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PROCESS FOR CONVERTING TRICHLOR ETHYLENE

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The invention relates to the production of technically valuable chlorinated hydrocarbons from trichlor ethylene.

It has been described that trichlor ethylene can be polymerized by the action of aluminum chloride to yield oils or substances of resin-like character. Furthermore it has been proposed to polymerize trichlor ethylene in the presence of organic vinyl esters to yield joint polymers with said esters. It is also known to use trichlor ethylene as a solvent for acrylic acid or its derivatives, when polymerizing the said compounds with the aid of oxygen or substances evolving oxygen.

It has been stated that the action of oxygen on trichlor ethylene even together with the action of ultra violet rays yields only dichlor acetyl chloride and no polymeric compounds.

It was surprising therefore that according to the present invention trichlor ethylene can be polymerized per se by treating with a peroxide. The polymeric compounds which are obtained by the new process are however quite different from the oils or resin-like substances obtained by the action of aluminum chloride on trichlor ethylene. The reaction products obtained from trichlor ethylene treated with peroxides are substantially dimeric and trimeric, liquid products besides some higher polymeric substances.

Suitable peroxides to be used according to the invention are inorganic peroxides and organic peroxides, e. g., benzoyl peroxide or tetrahydronaphthalene peroxide.

Trichlor ethylene can be treated with peroxides in admixture with symmetrical dichlor ethylene. In this case polymeric trichlor ethylenes, polymeric symmetrical dichlor ethylenes and addition products which contain trichlor ethylene and symmetrical dichlor ethylene are obtained.

Besides peroxides, heat or pressure alone or combined together may be employed to assist the polymerization.

The new process is especially advantageous since the splitting off of hydrogen chloride (effected by aluminum chloride in any case) is avoided practically completely when temperatures lower than about 150° C. are used. Above 150° C. decomposition (especially splitting off of hydrogen chloride) occurs and the reaction vessels may be affected.

The reaction may conveniently be carried out by boiling at atmospheric pressure using a reflux condenser, although lower or higher temperatures can also be used. By working at higher temperatures (using a pressure of at least the vapour pressure of trichlor ethylene) somewhat higher yields are obtained in shorter time.

At all temperatures the dimeric compound preponderates. At lower temperatures the yield of trimeric and higher polymeric compounds the highest of which show wax-like character is a little better than at higher temperatures.

The part of the starting material which has not undergone polymerization can be recovered by distillation and in a further process be treated with peroxides so that finally practically the whole of the starting material can be converted into polymers.

The lower polymers can be isolated by fractional distillation. They are suitable as non-combustible solvents, diluents, detergents, softening agents, insecticides, isolating materials, especially for electrical purposes, etc. They may also be used for the making of synthetic products.

The following examples illustrate the invention, but the invention is not restricted to the given examples.

Example 1

100 parts by weight of trichlor ethylene are boiled for 45 hours (using a reflux condenser) with 2 parts by weight of benzoyl peroxide. The reaction product may be filtered and the unaltered trichlor ethylene is recovered from the filtrate by distillation at atmospheric pressure. The higher boiling parts are fractionated at 15 mm. pressure, with the following result:

87–110° C.	.8 part by weight
110–115° C. (dimeric trichlor ethylene $C_4H_2Cl_6$)	24.1 parts by weight (specific gravity 1,662 at 29° C.)
115–190° C.	1.6 parts by weight
190–197° C. (trimeric trichlor ethylene $C_6H_3Cl_9$)	2.9 parts by weight
Solid residue	.5 part by weight

The dimeric trichlor ethylene shows a boiling point of 228–229° C. at 762 mm. pressure, a specific gravity of 1,671 at 20° C., an index of refraction n_D of 1,5457 at 20° C. and a dielectric constant of 3,97 at 20° C.

Example 2

100 parts by weight of trichlor ethylene and 2 parts by weight of benzoyl peroxide are heated to 100–115° C. for 15 hours in a closed tube. The unaltered trichlor ethylene is distilled off and the remainder is fractionated at 15 mm. pressure, with the following result:

	Parts by weight
110–114° C.	14.1
195–200° C.	.5
Solid residue	3.2

Example 3

100 parts by weight of trichlor ethylene and 1 part by weight of benzoyl peroxide are heated to 90–100° C. for 7 hours in an earthen vessel being in an iron autoclave, under a pressure of added

nitrogen of 50 atmospheres. The unaltered trichlor ethylene is distilled off and the remainder is fractionated at 15 mm. pressure, with the following result:

	Parts by weight
100–115° C.	25.5
190–200° C.	4.0
Solid residue	.5

Example 4

The working is carried out as in Example 1, but instead of 2 parts by weight of benzoyl peroxide 1 part by weight of tetrahydronaphthalene is used. The yield is lower.

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