

[54] **LOW TEMPERATURE MELT
CHLORINATION PROCESS**

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[57] **ABSTRACT**

A melt chlorination process which produces tetrachloroethane by chlorinating ethylene, vinyl chloride, ethylene dichloride, and mixtures thereof, with a melt consisting essentially of iron chloride, copper chloride, alkali metal chloride(s) and water by dispersing the material to be chlorinated in the melt whereby said material is chlorinated by the melt, wherein certain proportions and process conditions are utilized to provide desired product selectivity.

13 Claims, No Drawings

LOW TEMPERATURE MELT CHLORINATION PROCESS

BACKGROUND OF THE INVENTION

Many methods have been proposed in the prior art for randomly or selectively producing chlorinated hydrocarbons from hydrocarbons and/or chlorohydrocarbons in processes involving modified Deacon-type chlorination procedures. In processes of this character, oxygen, the hydrocarbon and/or chlorohydrocarbon to be chlorinated, and chlorine or HCl as the chlorinating agent, are brought into contact at elevated temperatures with a metal halide catalyst, usually a copper chloride-containing catalyst. Where HCl is utilized as the feed material, it is believed that a preliminary oxidation of the HCl takes place resulting in the formation of water and elemental chlorine. The chlorine produced then reacts with the hydrocarbon and/or chlorohydrocarbon feed to produce further quantities of HCl and a chlorinated derivative of the feed material. When chlorine is utilized as the chlorinating agent, it is believed that an initial chlorination of the hydrocarbon and/or chlorohydrocarbon takes place which generates HCl. The HCl thus generated is converted by the conventional Deacon reaction to chlorine and water.

In recent years considerably emphasis has been laid on fluid bed processes for conducting such oxychlorination procedures since the reactions involved are highly exothermic and the removal of heat usually becomes a problem of considerable moment. In conducting fluidized bed oxychlorination procedures of this type, however, many difficulties are encountered. For example, in some instances the fluidized bed does not provide sufficient contact with the initial feed to produce complete chlorination or high yields of substitutive chlorination. Also, the fluidized bed becomes hard to handle in high temperature chlorination procedures. Consequently, many methods have been devised for providing adequate cooling of the fluidized bed catalyst particles employed during reaction. Various carriers have been tested to determine the best materials from the standpoint of thermal conductivity, lack of attrition during fluidization, and other similar considerations in order to arrive at a material suitable for use as a support for the catalyst material employed during the chlorination reaction. Product recovery from the reaction zones without injuring the catalyst particles is also another problem encountered in this area. Many of the gas mixtures fed are highly explosive under certain conditions so that proper mixing of them is an extremely important factor. In addition, corrosion of materials of construction utilized in forming the reactors involved, and the selection of the proper size of the reactors for the purpose of providing maximum productivity are also problems. It has also been found that when conducting these processes in large reactors (2 feet or more in diameter), a considerable sacrifice in overall efficiency of the process contemplated is experienced.

The commercial success of these processes is due largely to the demand for halogenated compounds containing from one to ten carbon atoms; however, there is a great need for improvement of these processes. For example, it would be highly desirable to reduce the contact time normally associated with fixed bed operations, while eliminating the difficulties associated with fluidized solids operation such as catalyst attrition and catalyst vaporization which appears to be more pronounced with highly active catalysts. While the moving bed solves some of these difficulties, it is not without its own particular problems such as those derived from the mechanical transportation of catalysts throughout a zone and the existence of "hot spots" in the catalyst bed. The heat of reaction generated on the surface of the solid permits direct oxidation of the hydrocarbon and/or chlorohydrocarbon to produce undesirable oxides of carbon.

The more active metal halide catalysts such as, copper chloride, are more volatile at required halogenation temperatures and thus, it is difficult to retain the catalyst in the system and maintain the activity of the catalyst mass over an extended period of time. In such systems the volatilized catalyst must be

recovered by condensation or other troublesome methods and returned in a supported state to the reaction zone. Thus, the economics of operating with fluidized catalysts is poor in spite of the fact that such a system provides better temperature control and higher yield of product for a given period of operation.

