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(54) IMPROVEMENTS IN OR RELATING TO A PROCESS FOR RECOVERING CHLORINE VALUES FROM MOLTEN METAL CHLORIDE CHLORINATING AGENTS

(71) We, THE LUMMUS COMPANY, of 1515 Broad Street, Bloomfield, N.J. 07003, United States of America, a corporation organised and existing under the laws of the State of Delaware, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

5 This invention relates to a process for recovering chlorine values, and more particularly, to the recovery of chlorine values from a gas withdrawn from a melt oxidation zone.

10 In a process for producing chlorinated hydrocarbons by the use of molten salts, a molten salt mixture containing a multivalent metal chloride in its higher and lower valence states is contacted with molecular oxygen to effect oxidation of the salt mixture. It has been found that the gas stream withdrawn from the melt oxidation zone contains chlorine, and the overall efficiencies of the process can be improved by effectively recovering chlorine from such gas.

15 The present invention seeks to provide a process for the recovery of chlorine values from a gas withdrawn from a melt oxidation zone and to improve the recovery of chlorine values in a process for producing chlorinated hydrocarbons.

20 According to this invention there is provided a process for oxidising with gaseous oxygen in an oxidation reaction zone a molten salt mixture containing a metal chloride (which metal chloride has at least two valence states) in a higher and lower valence state, which comprises: withdrawing from the oxidation reaction zone an effluent gas containing water vapour and chlorine; contacting the effluent gas in a chlorine separation zone with activated carbon to convert chlorine to hydrogen chloride; withdrawing from the chlorine separation zone as gas substantially free of chlorine and containing water vapour and hydrogen chloride produced from the chlorine; recovering aqueous hydrogen chloride 25 from said gas; and introducing recovered aqueous hydrogen chloride into said oxidation reaction zone.

30 In a preferred process in accordance with the present invention, a molten salt mixture containing a multivalent metal chloride in its higher and lower valence states is contacted in a reaction zone with oxygen such as molecular oxygen, together with recycled aqueous hydrogen chloride, and optionally, a feed gas containing chlorine, hydrogen chloride or mixtures thereof, to effect oxidation of the salt. Recovery of chlorine values from the aqueous hydrogen chloride (and also those present in the gas feed) is effected by production of the higher valent metal chloride. The gas withdrawn from the reaction zone contains chlorine (in amounts up to the salt chlorine vapour pressure at the oxidation conditions), and the chlorine content of the gas is converted to gaseous hydrogen chloride by contact with water vapour (steam) and activated carbon. The hydrogen chloride is then recovered, as aqueous hydrogen chloride, and recycled (with or without concentration thereof) to the reaction zone to recover the chlorine values thereof.

35 Preferably, a gas stream containing chlorine, hydrogen chloride or mixtures thereof, is also introduced, as feed, into the oxidation reaction zone to recover the chlorine values thereof. The gas generally includes both chlorine and hydrogen chloride, and is preferably a chlorinated hydrocarbon combustion gas, generated by the burning of waste chlorinated hydrocarbons; and in particular, a combustion gas generated in a process for producing chlorinated hydrocarbons.

40 The salt mixture generally contains the higher and lower valent chlorides of either man-

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ganese, iron, copper, cobalt, chromium, or mixtures thereof, preferably the higher and lower valent chlorides of copper. The molten mixture may also include a metal salt melting point depressant which is non-volatile and resistant to the action of oxygen, at the process conditions, in order to maintain the multi-valent metal chloride in the form of a melt. The melting point depressant is generally either an alkali metal chloride or a heavy metal chloride; i.e. heavier than copper, of Groups I, II, III and IV of the Periodic Table. The preferred melting point depressant is potassium chloride. A preferred molten salt mixture contains from about 20% to about 40%, by weight, potassium chloride, with the remainder being copper chlorides. 5

