TECHNOLOGIES FOR PRODUCTION OF CHLADONS BY A METHOD OF GAS PHASE CATALYTIC HYDROFLUORINATION

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Chlorofluorocarbons and bromofluorocarbons (chladons and halons) as compounds possessing a number of unique properties such as chemical inertness, non-toxicity, explosion and fire safety, were widely used in engineering as aerosol propellants, refrigerants, foaming agents for plastics, solvents, high-performance extinguishers etc.

But the ozone depleting property of some chlorine- and bromine-containing compounds revealed in the 80-ties attracted attention to a large group of industrial chladones as potentially dangerous substances containing chlorine and bromine in their composition. The Montreal Protocol (MP) on substances that deplete the ozone layer was adopted in 1987y. As by this moment the depleting role of chlorine and bromine had been confirmed by a number of research teams, the Addendum to the MP listed ozone depleting substances (ODS) subject to regulation by all countries being the parties to the MP. This Addendum contained chlorofluorocarbons (CFC), bromofluorocarbons (halons) and some chlorohydrocarbons (CHC). The MP obliged the Parties to reduce consumption, production and import/export of ODS.

The Soviet Union was one of the first-rate manufacturers of ODS: in 1987y its share in ODS production made 15% of the world volume (approximately 200 thousand tons). At the same time the Soviet Union was one of the largest consumers and outstanding exporter of ODS that supplied not only all republics of the former USSR but also a whole number of European and Asian countries. Six large chemical plants in Russian Federation produced ODS. Almost all industry branches in RF were consumers of chladones [1,2].

FSUE RSC "Applied Chemistry" together with a number of research institutes of RF have made a great effort to convert domestic industry to a new class of chemical substances instead of the prohibited ODS.

As a result of their investigations a nomenclature of new chladones was suggested: hydrofluorocarbons 134a (CF_2CFH_2), 152a (CF_2HCH_3), 125 (CF_3CF_2H), 32 (CH_2F_2) etc. The main difference of ozone-friendly compounds from ODS is that their molecules does not contain chlorine and bromine atoms that may participate in "bromine" or "chlorine" cycle of the ozone depletion. Besides the zero value of ozone depleting potential (ODP) and the value of global warming potential (GWP), the main criteria in the choice of ODS alternatives is proximity of physical, chemical and maintenance properties to the analogues characteristics of ODS to be replaced.

The main nomenclature of ozone friendly compounds adopted for development and implementation into the industrial manufacture in Russian Federation is given in Table 1.

Table 1. *Nomenclature of hydrofluorocarbons accepted for development and implementation into the industry of Russian Federation and their main properties [3]*

Index	Unit	HFC 23	HFC 32	HFC 125	HFC 134	HFC 134a	HFC 143a
Formula		CHF_3	CH_2F_2	C_2F_5H	CHF_2CHF_2	CH_2FCF_3	CF_3CH_3
Molecular weight		70.1	52.024	120.022	102.03	102.03	84.041
Boiling temperature at pressure of 0,1 MPa	^oC	-82.2	-51.7	-48.5	-22.5	-26.5	-47.6
Freezing temperature	^oC	-155.15	-136	-103	-89.0	-101	-111.3
Critical temperature	^oC	25.85	78.4	67.7	110.25	101.5	73.1
Critical pressure MPa	MPa	4.82	5.843	3.39	3.77	4.06	4.11
Concentration limits of flame propagation in air	% vol.	-	14.2-30.0	-	-	-	9.2-18.4

Index	Unit						
Self-ignition temperature	°C	765	504	--	630	--	720
Ozone depleting potential (ODP)	Relatively CFC11	0	0	0	0	0	0
Global warming potential (GWP)	Relatively CO_2	14800	880	3800	1200	1600	5400
Toxicity: Permissible limit of exposure (DuPont) ppm (vol./vol.)	ppm (vol./vol.)	1000	1000	--	1000	--	--
MPCw.a.	mg/m^3	3000	3000	1000	--	3000	3000
Danger class		4	4	4	--	4	4