Therefore, it is readily apparent that a new chlorination process is needed which overcomes the above difficulties by providing a more economic and commercially feasible chlorination process. Additionally, a better chlorination process is desired to provide improved contact between the hydrocarbon and/or chlorohydrocarbon and chlorinating agents in conjunction with good temperature control of the reaction zone. Furthermore, a selective chlorination process (i.e., a process that produces predominantly one specific chlorinated product in high yields) is in great demand throughout the industry.

SUMMARY OF THE INVENTION

A chlorination process which comprises chlorinating a material of the group consisting of C_1 to C_{10} hydrocarbons, incompletely chlorinated derivatives of C_1 to C_{10} hydrocarbons, and mixtures thereof, at a temperature within the range of 100°C. – 250°C. by means of a melt comprising iron chloride, copper chloride, alkali metal chloride(s) and water by dispersing the material to be chlorinated in the melt whereby said material is chlorinated by the melt, wherein:

- the alkali metal chloride is selected from the group consisting of LiCl, a LiCl/KCl mixture, a LiCl/NaCl mixture, a LiCl/RbCl mixture, a LiCl/CsCl mixture and mixtures thereof, provided that the alkali metal chloride comprises at least 30 mole percent LiCl;
- the mole ratio of iron chloride to copper chloride is from about 20:1 to about 1:1;
- the mole ratio of alkali metal chloride to combined moles of iron chloride and copper chloride is from about 0.5:1 to about 2:1;
- the water is present in an amount within the range of 0.1 percent–6 percent based on the weight of the melt; and
- at least some of the iron chloride is maintained as ferric chloride and all of the copper chloride is maintained as cupric chloride.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred process of this invention involves chlorinating ethylene, ethylene dichloride, vinyl chloride or mixtures thereof, to produce high yields of tetrachloroethane by contacting the ethylene, ethylene dichloride, vinyl chloride or mixtures thereof with the above-described melt. In addition, the process of this invention is equally applicable to the chlorination of many other C_1 to C_{10} hydrocarbons and their incompletely chlorinated derivatives, and more specifically, to C_2 to C_{10} unsaturated hydrocarbons and their chlorinated derivatives. However, since ethylene is one of the preferred starting materials, the discussion throughout the specification is directed to the chlorination of ethylene, without intending to limit the scope of this invention to ethylene.

It is pointed out that when chlorinating ethylene, the preferred process of this invention effects a high selectivity toward tetrachloroethane. The terminology "high selectivity" is intended to designate that at least 50 mole percent of the chlorinated product is tetrachloroethane, with a preferred selectivity being at least 70 percent tetrachloroethane.

The preferred process of this invention is also directed to producing "high yields" of chlorinated hydrocarbons. The terminology "high yields" means that a high percentage (at least 70 percent) of the starting material is converted to chlorinated hydrocarbons, with the yield losses being represented by CO , CO_2 and any other oxygen-containing byproducts. More specifically, "high yields" of tetrachloroethane are desired with the yield losses being CO , CO_2 and any other oxygen-containing byproducts. In order to achieve high yields, the melt

composition (e.g., LiCl, water, etc.), temperature, HCl partial pressure and oxide content must be optimized within the teachings of this invention.

