, however, and particularly in combinations wherein the first stage is smaller than succeeding stages, it is also expedient to have a direct reflux to each zone. It is thus apparent that the system composition in each of the several stages can be varied by several means as above described.

One factor to be carefully observed in embodiment such as illustrated by Figure 2 is that the streams of reacted mixture between the several stages should flow at a relatively steep angle. It has been found that if partially reacted sodium lead alloy particles are allowed to remain in a quiescent state while at reacting temperatures, and in contact with an ethylating liquid, that they tend to adhere together and form masses which plug transfer lines. This difficulty is, however, avoided by providing for passage of the streams at relatively steep angles. It is found that providing a transfer angle of at least 45° will assure steady flow. It is believed that this angle is a function of the roughness of commercially available piping, and that specially finished conduit will permit lower transfer angles where desired.

Apparatus for an additional embodiment having particular features of merit is illustrated in Figure 3. Referring to Figure 3, a common envelope or drum 51 is compartmentalized into three separate zones 52, 53, 54 of approximately equal size by dams 55, 56. Multiple agitator assemblies 57, 58, 59 are provided in each of the zones, being driven by externally mounted motors 60, 61, 62.

A feed system is provided for comminuted solid alloy, including a feed screw conveyor 63, a stand pipe 64, and block valves 65, 66. The alloy supply is maintained in a hopper 67. The stand pipe 64 is intermittently charged with alloy by opening and then closing the top valve 66. The alloy in the stand pipe is then pressurized by an inert gas supplied through an auxiliary line 68. The bottom valve is then opened to allow alloy to be fed by the screw conveyor 63 into the initial reaction zone 52. Ethyl chloride liquid, or other ethylating liquid, is also concurrently fed to the initial stage 52 through a feed line 69.

In operation, the reacting mixture flows by gravity through the several zones in series. An important feature of this embodiment is that special devices are supplied to provide for control or variation of the level of withdrawal from the first two stages to the succeeding stage. It has been found that this feature provides highly desirable flexibility in that it makes possible alteration and control of the solids and liquid distribution within one of the individual zones substantially independently of the proportions in the feed stream. Therefore, variation of the degree of agitation employed is not essential for this purpose.

To further illustrate the mechanism provided for the above-mentioned feature, reference is made to Figure 4, this figure being a view of the transverse section 4—4 of the apparatus shown in Figure 3. The elements of this device include a slide plate 70, having a horizontally positioned slot 71 therein. The slide plate is snugly held against the dam 55 by slide angles 76 which has a square or rectangular hole 73 therein, the vertical dimensions being appreciably greater than the slot 71 in the slide plate. A rod 72 is affixed to the slide plate and passed through a gland 74 to allow vertical adjustment. The adjustment is provided as desired by the hand wheel 75 which engages the upper, threaded portion of the slide plate 70. In operation, the discharge of slurry from the initial zone 52 to the succeeding zone 53 (or similarly, from the second zone 53 to the final zone 54) can be readily varied from a lever near the top of the first zone to a point at or near the midpoint of the vertical depth.

Generally, the operation of the process in the above described apparatus is similar to the process as described in connection with Figure 2. Vapors from each stage are collected and liquified by the condensers 77, 78, 79. The finally reacted slurry is discharged from the last stage 54 through a line 80 to subsequent recovery operations.

It will be evident from the foregoing description and examples that the process is capable of numerous variations. Among the factors which can be varied without fundamental alteration of the process characteristics are the degree of agitation, the ratio of liquid ethylating agent to alloy, throughput time, and the number of stages employed. As heretofore stated, the reacting mixture of liquids and solids is agitated in a nonideal manner, that is the solids are not uniformly distributed throughout the liquid, although the liquid phase in any individual zone is virtually homogeneous. To provide such agitation the horsepower input in the agitation system is limited. Thus in every case, drive capacity of below 0.5 horepower per cubic foot of reaction mixture is provided, the preferred work input being about 0.1 shaft horsepower per one cubic foot to two cubic feet of reaction mixture. Although nonideal agitation is provided, nevertheless, other attributes of efficient agitation practice are adhered to. Thus, it is generally preferred to use a plurality of agitating elements (which may be either turbine type agitators or propellers) having a sweep of about 40 to 50 percent of the agitation zone area. In virtually all instances wherever a plurality of agitator elements are provided, the lowermost element is positioned within a distance of from one-fourth to one-half of its diameter to the bottom of the zone.

As heretofore stated, the ratio of liquid ethylating agent to sodium lead alloy fed can be varied, from above a liquid: solid proportion of 2:1 on up, although feed ratios of over 6:1 should be avoided because they impose an unnecessary burden on the recovery section or operations. A preferred feed ratio, and a preferred internal ratio in a specific reaction zone, is from 3.5:1.0 to 4.5:1.0.

Any plurality of separate stages in series attains the objects of the process, at least in part. The preferred maximum number of stages is three, and in fact, further increasing the number of separate stages will tend to depress the ultimate yield because every additional stage moves the process closer to an approximation of a batch operation which, as has been explained heretofore, does not provide any ultimate yield benefits. Accordingly, it is preferred to operate from two to three separate series stages. In addition to some latitude in the number of stages permissible, it is not essential that each zone or stage should be the same in size. Thus, a first zone can be smaller or larger than the succeeding zones. Similarly, the final zone may contain a smaller volume of reacting mixture than the preceeding zones. In all cases, it is preferred, for practical reasons, to limit the variance in volume to a factor of four, that is, the ratio in volume of the largest to the smallest stage should not exceed about 4:1.

