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HOE 93/F 366

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Process for preparing highly chlorinated paraffins

In the preparation of chlorinated hydrocarbons containing from 14 to 40 carbon atoms and having a chlorine content of more than 60%, the chlorination is carried out in a solvent, since the melt viscosity of the chlorinated paraffins formed is very high and chlorine exchange between the gaseous and the liquid phase no longer takes place normally. The solvent used is principally carbon tetrachloride, recently chloroform too. The use of chlorofluorocarbons is also described in the literature (cf. DE 2 150 599). The conversion to the chloroparaffins is carried out using liquefied chlorine and in the presence of a free-radical-forming catalyst, such as, for example, organic peroxides, or under the action of ultraviolet rays, X-rays, etc.

Since chlorinated hydrocarbons, because they have properties hazardous to health and to the environment, require particular expense in handling, it is an object of the invention to reduce their amount in the production circuit as far as possible.

It has been found that the preparation of high chlorinated paraffins is also possible in the absence of a solvent.

The invention accordingly provides a process for preparing highly chlorinated paraffins having a chlorine content of more than 60% by weight at a temperature of from 75 to 105°C and a pressure of up to 10 bar by reacting a paraffin having from 14 to 40 carbon atoms with liquid chlorine, wherein the reaction is carried out in the presence of from 0.5 to 3% by weight of water, based on the final product.

Starting materials used in the process of the invention

are saturated or unsaturated hydrocarbons having from 14 to 40, preferably from 17 to 24, carbon atoms, which can already contain chlorine atoms ("prechlorinated"). These materials include the various types of paraffin, for example n-paraffins, α -olefins.

The chlorination is carried out by means of liquid chlorine. The pressure in the reaction vessel is accordingly up to 10 bar, preferably from 2 to 6 bar. The reaction temperature is from 75 to 140°C, preferably from 80 to 105°C.

The reaction is carried out in the presence of a free-radical-forming catalyst. The bonds of -COOC-, -COOOC- and -CNNC- compounds dissociate even at lower temperatures and form free radicals.

Preferably, the free-radical-forming catalyst comprises an azo compound, for example an azonitrile such as α,α -azobisisobutyronitrile, or an organic peroxide such as benzoyl peroxide or dilauroyl peroxide or an organic hydroperoxide. Preference is given to using α,α -azobisisobutyronitrile and dilauroyl peroxide.

However, it is also possible to form free radicals using ultraviolet light or other ionizing radiation, for example X-rays.

The reaction of the paraffins with the chlorine is carried out in the presence of water which absorbs the hydrogen chloride formed during the reaction, or dilute hydrochloric acid. The amount of water at the beginning of the reaction is from 0.5 to 3% by weight, based on the final product, or from 1 : 6 to 1 : 15, based on hydrocarbon used.

The process of the invention can be carried out in various types of apparatus. Possibilities are stirred reactors, falling-film reactors, loop reactors,



bubble-column reactors. The essential point is that intensive mixing of the aqueous and organic phases takes place. Preference is given to using a stirred reactor with an impeller stirrer.

5 The process of the invention makes it possible to prepare highly chlorinated paraffins in a simple manner. It has been found that the presence of hydrochloric acid even at the high temperatures has no deleterious effect on quality. The separation of the chloroparaffin from the
10 hydrochloric acid is very good under these conditions. An emulsion layer which inhibits the transport of the chloroparaffin into downstream equipment does not occur.

The following examples illustrate the invention.

The experiments were carried out in a stirred reactor of
15 enamelled steel having a volume of 8 m³ and fitted with an impeller stirrer. The reaction mixture was stirred with the stirrer having 3 blades in association with deflectors, i.e. baffles. The chlorinator was provided with lines by means of which the raw materials such as
20 paraffin, water or dilute hydrochloric acid, the solvent and also the free-radical initiator were fed in. There was present a dip pipe for continuously feeding in liquid chlorine, which pipe advantageously dips into the reaction mixture and, if possible, ends below the level of
25 the stirrer. In each experiment, the amount of water or hydrochloric acid was calculated in such a way that during chlorination there was formed hydrochloric acid having a strength of from 29% (m/m) to 35% (m/m), so that it was not necessary to conduct away the hydrogen
30 chloride formed in the chlorination.

The chlorination unit was made safe by means of pressure and temperature measuring devices.



Comparative Example A

A mixture of 730 kg of paraffin hydrocarbons having from 17 to 26 carbon atoms in the molecule, 1600 kg of carbon tetrachloride (40% (m/m) based on the chloroparaffin prepared) and 3900 kg of water was reacted with 3570 kg of liquid chlorine in the presence of 0.3% of dilauroyl peroxide, based on the chloroparaffin prepared, at a temperature of from 84 to 103°C and a pressure which was increased up to 5.3 bar during the course of the chlorination. The desired amount of chlorine could be introduced over a period of about 5 hours, with the chlorine introduced having reacted completely, i.e. to more than 99.9% (m/m). After chlorination was complete, the stirrer was turned off to achieve phase separation within 10 minutes. The organic phase was drained to remove the solvent.