Accordingly, the preferred embodiment is directed to a continuous chlorination process which comprises chlorinating ethylene, to produce a chlorinated product which contains at least 50 mole percent of tetrachloroethane, at a temperature within the range of from 125°C.-225°C., by means of a melt comprising iron chloride, copper chloride, alkali metal chloride(s) and water by dispersing the ethylene in the melt, the melt being the continuous phase, whereby said ethylene is chlorinated by the melt; withdrawing a gaseous effluent from the reaction zone which contains unreacted starting material and the resulting chlorinated hydrocarbon products and recovering the chlorinated hydrocarbon products from the effluent as the products of the process; and regenerating the melt with a regenerating system selected from the group consisting of a chlorine-containing gas, a combination of an oxygen-containing gas and hydrogen chloride, and mixtures thereof, wherein:

- a. the alkali metal chloride is selected from the group consisting of LiCl, a LiCl/KCl mixture, a LiCl/NaCl mixture, a LiCl/RbCl mixture, a LiCl/CsCl mixture and mixtures thereof, provided that the alkali metal chloride comprises at least 30 mole percent LiCl;
- b. the mole ratio of iron chloride to copper chloride is from about 10:1 to about 5:1;
- c. the mole ratio of lithium chloride to combined moles of iron chloride and copper chloride is from about 0.7:1 to about 1.3:1;
- d. the water is present in an amount within the range of 0.5 percent-3 percent based on the weight of the melt; and
- e. at least 75 percent of the iron chloride is maintained as ferric chloride and all of the copper chloride is maintained as cupric chloride.

Generally, as ethylene is chlorinated, with the progressive addition of chlorine and splitting out of HCl, the chlorination products are as follows: ethylene dichloride (1,2-dichloroethane), vinyl chloride, 1,1,2-trichloroethane, dichloroethylene (DCE), tetrachloroethane, trichloroethylene, pentachloroethane, perchloroethylene and hexachloroethane. The employment of the various process parameters of this invention results in a high selectivity of product to at least 50 percent symmetrical tetrachloroethane in the preferred embodiment, with smaller amounts of the incompletely chlorinated derivatives (e.g., ethylene dichloride, vinyl chloride, and 1,1,2-trichloroethane) being produced; very minor amounts of the more completely chlorinated derivatives (e.g., pentachloroethane, perchloroethylene and hexachloroethane) may also be produced.

The chlorination process of this invention involves the use of a particular melt which contains water and certain metal chlorides in critical proportionate amounts to produce the desired selectivity of product. The essential components of the melt composition are ferric chloride, cupric chloride and lithium chloride. The ferric chloride and cupric chloride are considered to have at least two functions; they act as chlorinating agents and also as dehydrohalogenating agents. The function of the lithium chloride is to reduce the vapor pressure of ferric chloride and also to reduce the chlorinating power of the ferric chloride and cupric chloride in order that the chlorination product can be stopped selectively, for example, in the case of ethylene, at dichloroethylene. The alkali metal chloride also is necessary to produce a melt and to moderate the dehydrohalogenating (HCl cracking) reaction.

Small amounts of water must be present in the melt to produce the desired chlorination rates at low temperatures. Generally, from 0.1 percent-6 percent, by weight, based on the weight of the melt; a preferred range is 0.5 percent-3 percent. Below 0.1 percent water, the melt is not fluid enough; above 6 percent water, high yield losses to CO and CO₂ occur. Consequently, this water content is critical to the successful operation of this invention.

Since ferric chloride and cupric chloride are the chlorinating agents, there must be some of each chloride present in the melt at all times. One of the essential features of this invention is that at least some of the iron chloride be maintained as ferric chloride and all of the copper chloride be maintained as cupric chloride. The numerical amount is not significant in the broad scope of the invention; any small amount of ferric chloride provides an operable process. However, for all practical purposes, at least 10 mole percent of the iron chloride must be maintained as ferric chloride. The preferred parameters require at least 75 mole percent of the iron chloride to be maintained as ferric chloride. As for the copper chloride, it all must be cupric chloride to provide good chlorination rates at these low temperatures, in the presence of water.

The proportions of iron chloride to copper chloride are a critical feature of this invention. Generally, the mole ratio of iron chloride to copper chloride is from 20:1 to 1:1. The preferred proportions range from about 10:1 to about 5:1. While the use of larger or smaller amounts of these chlorides will chlorinate and provide an operable process, the selective process of this invention will not tolerate any variation in proportions outside of the above-specified proportions.

