Non-ozone-depleting hydrofluorocarbons

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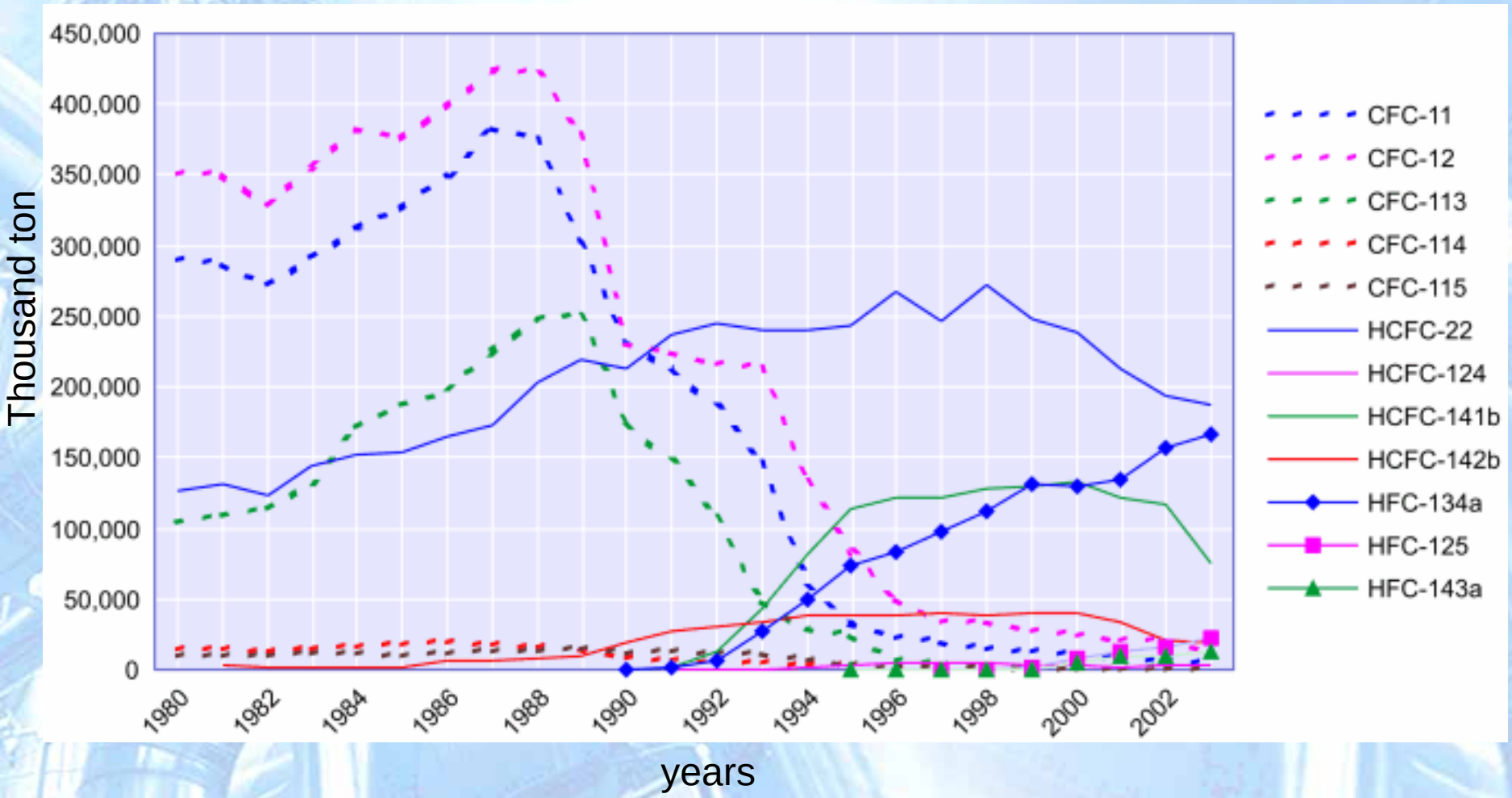
Classification of the main industrial hladons by their environmental properties

Action on ozone layer	Substance	ODP	GWP (direct, time horizon -100 years)	International regulating document
Ozone-depleting	Chloroflurocarbons (CFC)	≥0,1	≥10300	Montreal protocol Annex A, Group I, Annex B, Group I
Transient	Hydrochlorofluoro carbons (HCFC)	0≤0,1	≥2300	Montreal protocol Annex C, Group I
Non-ozone-depleting	Hydrofluorocarbons (HFC)	0	≤140	Kyoto protocol
	Fluorocarbons (FC)	0	≥11400	Kyoto protocol