The oxidation reaction zone is generally operated at a temperature of from 600°F to 900°F, preferably a temperature of from 750°F to 870°F, and a pressure of from 1 to 20 atmospheres. The contacting of the feed and melt is generally effected in a counter-current fashion, although co-current operation is also possible. The oxygen which is added to the oxidation reaction zone can be in a quantity corresponding to that required to convert the hydrogen chloride values to the higher valent metal chloride, and is preferably introduced in excess of such amounts in order to provide for net production of oxychloride in the melt, whereby in the oxidation reaction zone, the molten salt mixture is enriched in the higher valent metal chloride content thereof, and in addition, oxychloride is generated. 10

The contacting with activated carbon is generally effected at a temperature of from 100°F to 250°F, and preferably a temperature of from 115°F to 215°F. The contacting pressure is generally from 15 to 100 psia and preferably from 25 to 70 psia. It has been found that the use of such conditions provides the added advantage of reduced carbon oxidation. 15

The activated carbon is preferably one with a low ash content; e.g. less than 1% ash, to permit consumption of the carbon without leaving an ash residue which could lead to contamination of the molten salt through leaching by recovered hydrochloric acid. The activated carbon preferably has a high surface area; for example, 500 m²/gm or greater. 20

The following theoretical discussion is given to provide a better understanding of the invention and whilst the applicants believe that the theoretical discussion is correct the discussion is given on the understanding that if the discussion is found to be inaccurate in any respect the validity of the claims will not be affected solely for that reason. 25

It is believed that in a process in accordance with the invention chlorine is converted to hydrogen chloride by two different mechanisms. In one, chlorine and water vapour react directly with carbon as follows: 30

$$(1) \text{Cl}_2 + \text{H}_2\text{O} + 1/2\text{C} \rightleftharpoons 2\text{HCl} + 1/2\text{CO}_2$$

In addition, chlorine and water vapour are adsorbed by the carbon and all or a portion of the adsorbed chlorine is converted to hydrogen chloride as follows: 35

$$(2) \text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HOCl}$$

$$(3) \text{HOCl} \rightleftharpoons \text{HCl} + 1/2\text{O}_2$$

After a period of operation, the bed no longer effectively converts chlorine to hydrogen chloride, as shown by chlorine breakthrough, as a result of carbon consumption (Equation (1)). At such a time, the bed is taken off-stream for replacement of the carbon, and another bed is placed on stream. The bed is initially purged of chlorine and hydrogen chloride to permit safe opening of the vessel by operators, and such purging can be effected by use of an inert gas. In general, such purging is effected at temperatures of from 200° to 350°F, however, such temperature conditions are illustrative only, in that purging can be effected at other temperatures. The purge gas, subsequent to contact with the activated carbon contains chlorine and/or hydrogen chloride, generally both chlorine and hydrogen chloride, desorbed from the bed. The purge gas is preferably introduced into the activated carbon bed which is on-stream to recover the chlorine values therefrom. After replacement of the carbon, the replenished bed is heated to reaction conditions, preferably by contact with an inert gas at the appropriate temperature. 40

Thus according to another aspect of this invention there is provided a process for oxidizing in an oxidation reaction zone a molten salt mixture containing a metal chloride (which metal chloride has at least two valence states) in its higher and lower valence state by contacting the molten salt mixture with gaseous molecular oxygen and recycle aqueous hydrogen chloride at a temperature of from 600°F to 900°F to produce an oxidized melt and recover chlorine values by enriching the higher valent metal chloride content of the molten salt mixture and recovering the molten salt from the oxidation reaction zone, comprising withdrawing from the oxidation reaction zone an effluent gas containing water vapour and chlorine, said chlorine being present in an amount up to the chlorine vapour pressure of the molten salt mixture, cooling the effluent gas, contacting the effluent gas in a chlorine separation zone with activated carbon to convert chlorine to hydrogen chloride, said contacting being effected at a temperature of from 100°F to 250°F and a pressure of 45

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from 15 to 100 psia, withdrawing from the chlorine separation zone a gas substantially free of chlorine and containing water vapour and hydrogen chloride produced from the chlorine, recovering aqueous hydrogen chloride from said gas, and introducing recovered aqueous hydrogen chloride into said oxidation reaction zone.

