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CHLORINATING ETHYLENE HYDROCARBONS

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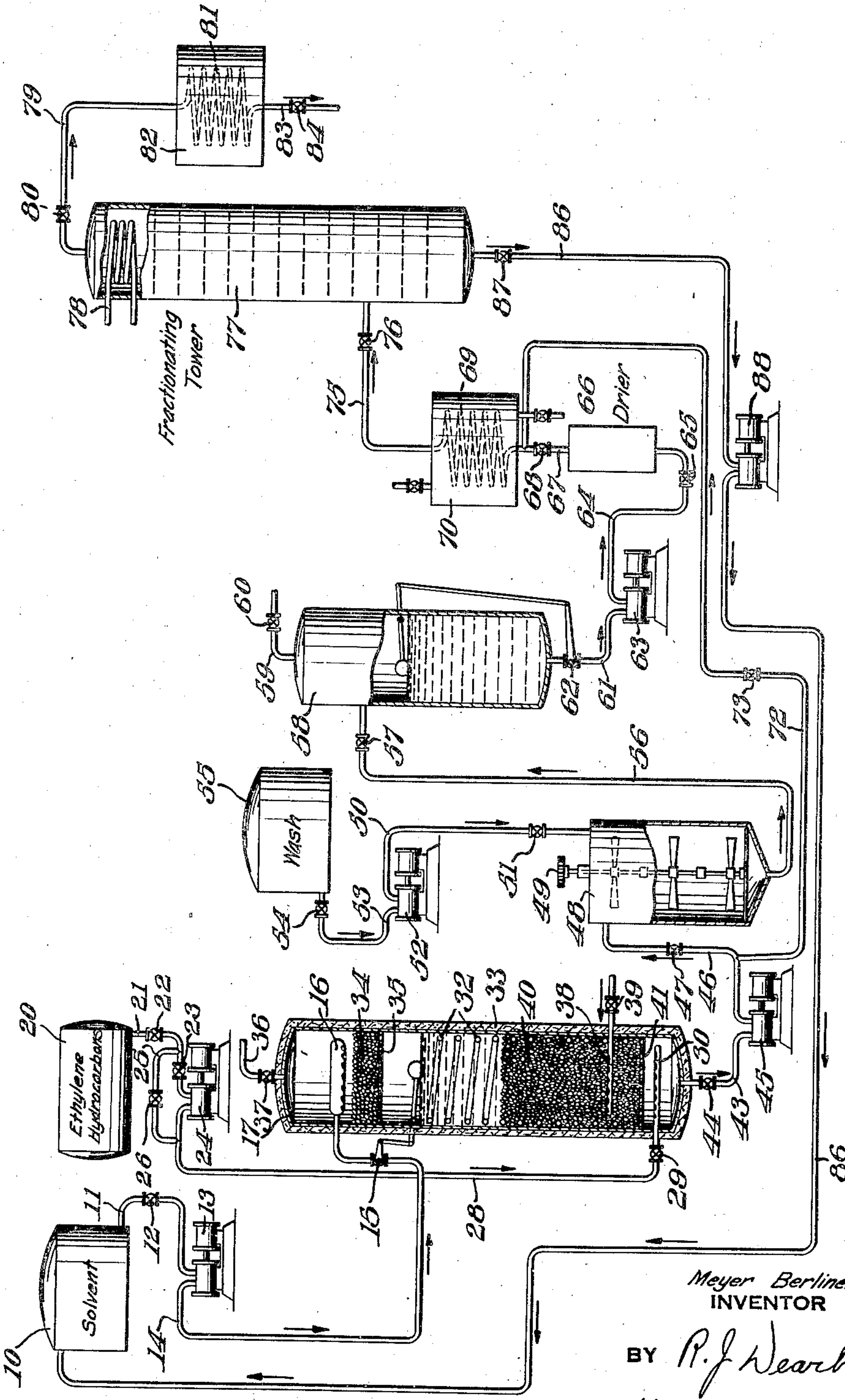

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CHLORINATING ETHYLENE HYDROCARBONS

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7 Claims. (Cl. 260—162)

This invention relates to the halogenation of hydrocarbons of the ethylene series and more particularly to a process of chlorinating ethylene hydrocarbons whereby the dichlor derivatives of the hydrocarbons are produced.