Lithium chloride is the essential alkali metal chloride which is used in the process of this invention. While the use of KCl and NaCl alone provide operable processes, it is essential that at least 30 mole percent of the alkali metal chloride be LiCl to produce the selective chlorinating power at the low temperatures used in the aqueous process of this invention. The mole ratio of alkali metal chloride to the combined moles of iron chloride and copper chloride is from about 0.5:1 to about 2:1. A preferred range is from about 0.7:1 to about 1.3:1.

The relatively low temperatures at which the melt chlorination process of this invention is carried out are generally within the range of 100°C.-250°C. It is desirable to operate in this range to be able to use metallic materials as materials of construction (e.g., nickel and titanium) in reaction vessels, etc. The temperatures range is dependent upon the metal chloride salt mixture which is utilized and the desired product. Conversely, lower temperatures may be used where lower chlorination rates are acceptable or where pressures greater than one atmosphere are utilized. A temperature range of 200°C.-500°C. is generally preferred for olefins. The temperature range of 125°C.-225°C., in the preferred process, where ethylene, ethylene dichloride, vinyl chloride or mixtures thereof are used as the starting materials, is the temperature at which a high selectivity to tetrachloroethane results, i.e., at least 50 mole percent tetrachloroethane.

The pressure employed in the chlorination process can vary considerably and be as high as 50 atmospheres. A pressure within the range of 1 to 10 atmospheres is preferred. The pressure utilized is restricted by materials of construction and the problems of handling the melt at the high operating temperatures of this invention.

The atmosphere employed in the melt and surrounding the melt, in the preferred chlorination process, is essentially free of any substantial amount of added elemental chlorine. This terminology is intended to exclude the presence or addition of free chlorine to the reaction zone for the purpose of directly chlorinating the hydrocarbon. Since this process involves using the melt itself as the chlorinator, no free elemental chlorine is required or used to directly chlorinate the hydrocarbon. However, the melt itself might give off minor amounts of elemental chlorine through decomposition of the metal chlorides. Also, free chlorine may be added to the reaction zone to regenerate the melt. However, the chlorine, even when premixed with the feed, will preferentially oxidize (chlorinate) the FeCl₂ to FeCl₃ and the CuCl to CuCl₂ rather than enter into the hydrocarbon chlorination reaction. Therefore, the terminology "atmosphere essentially free of elemental chlorine" is intended to permit the presence, in the reaction zone, of minor amounts of elemental chlorine which are given off by the melt, or used to regenerate, but not the presence or addition of any elemental chlorine, separate and

apart from the melt, which would in fact chlorinate the hydrocarbon.

The hydrocarbons suitable for the chlorination reactions described herein include saturated aliphatics such as methane, ethane, propane, the butanes, and hydrocarbons containing up to ten carbon atoms; unsaturated aliphatic hydrocarbons, such as ethylene, propylene, the butylenes, butadiene, isoprene and hydrocarbons containing up to about ten carbon atoms including isomeric types; and aromatically unsaturated hydrocarbons, such as benzene, toluene, xylene, styrene, etc. Also, their incompletely chlorinated derivatives can be used. The terminology "incompletely chlorinated derivatives" is intended to include hydrocarbons containing at least one hydrogen atom which can be replaced by chlorine. For example, vinyl chloride, ethylene dichloride, 1,1,2-trichloroethane, symmetrical and/or unsymmetrical tetrachloroethane, chlorobenzene, etc., can be used as starting materials. Of this group, the preferred hydrocarbons are the olefins containing from two-five carbon atoms, and most preferably, ethylene. Additionally mixtures of these materials can be used as the starting materials (feed stock).