5 In order that the invention may be more readily understood and so that further features thereof may be appreciated the invention will now be described by way of example, with reference to the accompanying drawing which is simplified schematic flow diagram of one process in accordance with the invention.

10 The particular process, which will be described by way of example, and which is illustrated in the accompanying drawing is a process for producing chlorinated methanes.

15 Referring to the drawing, a molten chloride salt, such as a mixture of potassium chloride, cupric chloride and cuprous chloride, in line 10 is introduced in the central part of an oxidation vessel 11 which is maintained at a temperature within the range 600°F-900°F and preferably in the range 750°F-870°F, and at a pressure of from 1 to 20 atmospheres. A compressed gas containing molecular oxygen, such as air, in line 12, an aqueous solution of hydrogen chloride, in lines 13 and 14, obtained as hereinafter described, and a by-product combustion effluent, in line 15, obtained as hereinafter described, and comprising chlorine, hydrogen chloride, as well as carbon oxides, water vapour, nitrogen and possibly unreacted oxygen, are combined in line 16 and introduced as a feed into the lower part of oxidation vessel 11.

20 As a result of the countercurrent contact between the feed introduced through line 16 and the descending molten salt mixture, introduced through line 10, the salt is oxidised to produce copper oxychloride, and the hydrogen chloride and chlorine introduced as aqueous hydrogen chloride, are selectively reacted with the molten salt to produce cupric chloride. In addition, the water introduced with the aqueous hydrogen chloride is vapourised. The amount of oxygen present in the gas introduced through line 12 is in an amount in excess of that required to react with the hydrogen chloride, and thus the molten salt mixture is enriched in the higher valent metal chloride content thereof and there is net production of copper oxychloride.

25 30 An effluent gas, including water vapour, nitrogen, carbon oxides, chlorine and hydrogen chloride rises into the top of vessel 11 wherein the gas is combined with a lift gas, as hereinafter described, which is introduced through line 17. The combined gas is directly contacted in the top of vessel 11 with a spray of aqueous hydrogen chloride quench liquid introduced through line 18 to cool the combined gas and eliminate any vapourised and entrained salts therefrom. The effluent gas is cooled to a temperature at which the molten salt is still in the form of a melt to permit the molten salt to flow back into the reactor 11.

35 40 The cooled gaseous stream withdrawn from reactor 11 through line 19 is introduced into a quench vessel 21, wherein the gaseous stream is directly contacted with an aqueous hydrogen chloride stream introduced through line 22. The quenching in vessel 21 is effected in a manner such that the aqueous hydrogen chloride quench liquid introduced through line 22 is partially vapourised which produces a remaining aqueous hydrogen chloride quench liquid having a higher concentration of hydrogen chloride. The quenching in vessel 21 also functions to separate any remaining entrained salt from the gaseous effluent. In a preferred process, quenching in vessel 21 is effected in manner to cool the effluent to a temperature of 200-250°F.

45 50 The remaining liquid aqueous hydrogen chloride quench liquid, containing any remaining salt, is withdrawn from vessel 21 through line 13 and introduced, as recycle, into reactor 11.

55 60 The effluent gas, now also containing vapourised quench liquid, is withdrawn from vessel 21 through line 23, and is introduced into a direct contact quench tower 24 of a type known in the art, wherein the gas is cooled by direct contact with further aqueous hydrogen chloride quench liquid introduced through line 25. The quenching in tower 24 is controlled in a manner such that not all of the hydrogen chloride present in the feed gas supplied through line 23 is recovered therefrom since such complete recovery, if accomplished, would be accompanied by an unacceptable corresponding amount of water condensation. In accordance with a preferred embodiment of the present invention, condensation is preferably controlled to condense an aqueous hydrogen chloride solution having a hydrogen chloride concentration of 8% to 20%, preferably from 10% to 18%, all by weight. In general, such a result can be achieved by effecting cooling of the gas introduced into tower 24 to a temperature of from 120°F to 250°F.