My invention contemplates a method of chlorinating hydrocarbons of the ethylene series wherein hydrocarbons such as ethylene, propylene, butylene, and the like, are reacted with chlorine in the presence of high boiling chlorinated compounds such as the trichlor and tetrachlor derivatives of propane and butane, or mixtures of these compounds, whereby high yields of the dichlor derivatives of the ethylene hydrocarbons are obtained. The reaction mixture may then be freed from dissolved chlorine and the hydrochloric acid by a suitable procedure, after which the reaction mixture is subjected to a distillation step. By means of the distillation operation, the desired dichlor derivatives are segregated as a separate fraction while the high boiling chlor derivatives are separated and recycled to the chlorination reaction.

The preparation of dichlor derivatives of ethylene hydrocarbons has always presented considerable difficulty and numerous expedients have been proposed to overcome this. The most success apparently has been had by employing solvents which dissolve both the chlorine and the hydrocarbons. In this connection, cognizance is had of U. S. Patent No. 1,231,123 issued to Benjamin T. Brooks and Dillon F. Smith. This patent discloses the preparation of dichlor derivatives of ethylene hydrocarbons by reacting these hydrocarbons with chlorine in the presence of a mutual solvent. As mutual solvents the inventors propose chloroform, carbon tetrachloride, carbon disulfide tetrachlorethane, and dichlorinated ethylene hydrocarbons.

I have discovered that by employing the trichlor and tetrachlor derivatives of propane and butane, higher yields of the dichlor derivatives of the ethylene hydrocarbons can be obtained than are possible when using the mutual solvents disclosed by Brooks and Smith.

In the practice of my invention, I may employ either a mixture of the trichlor and tetrachlor derivatives of propane and butane or any one of these compounds or any mixture thereof. The choice of the proper solvent or solvent mixture is determined largely by the character of the ethylene hydrocarbons undergoing reaction, as well as upon the economies which control any particular dichlorination reaction.

The chlorination reaction which forms the basis of my invention is most effectively carried out by maintaining a body of one of the above solvents or any mixture of these, and passing thereinto chlorine and the ethylene hydrocarbons to be chlorinated. When conducted in this way, the reaction is quite rapid and smooth, and a high percentage of the dichlor derivatives is formed. Although the reaction is advantageously carried out at a low temperature such as of the order of 5° C., lower or higher temperatures may be used, the choice of the proper temperature being dependent upon the type or types of ethylene hydrocarbons undergoing reaction. The reaction is advantageously carried out under a pressure in the neighborhood of atmospheric. However, in certain applications of the invention, it may be desirable to use higher pressures which may be as high as 200 pounds per square inch or higher.

The above described invention has been incorporated in a chlorination procedure which will be readily understood by reference to the accompanying drawing which shows in diagrammatic sectional elevation a suitable apparatus for efficiently carrying out the process.

In the figure, the numeral 10 refers to a storage for the solvent. This vessel is connected through the line 11 and the valve 12 with the inlet side of the pump 13. This pump is connected by the line 14 controlled by the automatic float-controlled valve 15 with the spray 16 which is supported in an upper portion of the reaction vessel 17.

The numeral 20 refers to a storage tank for ethylene hydrocarbons which is connected through the line 21 and the valves 22 and 23 with the inlet side of the pump 24. This pump is connected by the line 28 controlled by the valve 29 with the spray 30 which is situated at a lower point in the reaction chamber 17. A bypass line 25 controlled by the valve 26 connects line 21 at a point intermediate the valves 22 and 23 with the line 28.

The reaction chamber 17 is preferably an elongated vessel so constructed as to withstand the pressure used in the process and also constructed of such material as is proof against the corrosive by-products that are formed in the course of the reaction. The vessel is provided with cooling coils 32 for maintaining the reaction mixture at the proper temperature and with insulation 33 to prevent absorption of heat from the surrounding atmosphere. The vessel is also provided at a point below the spray 16 with a bed 34 of distributing material such as Raschig rings, tile, pumice stone, or the like, supported on a foraminous plate 35. This bed acts both as a distributing means for the solvent which is injected into the vessel and also serves to minimize the loss of reagents by the formation of mists. The top of the vessel is provided with a vapor drawoff line 36 controlled by the valve 37 which connects the vessel with a storage provision or an apparatus for recovering any unreacted ethylene hydrocarbons. There is inserted into a lower point of the vessel a spray 38 which is connected through the valve 39 with a source or supply of chlorine. There is provided at a point immediately above the spray 30 a bed 40 of distributing material such as Raschig rings, tile, pumice, or the like which is supported on a foraminous plate 41. This bed which may be of varying depth serves to facilitate the interaction of the reactants.