The process of this invention involves providing good contact between the hydrocarbon gas and the melt. The gas can be distributed in the melt or the melt can be distributed in the gas. The melt can be the continuous phase or the discontinuous phase. An effective method that may be used is to disperse the gas in the body of the melt. The dispersal may be effected by forcing the gas, in the form of fine bubbles, to ascend through the melt, by any known means. Typical means include porous plates, or porous thimbles, a suitable bubbling apparatus or a sparger. A stirring apparatus may also be used. Several stages may be used, with the gas being dispersed into the melt at several different positions in the apparatus, while the melt is passed continuously from one stage to another. In the preferred process, it is an essential requirement that the hydrocarbon gas be dispersed and finely distributed throughout the melt to provide good contact between the hydrocarbon gas and the melt, and to obtain a reasonable reaction rate. The size or fineness of the bubbles also has an effect on the reaction rate. The reaction rate increases directly with an increase in the fineness of the hydrocarbon gas bubbles, an increase in the amount of agitation utilized to disperse the hydrocarbon gas in the melt, or any increased overall contact of the hydrocarbon gas with the melt. However, the scope of this invention is not intended to be limited to any particular dispersing mechanisms. Comparatively speaking, if slower reaction rates and chlorination rates can be tolerated, there is no necessity for a thorough dispersion of the hydrocarbon gas in the liquid melt as is required in the preferred embodiment of the invention.

The process of this invention can be carried out as follows: the required amounts of each metal salt, in solid form, are mixed together to obtain even distribution of the respective salts in the salt mixture. This salt mixture is added to a reaction vessel where it is heated to a temperature within the range of 100° C.-250° C. whereby a melt of the salt mixture is obtained. If any of the metal salts were melted separately, various operating problems would arise. For example, if ferric chloride were melted separately, it would vaporize and boil off (e.g., sublime at high temperatures). If the alkali metal salts were melted separately, very high temperatures would be required since they have high melting points. Therefore, by using a mixture of the metal salts, a melt or molten solution of the metal salts can be readily obtained at the operating temperatures of this process. Water may be added at this stage.

Then ethylene (or any other suitable hydrocarbon or chlorohydrocarbon) is fed to the reaction vessel through any appropriate inlet means. It is a matter of choice and designing skill to decide whether the ethylene enters through the side, top or bottom of the reaction vessel. It is preferred, however, that the ethylene enter the reaction vessel near the bottom to give the ethylene a longer contact time with the melt. The ethylene is chlorinated and the chlorinated hydrocarbon reac-

tion products, containing at least 50 percent tetrachloroethane, begin to vaporize and rise to the top of the reaction vessel. An outlet is provided, usually at the top of the reaction vessel, where the reaction products can be drawn off; a condensation system, and possibly a scrubber system, could also be provided to recover and/or recycle any unreacted ethylene. The above-described process is essentially a batch-type process; when the cupric chloride becomes reduced, this batch process would not chlorinate to the desired high selectivity and high yield of tetrachloroethane. The batch process would have to be stopped in order to regenerate the melt. A suitable batch operation can be carried out by alternatively chlorinating the hydrocarbon (i.e., ethylene), and then regenerating the melt with a chlorine-containing gas, a combination of an oxygen-containing gas and hydrogen chloride, or a mixture thereof, prior to the next chlorination run.

The preferred regenerating system comprises a combination of an oxygen-containing gas and hydrogen chloride. This includes the use of mixtures of an oxygen-containing gas and HCl as well as the stepwise use of an oxygen-containing gas and HCl (and visa versa). Any regenerating procedures involving the use of an oxygen-containing gas and hydrogen chloride are applicable.

The terminology "a chlorine-containing gas" includes free elemental chlorine, a mixture of chlorine and oxygen, a mixture of chlorine and hydrogen chloride, and mixtures of chlorine and any other gases which are compatible with the chlorination system. The terminology "an oxygen-containing gas" encompasses free elemental oxygen and mixtures of oxygen and other gases which are compatible with the chlorination system. Air is an economical oxygen-containing gas which can be used.