The chloroparaffin had a chlorine content of 72% (m/m); the yield was 2500 kg of solid chloroparaffin.

Comparative Example B

The chlorination was carried out in a similar manner to that described in comparative example A, except that chloroform was used in place of carbon tetrachloride and the amount of chlorine fed in was increased by the amount required to chlorinate the chloroform used to carbon tetrachloride. The chloroparaffin obtained had a chlorine content of about 72% (m/m); the phase separation was achieved within 10 minutes in the chlorination at from 84 to 102°C.

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Comparative Example C

At otherwise constant amounts used, the experimental conditions were changed by reducing the amounts of carbon tetrachloride as solvent to 1400 kg corresponding to 36% (m/m), based on the chloroparaffin prepared. At a chlorination time of about 5.5 hours and a phase

separation time of about 10 minutes at a temperature of
from 84 to 102°C, there were prepared 2500 kg of chloro-
paraffin having a chlorine content of 72% (m/m). The
drainage time into the downstream equipment to remove the
5 solvent was 10 minutes.

Comparative Example D

At otherwise constant amounts used, the experimental
conditions were changed by reducing the amounts of carbon
tetrachloride as solvent to 900 kg corresponding to 26%
10 (m/m), based on the chloroparaffin prepared. At a
chlorination time of about 5.5 hours and a phase separa-
tion time of 20 minutes at a temperature of 95°C, there
were prepared 2500 kg of chloroparaffin having a chlorine
content of about 72% (m/m). An emulsion layer was ob-
15 served between the phases. The drainage of the product
into the downstream equipment took 12 minutes and was
only slightly hindered.

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Comparative Example E

At otherwise constant amounts used, the experimental
20 conditions were changed by reducing the amounts of carbon
tetrachloride as solvent to 600 kg corresponding to 19%
(m/m), based on the chloroparaffin prepared. At a
chlorination time of about 5.5 hours and a phase separa-
tion time of 25 minutes at a temperature of 94°C, there
25 were prepared 2500 kg of chloroparaffin having a chlorine
content of about 72% (m/m). An emulsion layer was ob-
served between the phases, which layer was, in terms of
amount, significantly greater than in experimental
example D. The drainage time into the downstream equip-
30 ment to remove the solvent was increased to 23 minutes.

Comparative Example F

At otherwise constant amounts used, the experimental
conditions were further changed by reducing the amounts

of tetrachloromethane to 300 kg corresponding to 11% (m/m), based on the chloroparaffin prepared. At a chlorination time of about 7 hours and a phase separation of about 40 minutes at a temperature of 94°C, there were prepared 2500 kg of chloroparaffin having a chlorine content of about 72% (m/m). The drainage time into the downstream equipment for removing the solvent was increased to about 60 minutes. Owing to a thick emulsion layer between the two phases, the time for distilling off the solvent was considerably increased as a result of entrained hydrochloric acid.

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Example 1



At otherwise constant amounts used, the experimental conditions were further changed by entirely omitting the solvent carbon tetrachloride or chloroform. At a chlorination time of about 7.5 hours and a phase separation time of about 30 minutes, which owing to the absence of solvent could be carried out at a temperature of 135°C, 2500 kg of chloroparaffin were again prepared. The phase separation was very good without signs of an emulsion layer. The hydrochloric acid phase was very clean and free of chloroparaffin flocs. The drainage time into the downstream apparatus was 55 minutes. Owing to the good phase separation, residual amounts of hydrochloric acid were quickly and completely removed from the chloroparaffin phase.

To achieve an acceptable chlorination time even without solvent, the gap between the impeller stirrer and the bottom of the reactor has to be so small, and the diameter of the stirrer has to be so designed, that the chloroparaffin/paraffin mixture drawn in is sufficiently well dispersed and intimately mixed with the aqueous phase and the chlorine present. The reaction of the chlorine with the chloroparaffin/paraffin mixture was then ensured. After reaction was complete, the mixture was heated to a temperature of up to 140°C, to achieve

satisfactory separation of the phases.

Example 2

5 In further experiments, under the same experimental
conditions and with constant amounts used in a similar
manner to example 1, the paraffin hydrocarbon used was
varied in terms of chain-length distribution. In each
case, after chlorination was complete phase separation
was achieved at temperatures up to 140°C, without an
emulsion layer interfering with further workup being
10 observed.

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Claim

1. A process for preparing highly chlorinated paraffins having a chlorine content of more than 60% by weight at a temperature of from 75 to 105°C and a pressure of up to 10 bar by reacting a paraffin having from 14 to 40 carbon atoms with liquid chlorine, wherein the reaction is carried out in the presence of from 0.5 to 3% by weight of water, based on the final product, and in the absence of a solvent.



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