Table 1. *Continuation*

Index	Unit	HFC 152a	HFC 227ea	HFC 236fa	HFC C336	HFC C438	HFC 43-10mee
Formula		CH_3CHF_2	CF_3CFHCF_3	$CF_3CH_2CF_3$	$C_4F_6H_2$-cyclo	$C_5F_8H_2$-cyclo	$CF_3CHFCHFCF_2CF_3$
Molecular weight		66.05	170.03	152.039	164	214	252.053
Boiling temperature at pressure of 0,1 MPa	°C	-24.55	-18.3	-0.7 (-1.4)	63	79	47.0
Freezing temperature	°C	-117.0	-131.2	-93.6	--	--	-80
Critical temperature	°C	113.5	103.5	130.7	--	--	--
Critical pressure MPa	MPa	4.491	2.95	3.18	--	--	--
Concentration limits of flame propagation in air	% vol.	3.9-16.9	-	-	--	--	--
Self-ignition temperature	°C	453	>650	--	--	--	--
Ozone depleting potential (ODP)	Relatively CFC11	0	0	0	--	--	0
Global warming potential (GWP)	Relatively CO_2	190	3800	9400	--	--	1700
Toxicity: Permissible limit of exposure (DuPont) ppm (vol./vol.)	ppm (vol./vol.)	1000	--	--	--	--	--
MPCw.a.	mg/m^3	3000	--	--	--	--	--

In the development of technologies for ozone friendly hydrofluorocarbons at the plants in RF were used two production methods depending on their structure and taken into account existing production facilities of replaced CFC 11, 12, 113:
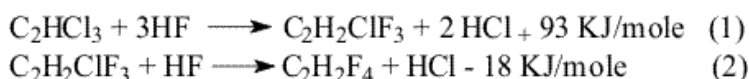- liquid phase fluorination with anhydrous hydrogen fluoride of organochlorine compounds (HFCs 152a, 32, 143a etc.);
- gas phase catalytic fluorination of organochlorine compounds with anhydrous hydrogen fluoride

   But the liquid phase hydrofluorination method has a number of limitations:
- replacement of the chlorine atom by fluorine in -CH2Cl and =CHCl groups proceeds with a great difficulty;
- catalyst $SbCl_nF_{5-n}$ in the hydrofluorination may act as a chlorinating agent with formation of ozone depleting chlorofluoroalkanes.

   Taken that into account to obtain hydrofluorocarbons with a great fluorine content in the molecule (CF_3-CFH_2, CF_3-CF_2H) the gas phase catalytic method of hydrofluorination is used.

   The peculiarities of gas phase catalytic hydrofluorination are seen on the example of 1,1,1,2-tetrafluoroethane (HFC-134a) synthesis from trichloroethylene and hydrogen fluoride. The synthesis process runs in two stages (Scheme 1):

$$C_2HCl_3 + 3HF \longrightarrow C_2H_2ClF_3 + 2HCl + 93\ KJ/mole \quad (1)$$
$$C_2H_2ClF_3 + HF \longrightarrow C_2H_2F_4 + HCl - 18\ KJ/mole \quad (2)$$
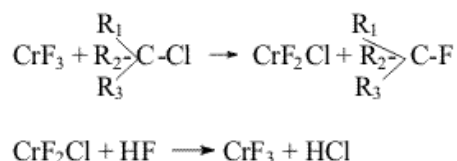
Scheme 1

   It follows from the experimental data and thermodynamic calculation of stage (1) of the process that HFC133a content in the organic share of the synthesis products may reach 90-98%.

   Stage (2) is reversible. In dependence on the conditions the contentof HFC 134a in the organic share of the synthesis products may make 10-40% by volume (from organic part of the synthesis products). For the process there is used a chromine-magenesium-fluoride catalyst [3, 16] manufactured from magnesium fluoride powder by saturation with chromium chloride solution followed by mixing, moulding, drying and treatment with hydrogen fluoride with the purpose to convert chromium chloride ($CrCl_3$) into chromium fluoride (CrF_3) [4, 5].
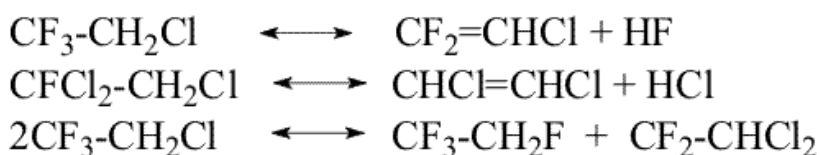
   The study of the mechanism of the catalyst effect in the present process has shown that the catalyst acts as a carrier of fluorine and chlorine atoms [6-8]. It is suggested that the process of hydrofluorination of chlorofluoroethanes runs according to scheme (2):

