transfair

CFC free refrigerator technology

technologie de réfrigérateur sans CFC

FCKW freie Kühl-schranktechnologie

GmbH

Transfair Engineering:

Refrigerator insulation material today

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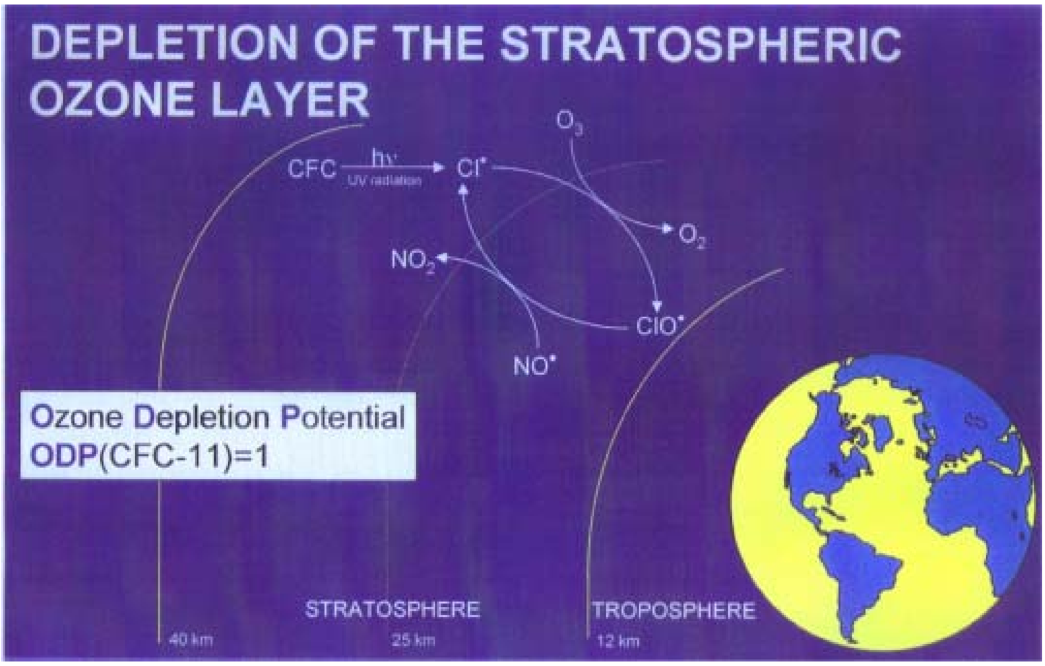
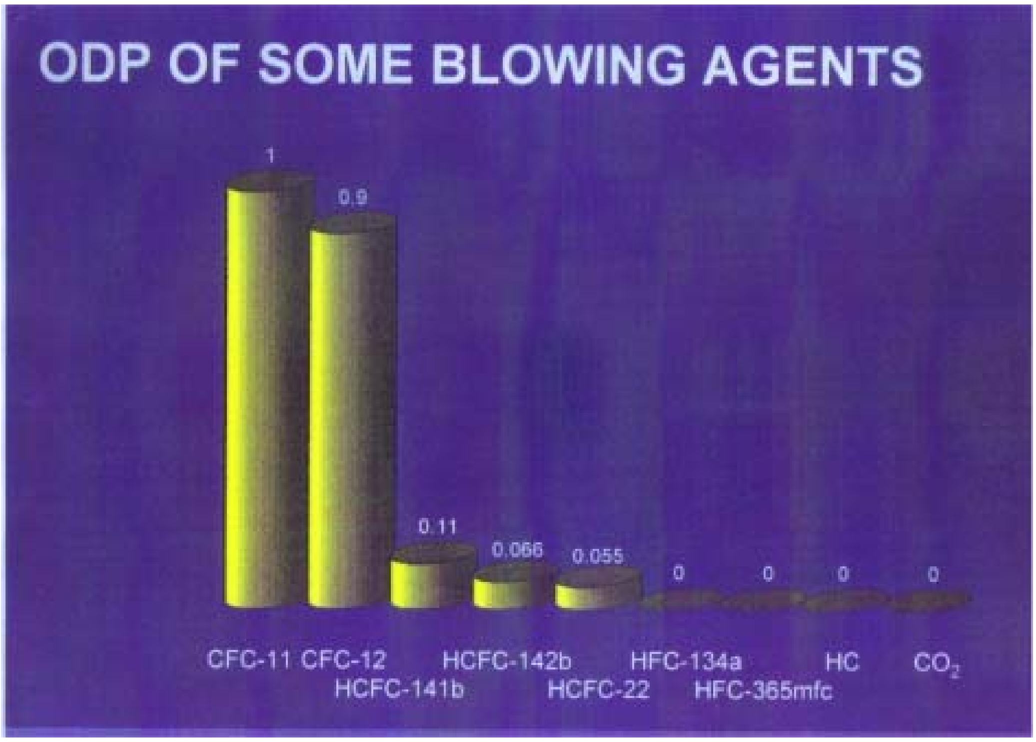
Content:

1. Ozone Depletion Substances (ODS) and regulation

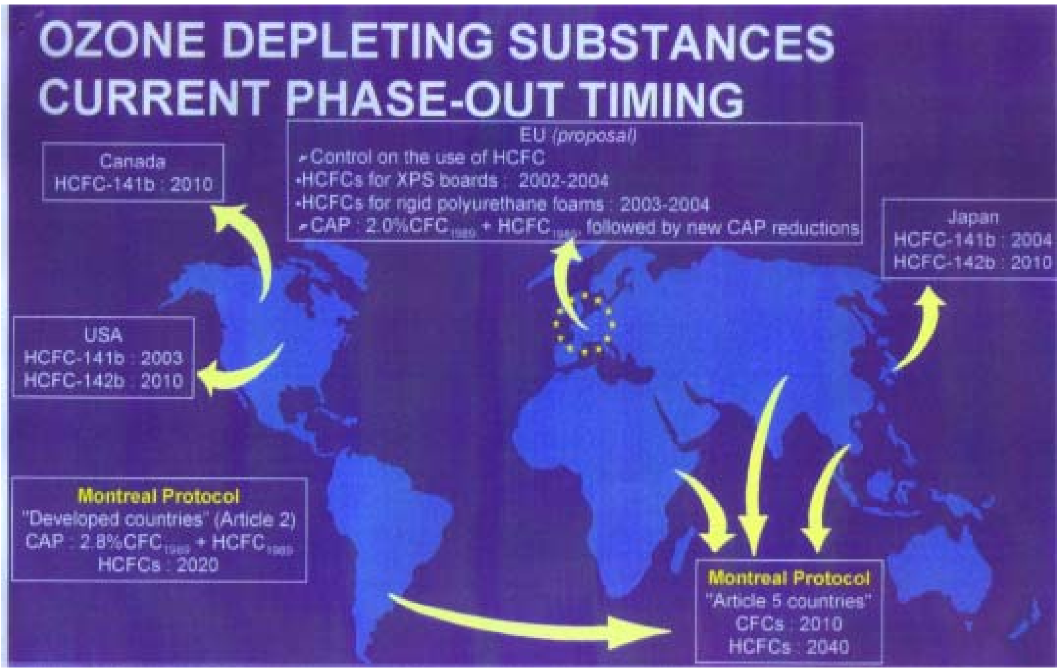
Some chemical substances are destroying the ozone layer in the stratosphere which filters dangerous short wave UV_B radiation causing skin cancer and influence negatively the growing of plants. The absorption of this short high energetic waves are made by the $O_2+0^- = O_3^-$ highly disturbed by these ODS (CFC, HCFC, Halons). The refrigerator industries had used CFC-11 as blowing agent in foam and CFC-12 as refrigerant, and still are using in USA, Japan and some other areas HCFC-141b.



1.1. Ozone Depletion Potentials of some blowing agents in use



1.2. International conventions (Montreal and Kyoto Protocol) and national legislation to phase out the use of Ozone Depletion Substances



The last 3 pictures are from Elf Atochem.

