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Description

Process for removing olefinic impurities from fluorinated C_3 - C_6 -hydrocarbons

5 The invention relates to a process for removing olefinic impurities from fluorinated C_3 - C_6 -hydrocarbons. These compounds are provided as substitutes for the ozone-endangering completely halogenated chlorofluorocarbons. In order to be able to use the fluorinated C_3 - C_6 -hydrocarbons in the refrigeration technology area or as
10 propellants for pharmaceutical aerosols or rigid polyurethane foams, interfering and toxic olefinic impurities, which are formed in the synthesis - some only in traces - must be completely removed. This is not possible on an economically tolerable scale by
15 conventional physical methods such as distillation or adsorption. Therefore a possible method must be sought of converting the interfering impurities into non-toxic compounds by reaction with suitable substances or of converting them into those compounds which can be
20 separated off from fluorinated C_3 - C_6 -hydrocarbons by a physical route with small expenditure.

It has now proved to be expedient to react the olefins, such as 1,1,1,3,4,4,5,5,5-nonafluoro-2-(trifluoromethyl)-2-pentene (HFH), which are formed in the preparation of,
25 for example, isodihydroperfluorohexane (IDPH; 1,1,1,2,3,4,5,5,5-nonafluoro-2-(trifluoromethyl)-pentane), with alcohols in the presence of bases. In this case, only compounds are formed which can easily be separated off from IDPH by distillation. Moreover, IDPH
30 is not attacked and the reaction proceeds rapidly and quantitatively.

The removal of olefinic impurities from 1,1,1,2,3,3,3-heptafluoropropane (R 227) by reaction with alcohols in the presence of salts is already described in
35 German Patent Application P 4 115 025.2, which is not a

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prior publication.

Although Chemical Abstracts 1971, volume 13: 60600w discloses that a mixture of higher-boiling ethers and esters can be prepared from 2-H-pentafluoropropene and alcohols in the presence of KOH, the conversion rates are not quantitative. Therefore, it was not to be expected that traces of HFH and other olefins, dissolved in IDPH, can be quantitatively removed by reaction with alcohols. Moreover, azeotrope formation with alcohols was to be feared.

The invention relates to a process for removing olefinic impurities of the formula $C_nH_mF_pCl_q$, where $n = 2 - 6$, $m = 0 - 8$, $p = 1 - 12$, $q = 0 - 8$ and $m + p + q = 2n$, from fluorinated C_3 - C_6 -hydrocarbons, with the exception of 1,1,1,2,3,3,3-heptafluoropropane (R 227), which comprises bringing the contaminated fluorinated C_3 - C_6 -hydrocarbons into contact with an alcohol and a base at temperatures of -20 to 100°C and pressures of 1 to 50 bar and, simultaneously or subsequently, distilling off the fluorinated C_3 - C_6 -hydrocarbons.

The fluorinated C_3 - C_6 -hydrocarbon used is preferably 1,1,1,3-tetrafluoropropane, 1,1,1,4,4,4-hexafluorobutane, 1,1,1,2,3,4,4,4-octafluorobutane, 1,1,2,2,3,3,4,4-octafluorobutane or 1,1,1,2,3,4,5,5,5-nonafluoro-2-(tri-fluoromethyl)-pentane.

A monohydric alcohol is preferably used of the formula $C_aH_{2a+1}OH$, $C_aH_{2a}(OH)_2$, $C_aH_{2a-1}OH$ or $C_aH_{2a-2}(OH)_2$, where $a = 1$ to 6, in particular where $a = 1$ to 3. Methanol, ethanol, i-propanol and ethylene glycol (glycol) are particularly suitable.

The bases used are preferably those whose pK is 8 to 14, in particular NaOH, KOH or Na phenolate.

The temperature is preferably at 0 to 50°C and the



pressure is preferably 1 to 10 bar. Based on fluorinated C₃-C₆-hydrocarbon, the amount of alcohol is preferably 0.5 to 20% by weight, in particular 0.5 to 10% by weight, and the amount of base is preferably 0.01 to 10% by weight, in particular 0.01 to 5% by weight.

The invention is intended to be described in more detail by means of the following examples.

Examples 1 to 9:

A heatable stirred autoclave (V = 300 ml) was charged with 100 g of isodihydroperfluorohexane (IDPH), which contained approximately 500 ppm of 1,1,1,3,4,4,5,5,5-nonafluoro-2-(trifluoromethyl)-2-pentene (HFH), and with 10 g of an alcohol and 1 g of a base. The autoclave was then heated to 50°C and stirred for 8 hours at this temperature. The content of HFH was followed by gas chromatography. The alcohols and bases used and the results are presented in Table 1.

Table 1

	<u>Alcohol</u>	<u>Base</u>	<u>Content of HFH [ppm] after 8 hours</u>
20	Methanol	NaOH	B.D.L.*
	Methanol	KOH	B.D.L.*
	Methanol	Na acetate	380
	Methanol	Na ₂ HPO ₄	450
	Methanol	Pyridine	280
25	Methanol	Na phenolate	50
	Ethanol	NaOH	B.D.L.*
	i-Propanol	NaOH	40
	Glycol	NaOH	B.D.L.*

Example 10:

A distillation vessel was charged with 80 kg of IDPH, which contained approximately 500 ppm of HFH, and with 800 g of methanol and 50 g of KOH. The vessel was then

* B.D.L. = Below detection limit (< 1 ppm)

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heated to 40°C and stirred for 12 hours at this temperature. The content of HFH had afterwards fallen to below 10 ppm.



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Patent claims:

1. A process for removing olefinic impurities of the formula $C_nH_mF_pCl_q$, where $n = 2 - 6$, $m = 0 - 8$, $p = 1 - 12$, $q = 0 - 8$ and $m + p + q = 2n$, from fluorinated C_3 - C_6 -hydrocarbons, with the exception of 1,1,1,2,3,3,3-heptafluoropropane (R 227), which comprises bringing the contaminated fluorinated C_3 - C_6 -hydrocarbons into contact with an alcohol and a base at temperatures of -20 to 100°C and pressures of 1 to 50 bar and, simultaneously or subsequently, distilling off the fluorinated C_3 - C_6 -hydrocarbons.
2. The process as claimed in claim 1, wherein the fluorinated C_3 - C_6 -hydrocarbon used is 1,1,1,3-tetrafluoropropane, 1,1,1,4,4,4-hexafluorobutane, 1,1,1,2,3,4,4,4-octafluorobutane, 1,1,2,2,3,3,4,4-octafluorobutane or 1,1,1,2,3,4,5,5,5-nonafluoro-2-(trifluoromethyl)-pentane.
3. The process as claimed in claim 1 or 2, wherein an alcohol of the formula $C_nH_{2n+1}OH$, $C_nH_{2n}(OH)_2$, $C_nH_{2n-1}OH$ or $C_nH_{2n-2}(OH)_2$, where $n = 1 - 6$, preferably $n = 1 - 3$, is used.
4. The process as claimed in one of claims 1 to 3, wherein a base is used whose pK is 8 to 14.
5. The process as claimed in one of claims 1 to 4, wherein the procedure is carried out at 0 to 50°C and 1 to 10 bar.
6. The process as claimed in one of claims 1 to 5, wherein the alcohol used is ethylene glycol, methanol, ethanol or i-propanol.
7. The process as claimed in one of claims 1 to 6, wherein the base used is NaOH, KOH or Na phenolate.

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8. The process as claimed in one of claims 1 to 7, wherein 0.5 to 20% by weight of alcohol and 0.01 to 10% by weight of base are used, based on the fluorinated C₃-C₆-hydrocarbon.



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