The preferred process of this invention is a continuous process whereby the melt is continually chlorinating ethylene, being regenerated, and/or recycled. The continuous process of this invention can be operated as either a single-stage operation or a multi-stage operation. In a single-stage continuous process, one reaction vessel is used. While the chlorination is taking place and the ferric chloride and cupric chloride are being reduced to ferrous chloride and cuprous chloride, a chlorine-containing gas, a mixture of an oxygen-containing gas and hydrogen chloride or a mixture thereof are added to regenerate the melt. Thus, the ethylene is continuously chlorinated by the melt and drawn off in high yields of tetrachloroethane at the same time that the melt is being regenerated to provide the required ferric chloride and cupric chloride to chlorinate the ethylene. If a chlorine-containing gas is added to regenerate the melt, preferably the chlorine will be supplied in a separate section or zone of the reaction vessel so that the atmosphere in the reaction zone is essentially free of any substantial amount of elemental chlorine. A typical reaction vessel might contain a central conical section for reacting the hydrocarbon with the melt and a separate side section between the conical section and the walls of the vessel for regeneration of the reduced melt.

The multi-stage continuous process requires use of two or more vessels or reaction zones. The first vessel would be the reaction vessel in which the actual chlorinating is done. The reduced melt containing ferrous chloride and cuprous chloride would then be pumped to another vessel to be oxidized and thereby regenerated to the ferric state. Into the second and any succeeding vessels is introduced a combination of an oxygen-containing gas (e.g. air) and HCl, a chlorine-containing gas, or a mixture thereof. Also, any byproduct water may be removed from the melt in the regeneration zone or in a separate zone. The regenerated melt containing ferric chloride and cupric chloride would then be recycled to the original reaction vessel to chlorinate the unchlorinated ethylene.

The amount of oxygen absorbed by the melt is controlled by the rate of passage of the oxygen-containing gas over and through the melt in the regeneration contact zone(s), the pressure of the oxygen-containing gas, the length of the contact

zone and the efficiency of the overall regeneration system. Moderate pressures generally give rapid and efficient absorption of oxygen in the melt although operations at atmospheric pressure give satisfactory results. Air pressures between 1 to 50 atmospheres may be employed, however, the preferred range is between 1 and 10 atmospheres. When air is utilized as the gas, absorption of from 35 to 75 percent of the oxygen from the contacting air is readily obtainable. In general, it is not practical to attempt to remove all the oxygen from the air passing through the regeneration zone.

An alternative regeneration reaction is as follows:

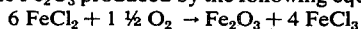


The melt utilized in the process of this invention may optionally contain other ingredients. Iron oxide (Fe_2O_3) may be added to the melt in quantities which saturate the melt with iron oxide. In terms of quantity, this is a very small amount (e.g., less than 5 mole percent of the melt) since this oxide is very insoluble in the melt system. At melt temperatures, Fe_2O_3 is believed to equilibrate with FeCl_3 to form FeOCl as shown by the following equation:



Therefore, both Fe_2O_3 and FeOCl are considered to be present in the melt.

In a batch process, the Fe_2O_3 is added in a specified amount to saturate the melt or it is generated in situ by oxidation of FeCl_2 in a partially reduced melt. In a continuous process where oxidation is being carried out at all times, the melt may contain some Fe_2O_3 produced by the following equation:



The amount of Fe_2O_3 that can be added to the melt to absorb HCl can be as much as 5 mole percent of the melt, but a sacrifice in yield loss to CO and CO_2 is likely to occur.

It is pointed out that the process of this invention is directed to chlorinating "by means of" a melt (molten salts) as distinguished from chlorinating "in" the melt or molten salt. It is the melt itself which does the chlorinating in the process of this invention and not any other liquid or gaseous additives. The process is significantly different from chlorinating with elemental chlorine because elemental chlorine gives a random product distribution whereas the process of this invention is selective and produces high yields. Chlorinating by means of a melt provides additional significant advantages over the prior chlorination processes. There is a uniform temperature throughout the melt and, consequently, a uniform chlorination rate. There is no agglomeration of catalyst particles as in a fluidized bed. More complete chlorination rates are available due to the presence of massive amounts of the chlorinating composition in the melt. In short, the melt chlorination process of this invention provides a more effective means for chlorinating.