The time of ethylation or residence time is another factor which has some effect on performance. It would be expected that an extremely long ethylation period might produce beneficial results, or at least, produce no adverse results. However, in one two-stage ethylation wherein an extended time of approximately 120 minutes was provided, the ultimate yield was no better than obtained in single stage operation. For this reason, it is inferred that under such conditions, there is no opportunity for some of the advantages of multi-stage operations to be exhibited, and hence it is preferred that the total time of ethylation be confined to not over about 60 minutes, the preferred range being from 30 to 60 minutes.

The mode of introduction, and the physical form of alloy introduced to the process are not extremely critical. Embodiments of the process have been operated with good results employing alloy prepared by crushing massive cast slabs of the metal. Another form of alloy successfully employed has been a super reactive alloy in the form of thin flakes cast on a rotating cylinder and quickly cooled. Still another suitable form of alloy is the feeding in a liquid state. The primary effect of such alterations is the effect on the recovery of alloy manufacture and the reaction rate in the initial stages of the ethylation, rather than on the ultimate yield.

The process is not limited to a specific ethylation reaction, but is applicable to ethylation reactions involving sodium-lead alloys of relatively high sodium content. For example, the process is applicable in the ethylation of alloys of the composition corresponding to the formula Na_2Pb, or with lesser and greater proportions of sodium. In addition, alloys with other alkali metal components are suitable feed components and similar benefits will be realized. For example, alloys containing potassium, either as the sole alkali metal, or as a component of a ternary alloy, can be advantageously ethylated by the process.

Although ethyl chloride is the preferred ethylating agent, other ethylating agents may be substituted for the ethyl chloride and the benefits of the method will be realized, although in varying degree. Examples of alternative ethylating agents which can thus be substituted for the ethyl chloride are ethyl bromide, ethyl iodide, and diethyl sulfate. As a practical matter, ethyl chloride will be most widely used owing to the cheapness and availability of this chemical.

This application is a continuation-in-part of our application Serial No. 244,514, now Patent Number 2,644,827, issued July 7, 1953.

The foregoing description of the process illustrates the effectiveness with which the objects of the invention are attained. Having fully described the invention and the best manner in which it is carried out, what we claim is:

1. The process for continuous noncatalyzed manufacture of tetraethyllead comprising ethylating an essentially monosodium lead alloy with an excess of liquid ethyl chloride in from two to three separate ethylation zones arranged in series, agitating the ethylation mixture in each of said zones only sufficiently to maintain the reacting and the reacted solids in non-uniform distribution in a liquid solution of tetraethyllead in ethyl chloride, withdrawing a slurry of solids in the liquid from each zone at a point remote from the bottom of said zone, said solids being more ethylated than the solids in the said zone, the feed to the initial zone being at least 2 parts by weight of ethyl chloride to 1 part of alloy, the slurry withdrawn from the final zone being discharged to recovery operations and the slurry from each other zone being fed to the next following zone, the total ethylation time being maintained from about 30 to about 60 minutes.

2. The process of claim 1 further defined in that the process is carried out in three ethylation zones of equal volume, and the feed to the initial zone includes from about 3.5 to 4.5 parts by weight of ethyl chloride to 1 part of alloy.

3. A continuous non-catalyzed process for manufacture of tetrathyllead comprising ethylating, at a temperature of about 80° to 90° C., monosodium lead alloy with an excess of liquid ethyl chloride in three separate ethylation zones of equal volume arranged in series, the ethylation mixture in each of said zones being agitated at the rate of from 0.05 to 0.5 shaft horsepower per cubic foot of reaction mixture, thereby providing non-uniform distribution of the reacting and reacted solids in a liquid solution of tetraethyllead in ethyl chloride, withdrawing a slurry of solids in the liquids from each zone at a point remote from the bottom of the zone, said solids being more ethylated than the solids in the said zone, the feed to the initial zone being from 3.5 to 4.5 parts by weight of ethyl chloride, the heat of reaction in each of the zones being removed at least in part by vaporizing a portion of the ethyl chloride therein, the vaporized ethyl chloride being condensed and returned to the first zone, the slurry withdrawn from the final zone being discharged to recovery operations and the slurry from each other zone being fed to the next following zone, the total ethylation time being maintained from about 30 to about 60 minutes.

4. The process of claim 1 further defined in that the process is carried out in two ethylation zones, the second zone being approximately one-fourth the volume of the first zone.

5. A continuous noncatalyzed process for manufacture of tetraethyllead comprising ethylating monosodium lead alloy with an excess of liquid ethyl chloride in three separate ethylation zones of substantially equal volume arranged in series, said ethylation zones being hereafter referred to as the first, second and third zones, the first and second zones having a common boundary, and the second and third zones having a common boundary, said boundaries being provided with communication ports between the said zones at a point remote from the bottom of the zones, the ethylation mixture in each of said zones being agitated at the rate of from about 0.1 to 0.5 shaft horse power per cubic foot of reaction mixture, thereby providing nonuniform distribution of the reacting and reactant solids in a liquid solution of tetraethyllead in ethyl chloride, withdrawing a slurry of solids in the liquid from each zone at a point remote from the bottom of the zone, said solids being more ethylated than the solids in the said zone, the feed to the initial zone being from 3.5 to 4.5 parts by weight of ethyl chloride, the heat of reaction in each of the zones being removed at least in part by vaporizing a portion of the ethyl chloride therein, the vaporized ethyl chloride from each of the first, second and third zones being condensed and returned to the zone from which it is vaporized, the slurry withdrawn from the final zone being discharged to recovery operations and the slurry from each other zone being fed to the next following zone, the total ethylation time being maintained from about 30 to about 60 minutes.

6. The process of claim 3 further defined in that the slurry streams withdrawn from the zones and transferred to subsequent zones are withdrawn and passed through a straight path downwardly inclined at least 45° to the horizontal.

References Cited in the file of this patent

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