Phaseout time schedule for MP-regulated substances

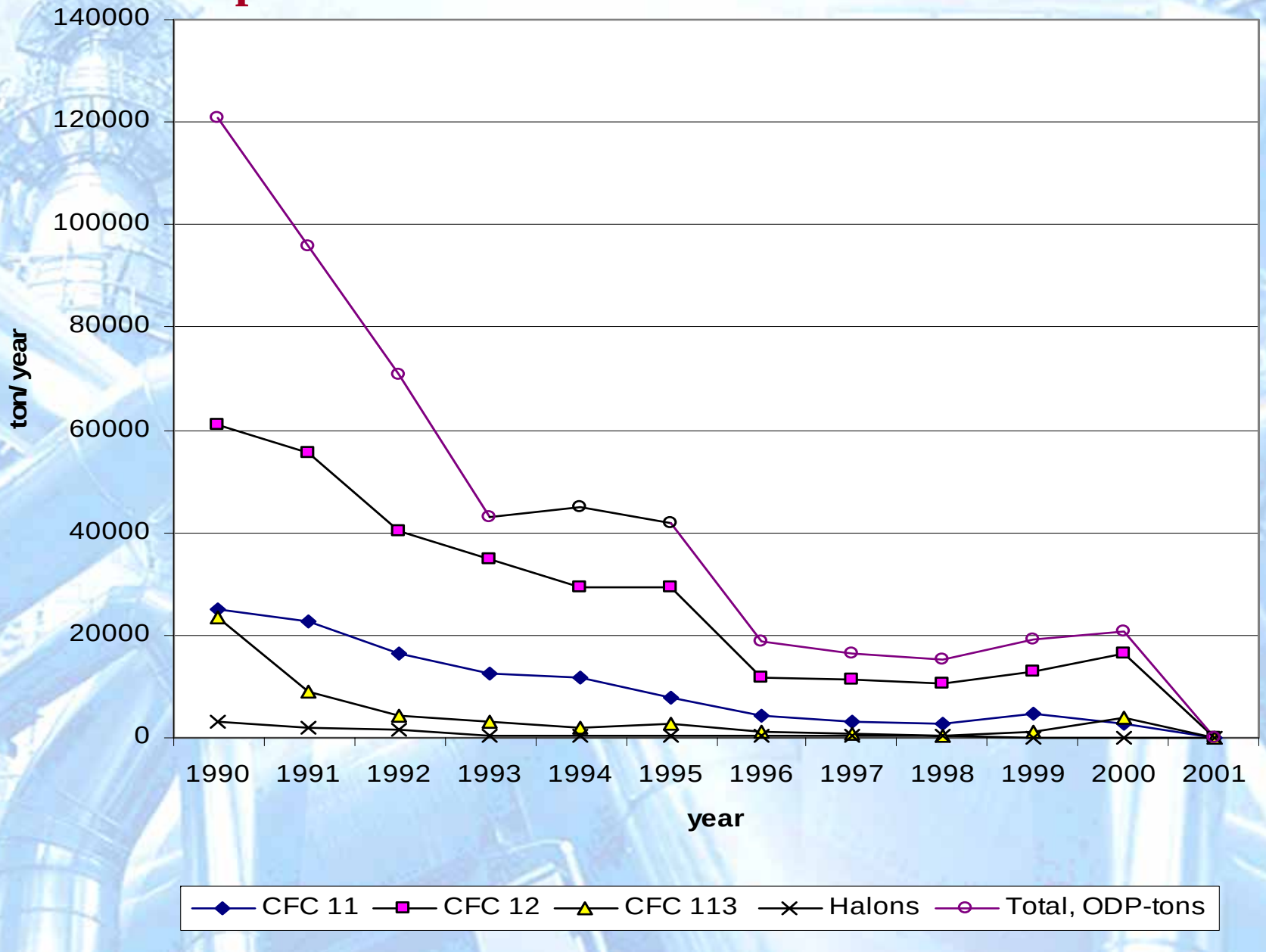
Substance	CFC	Halons	CFC	CTC	MCF	HCFC	HBFC	Methyl bromide	Bromochloro methane
MP Article	2A	2B	2C	2D	2E	2F	2G	2H	2I
MP Annex, Group	A, Gr.I	A, gr.II	B, gr.I	B, gr.II	B, gr.III	C, gr.I	C, gr.II	E	C, rp.III
Industrial countries (Article 2A)									
Beginning of regulation	1992	1992	1993	1995	1993	1996	1996	1995	2002
Total phaseout	1996	1994	1996	1996	1996	2030	1996	2005	2002
Developing countries (Article 5A) – ten years delay									
Beginning of regulation	2002	2002	2003	2005	2003	2016	1996	2002	2002
Total phaseout	2006	2004	2006	2006	2006	2040	1996	2007	2007

Total world manufacture of non-ozone-depleting and transient hladons in 1980-2003.