$$CrF_3 + R_2\!\!\underset{R_3}{\overset{R_1}{>}}\!\!C\text{-}Cl \rightarrow CrF_2Cl + R_2\!\!\underset{R_3}{\overset{R_1}{>}}\!\!C\text{-}F$$

$$CrF_2Cl + HF \longrightarrow CrF_3 + HCl$$

Scheme 2

   where chromium fluoride substitutes chlorine by fluorine in chlorofluoroethanes changing its composition to CrF_2Cl,after that hydrogen fluoride replaces chlorine with fluorine in active catalyst part to form hydrogen chloride and CrF_3. This mechanism seems more probable than mechanism [9, 10] that contains the stage of interaction of HF and chloroalkane molecules absorbed on neighboring active centers of the catalyst.
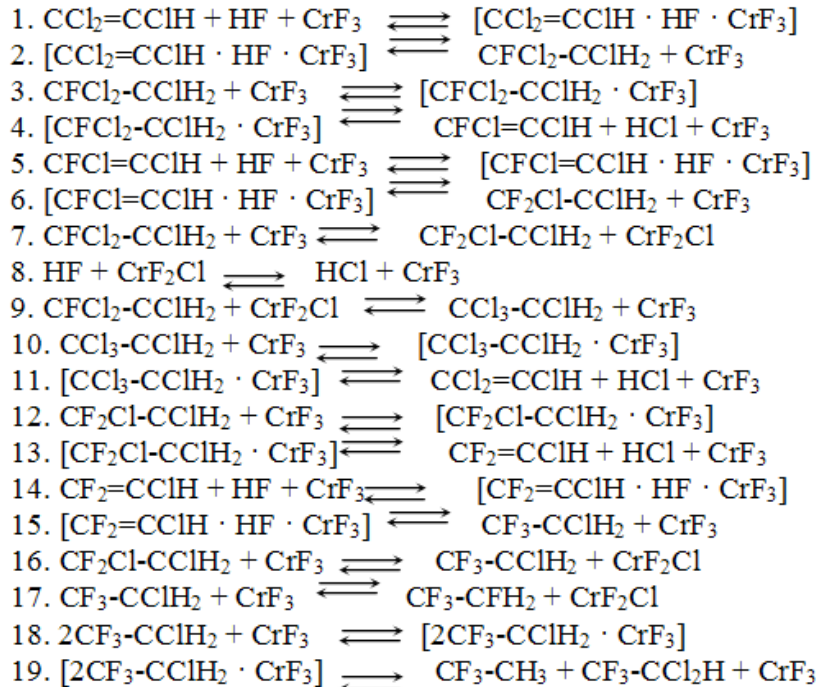
   Besides the main hydrofluorination processes this catalyst is used for the reactions of dehydrofluorination, dehydrochlorination and disproportionation (Scheme 3)

$$CF_3\text{-}CH_2Cl \longleftrightarrow CF_2\text{=}CHCl + HF$$
$$CFCl_2\text{-}CH_2Cl \longleftrightarrow CHCl\text{=}CHCl + HCl$$
$$2CF_3\text{-}CH_2Cl \longleftrightarrow CF_3\text{-}CH_2F + CF_2\text{-}CHCl_2$$

Scheme 3

   The obtaining unsaturated fluorine-containing compounds(particularly CF_2=CHCl that forms azeotrope with 1,1,1,2-tetrafluoroethane) in future make more difficult the desired product separation from the reaction mixture. Obviously the mechanism of these processes is connected with formation of active transition complexes on the catalyst surface.
As a whole, taken into account the said assumptions the process of hydrofluorination of trichloroethylene may be given as the following sequence of the stages (Scheme 4):