The lowermost point of the reaction vessel 17 is connected by the line 43 controlled by the valve 44 with the pump 45 which discharges through the line 46 and the valve 47 into the top of the washer 48. The washer comprises essentially a vessel provided with a mechanical agitating device 49. It is connected through the line 50 controlled by the valve 51 with the discharge side of the pump 52. The inlet side of this pump is in turn connected through the line 53 and the valve 54 with the storage tank 55 for wash liquid. The bottom of the washer is provided with a discharge line 56 controlled by the valve 57 which connects it with the settling chamber 58. This chamber is provided at its uppermost point with a discharge line 59 controlled by the valve 60 which leads to a sump, while the bottom of the vessel discharges through the line 61 and the automatic float-controlled valve 62 into the intake side of the pump 63. The discharge side of this pump is connected through the line 64 and the valve 65 with the drying chamber 66. This drying chamber is a vessel containing drying chemicals such as anhydrous calcium chloride, anhydrous copper sulfate or any other material which readily absorbs water and which does not detrimentally affect the products of the chlorination. The drier is connected by the line 67 controlled by the valve 68 with the heating coil 69 situated in the heater 70.

In order to permit of the by-passing of the washing and drying apparatus, there is provided the by-pass line 72 controlled by the valve 73 which connects the line 46 at a point intermediate the pump 45 and the valve 47 with the line 67 intermediate the valve 68 and the inlet to the heating coil 69.

The heater 70 consists essentially of the heating coil 69 and a containing vessel through which a heating medium such as high pressure steam, hot oil or the like may be circulated. The outlet of the heating coil 69 is connected through the line 75 and the expansion valve 76 with a lower point of the fractionating tower 77. This tower is advantageously provided at an upper point of its structure with a cooling coil 78 which serves to provide reflux for the fractionating operation. The top of the tower is connected through the line 79 controlled by the valve 80 with the coil 81 of the condenser 82. The outlet side of this condenser discharges through the line 83 controlled by the valve 84 to a suitable storage. The bottom of the fractionating tower is connected by the line 86 controlled by the valve 87 through the pump 88 with the storage tank 10.

In a typical operation of the present process, an ethylene hydrocarbon or a mixture of ethylene hydrocarbons is drawn from the storage tank 20 and delivered under its own pressure or by pump pressure to the line 28 and thence to the spray 30 situated within the reaction chamber 17. There is simultaneously delivered into the upper portion of the reaction chamber through the spray 16 a quantity of one of the previously described solvents which may consist either of a trichlor or tetrachlor derivative of propane or butane or any mixture of these derivatives. The quantity of solvent supplied is automatically controlled by means of the float-controlled valve 15. There is also injected into the reaction vessel through the spray 38 a measured and controlled quantity of chlorine.

The chlorine and ethylene hydrocarbon or hydrocarbons are mutually dissolved by the solvent and a rapid reaction resulting in the formation of the dichlor derivatives of the ethylene hydrocarbon or hydrocarbons occurs.

The temperature maintained with the reaction chamber 17 must be kept within closely controlled limits in order to effect the highest possible conversion of the ethylene hydrocarbons into dichlor derivatives. Although no specific temperature can be given since the same is dependent on the pressures used in carrying out the reaction, as well as on the types of ethylene hydrocarbons undergoing chlorination, in most cases temperatures below 60° F. may be employed with advantage.

The products of the reaction become dissolved in the solvent and this solution is continuously withdrawn from the bottom of the reaction chamber through the line 43 and delivered to the pump 45 which delivers the same either directly to the heater 70 or else through the washing and drying apparatus. In the latter case, the solution of dichlor derivatives in solvent is delivered under a suitable pressure into the washing chamber 48 wherein the solution is washed with water or an aqueous alkaline solution in order to free it from free chlorine or hydrochloric acid. This is accomplished by thoroughly agitating the solvent solution of dichlor derivatives with the wash liquid and then delivering the mixture to the separatory chamber 58 wherein the dichlor derivatives in solvent are caused to separate from the spent wash liquid. The latter is drawn off and passed to a sump while the former are charged by means of the pump 63 through the drying chamber wherein any remaining water is removed by the hygroscopic drying materials contained therein. The dried solution of dichlor derivatives in solvent is then delivered to the coil 69 of the heater 70 wherein it is heated to an elevated temperature above the vaporization temperature of the dichlor derivatives. The heated solution is then passed through the expansion valve 76 into a lower point of the fractionating tower 77 where the dichlor derivatives are separated from the solvent liquid. The former are vaporized and are delivered from the top of the tower to the condenser 82 where they are condensed. The solvent liquid, on the other hand, collects as a pool at the bottom of the fractionating tower 77 from which it is drawn through the line 86 by means of the pump 88 and returned to the solvent storage tank 10.