Meeting the requirements of Vienna Convention (1985) and Montreal Protocol (1987), Russian Federation in 2000 stopped the manufacture of ozone-depleting hladons used for aerosol propellants, refrigerants, foaming agents, solvents, fire extinguishants, etc.

ODS phaseout in Russian Federation in 1989-2000

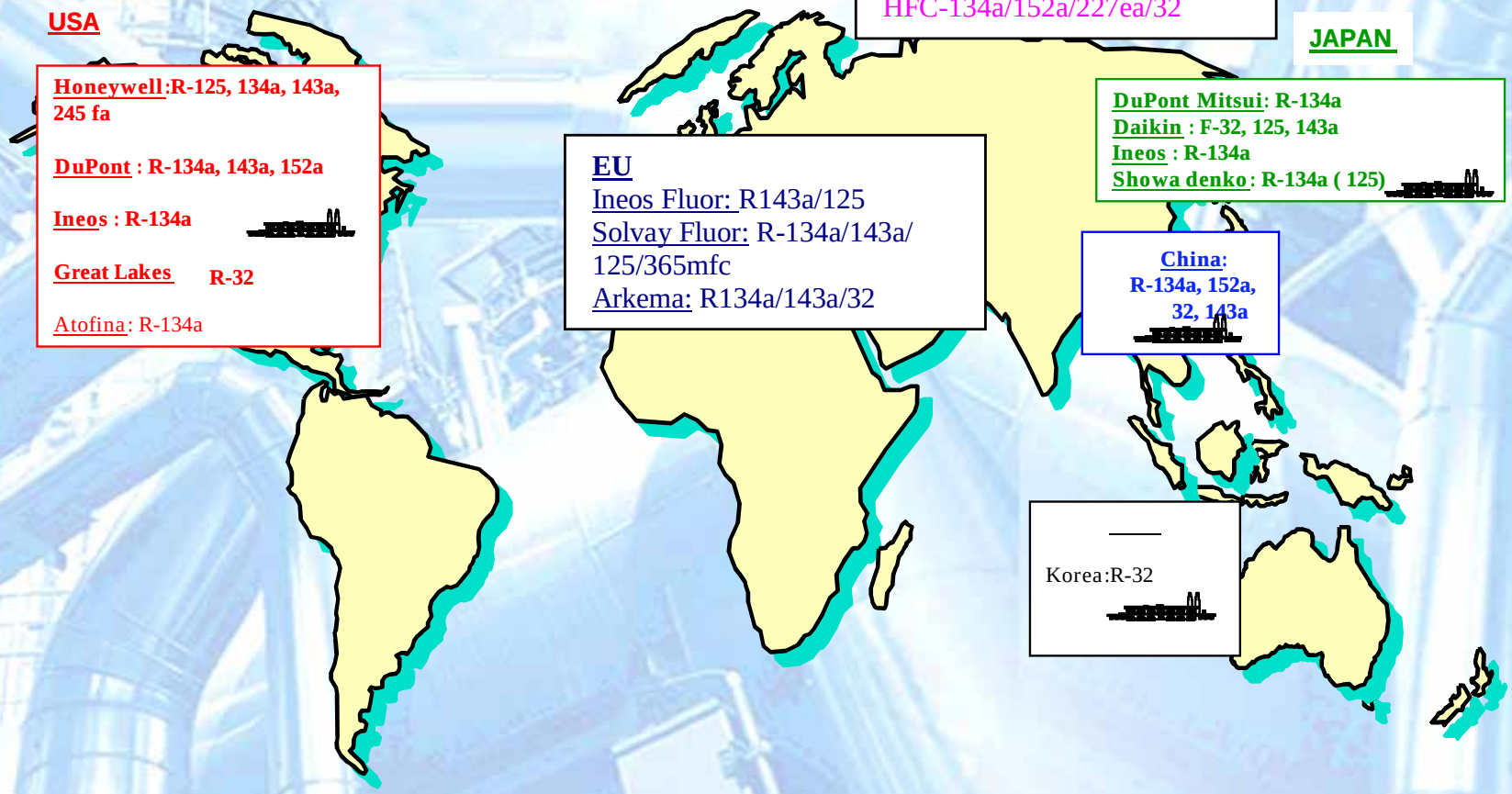


Federal reserve (ODS banks)
was established in order to provide
military equipment with
those substances till 2005
Currently the supplies are nearly
exhausted,
and implementation of full-value ODS
substituents in military industry is an
urgent challenge.