2. Global Warming Potential (GWP) and Total Equivalent Warming Impact (TEWI)

Substance released into the atmosphere can cause global warming to be avoided. **Therefore chemical substances are classified with their Global Warming Potential (GWP).** 1993 an international climate conference in Brazil was started and regular continued to reduce the global warming. To make a correct environmental balance on global warming of such substances used in insulation we have to take into account if by the use of a substance for example with higher GWP as blowing agent energy could be saved or not so that the total impact on global warming, the so called **Total Equivalent Warming Impact (TEWI)** could deviate from the GWP-value of a substance. Energy is mainly produced by burning of fossil Hydrocarbon producing CO_2 with a high GWP. Using a refrigerator with a lower insulation as result of lower k-value of the used materials (thermal transmission coefficient of an insulation)– even if the substances have no or low GWP, can often cause totally higher global warming as a good insulated refrigerator using even a substance with higher GWP. Also the energy used for manufacturing as well as the one used for their destroy or recycling have to be taken into account. Therefore the balance of the total lifetime cycle have to be made to enable a correct comparison. **In refrigeration lowest energy consumption seems the most relevant factor of the global warming effect** – at least in all countries which uses mainly fossil energy for generating electricity.

Ageing of foam. But we also should not look only on initial values after manufacturing, as it is part of the refrigerator standards, but on values over the full lifetime of a refrigerator. For example CFC-11 and HCFC-141b used as blowing agent in foam produce foam with excellent initial k-values in the range of 17 mW/m*K (CFC-11) respective 17.5 mW/m*K (HCFC-141b); but after 310 days (CFC-11) respective 280 days (HCFC-141b) because of faster diffusion of this small molecules out of the cellular foam matrix, their k-values of foam became higher, that means lower insulating, as if larger blowing agent molecules, like Cyclopentane (18 mW/m*K) or HFC-365mfc (18 mW/m*K; not yet optimised). The speed of ageing depends from

- the temperatures the foam is exposed during life,
- the skin of foam (in the refrigerator one side in direction of cold storage are plastic like Polystyrene or ABS and the other side is quite good sealing steel),
- the size of molecule,
- the partial vapour pressure, which in case of Cyclopentane is slightly reduced because of partial solubility inside the foam matrix.

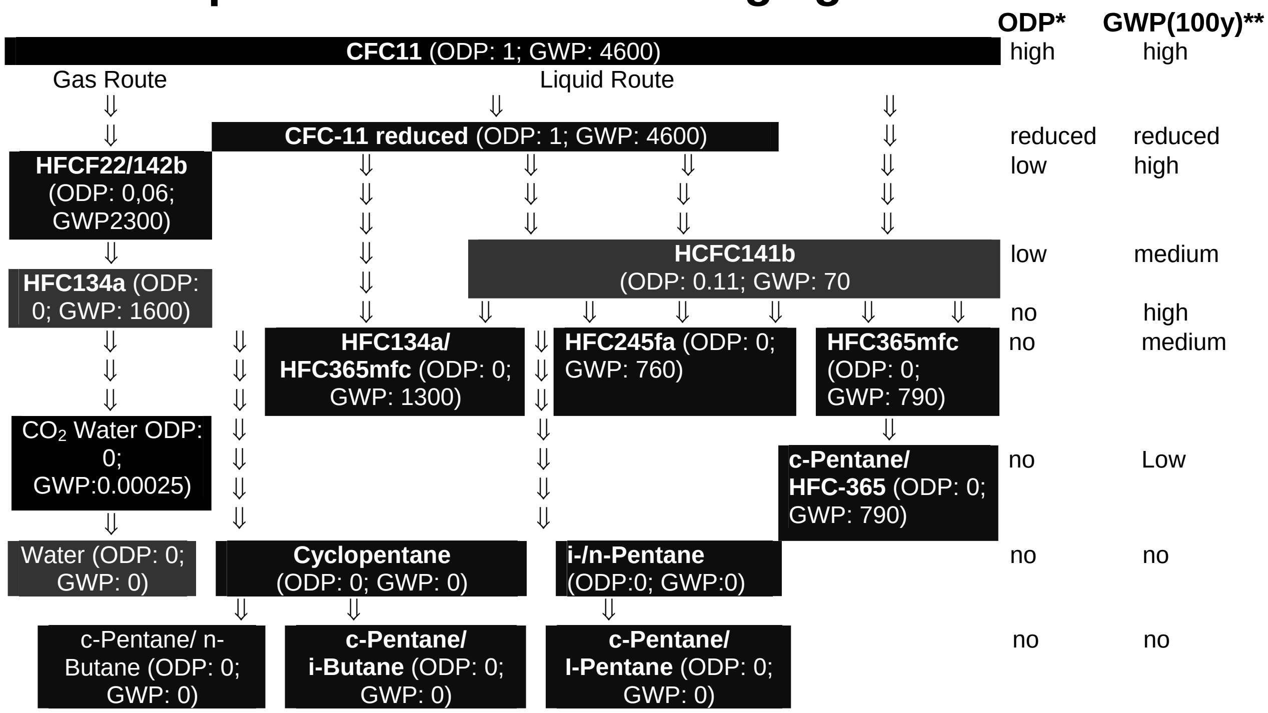
After 6-9 years the k-values of foam produced with different blowing agents will become similar to each other in the range of 27-28 kW/m*K, that is the value after complete diffusion of the blowing agent, so that the foam matrix is only filled by air. Therefore the discussion which blowing agent are the best should not to be taken too serious if the k-values are deviating only by 1kW/m*K - except under ODP, health aspect and bid differences of GWP values.