Comparative experiments have been conducted on the preparation of dichlor derivatives of mixed ethylene hydrocarbons and comprising particularly ethylene, propylene and butylene. These hydrocarbons were reacted with chlorine in the presence of different solvents. The solvents employed were:

1. The dichlorides of the hydrocarbons formed by the chlorination of the hydrocarbons used in the experiments.
2. Symmetrical tetrachlorethane.
3. A mixture of trichlor and tetrachlor propanes and butanes having a boiling range of approximately 130° to 205° C.

The procedure that was followed consisted in maintaining a body of the particular solvents at a temperature of 41° F. and introducing thereinto chlorine and the mixed ethylene hydrocarbons. The controlling prime variables were maintained substantially uniform and constant. These included the temperatures, pressures and quantity of reagents delivered to the reaction zone in a unit of time. The solvents containing the dichlor derivatives were then subjected to a distillation operation and the dichlor derivatives separated as distinct fractions. The yields obtained with the solvents set forth above were as follows:

Solvent	Yield in percent of theoretical	
	Olefin basis	Chlorine basis
1. Dichlorides of mixed ethylene hydrocarbons	54.1	64.8
2. Symmetrical tetrachlorethane	54.9	64.1
3. Mixed trichlor and tetrachlor propanes and butanes	68.6	76.8

These results indicate that the solvents which I have discovered permit of increased yields of ethylene hydrocarbon dichlorides over the solvents proposed in the past.

Although I have described this invention in connection with the preparation of dichlor derivatives of ethylene hydrocarbons present in high concentrations, the reaction may nevertheless be advantageously used in dichlorinating ethylene hydrocarbons present in cracking gases or other hydrocarbon gases containing ethylene hydrocarbons. The process may also be employed in direct connection with a fractionating operation or similar process where cracking gases are stripped of their ethylene hydrocarbon content and the latter, when separated, submitted to the process which forms the basis of my invention.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A method of preparing dichlor derivatives of ethylene hydrocarbons which comprises reacting the ethylene hydrocarbons with chlorine in the presence of a mixture of trichlor and tetrachlor propanes and trichlor and tetrachlor butanes.

2. The method of preparing dichlor derivatives of ethylene hydrocarbons which comprises maintaining a body of a mixture of trichlor and tetrachlor propanes and trichlor and tetrachlor butanes, and passing thereinto a stream of chlorine and a stream of the ethylene hydrocarbons.

3. The method of preparing dichlor derivatives of ethylene hydrocarbons which comprises reacting the ethylene hydrocarbons with chlorine in the presence of a mixture of trichlor and tetrachlor propanes and trichlor and tetrachlor butanes at a temperature of in the neighborhood of 5° C.

4. The method of preparing dichlor derivatives of ethylene hydrocarbons which comprises reacting the ethylene hydrocarbons with chlorine in the presence of a mixture of trichlor and tetrachlor propanes and trichlor and tetrachlor butanes and under superatmospheric pressure.

5. The method of preparing the dichlor derivatives of ethylene hydrocarbons which comprises reacting the ethylene hydrocarbons with chlorine in the presence of a solvent consisting of trichlor and tetrachlor propanes and trichlor and tetrachlor butanes whereby the so-formed dichlor derivatives become dissolved in the solvent together with unreacted chlorine and hydrochloric acid, washing the reaction product to remove the chlorine and hydrochloric acid and finally separating the dichlor derivatives from the solvent by distillation, and returning the solvent to the reaction.

6. A method of preparing dichlor derivatives of ethylene hydrocarbons which comprises reacting the ethylene hydrocarbons with chlorine in the presence of a solvent selected from the group consisting of trichlorpropane, trichlorbutane, tetrachlorpropane, and tetrachlorbutane.

7. A method of preparing dichlor derivatives of ethylene hydrocarbons which comprises reacting the ethylene hydrocarbons with chlorine in the presence of a solvent comprising a mixture of solvents selected from the group consisting of triclorpropane, trichlorbutane, tetrachlorpropane, and tetrachlorbutane.

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