HFC world manufacture; geographical location of production facilities.

HFC Producers
R-32/R-125/R-143a/R-134a/R-152a/R-227ea

Production capacity



Russian Federation
various producers:
HFC-134a/152a/227ea/32

USA

Honeywell:R-125, 134a, 143a, 245 fa

DuPont : R-134a, 143a, 152a

Ineos : R-134a

Great Lakes R-32

Atofina: R-134a

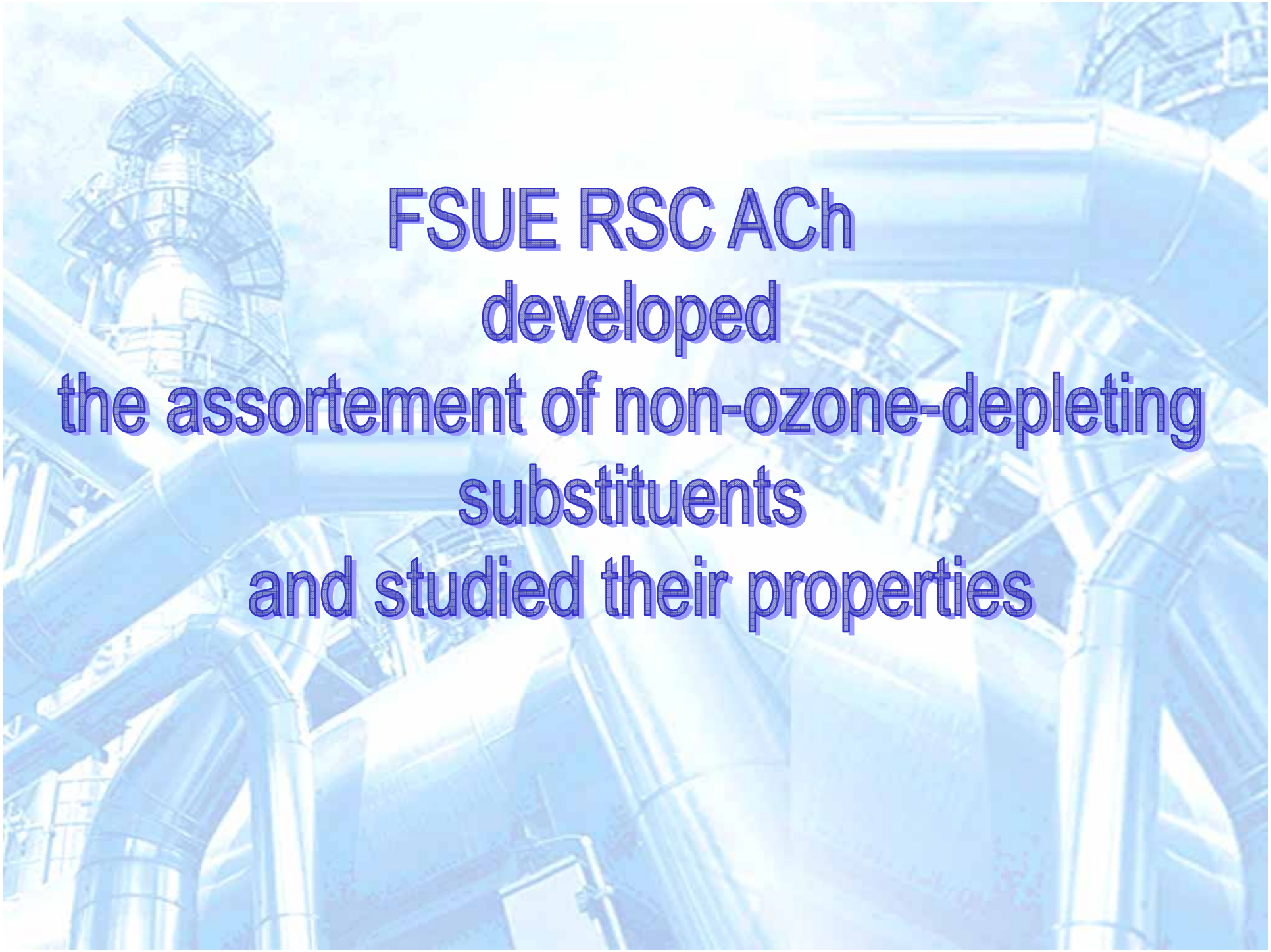
EU
Ineos Fluor: R143a/125
Solvay Fluor: R-134a/143a/ 125/365mfc
Arkema: R134a/143a/32

