

ALIEN PROPERTY CUSTODIAN

METHOD FOR PRODUCING UNSATURATED CHLORINATED HYDROCARBONS CON- TAINING FOUR CARBON ATOMS

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In my patent applications Serial No. 212,823 and Serial No. 221,264 there are described methods for polymerizing chlorinated ethylenes such as dichlor ethylene and trichlor ethylene, the main product of the polymerization being a dimeric product such as dimeric dichlor ethylene having the formula $C_4H_4Cl_4$ and dimeric trichlor ethylene having the formula $C_4H_2Cl_6$. It has been found that such chlorinated ethylenes which are compounds containing four carbon atoms and at least four chloride atoms in their molecules and which can be prepared according to the method described in the above cited applications or by other methods e. g. by application of pressure and high temperatures to the said chlorinated ethylenes, may be converted to technically valuable unsaturated chlorinated hydrocarbons containing four carbon atoms in their molecule by splitting off a molecule containing chlorine i. e. either hydrogen chloride or chlorine.

The splitting off may be carried out by methods known per se, so the hydrogen chloride may be splitted off by an alkaline substance or by catalysts, and the chlorine may be splitted off by application of metals.

The products which are obtained by the described processes of splitting off hydrogen chloride or chlorine are proposed to be chlorinated derivatives of butadiene. They may be used high boiling solvents and/or softening agents, insecticides, insulating materials for electrical purposes etc. They are almost non-combustible, the more the higher the chlorine contents are.

The new compounds may be converted to resin-like compounds for use as plastic materials by treating them with aluminium chloride or similar catalysts. The new artificial resins which are obtained in form of powder may be used for moulded articles e. g. sheets or plates by the application of pressure and heat to the powder.

The new resins show a high molecular weight and are probably polymers of the starting materials.

Instead of the pure compounds with four carbon atoms, mixtures of two or more of the said compounds or mixtures of the said compounds with other substances especially unsaturated substances may be treated with aluminium chloride or similar catalysts according to the invention.

The reaction which yields substances of high molecular weight may be carried out in the presence or absence of solvents and/or diluents. The reaction occurs very easily if the starting materials have a low percentage of chlorine, e. g. $C_2H_2Cl_2$ reacts below room temperatures. The

reaction of substances showing higher chlorine percentage is preferably carried out by using higher temperatures.

Instead of aluminium chloride the addition products of aluminium chloride with other salts may be used e. g. with sodium chloride, lithia chloride or aluminium bromide and similar catalysts.

It was surprising that aluminium chloride and similar catalysts are suited for the production of high-molecular substances, since high temperatures, oxygen and peroxides alone or combination which each other have proved to be unsuitable.

The high molecular substances obtained are almost non-combustible and show a high insulating power, e. g. for electrical purposes. They may be combined with other artificial matter as for instance condensation products from formaldehyde and phenol or urea and the like, polymeric vinyl, acrylic or methacrylic compounds or the like, e. g. polymeric vinyl acetate, vinyl chloride, vinyl ethers, vinyl carbazole, vinyl acetylene, styrene, butadiene, monochlorbutadiene, acrylic and methacrylic acid and especially their esters and nitriles, furthermore with esters and ethers of cellulose, waxes, natural resins such as rosin, fillers, pigments, dyestuffs, softening agents. The additional substances may be used alone or in any desired combination. The high molecular substances obtained according to the invention are preferably mixed with low molecular, liquid starting products, especially with polymerizable substances. The polymeric chlorinated butadiens which are obtained according to the invention are for instance moistened with liquid monomeric esters of acrylic acid and polymerized to a rubber-like, non-sticky mass.

Examples

1. 250 g zinc dust are suspended by stirring in 250 ccm methyl alcohol and 500g dimeric dichlor ethylene are added within an hour. The temperature of the solution is raised to 70-75°C. In order to complete the reaction the whole may be heated to 75-80°C for some time. Two layers are obtained. The upper layer which is clear is separated and fractionated at 15 mm pressure. A yield of 70-80% of a chlorinated hydrocarbon showing a constant boiling point, is obtained.