The invention is illustrated by the following examples. In the examples and elsewhere in the specification, unless indicated otherwise, all parts, proportions and percentages of materials or components are in mole percent, based on the moles of melt. However, the water is based on weight percent.

EXAMPLE 1

Into a glass reactor containing 2 liters of a melt comprising 3 moles CuCl_2 , 12 moles FeCl_3 , 3 moles FeCl_2 , 18 moles LiCl and 1 weight percent water was passed ethylene at the rate of 1 liter/minute. The melt was mechanically stirred at a temperature of 175°C . under atmospheric pressure. Approximately 85 mole percent of the ethylene fed was converted to a product comprising 78 percent s-tetrachloroethane and 21 percent ethylene dichloride.

EXAMPLE 2

The process of Example 1 was carried out except that no water was present in the reactor. It was not possible to product a melt until the temperature was raised to 275°C . At this temperature, the chlorination reaction proceeded. Approximately 85 mole percent of the ethylene was converted to a product

containing 21 percent s-tetrachloroethane, 32 percent ethylene dichloride and 26 percent perchloroethylene. This demonstrates that water is necessary to chlorinate at low temperatures; also the selectivity of product to s-tetrachloroethane is not high without water.

EXAMPLE 3

The process of Example 1 was carried out except that no copper chloride was used. Approximately 30 percent of the ethylene fed was converted to a product comprising 85 percent ethylene dichloride and 3 percent s-tetrachloroethane. This demonstrates that very little chlorination occurs in the absence of copper chloride.

EXAMPLE 4

The process of Example 1 was carried out with a melt comprising 3 moles CuCl_2 , 12 moles FeCl_3 , 3 moles FeCl_2 , 9 moles LiCl , 9 moles KCl and 1 weight percent water. Approximately 65 percent of the ethylene fed was converted to a product comprising 62 percent s-tetrachloroethane and 27 percent ethylene dichloride. This demonstrates that other alkali metals can be used together with LiCl but the desired high yields are not always obtained.

EXAMPLE 5

The used melt of Example 1 was regenerated by treatment with oxygen and HCl. Oxygen was passed through the melt (175°C .) at the rate of 1 liter/minute. Then the temperature of the melt was raised to 350°C . and HCl was passed through the melt at the same rate. The oxygen conversion was 95 percent while HCl conversion was 41 percent during the time required to regenerate. The melt was cooled to 175°C . and the chlorination process of Example 1 was repeated; the same chlorination products were produced in approximately the same quantities.

EXAMPLE 6

This example demonstrates the non-corrosive effects of a melt utilized in the low temperature process of this invention. Several strips of titanium were immersed in a melt comprising 2 moles CuCl_2 , 9 moles FeCl_3 , 2 moles FeCl_2 , 10 moles LiCl and 4 moles KCl . Utilizing the above melt at 200°C . (no water), the titanium exhibited a corrosion value of 1,000 mils/year. At 200°C . and 250°C . with 1 percent water in the melt, the corrosion values of less than 1 mil/year and 50 mils/year, respectively, were exhibited. Thus, it is apparent that the melt of this invention and process of using same avoid corrosion problems associated with prior chlorination processes, particularly when the same selective, high yield chlorination is desired.