65 An aqueous hydrogen chloride solution is withdrawn from tower 24 through line 26 and a first portion thereof passed through line 27 and cooler 28 for reintroduction into the quench tower 24 through line 25 to meet the cooling requirements therefor. A second portion of the aqueous hydrogen chloride is passed through line 29 for meeting the quenching requirements of the reactor 11 through line 18 and the requirements of vessel

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21 through line 22.

The gas withdrawn from tower 24 through line 32, contains inerts, water vapour, and some hydrogen chloride and chlorine, and this gas is introduced into reactor 33a of a pair 5 of reactors 33a and b, each containing a bed of activated carbon. The activated carbon has an ash content of less than 1% and a surface area of at least 500m²/gm. For purposes of explanation, reactor 33a is illustrated as being on-stream and reactor 33b is illustrated as having been recently taken off-stream for replenishment of the activated carbon. As a 10 result of the contact between the gas introduced through line 32 and the activated carbon in reactor 33a, which is at a temperature of from 100°F to 250°F, and which operates at a gas pressure of from 15lb psia to 100lb. psia, the chlorine is converted into hydrogen chloride. The most preferred temperature is from 115°F to 215°F and the most preferred 15 pressure is from 25 to 70 psia. The gas withdrawn from reactor 33a through line 34, is substantially free of chlorine, and contains increased amounts of hydrogen chloride, water vapour nitrogen and carbon oxides. The gas may also include some oxygen (See Equation 3 above). The gas in line 34 is introduced into a direct contact quench tower 35, of a type known in the art, wherein the gas is cooled by direct contact with aqueous hydrogen chloride quench liquid introduced through line 36. The quenching in tower 35 is controlled in a manner such that not all of the hydrogen chloride present in the gas is recovered 20 therefrom, as described above with reference to the operation of quench tower 24. Condensation is preferably controlled to provide a condensed aqueous hydrogen chloride solution having a hydrogen chloride concentration from 8% to 20%, preferably from 10% to 18%, all by weight. In general, such a result can be achieved by effecting cooling of the gas introduced into tower 35 to a temperature of from 100°F to 250°F.

An aqueous hydrogen chloride solution is withdrawn from tower 35 through line 37, 25 and a first portion thereof passed through line 38, including cooler 39, for re-introduction into the quench tower through line 36. A second portion of the aqueous hydrogen chloride is passed through line 14 for introduction into the oxidation vessel 11 to recover the chlorine values thereof. The aqueous hydrogen chloride in line 14 can be concentrated; e.g. by stripping of water, prior to introduction into oxidation vessel 11.

The gas withdrawn from tower 35 through line 41 is caustic and water-washed or scrubbed 30 in zone 42 to remove any remaining hydrogen chloride, and a portion thereof is released to the atmosphere through line 43. The remaining portion of the gas in line 44 is compressed in compressor 45, and the temperature thereof regulated in heat exchanger 35 46, prior to passage through lines 47 and 48 for use as a lift gas for transporting molten salt, as hereinafter described.

A portion of the compressed lift gas, in line 51 or line 55 (depending on temperature 40 conditions) is passed through the reactor 33b, containing activated carbon previously employed for removing chlorine from the gas in line 32, in order to strip chlorine and hydrogen chlorine therefrom, prior to replenishing the activated carbon. The lift gas, withdrawn from reactor 33b, in line 52 containing components desorbed from the activated carbon bed, in particular, chlorine and/or hydrogen chloride, is combined with the gas in line 32, which of course comprises effluent gas withdrawn from the oxidation reaction zone, with the chlorine values ultimately being recovered therefrom, as hereinabove 45 described. Alternatively, or in addition, the lift gas containing chlorine and/or hydrogen chloride in line 52 can be combined with lift gas in line 47 for ultimate re-using of chlorine values. After replenishment of the activated carbon, the bed in reactor 33b can be heated to operation conditions by a portion of the lift gas in line 51 or 55, and the reactor 33b can be substituted for reactor 33a and vice-versa to permit the bed in reactor 33a to be 50 replenished.