The boiling point is 30-35°C at 15 mm pressure, $d_{20} = 1.214$; $n_{D}^{20} = 1.523$. The chlorine percentage was found to be 57.82 (calculated 57.72 for $C_4H_4Cl_4$).

Whereas the dimeric dichlor ethylene does not

accept any bromine, the reaction product obtained by splitting off one molecule of chlorine is capable of accepting two molecules of bromine. The reaction seems to show that the new compound is a dichlor butadiene. The product is not the same as the one known 1,2-dichlorbutadiene.

Instead of zinc, iron may be used for splitting off the chlorine but zinc is preferred.

2. 300 g dimeric dichlor ethylene are cooled to 0°C and while stirring the calculated amount of potassium hydroxide dissolved in methyl alcohol is added with-in 3 hours. The formed potassium chloride is filtered off, the two layers are separated and fractionated at 15 mm pressure. A pure chlorinated hydrocarbon boiling at 52-53°C is obtained in a yield of 85% of the theoretical. $d_{20} = 1.382$; $n_{D}^{20} = 1.546$. The chlorine percentage was found to be 67.43 (calculated 67.02 for $C_4H_2Cl_2$). Bromine is added in a similar manner as to the product according to example 1.

3. 80 g zinc dust are suspended by stirring in 50 ccm methyl alcohol and 150 g dimeric trichlor ethylene are added at 70°C within an hour. A temperature of 70-80°C is then maintained for another hour, continuously stirring. The upper of the two layers formed is fractionated at 15 mm pressure. The product which is obtained in a yield of about 70%, shows a boiling point of 64-67°C at 15 mm pressure, the formula is $C_4H_2Cl_4$.

4. The compound $C_4H_2Cl_2$ obtained according to example 1 is polymerized in the following manner. 3 g of dry aluminum chloride are added to 50 ccm ethylene chloride. While stirring and maintaining a temperature of about 0°C, 50 g of the chlorinated hydrocarbon are added with in half an hour. The stirring is continued at 0°C for 3 hours. The formed pappy black product is washed twice with hydrochloric acid and then twice with pure water. The pap was filtered off and a bluish product in the form of a powder was obtained in a yield of about 95%. Plates or similar molded articles may be prepared by pressing

the powder at about 70-90° C under high pressure.

5. 30 g of the new compound obtained according to example 1 are cooled down to 0-5° C. While maintaining the low temperature and stirring 1 g of dry aluminum chloride is added. The reaction begins after 5-10 minutes and is complete after about 30 minutes. The products are washed with diluted hydrochloric acid and then with wather. The blackish raw product became light yellow by the washing process. It was filtered off and dried at 50-60° C. The light coloured powdery product was obtained in a good yield. Molded articles could be obtained by pressing as described in example 4.

6. The powder obtained according to example 4 or 5 was mixed with its own weight of monomeric ethyl acrylate and the mixture was kept at room temperature until the powder is swelled to some extent. The mass was then heated to 50° C for 24 hours adding some benzoyl peroxyde. The temperature is raised to 70° C left for 24 hours. The monomeric ethylacrylate yields the polymeric product and tough practically not sticky mixtures are obtained.

7. 50 g of the new compound obtained according to example 2 are heated to 50-70° C and while stirring 3 g dry aluminum chloride is added. The reaction begins after a short time and is practically complete after half an hour. The black tough product is washed with methyl alcohol and worked up according to example 4. The yield is about 95%.

8. 30 g of the new compound obtained according to example 3 are heated to 50° C and while stirring 2 g dry aluminium chloride is added. The temperature is then raised to 70° C. Reaction occurs immediately. The product was worked up according to example 4. The yield was about 95%.

Instead of 2 g aluminum chloride 3 g aluminum bromid may be used.

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