I claim:

1. A continuous chlorination process for the production of tetrachloroethane which comprises chlorinating a material of the group consisting of ethylene, vinyl chloride, ethylene dichloride, and mixtures thereof, at a temperature within the range of 100°C .– 250°C . by means of a melt consisting essentially of iron chloride, copper chloride, alkali metal chloride and water by dispersing the material to be chlorinated in the melt whereby said material is chlorinated by the melt; withdrawing a gaseous effluent from the reaction zone which contains unreacted starting material and the resulting chlorinated hydrocarbon products and recovering the chlorinated hydrocarbon products from the effluent as the product of the process; and regenerating the melt with a regenerating system selected from the group consisting of a chlorine-containing gas, a combination of an oxygen-containing gas and hydrogen chloride, and mixtures thereof, wherein:

a. the alkali metal chloride is selected from the group consisting of LiCl , a LiCl/KCl mixture, a LiCl/NaCl mixture, a LiCl/RbCl mixture, a LiCl/CsCl mixture and mixtures thereof, provided that the alkali metal chloride comprises at least 30 mole percent LiCl ;

- b. the mole ratio of iron chloride to copper chloride is from about 20:1 to about 1:1;
- c. the mole ratio of alkali metal chloride to combined moles of iron chloride and copper chloride is from about 0.5:1 to about 2:1;
- d. the water is present in an amount within the range of 0.1-6 percent based on the weight of the melt; and
- e. at least some of the iron chloride is maintained as ferric chloride and all of the copper chloride is maintained as cupric chloride.
2. A process in accordance with claim 1 wherein the regenerating system comprises a chlorine-containing gas.
3. A process in accordance with claim 1 wherein the regenerating system comprises a combination of an oxygen-containing gas and hydrogen chloride.
4. A process in accordance with claim 3 wherein the by-product water is removed from the melt in a zone separate from the reaction zone.
5. A process in accordance with claim 1 wherein the chlorination reaction and regeneration of the melt are carried out in the same zone.
6. A process in accordance with claim 2 wherein the regeneration of the melt is carried out in a zone separate from the chlorination reaction.
7. A continuous chlorination process for the production of tetrachloroethane which comprises chlorinating a material selected from the group consisting of ethylene, ethylene dichloride, vinyl chloride and mixtures thereof to produce a chlorinated product which contains at least 50 mole percent of tetrachloroethane, at a temperature within the range of from 125° C.-225° C. by means of a melt consisting essentially of iron chloride, copper chloride, alkali metal chloride and water by dispersing the material to be chlorinated in the melt, the melt being the continuous phase, whereby said material is chlorinated by the melt; withdrawing a gaseous effluent from the reaction zone which contains unreacted starting material and the resulting chlorinated hydrocarbon products and recovering the chlorinated hydrocarbon products from the ef-

fluent as the products of the process; and regenerating the melt with a regenerating system selected from the group consisting of a chlorine-containing gas, a combination of an oxygen-containing gas and hydrogen chloride, and mixtures thereof, wherein:

- a. the alkali metal chloride is selected from the group consisting of LiCl, a LiCl/KCl mixture, a LiCl/NaCl mixture, a LiCl/RbCl mixture, a LiCl/CsCl mixture and mixtures thereof, provided that the alkali metal chloride comprises at least 30 mole percent LiCl;
- b. The mole ratio of iron chloride to copper chloride is from about 10:1 to about 5:1;
- c. the mole ratio of lithium chloride to combined moles of iron chloride and copper chloride is from about 0.7:1 to about 1.3:1;
- d. the water is present in an amount within the range of 0.5-3 percent based on the weight of the melt; and
- e. at least 75 percent of the iron chloride is maintained as ferric chloride and all of the copper chloride is maintained as cupric chloride.
8. A process in accordance with claim 7 wherein the regenerating system comprises a chlorine-containing gas.
9. A process in accordance with claim 7 wherein the regenerating system comprises a combination of an oxygen-containing gas and hydrogen chloride.
10. A process in accordance with claim 9 wherein the by-product water is removed from the melt in a zone separate from the reaction zone.
11. A process in accordance with claim 9 wherein the chlorination reaction and regeneration of the melt are carried out in the same zone.
12. A process in accordance with claim 9 wherein the regeneration of the melt is carried out in a zone separate from the chlorination reaction.
13. A process in accordance with claim 9 which is carried out under pressure within the range of 1 atmosphere to 10 atmospheres.

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