Referring back to the oxidation vessel 11, a molten salt, now containing copper oxychloride, and enriched in the cupric chloride content thereof, is withdrawn from the bottom of vessel 11 through line 61 and is lifted by the lift gas in line 48 into a separation vessel 62, positioned adjacent to the top of a chlorination vessel 63. In separator 62, the molten salt is separated from the lift gas, with the molten salt being introduced into the top of the chlorination vessel 63 through line 64. The lift gas is withdrawn from vessel 62 through line 65, and combined with lift gas (used for transporting salt to the oxidation reactor 11), for introduction into the uppermost or quenching portion of vessel 11 through line 17, to thereby separate any entrained and vapourised salt therefrom.

Fresh feed methane in line 66, fresh feed hydrogen chloride and/or chlorine in line 67 60 and recycle components in line 68 are introduced into the bottom of the reactor 63 and they are contacted with the descending molten salt to effect chlorination of the methane and of recycle components.

Molten salt withdrawn from reactor 63 through line 69 is lifted by lift gas in line 47 into 65 a separation vessel 71, positioned adjacent to the top of reactor 11. In the separator 71,

the molten salt is separated from the lift gas, and introduced through line 10 into vessel 11. The lift gas is withdrawn from separator 71 through line 72 and combined with the lift gas in line 65 for introduction through line 17 into the top of the quenching section of the vessel 11.

5 A chlorination effluent is withdrawn from reactor 63 through line 81 and introduced into a separation and recovery section, schematically indicated as 82. In separation and recovery section 82, recycle components are recovered and recycled to reactor 63 through line 68. Chlorinated methane reaction product is recovered from separation section 82 through line 83.

10 Chlorinated hydrocarbons which are not recovered as reaction production, and are not suitable, as recycle, for the production of chlorinated methanes, are withdrawn from the separation and recovery section 82, through line 84, and introduced along with molecular oxygen in line 85, into a combustion zone 86, wherein the chlorinated hydrocarbons are burned to recover the chlorine values thereof. A combustion effluent, including hydrogen chloride, chlorine, carbon oxides, water vapour and nitrogen, and possibly oxygen, is withdrawn from combustion chamber 86 through line 15 for introduction into the reactor 11, as hereinabove described.

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20 The hydrogen chloride present in the effluent from reactor 11 can be recovered in a manner other than as particularly described in the specific example given above; e.g. by indirect cooling, instead of by direct quenching. Similarly, the partial vapourising quench step could be eliminated from the hydrogen chloride recovery.

25 In a further modification, the invention also relates to a process wherein a combustion gas is not introduced into the oxidation reactor 11. Similarly, the gas introduced into the reactor 11, if any, could contain either hydrogen chloride or chlorine, rather than a mixture thereof.

30 As another modification, the activated carbon could be purged by use of an extraneous stripping gas, such as an inert gas.

35 As yet a further modification, hydrogen chloride could be recovered from the effluent withdrawn from the activated carbon reactor by a method other than as described in the specific example given above; e.g. by indirect cooling or partial condensation.

40 As still another modification, the aqueous hydrogen chloride recovered in the quench tower 35 could be combined with the aqueous hydrogen chloride in line 22 for introduction into the quench vessel 21.

45 A process very similar to that specifically described above is also applicable to the production of C₂ chlorinated hydrocarbons, by the use of molten chloride salts. In the production of a chlorinated C₂ hydrocarbon, (such as vinyl chloride, trichloroethylene, or perchloroethylene) ethane and/or ethylene is employed as fresh feed, and in addition, the chlorination reactor is preferably either provided with a separate dehydrochlorination section or a separate dehydrochlorination vessel. Similarly, a process in accordance with the present invention is also applicable to the production of other chlorinated aliphatic hydrocarbons, such as chlorinated C₃ hydrocarbons, and to chlorinated aromatic hydrocarbons, such as chlorinated benzenes.