JAPAN

DuPont Mitsui: R-134a
Daikin : F-32, 125, 143a
Ineos : R-134a
Showa denko: R-134a (125)

China:
R-134a, 152a, 32, 143a

Korea:R-32


FSUE RSC ACh
developed
the assortement of non-ozone-depleting
substituents
and studied their properties

Main characteristics of hydrofluorocarbons (non-ozone-depleting hladons)

Hladon	Formula	Molecular mass	T boiling at 0.1MPa	T freezing	T self-ignition	ODP	GWP	MAC w.z. mg/m^3
			°C					
23	CHF_3	70,1	–82,2	–155,15	765	0	14800	3000
32	CH_2F_2	52,024	–51,7	–136	504	0	880	3000
125	C_2F_5H	120,022	–48,5	–103	-	0	3800	1000
134	CHF_2CHF_2	102,03	–22,5	–89,0	630	0	1200	-
134a	CH_2FCF_3	102,03	–26,5	-101	-	0	1600	3000
143a	CF_3CH_3	84,041	–47,6	–111,3	720	0	5400	3000
152a	CH_3CHF_2	66,05	–24,55	–117,0	453	0	190	3000
227ea	CF_3CFHCF_3	170,03	-18,3	-131,2	>650	0	3800	-
236fa	$CF_3CH_2CF_3$	152,039	-0,7	-93,6	-	0	9400	-
C336	$C_4F_6H_2$-cyclo	164	63	-	-	0	-	-
C438	$C_5F_8H_2$-cyclo	214	79	-	-	0	-	-
43-10mee	$CF_3CHFCHFCF_2CF_3$	252,053	47	-80	-	0	1700	-


FSUE RSC ACh
developed the technologies
for non-ozone-depleting substances manufacture
by gas-phase or liquid-phase hydrofluorination

Gas-phase catalyzed hydrofluorination (catalyst: CrF_3*MgF_2)

$$C_2HCl_3 + 3\,HF \rightleftharpoons C_2H_2ClF_3 + 2\,HCl + 93\ kJ/mole$$

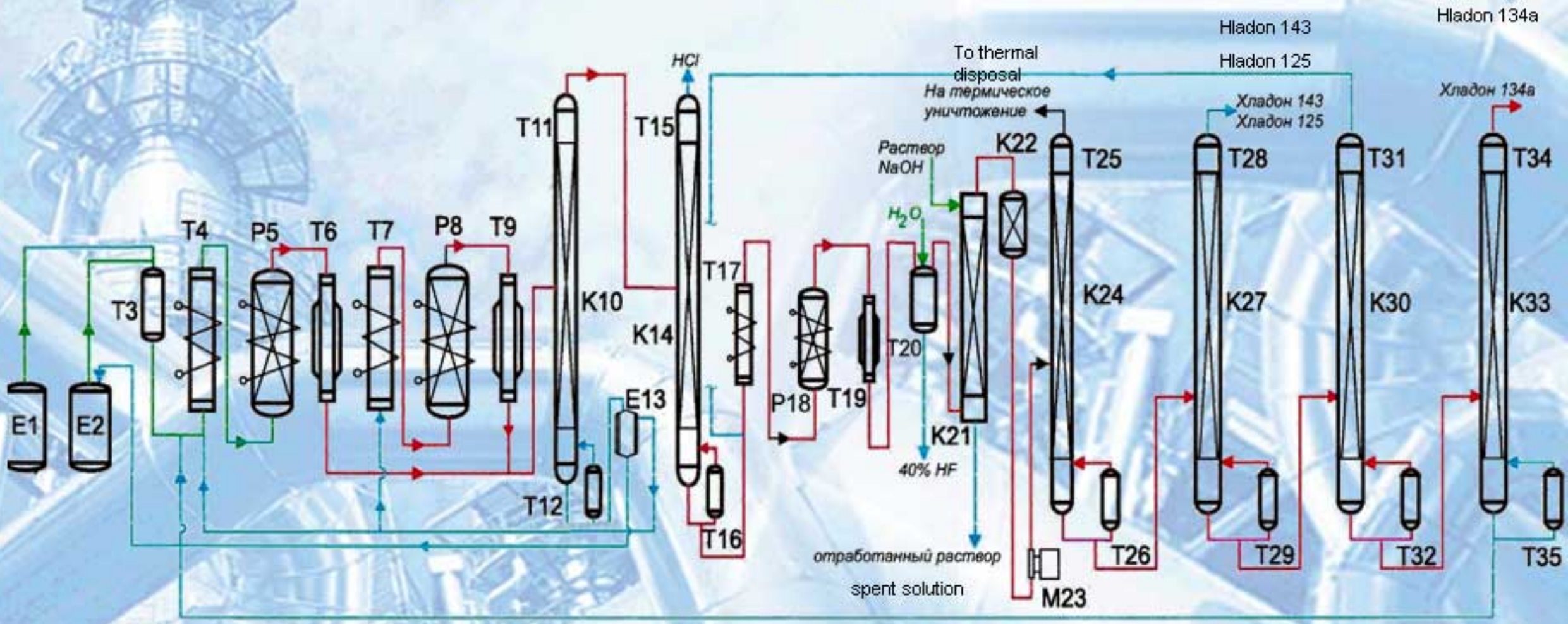
$$C_2H_2ClF_3 + HF \rightleftharpoons C_2H_2F_4 + HCl + 18\ kJ/mole$$

