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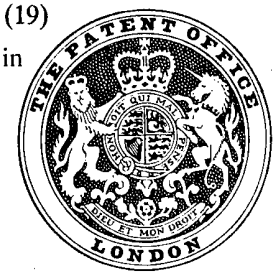

(54) PREPARATION OF DICHLOROETHANE

(71) We THE B.F. GOODRICH COMPANY, a corporation organised and existing under the laws of the State of New York, United States of America, of 277 Park Avenue, New York, State of New York 10017, United States of America, 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:

The present invention relates to the preparation of dichloroethane.

United States Patent specification 3,689,582 describes a process for recovering dichloroethane produced by the oxychlorination of ethylene in air by absorbing dichloroethane in an alkyl benzene absorbent having a boiling point within the range of 130° to 190°C., preferably from 135° to 180°C. The use of this solvent has not been completely satisfactory. In fact, fouling and plugging of the apparatus is frequent, probably because of the formation of polymers and this involves the use of pumps equipped with special seals and gaskets, as well as the use of filters suitable to retain solid particles. The frequency of the plant shut-downs reaches an extremely troublesome level. In addition there is often the escape to the atmosphere of foams entrained by the waste gases. The presence of foams in materials discharged to the atmosphere is dependent in part on humidity and represents a drawback also from the viewpoint of the absorption efficiency at the high temperatures at which the solvent is employed. A further deficiency is in solvent losses that increase as a function of the frequency of stopping the process.

According to the present invention there is provided a process for the preparation of dichloroethane which comprises oxychlorination of ethylene, the dichloroethane entrained by waste gases being recovered by absorption in a solvent, the solvent comprising at least one alkylbenzene having at least 12 carbon atoms and a boiling point greater than 190°C.

In preparing dichloroethane in an ethylene oxychlorination plant, ethylene is converted into dichloroethane through catalytic reaction with hydrochloric acid and oxygen, or other molecular oxygen-containing gases, according to the equation:

$$C_2H_4 + 2HCl + 1/2\ O_2 \longrightarrow C_2H_4Cl_2 + H_2O$$

Usually the oxygen is fed in excess in the form of air, and after separation of dichloroethane and reaction water, there is a large amount of inert gas still containing considerable amounts of useful product dichloroethane. These residual amounts of dichloroethane are recovered by absorption with suitable solvents.

These solvents are alkylbenzenes containing at least 12 and up to 16 carbon atoms; and having boiling points greater than 190°C., for example 195° to 255°C. Particularly useful are those alkylbenzenes having boiling points of 195 to 235°C., more preferably, 200° to 225°C. An example of useful solvent is diisopropyl benzene or mixtures of diisopropyl benzenes having boiling points in the range of 204 to 210°C. The solvent may contain at least 60% by weight of ortho-, meta- or para-diisopropyl benzene, or mixtures thereof. It was quite surprising in view of the clear teaching in United States Patent Specification No. 3,689,582 to find the diisopropyl benzenes so effective.

These solvents are inert toward dichloroethane and are exceptionally stable at operating temperatures. The solubility of dichloroethane vapors in these solvents is very high at low temperatures, even for very low partial pressures of dichloroethane. The separation of dichloroethane from the solution however is completely satisfactory when this is done

under vacuum at pressures below about 300 mm of Hg because of the very great differences between the vapor pressure of dichloroethane and the solvent. Since lower pressures are important, plant operations have been effective at 200 mm of Hg and while they may go as low as 10 mm of Hg, a more useful range will be from about 50 mm of Hg to less than 300 mm of Hg. The lower the pressure, the lower the temperature in the reboiler and one thus avoids problems related to operating the reboiling at higher temperatures.

When using the defined solvents, as the diisopropyl benzene solvents, and desorbing at pressures below 300 mm of Hg, i.e., about 200 mm of Hg, of diisopropyl benzene has been used in the claimed process on a commercial scale for two years (about 16,000 hours) with none of the problems associated with use of the solvents of the prior art. It is noted that in United States Patent Specification No. 3,689,582, the stability of that solvent was reported as 2000 hours.

The present invention is illustrated by the following Examples.

Example I

An ethylene feed stream was oxychlorinated with hydrochloric acid and air, and most of the resulting dichloroethane was condensed and separated, along with the reaction water, by cooling under a pressure of 3 kg/cm^2. The residual gases, containing 3.75% by weight of dichloroethane, were introduced into the bottom of an absorption column that operated at 2.5 kg/cm^2. For each kg of inflowing gas, 0.31 kg of an alkylbenzenes mixture having the following characteristics were fed to the top of the column:

specific heat at 150°C	0.577 kcal/kg/°C
diisopropylbenzenes content	81.9% by weight
distillation range	between 195° and 255°C. (ASTM D-850)
density (15/4°C.	0.8685 (ASTM D-1298)
viscosity at 50°C.	12. centistokes (ASTM D-445)
flash point (Pensky Martens method)	71°C. (ASTM D-93)
alkylbenzenes having 12 or more carbon atoms	95.7% by weight
cracking starting temperature	>450°C.

The solution leaving the column bottom, rich in dichloroethane, was fed to a desorption or stripping column complete with reboiler operating at 200 mm of Hg; the recovered dichloroethane containing less than 100 ppm of alkylbenzenes flowed out from the top of this column, while the hot alkylbenzenes (at 160°C.) flowed out from the bottom; these alkylbenzenes preheated the solution to be stripped and were then cooled down to 8°C. before being fed again to the absorption column top, where the temperature was kept at 20°C. and where the residual gases containing 15 ppm of dichloroethane were separated. After a 10,000-hour run the equipment exhibited insignificant soiling and no solids in suspension in the solvent were noticed. In practice the solvent losses did not exceed 0.7 kg per ton of dichloroethane produced.

Example II

The test of Example I was repeated, but with the following variations: the solvent was cooled down to 2°C. before being introduced into the absorption column, and the temperature at the top of said absorption column was kept at 14°C. The result was that the dichloroethane content of the gases vented to the atmosphere was lower than 3 ppm and the solvent consumption decreased to less than 0.5 kg per ton of dichloroethane produced. Also under these conditions no foam formed.

WHAT WE CLAIM IS:-

1. A process for the preparation of dichloroethane which comprises oxychlorination of ethylene, the dichloroethane entrained by waste gases being recovered by absorption in a solvent comprising at least one alkylbenzene having at least 12 carbon atoms and a boiling

point greater than 190°C.

2. A process as claimed in claim 1 in which the solvent contains 12 to 16 carbon atoms and has a boiling point range of 195°C. to 255°C.

3. A process as claimed in claim 2 in which the solvent has a boiling point of 195°C. to 235°C.

4. A process as claimed in claim 3 in which the solvent has a boiling point of 200°C. to 225°C.

5. A process as claimed in any of claims 1 to 4 in which at least 60% by weight of the solvent comprises ortho, meta or para-diisopropylbenzene or of mixtures thereof.

6. A process as claimed in any of claims 1 to 5 in which the solvent containing dichloroethane flows to a desorption column operating at a pressure less than 300 mmHg to recover dichloroethane from the solvent.

7. A process as claimed in claim 6 in which the solvent containing dichloroethane flows to a desorption column operating at a pressure of 50 to 200 mmHg to recover dichloroethane from the solvent.

8. A process for the preparation of dichloroethane substantially as hereinbefore described with particular reference to any of the foregoing examples.

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