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Potentially Acceptable Substitutes for the Chlorofluorocarbons: Properties and Performance Features of HFC-134a, HCFC-123, and HCFC-141b[1]

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Potentially acceptable substitutes are known for CFC-11 and CFC-12—the most important chlorofluorocarbons. HFC-134a could replace CFC-12 in air-conditioning and refrigeration and both HCFC-123 and HCFC-141b show promise as CFC-11 substitutes. The replacement molecules all have significantly reduced greenhouse and ozone depletion potentials compared to their fully halogenated counterparts. HCFC-123 is theoretically a less efficient blowing agent than CFC-11, but 141b is more efficient. Results from experimental foaming tests confirm these relationships and show that initial insulating values are slightly lower for 141b and 123 than 11. Both substitutes are nonflammable liquids. Based on its physical properties, HFC-134a is an excellent replacement candidate for CFC-12. In addition, it is more thermally stable than CFC-12. A new family of HFC-134a compatible lubricant oils will be required. The estimated coefficient of performance (COP) of 134a is 96–98% that of CFC-12. Subacute toxicity tests show HFC-134a to have a low order of toxicity. HCFC-123 reveals no serious side effects at a concentration of 0.1% in sub-chronic tests and the inhalation toxicity of 141b is lower than that of CFC-11 based on a 6-h exposure. Chronic tests on all the new candidates will have to be completed for large-scale commercial use. Allied-Signal is conducting process development at a highly accelerated pace, and we plan to begin commercialization of substitutes within 5 years.

KEY WORDS: blowing agents; chlorofluorocarbons; chlorofluorocarbon substitutes; physical properties; ozone depletion potential; toxicity.

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1. INTRODUCTION

It is certainly no secret that potentially acceptable substitutes are known for the most important chlorofluorocarbons (CFCs)—namely, 11 and 12. HFC-134a could replace 12 as the working fluid in a wide range of air-conditioning and refrigeration applications. Both HCFC-123 and HCFC-141b look promising as blowing agents for insulating foams. In addition, HCFC-22 and blends containing 22 appear eminently suited to the preparation of packaging foams and in refrigerant applications. From here, however, the list peters out very rapidly. There are few, if any, other replacements in the same league with 11 and 12, let alone in an advanced state of development. Therefore, it is important that we understand how well the substitutes perform and that we know the toxicity status of these materials and how soon they will be commercialized. In short, we must develop a clear picture of 134a, 123, and 141b.

Perhaps the best way to address the first issue would be to compare the properties and performance features of CFC-11 and CFC-12 with those of their respective substitutes in two major end use areas.

First, let us examine 123 and 141b as potential urethane insulation foam blowing agents.

2. HCFC-123 AND HCFC-141b: PHYSICAL PROPERTIES AND BLOWING AGENT PERFORMANCE

As shown in Table I, the atmospheric lifetimes and ozone depletion potentials for both are significantly lower than those for 11. In addition, greenhouse effects are reduced severalfold. Table II summarizes some of the basic properties of the fluids. HCFC-123 has a higher molecular weight than CFC-11, which means that it will be less efficient as a foam blowing agent. On a theoretical basis, the decrease in efficiency is 11%. Similarly, 123's higher thermal conductivity will result in foams with poorer insu-

Table I. Environmental Aspects of HCFC-123 and HCFC-141b

	CFC-11	HCFC-123	HCFC-141b
Formula	CCl_3F	$CHCl_2CF_3$	CCl_2FCH_3
Approx. atmospheric lifetime (years)	61	2	10
Ozone depletion potential[a]	1.00	≤0.02	≤0.11
Greenhouse warming potential[b]	0.42	0.01	0.05

[a] Relative to CFC-11, which is assigned the value 1.00.
[b] Relative to CFC-12, which is assigned the value 1.00.

