

# ALIEN PROPERTY CUSTODIAN

## PROCESS FOR MANUFACTURING AFTER-CHLORINATED POLYVINYL CHLORIDE

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The present invention relates to an improved process for manufacturing after-chlorinated polyvinyl chloride.

According to the process described in U. S. Patent No. 1,982,765 polyvinyl chloride is chlorinated by passing chlorine through an organic liquid such as carbon tetrachloride or tetrachlorethane in which the polyvinyl chloride is suspended.

Apart from the fact that by this method of working the chlorination occurs rather slowly and a multiple of the quantity of chlorine which is theoretically required escapes unconsumed and must be recovered, it is necessary to control continuously by taking test portions whether the desired chlorination degree has been attained. Moreover, care must be taken that the highest temperatures applied do not exceed the boiling point of the solvent used.

Now, I have found that this chlorination of polyvinyl chloride may be essentially simplified by performing it in the presence of an organic solvent, preferably a chlorinated aliphatic hydrocarbon, in a closed vessel under pressure. By addition of the quantity of chlorine necessary for the desired degree of chlorination, heating to the reaction temperature and cooling, if desired, when the chlorination has started, in order to remove an excess of reaction heat there is obtained after a short time and in a single manner a final product of definite properties, especially of a definite solubility. A further advantage resides in the fact that as suspending agent for the parent material there may also be used chlorinated hydrocarbons of low boiling point as, for instance, chloroform, from which the final product may be separated completely, for instance, by causing the reaction mixture to run into boiling water. Last not least, a smaller quantity of the solvent is used in the new process.

The following examples serve to illustrate the invention, the parts being by weight:—

*Example 1.*—50 parts of polyvinyl chloride of the degree of polymerization  $K=62.3$ , 800 parts of carbon tetrachloride and 50 parts of chlorine are heated in a roller or rocking autoclave at about 80° C. to 90° C. until reaction sets in. By cooling the temperature is kept at 100° C. to 110° C. After about 2 hours the chlorination has finished. The highest pressure amounts to about 9 to 10 atmospheres above atmospheric pressure. The reaction product which has separated contains 66.8 per cent. of chlorine. By suitably dosing the chlorine used, the contents of chlorine may be varied at will. The final products thus obtained

yield in tetrahydrofurfurane solutions of up to 15 per cent. strength.

*Example 2.*—22 parts of polyvinyl chloride of a  $K$ -value of 69.8, 300 parts of chloroform and 14 parts of chlorine are heated to 85° C. in a shaking autoclave. After the chlorination has set in, the vessel is cooled so that the temperature remains constantly at 90° C. to 100° C. The highest pressure during the reaction amounts to about 8 atmospheres above atmospheric pressure. After about 2 hours the chlorination has finished; the final product is separated by causing the reaction mixture to run into boiling water. The final product contains 63.2 per cent. of chlorine and yields in acetone solutions of 25 per cent. strength and in methylene chloride solutions of 20 per cent. strength.

*Example 3.*—A mixture of 30 parts of polyvinyl chloride of a  $K$ -value of 72.4, 300 parts of chloroform and 38 parts of chlorine yields after 2½ hours at a maximum temperature of 120° C. and a maximum pressure of 20 atmospheres a final product containing 67.3 per cent. of chlorine. It is insoluble in acetone, but yields in tetrahydrofurfurane clear solutions of 25 per cent. strength.

*Example 4.*—35 parts of polyvinyl chloride, 420 parts of tetrachlorethane and 35 parts of chlorine are heated in an autoclave to 85° C. In the course of 15 minutes the temperature rises to 90° C., care being taken by cooling that the temperature does not exceed 100° C. to 105° C. The maximum pressure amounts to 12 atmospheres above atmospheric pressure. Towards the end of the reaction the reacting liquor is heated to the said temperatures. After 1½ hours the reaction is finished. The final product contains 63.7 per cent. of chlorine and yields in acetone solutions of 25 per cent. strength and in methylenechloride solutions of 20 per cent. strength.

It is obvious that the invention is not limited to the foregoing examples or to the specific details given therein. Thus, for instance, other organic liquids which are inactive against chlorine may be used as suspending agents for the polyvinyl chloride under treatment. Although the reaction occurs very promptly it may be forwarded by addition of a chlorinating catalyst known per se in the art.

Furthermore, the process may be varied by introducing the desired amount of chlorine into the reaction vessel in stages so that always only limited quantities react with the polyvinyl chloride.

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