1. $CCl_2=CClH + HF + CrF_3 \rightleftharpoons [CCl_2=CClH \cdot HF \cdot CrF_3]$
2. $[CCl_2=CClH \cdot HF \cdot CrF_3] \rightleftharpoons CFCl_2\text{-}CClH_2 + CrF_3$
3. $CFCl_2\text{-}CClH_2 + CrF_3 \rightleftharpoons [CFCl_2\text{-}CClH_2 \cdot CrF_3]$
4. $[CFCl_2\text{-}CClH_2 \cdot CrF_3] \rightleftharpoons CFCl=CClH + HCl + CrF_3$
5. $CFCl=CClH + HF + CrF_3 \rightleftharpoons [CFCl=CClH \cdot HF \cdot CrF_3]$
6. $[CFCl=CClH \cdot HF \cdot CrF_3] \rightleftharpoons CF_2Cl\text{-}CClH_2 + CrF_3$
7. $CFCl_2\text{-}CClH_2 + CrF_3 \rightleftharpoons CF_2Cl\text{-}CClH_2 + CrF_2Cl$
8. $HF + CrF_2Cl \longrightarrow HCl + CrF_3$
9. $CFCl_2\text{-}CClH_2 + CrF_2Cl \rightleftharpoons CCl_3\text{-}CClH_2 + CrF_3$
10. $CCl_3\text{-}CClH_2 + CrF_3 \longrightarrow [CCl_3\text{-}CClH_2 \cdot CrF_3]$
11. $[CCl_3\text{-}CClH_2 \cdot CrF_3] \rightleftharpoons CCl_2=CClH + HCl + CrF_3$
12. $CF_2Cl\text{-}CClH_2 + CrF_3 \rightleftharpoons [CF_2Cl\text{-}CClH_2 \cdot CrF_3]$
13. $[CF_2Cl\text{-}CClH_2 \cdot CrF_3] \rightleftharpoons CF_2=CClH + HCl + CrF_3$
14. $CF_2=CClH + HF + CrF_3 \rightleftharpoons [CF_2=CClH \cdot HF \cdot CrF_3]$
15. $[CF_2=CClH \cdot HF \cdot CrF_3] \rightleftharpoons CF_3\text{-}CClH_2 + CrF_3$
16. $CF_2Cl\text{-}CClH_2 + CrF_3 \rightleftharpoons CF_3\text{-}CClH_2 + CrF_2Cl$
17. $CF_3\text{-}CClH_2 + CrF_3 \rightleftharpoons CF_3\text{-}CFH_2 + CrF_2Cl$
18. $2CF_3\text{-}CClH_2 + CrF_3 \rightleftharpoons [2CF_3\text{-}CClH_2 \cdot CrF_3]$
19. $[2CF_3\text{-}CClH_2 \cdot CrF_3] \rightleftharpoons CF_3\text{-}CH_3 + CF_3\text{-}CCl_2H + CrF_3$

Scheme 4

On the basis of the suggested mechanism with the use of the method of routes for complex reactions **11** a kinetic model for the process of synthesis of 1,1,1,2-tetrafluoroethane has been developed [12].

1. $$\frac{dc_1}{d\tau} = k'_{16}c_8 - k_{-16}c_1c_{11} - k'_{17}c_1 + k_{-17}c_3c_{11} + k'_{14}c_2c_{10} - k_Bc_1 - 2k'_{18}c_1^2 + 2k_Dc_1^2 + 2k_Cc_4c_{11}$$

2. $$\frac{dc_3}{d\tau} = k'_{17}c_1 - k_{-17}c_3c_{11}$$

3. $$\frac{dc_4}{d\tau} = k'_{18}c_1^2 - k_Dc_1^2 - k_Cc_4c_{11}$$

4. $$\frac{dc_5}{d\tau} = k'_{18}c_1^2 - k_Dc_1^2 - k_Cc_4c_{11} - k'_{20}c_5 + k_{-20}c_6c_{11}$$

5. $$\frac{dc_6}{d\tau} = k'_{20}c_5 - k_{-20}c_6c_{11} - k'_{21}c_6 + k_{-21}c_7c_{11}$$

6. $$\frac{dc_7}{d\tau} = k'_{21}c_6 - k_{-21}c_7c_{11}$$

7. $$\frac{dc_8}{d\tau} = k'_7c_{12} - k_{-7}c_8c_{11} - k'_{16}c_8 + k_{-16}c_1c_{11} - 0.5k_{12}c_8 + 0.5k'_{-13}c_{10}c_{11} + k'_5c_2c_{13}$$

8. $$\frac{dc_9}{d\tau} = -k'_1c_2c_9 + k_Ac_8c_{11} + k_Ec_9c_{11}$$

9. $$\frac{dc_{10}}{d\tau} = 0.5k'_{12}c_8 - 0.5k'_{-13}c_{10}c_{11} - k'_{14}c_2c_{10} + k_Bc_1$$