Values like
- the cabinet constant (= reverse heat leakage), that represents the energy needed to maintain the temperature difference of a cold storage to its environment,
- the pull down energy (this is a question of the efficiency of the cooling circuit and has nothing to do with the insulation), and last not least
- energy consumption of the refrigerator, depending on insulation, design and cooling circuit construction) are the most important factor of global warming to be considered in the refrigeration sector.

3. CFC-free insulation alternatives

To phase out the use of CFC-11 as blowing agent of polyurethane foam which destroys the protective ozone layer of the earth following technical routes the industries have tried:

3.1. Developments on foam blowing agents



Explanations: * ODP- Ozone depletion potential
** GWP- Global Warming Potential in 100 Year ITH, relative to CO_2 (WMO1999)

At moment refrigerator companies in USA and Japan are using HCFC-141b, in Europe nearly only Cyclopentane and Cyclopentane mixtures and in the rest of the world mainly Cyclopentane. The use of HCFC-141b have to be phased out in USA and Japan till end of 2002. Therefore no developing efforts are made anymore in this temporary solution.

The GWP of a molecule will also vary depending from the time interval considered. A 100-year time horizon is the most common on: 100 year ITH GWP (kg to CO_2 /kg). In 1999 the World Meteorological Organisation (WMO) (Report 8) has introduced new values for absolute GWP's with differ from the values introduced during the Climate Change Conference from 1995. We use the WMO 1999 values. So for a time being we have to pay attention which GWP values on which base are used to avoid comparison of 2 values generated by different systems. Therefore the GWP in the following table have soon to be adjusted to the newer standards.

3.2. Most relevant foam selection criteria: k-Values and densities of different blowing agents

The 2 most important criteria of selecting foam material are the thermal conductivity (k-value) and the density: The lower the thermal conductivity is the less energy will be lost, the less density is reached, the less material is needed to fill a cavity, the less it costs.

The following table contain compared test data under production conditions as made by foaming material producers (BASF-Elastogran, Huntman-I.C.I, Bayer and Dow), by some refrigerant producers, for HFC-365mfc (Solvay, licence of Bayer) and HFC-245a (Honeywell) by blowing agent producers. The overall density have a range: the lower range values can be reached in simpler cabinet geometry foamed in bath position and if the filling hole is centralised on the bottom point (so called top flow technology) while the upper overall density value is reached by longer foam rising ways filled from compressor compartment side or top plate side. Only in few single case their were deviations with worse values outside the given range as a result of not optimal production or material conditions. We did not take into consideration special controlled "laboratory" conditions which often could reach 1-2 mW/m*K better k-values as to be realised in running production even with strict quality control on material, machines and process. We estimate that the HCF-365mfc and HCF-245fa values could be improved in the future by 1-1.5mW/m*K similar to the values reached by other blowing agents after 2-3 years of research when the systems will be optimised.