Table II. Physical Properties of HCFC-123 and HCFC-141b

	CFC-11	HCFC-123	HCFC-141b
Molecular weight	137.4	152.9	116.9
Boiling point (°C)	23.8	27.9	32.1
Freezing point (°C)	−111.1	−107.2	−103.3
P_{vap} (kPa)[a]	105.63	91.29	79.98
K_{vap} ($mW \cdot m^{-1} \cdot K^{-1}$)	8.222	10.397	10.022
Liquid density ($kg \cdot m^{-3}$)[a]	1476.	1462.	1232.
ΔH_{vap} ($kJ \cdot mol^{-1}$)	24.76	26.30	25.86
Liquid viscosity ($mPa \cdot s$)[a]	0.412	0.481	0.430
Solubility in H_2O (ppm)[a]	950.	2100.	660.
H_2O solubility (ppm)[a]	70.	662.	420.
Polyol solubility limit (wt %),[a] Terate 203	9.7	96.4	24.4

[a] Measured at 25°C.

lating values. The decreases in efficiency and in insulating power represent the biggest drawbacks to the use of 123.

HCFC-123 is a more powerful solvent toward polyols than 11. From Table II, one can see the significant difference in compatibility with an aromatic polyester polyol. Thus, the miscibility problems associated with 11 are not evident with 123, which is an advantage. However, this is a double-edged sword because increased solvency can impact other aspects of foam behavior such as dimensional stability and compressive strength. Most other physical properties of 123 are similar to those of 11.

HCFC-141b is theoretically 24% more efficient than 123 due to its lower molecular weight—a considerable advantage. The solvency of 141b is intermediate between that of 123 and that of 11 and its vapor–thermal conductivity is similar to that of 123.

The flammability characteristics (Table III) of the alternate fluorocarbons are an important factor in almost every application. HCFC-123, like 11, does not have a flash point and is, therefore, classified as a nonflammable liquid. Nor does the vapor phase of 123 possess flame limits under ambient conditions. HCFC-141b is a nonflammable liquid but its vapor is flammable over a narrow range of composition. This does not preclude its use, although it may require changes to the foam manufacturing process in some circumstances. However, this is not the complete story. One needs to be concerned about any possible increase in foam fuel value due to the new blowing agent. Based on the limited data available to date, it is difficult to say for sure that 123 and 141b do not adversely affect foam

Table III. Flammability Characteristics of HCFC-123 and HCFC-141b

	CFC-11	HCFC-123	HCFC-141b
Flash point[a]	None	None	None
Vapor flame limits[b]			
Ambient	None	None	7.6–17.2 vol%
$T = 95°C$	None	None	7.3–18.5 vol%
Foam flammability[c]		—Limited data—	

[a] Open cup (ASTM D 1310-67) and closed cup (ASTM D 56-82).
[b] For comparison, flame limits of HCFC-142b measured using the same apparatus are 8.0–15.4 vol%.
[c] Available data are equivocal.

flammability. It is likely that they will prove satisfactory, but more tunnel testing will be needed to prove the point.

Table IV shows the results from some experimental foaming tests. Here the same base formulation was used to prepare the foams by substituting 123 and 141b for 11. We see from the table that 25% more 123 by weight is required to achieve the same density foam as 11. This greater than the molecular weight replacement ratio is probably attributable to the higher solubility of 123 in the formulation, which causes the blowing agent to remain dissolved in the polymerizing mixture until later in exotherm. On

Table IV. Rigid Urethane Foam Properties

	Blowing agent		
	CFC-11	HCFC-123	HCFC-141b
Density ($kg \cdot m^{-3}$)	32.03	32.03	32.03
K factor[a] ($mW \cdot m^{-1} \cdot K^{-1}$)	18.72	20.16	21.60
Dimensional stability[a]			
% vol change (−40°C, 24 h)	−0.4	0.37	−0.93
% vol change (70°C, 16 h)	0.4	1.54	0.23
Compressive strength (kPa)			
∥ to rise	232.4	234.4	229.6
⊥ to rise	142.0	121.3	104.1
% open cells	9.3	6.5	7.3
Mole of blowing agent	0.255	0.285	0.254
Mass of blowing agent	35.	43.6	29.7
Relative efficiency	1.000	1.246	0.849

[a] Five-day-old foam.

the other hand, only 85% as much 141b as 11 is required, very close to theoretical. The initial K factors for both 141b and 123 are higher than that for 11 as expected. Other foam properties such as dimensional stability, compressive strength, and percentage of open cells are essentially equivalent. The differences are not significant.

A similar picture emerges with different formulations and different density foams. However, in many instances K factors for both 123 and 141b are closer to that for 11 than shown here.