50 The invention will be further described with respect to the following example which relates to the process particularly described with reference to the drawing, and which provides detailed information concerning the precise operation of temperatures of the various stages of the process together with the composition of various streams when the process has reached a steady state.

EXAMPLE

50 The activated carbon reactor 33a is operated at a pressure of 46 psig, an inlet temperature of 175°F and an outlet temperature of 180°F.

55 The quench tower 35 is operated at an overhead temperature (line 41) of 155°F, a bottoms temperature (line 37) of 165°F and a quench inlet (line 36) temperature of 145°F.

The composition of the streams are as follows:

	Line 32			Line 34			Line 34			Line 41			Line 14		
	lb mole/ hr	lb/ hr	lb mole/ hr	lb mole/ hr	lb/ hr	lb mole/ hr	lb mole/ hr	lb/ hr	lb mole/ hr	lb/ hr	lb mole/ hr	lb/ hr	lb/ hr	lb/ hr	
Cl ₂	2419.1	67735	2419.1	67335	2419.1	67735	2419.1	67735	2419.1	67735	2419.1	67735	2419.1	67735	
O ₂	119.7	3830	120.9	3868	120.9	3868	120.9	3868	120.9	3868	120.9	3868	120.9	3868	
CO ₂	26.7	1175	27.5	1210	27.5	1210	27.5	1210	27.5	1210	27.5	1210	27.5	1210	
HCl	0.5	18	8.5	310	0.3	11	0.3	11	0.3	11	0.3	11	0.3	11	
H ₂ O	287.8	5186	283.8	5114	148.8	2681	148.8	2681	148.8	2681	148.8	2681	148.8	2681	
	<u>2857.8</u>	<u>78228</u>	<u>2859.8</u>	<u>78237</u>	<u>2716.6</u>	<u>75505</u>	<u>2716.6</u>	<u>75505</u>	<u>2716.6</u>	<u>75505</u>	<u>2716.6</u>	<u>75505</u>	<u>2716.6</u>	<u>75505</u>	

Preferred embodiments of the present invention are particularly advantageous in that substantially all chlorine values are recovered. In particular, the chlorine values which would normally be lost in the gas withdrawn from a molten salt oxidation reactor are effectively recovered and utilised in the chlorination process. In addition, the gases purged to the atmosphere will meet air pollution requirements; e.g. in some cases, <30 ppm chlorine.

WHAT WE CLAIM IS:

1. A process for oxidising with gaseous oxygen in an oxidation reaction zone a molten salt mixture containing a metal chloride (which metal chloride has at least two valence states) in a higher and lower valence state, which comprises: withdrawing from the oxidation reaction zone an effluent gas containing water vapour and chlorine; contacting the effluent gas in a chlorine separation zone with activated carbon to convert chlorine to hydrogen chloride; withdrawing from the chlorine separation zone a gas substantially free of chlorine and containing water vapour and hydrogen chloride produced from the chlorine; recovering aqueous hydrogen chloride from said gas; and introducing recovered aqueous hydrogen chloride into said oxidation reaction zone. 5

2. A process as claimed in claim 1 wherein chlorine or hydrogen chloride, or a mixture thereof, is also introduced into the oxidation reaction zone. 10

3. A process as claimed in any one of the preceding claims, wherein the said metal chloride is a chloride of manganese, iron, chromium, cobalt, copper or a mixture thereof. 15

4. A process as claimed in any one of the preceding claims, wherein the molten mixture contains cuprous and cupric chloride. 15

5. A process as claimed in any one of the preceding claims, wherein the effluent gas is contacted with activated carbon at a temperature of from 100°F to 250°F. 15

6. A process according to claim 5, wherein the effluent gas is contacted with the activated carbon at a temperature of from 115°F to 215°F. 20