mechanism:

$$CrF_3 + \begin{matrix} & R_1 & \\ R_2 & - & C\text{-}Cl \\ & R_3 & \end{matrix} \rightleftharpoons CrF_2Cl + \begin{matrix} & R_1 & \\ R_2 & - & C\text{-}F \\ & R_3 & \end{matrix}$$

$$CrF_2Cl + HF \rightleftharpoons CrF_3 + HCl$$

Basic flow-diagram for the synthesis of hladon 134a.



E1 - vessel with hydrogen fluoride

E2 – vessel with trichloroethylene

T3 – evaporator

T4, T7, T17 –electric heaters

P5, P8, P18 –reactors

T6, T9, T19 – coolers

K10, K14, K24, K27, K30, K33 – rectification columns

E13 – stratificator

T20 – absorber

T11, T15, T25, T28, T31, T34 - refluxers

T12, T16, T26, T29, T32, T35 - boilers

K21 – neutralization column

K22 – drying column

M23 – compressor

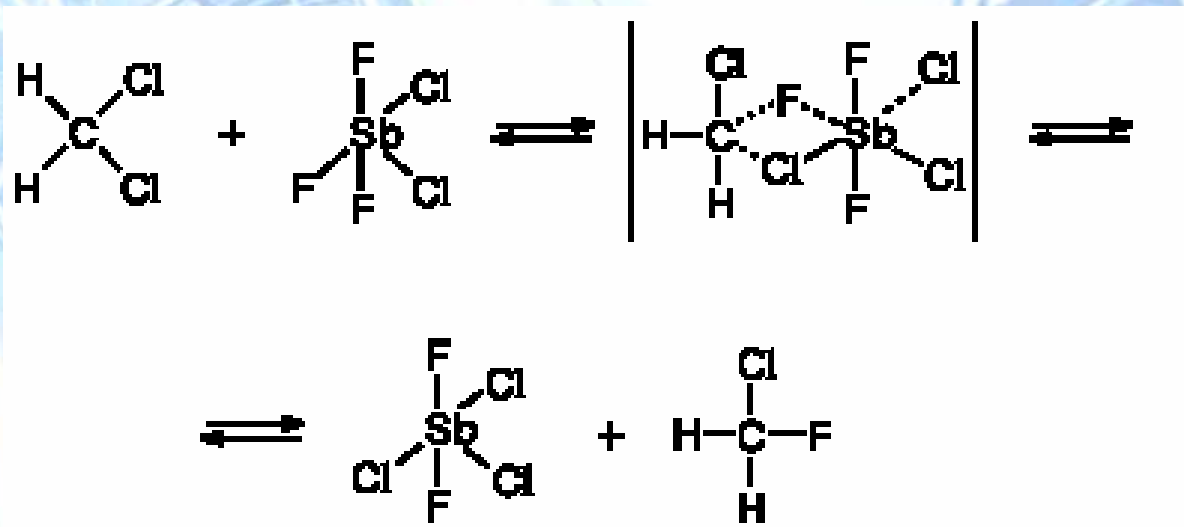
Liquid-phase catalyzed hydrofluorination. (Catalysts: $SbCl_5$, $SnCl_4$)