Table: Blowing Agents, physical properties, ODP- and GWP-values

Blowing agent	Boiling point	Mol weight	Heat transmission mW/k*K		% Agent on Polyol	Densities(kg/m^3)		ODP	GWP[3] 100y
			Blow.Agent	Foam at 10°C[2]		Core	overall		
CFC-11	24°C	137.4	8	**17 ± .5**	36%	**29.5 ± .7**	31-33	1	4600
CFC-11 red.	24°C	137.4	8	**17 ± .5**	18%	**32.5 ± .7**	33-35.4	1	4600
HCFC-22	-41°C	86.5	13	**40/60 Mixed: 20 ± 1**	8% 12%	**34.5 ± .9**	35.5-37.5	0.06	1900
HCFC-142b	-10°C	100.5	12						2300
HFC-134a	-26.5°C	102	15	**20.3 ± 1**	13%	**38 ± 1**	39-41	0	1600
HCFC-141b	32.1°C	117	9.7	**18 ± .5**	25%	**33.5 ± .7**	35-37	0.11	700
HFC-356mfc	40.2°C	148	10.6	**20 ± 1**	15%		34-36	0	790[4]
HFC-245fa	15.3°C	134	12.2	**18.2 ± .5**	23.5% ?	**?**	?	0	990
c-Pentane/72.5 %HFC-356mfc	32°C azeotrop	70 148	11.1 azeotrop	**18 ± 1**	26% azeotrop			0	790
c-Pentane II	49°C	70	10	**19 ± .6**	13%	**34 ± .8**	35-37	0	<0.1
c-Pentane III	49°C	70	10	**18 ± .5**	16%	**32 ± .7**	33-35	0	0
c-Pentane/ i-Butane	49°C -11.7°C	70 58,1	10 17	**19.5 ± .7**	c-P:12-13% i-B: 1.5-2%	**31 ± .7**	32-34	0	0
c-Pentane/ i-Pentane	49°C 27.8°C	70 72.1	10 13	**19.5 ± .7**	c-P: 8-9% i-P: 3-4%	**32 ± .7**	33-35	0	0
c-Pentane/ n-Butane	49°C -135°C	70 58,1	10 17	**19.5 ± .7**	c-P:13% n-P: 1.3%	**31 ± .7**	32-34	0	0
n-Pentane/ i-Pentane	36.1°C 27.1°C	72.2 72.1	14 13	**20 ± 1**	n-P: 8% i-P: 3%	**32 ± .7**	33-35	0	0
CO_2 sublimated	-78.5°C	44	17	**25 ± 1**	?	**40 ± 1**	41-43	0	1000[5]
Air =after 6-9 y	-	29	29	**28 ± .5 ± .5**	-	**-**	-	0	0

[2] At –20°C the k-values are often higher than at +20°C for low boiling materials. Lowest values are often reached in the range of 15-20°C. To receive a more realistic k-value we selected the comparison value on 10°C as average value because freezers are inside <-20°C, representing normally 33% of refrigeration volume, refrigerator inside 3-8°C and environment temperature for both are 18-38°C for subtropical class, up to 18-43°C for tropical class. Because of a condensation effect for lower temperatures underneath 0°C Cyclopentane foam have significant lower K-values than CFC-11.
[3] see remarks to changes of standardisation of GWP
[4] Old IPCC 1996 value, which probably have to be creased by 20% to make in comparable with WMO 1999 values
[5] The value of CO_2 can also be 0 id CO_2 is taken from air and not by burning of fossil Hydrocarbon.

The data base of HFC-245fa is incomplete and on HFC-365mfa still very small. We did not mentioned anymore HCFC-123 which did not pass the health test (PAFT) as well as HFC-152a, because relevant research data were not yet presented or not known yet by us.

A Handicap for the replacement of HCFC-141b by HFC-245 or HFC-365mfa is the high prices of these 2 blowing agents. US$ 9,00 per kg HFC-245fa and US$ 5,50 for HFC-365mfa is much more expensive than Cyclopentane.

Besides environmental aspects and density, which means cost of foam per refrigerator (the lower density can be reached the cheaper is the foam), an effective production is a decisive criterion for the economic efficiency of PU foams. The production efficiency are influenced by

- foam material characteristics , specially the demoulding behaviour and flow behaviour, and also by - the used technology: foaming machines, the supporting jigs, opening and closing speed, heating, mixing heads, cabinet carriage and their movement speed, which we will analyse separately. First we will concentrate of the foam material itself and after reanalysing many articles and research reports in this field we decided to cite an article of **Udo Rotermund, Gottfried Knorr, Holger Seifert, Werner Wiegmann: Technical Comparison of Various Blowing Agents with Different PU-Systems set for the Appliances Industry, Elastogran (BASF), 2000.**