10. $$\frac{dc_{12}}{d\tau} = k'_1c_2c_9 - k'_7c_{12} + k_{-7}c_8c_{11} - 0.5k'_3c_{12} + 0.5k'_4c_{11}c_{13}$$

11. $$\frac{dc_{13}}{d\tau} = 0.5k'_3c_{12} - 0.5k'_4c_{11}c_{13} - k'_5c_2c_{13}$$

12. $c_2 = c_2^0 - 3(c_1-c_1^0) - 4(c_3-c_3^0) - 3(c_4-c_4^0) - 3(c_5-c_5^0) - 4(c_6-c_6^0) - 5(c_7-c_7^0) - 2(c_8-c_8^0) - 2(c_{10}-c_{10}^0) - (c_{12}-c_{12}^0) - (c_{13}-c_{13}^0)$

13. $c_{11} = c_{11}^0 + (c_1^0-c_1) + 2(c_5^0-c_5) + (c_6^0-c_6) + 2(c_8^0-c_8) + 3(c_9^0-c_9) + (c_{10}^0-c_{10}) + 3(c_{12}^0-c_{12}) + 2(c_{13}^0-c_{13})$

where: c_1 is concentration of $CF_3\text{-}CClH_2$,
c_2 - HF, c_3 - $CF_3\text{-}CFH_2$, c_4 - $CF_3\text{-}CH_3$,

c_5 - CF_3-CCl_2H, c_6 - CF_3-$CFClH$, c_7 - CF_3-CF_2H,
c_8 - CF_2Cl-$CClH_2$, c_9 - C_2HCl_3, c_{10} - CF_2=$CClH$,
c_{11} - HCl, c_{12} - $CFCl_2$-$CClH_2$, c_{13} - $CFCl$=$CClH$,

$$k'_i = k_i \cdot [CrF_3], \qquad k_A = = 2\,\frac{k'_{14}k_{13}k_{12}}{k'_{-13}k_{-14}}, \qquad k_B = \frac{k_{-1}k_{-10}}{k'_{10}+k_{11}},$$

$$k_C = \frac{k_{-3}k'_{-4}}{k_{-3}+k_4}, \; k_D = \frac{k_{-3}k'_3}{k_{-3}+k_4}, \qquad k_E = \frac{k_{-14}k'_{14}k'_{-15}}{k_{15}k'_{-13}}$$

In the search of the kinetic model constants for numerical integration of the system of ordinary differential equations there was used LSODA method [12]. The found values of the kinetic constants are given in Table 2.

Table 2. *Parameters of Arrhenius equation for the process of production of 1,1,1,2-tetrafluoroethane from trichloroethylene*

k_i	ln$A$	$E_{act.}$, kJ/mole	k_i	ln$A$	$E_{act.}$, kJ/mole	k_i	ln$A$	$E_{act.}$, kJ/mole
k'_1	33.8	125.2	k'_{14}	12.2	41.9	k'_{21}	17	97
k'_3	38.7	146.1	k'_{16}	16.5	70	k_{-21}	26.5	103
k'_{-4}	58.7	207.7	k_{-16}	19.5	85	k_A	43	209.3
k'_5	46.7	162.4	k'_{17}	11.7	76.6	k_B	29.5	188.4
k'_7	16	66.5	k_{-17}	15.6	51.1	k_C	8.5	20.9
k_{-7}	23	126.0	k'_{18}	26.2	148.5	$k_D{\sim}0$		
k'_{12}	17	83.7	k'_{20}	33	74.6	$k_E{\sim}0$		
k'_{-13}	23.7	83.7	k_{-20}	30	115			

The kinetic model adequately describes the course of processes (1) and (2) (Scheme 1) within the following range of parameters: temperature of 175-420^{0}C; mole ratio of the reagents: HF:C_2HCl_3 =(3.4-13.6) : 1; HF: $C_2H_2ClF_3$=(4-20):1.

The process analysis with the use of the kinetic model has shown that the optimal conditions for stages (1) and (2) (Scheme 1) substantially differ (exothermic and endothermic processes), stage (1) is to be carried out at a lower temperature in comparison with stage (2) etc.