$$SbCl_5 + HF \xrightarrow{K_0} SbCl_nF_{5-n} + HCl$$

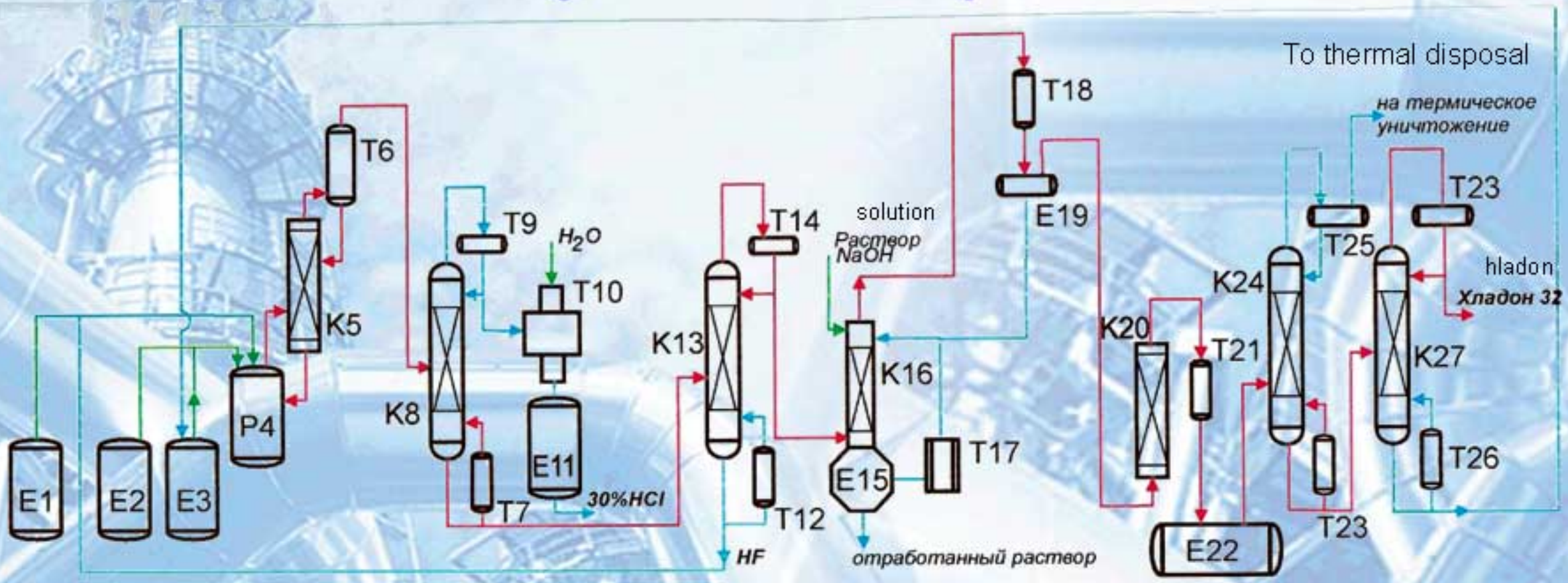
$$CH_2Cl_2 + SbCl_nF_{5-n} \xrightarrow[HF]{K_1} CH_2ClF + SbCl_{n+1}F_{4-n} + HCl$$

$$CH_2ClF + SbCl_nF_{5-n} \xrightarrow[HF]{K_2} CH_2F_2 + SbCl_{n+1}F_{4-n} + HCl$$

mechanism:



Principal flow-diagram for the synthesis of hladon 32.