7. A process as claimed in any one of the preceding claims, wherein the contacting with activated carbon is effected at a pressure or from 15 psia to 100 psia. 20

8. A process as claimed in claim 7, wherein the contacting with activated carbon is effected at a pressure of from 25 to 70 psia. 25

9. A process as claimed in any one of the preceding claims, wherein the chlorine separation zone includes first and second reactors, said contacting with activated carbon being effected in one reactor, the other reactor containing activated carbon previously employed for separation of chlorine, said process further comprising: contacting the activated carbon in the said other reactor with a portion of the gas remaining subsequent to recovery of aqueous hydrogen chloride to effect purging of the activated carbon by desorbing adsorbed chlorine and hydrogen chloride. 25

10. A process as claimed in claim 9, wherein the gas containing desorbed chlorine and hydrogen chloride is combined with the effluent gas withdrawn from the oxidation reaction zone. 30

11. A process as claimed in any one of the preceding claims, wherein the effluent gas which is contacted with the activated carbon includes hydrogen chloride, nitrogen and carbon dioxide. 35

12. A process as claimed in any one of the preceding claims, wherein aqueous hydrogen chloride recovered from the gas withdrawn from the chlorine separation zone is concentrated prior to recycle to the oxidation reaction zone. 40

13. A process claimed in any one of the preceding claims, wherein the activated carbon has an ash content of less than 1% and a surface area of at least 500 m²/gm. 40

14. A process according to any one of the preceding claims, wherein the oxidation reaction zone is at a temperature within the range of 600°F to 900°F and a pressure of between 1 and 20 atmospheres. 45

15. A process according to claim 12, wherein the oxidation reaction zone is at a temperature within the range of 750°F to 870°F. 45

16. A process according to any one of the preceding claims, wherein the molten salt mixture includes a melting point depressant. 50

17. A process according to claim 16, wherein the melting point depressant is potassium chloride. 50

18. A process according to any one of the preceding claims comprising the further steps of moving molten salt from said oxidation reaction zone, contacting the salt with a hydrocarbon to effect chlorination thereof, and subsequently returning the salt to the oxidation reaction zone. 55

19. A process according to claim 18, wherein waste chlorinated hydrocarbons produced by the process are burnt, and the combustion gas thus generated is introduced to said oxidation reaction zone. 55

20. A process for oxidizing in an oxidation reaction zone a molten salt mixture containing a metal (which metal chloride has at least two valence states) in its higher and lower valence state by contacting the molten salt mixture with gaseous molecular oxygen and recycle aqueous hydrogen chloride at a temperature of from 600°F to 900°F to produce an oxidized melt and recover chlorine values by enriching the higher valent metal chloride content of the molten salt mixture and recovering the molten salt from the oxidation reaction zone, comprising withdrawing from the oxidation reaction zone an effluent gas containing water vapour and chlorine, said chlorine being present in an amount up to 60

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the chlorine vapour pressure of the molten salt mixture, cooling the effluent gas, contacting the effluent gas in a chlorine separation zone with activated carbon to convert chlorine to hydrogen chloride, said contacting being effected at a temperature of from 100°F to 250°F and a pressure of from 15 to 100 psia, withdrawing from the chlorine separation zone a gas substantially free of chlorine and containing water vapour and hydrogen chloride produced from the chlorine, recovering aqueous hydrogen chloride from said gas, and introducing recovered aqueous hydrogen chloride into said oxidation reaction zone. 5

21. A process for oxidizing a salt mixture substantially as herein described with reference to the accompanying drawing. 10

10 22. A process for preparing a chlorinated hydrocarbon substantially as herein described with reference to the accompanying drawing.

23. A process according to claim 1 and substantially as herein described with reference to the example. 15

15 24. An oxidized salt mixture whenever prepared by a method according to any one of the preceding claims.

25. A chlorinated hydrocarbon whenever prepared by a method according to any one of claims 18, 19 or 22. 15

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