Therefore the synthesis of HFC 134a is reasonable to carry out according to the two-reactor scheme. For the choice of the optimal scheme of the reactor unit there was used a mathematical model of adiabatic reactor with stationary bed of chromium-magnesium-fluoride catalyst:

$$u \cdot dC_i/dx = R_i$$
$$\rho \cdot C_p \cdot u \cdot dT/dx = \Sigma(\Delta H_j \cdot r_j)$$
$$\text{where} \qquad R_i = \Sigma \upsilon_i \cdot r_j$$

C_i = concentration of component **i** in the gas mixture, mole/m^3;
X = reactor length, m; T= temperature, K;
R_i = rate of changing component i concentration as a result of chemical reactions, mole/(m$^3 \cdot$ s);
υ_i = number of i-th component moles participating reaction j;
r_j = rate of reaction j, mole/(m$^3 \cdot$ s);
ρ =density of the gas mixture depending on the concentration of components and temperature (ρ(C, T)), kg/m^3;

u = linear velocity of the mixture, m/s;
C_p =average heat capacity of the mixture, J/ (kg*K);
ΔH_j = heat effect of reaction j, J/mole;

Four variants of the reaction unit organization given in Fig.1 have been considered:
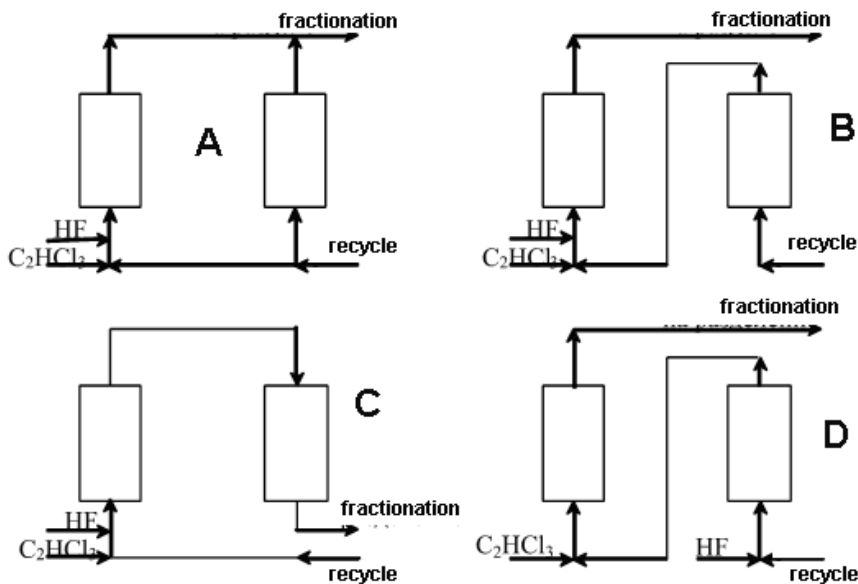
Fig.1. Variants of two-reactor scheme of 1,1,1,2-tetrafluoroethane synthesis

The calculations according to the above stated mathematical model have shown that the maximal output of HFC-134a provides variant A [13] (see Table 3).

Table 3. *Analysis of the reaction unit for synthesis of 1,1,1,2-tetrafluoroethane (TFE)*

Reaction unit scheme	A	B	C	D
TFE output, kg/s*	0.0268	0.0237	0.0218	0.0238

*The calculation were performed at the following basic data:
HF consumption: 60.86 kg/h;
C_2HCl_3 consumption: 97,54 kg/h;
Recycle consumption: 1121.5kg/h;
For scheme A: recycle to the first reactor: 166.44 kg/h;
Recycle to the second reactor: 955.07 kg/h;

According to variant **A** the first reactor is fed with hydrogen fluoride, trichloroethylene and part of the recycling mixture(to hold the temperature regime) in which the total content of HF and 1,1,1-trifluorochloroethane is more than 99%, the second reactor is fed with main part of the recycling mixture ("recycle") of the same composition; the flows from the reaction zones are united and directed to separation of hydrogen chloride, low-boiling products and 1,1,1,2-tetrafluoroethane while the high-boiling substances are returned as a recycle to the synthesis unit.

The standard process flowsheet for synthesis of ozone friendly HFCs has been developed by the method of gas phase catalytic hydrofluorination (pentafluoroethane, for example) [14]. The technology of production of HFC116 [15] was developed for processes of plasmachemical etching in microelectronics and the technology for HFC 23 [17] manufacture was developed for filling low-temperature refrigerating machines.

Industrial facilities for ozone friendly HFCs in Russian Federation have been created and are creating on the basis of the investigations carried-out.

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