E1 – HF vessel

E2 – methylene chloride vessel

E3 – chlorine vessel

P4 – synthesis reactor

K5 – super-reactor column

T6, T9, T14, T25, T28 – refluxers

T7, T12, T23, T26 – boilers

K8, F13, K24, K27 – rectification columns

spent solution

T10-absorber

E11 – stratificator

K16, E15, T17 – crude hladon 32 neutralization unit

T18 – freezer

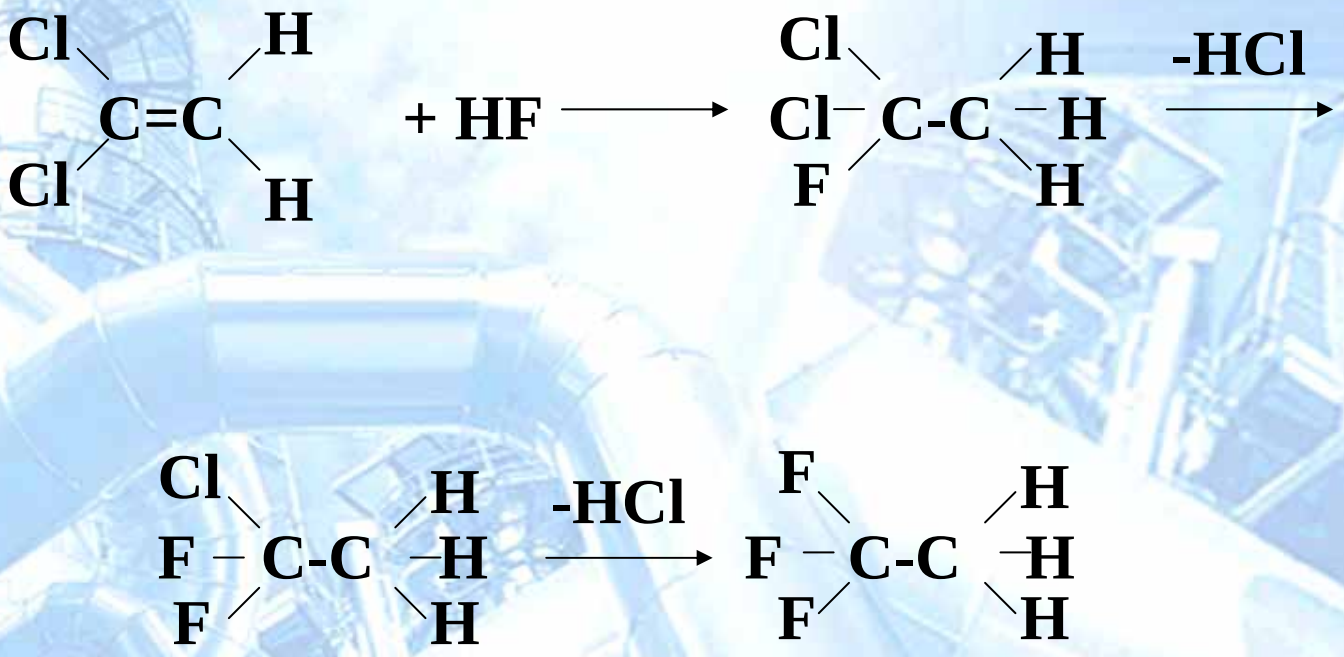
E19 – vessel

K20 – drying column

T21 – condenser

E22 - vessel

Liquid-phase hydrofluorination (not catalyzed)




FSUE RSC ACh
is implementing
non-ozone-depleting ODS substituents
in the industrial sector of Russian Federation

Manufacturing plants:

- Altaihimprom – JSC «Altaihimprom» (Yarovoe)
- AEChK – JSC «Angarskiy Electrolysis Plant» (Angarsk);
- VOCCO – JSC «Chimprom» (Volgograd);
- Halogen – JSC «Halogen» (Perm);
- Kaustic – JSC «Kaustic» (Volgograd);
- KChChK – JSC «Kirovo-Chepetzkiy Chemical Amalgamation» (Kirovo-Chepetzk);
- FSUE RSC ACh – FSUE RSC «Applied Chemistry» (St.Petersburg);
- ROZ - JSC «Redkinskiy Pilot Plant» (Redkino);
- Astor - JSC «Astor» (St.Petersburg)

NODS and transient	Manufacturer	Capacities	
		Consuming sector	(t/year)
HFC-134a		Refrigerants, aerosol propellants, solvents, foaming agents	suspended
HFC-23	ROZ RSC ACh	refrigerants, fire extinguishants	200 50
HFC-32		refrigerants	suspended
HFC-152a	Kaustic	refrigerants, aerosol propellants	4000
HFC-143a	KChChK	refrigerants	100
HFC-125	HALOGEN	refrigerants, fire extinguishants	1000
HFC-227ea	RSC ACh	refrigerants, aerosol propellants solvents, fire extinguishants	30
	KChChK		30
FC-218	KChChK	refrigerants, aerosol propellants, fire extinguishants, electronic gases	120
			100
	HALOGEN		40
FC C318	KChChK	refrigerants	100
	HALOGEN		40
Transient hladons:			
HCFC-141b, 142b	Altaihimprom	Solvents, Foaming agents	3000
HCFC-142b	KChChK	Foaming agents	2000
HCFC-22	VOCCO	refrigerants, aerosol propellants Half-products in fluoroplast manufacture	12000
	KChChK		20000
	HALOGEN		12000
HCFC-21	HALOGEN	refrigerants, aerosol propellants	100


It is necessary to continue
the development of
the new generation of
non-ozone-depleting substances
with zero ODPs and low GWPs