Overall, the results to date are encouraging. Clearly 141b is more efficient than 123. However, both blowing agents give K factors close to that of 11 and foam properties are unaffected by the substitutes. The major unknowns are foam flammability with the substitutes and their toxicities. Section 4 contains a summary of toxicity test results on the various chlorofluorocarbon substitutes.

3. HFC-134a: PHYSICAL PROPERTIES AND PERFORMANCE

Let us turn now to a comparison between CFC-12 and HFC-134a, its potential replacement for a wide range of air-conditioning and refrigeration applications.

Table V indicates that the small difference between the boiling point

Table V. Typical Physical Properties of HFC-134a

	HFC-134a	CFC-12
Chemical formula	CF_3CH_2F	CCl_2F_2
Molecular weight	102.03	120.93
Freezing point (°C)	−101	−158
Normal boiling point (°C)	−26.2	−29.8
Critical temperature (°C)	101.1	112.0
Critical pressure (kPa)	4067	4116
Critical density ($kg \cdot m^{-3}$)	512.2	558.1
Liquid density at 25°C ($kg \cdot m^{-3}$)	1207.3	1310.9
Specific heat of liquid at 25°C ($kJ \cdot kg^{-1} \cdot °C^{-1}$)	1.430	0.870
Specific heat of vapor at constant pressure (1 atm) and 25°C ($kJ \cdot kg^{-1} \cdot °C^{-1}$)	0.851	0.587
Heat of vaporization at NBP ($kJ \cdot kg^{-1}$)	217.8	167.24
Liquid thermal conductivity at 25°C ($mW \cdot m^{-1} \cdot K^{-1}$)	80.38	65.49
Vapor thermal conductivity at a pressure of 1 atm ($mW \cdot m^{-1} \cdot K^{-1}$)	14.15	9.63
Liquid viscosity at 25°C ($mPa \cdot s$)	0.211	0.223
Flammability limits (vol %)	Nonflammable	Nonflammable

Table VI. Substitution Potential of HFC-134a Automotive Air-Conditioning

Key physical requirements	HFC-134a performance rating[a]
Moderate–high critical temperature	0
Required thermodynamic properties	0
High thermal stability	+1
High miscibility with 500 SUS oils	−1
Low hose permeation rate	0
Product safety in use	(0)
Minimum space/weight demand	(0)
Maximum fuel efficiency	(0)
Good elastomer compatibility	0
Low copper plating (ref/oil)	+1
Compatible with desiccants	Inc.

[a] Relative to CFC-12: +1, better; 0, similar; −1, poorer; ( ), estimated.

of 12 and that of 134a coupled with the nonflammability and non-ozone depletion of the latter makes it a prime replacement candidate for 12. There are few, if any, other molecules with these attributes. In addition, the low molecular weight of 134a and its high latent heat are advantages in refrigeration systems. However, the high specific heat compared to 12 is a negative factor. The liquid thermal conductivity is a plus in refrigeration —while most other properties of 134a are quite acceptable.

Now we can take a look at the substitution potential of 134a in both air-conditioning and refrigeration.

We have observed experimentally (Table VI) that 134a is more thermally stable than 12 and less copper plating occurs with 134a/lubricant oil mixtures—the latter probably more attributable to the lubricant than the refrigerant. Again, in other respects including hose permeation and elastomer compatibility, 134a is about equal to 12—the major drawback is

Table VII. Substitution Potential of HCFC-134a Refrigeration

Key physical requirements	HFC-134a performance rating[a]
High miscibility with lower-viscosity oils	(−)
Motor winding/insulation compatibility	Inc.
Low copper plating (Ref/oil)	(+)
High lubricity of ref/oil mixture	(−)
High thermal stability	+
High dielectric properties	Inc.

[a] Relative to CFC-12: +1, better; 0, similar; −1, poorer; ( ), estimated.

the immiscibility of 134a with conventional refrigeration oils. It is quite likely that a totally new 134a compatible family of lubricant oils will have to be developed for both air conditioning and refrigeration. Work along these lines is well under way at Allied-Signal and other organizations.

In refrigeration applications (Table VII), 134a exhibits a good thermal stability, but we will need compatible lubricant oils.

The COP, or coefficient of performance, is a way of describing the energy efficiency of a vapor compression cycle. The COP for a refrigerant can be calculated from its thermodynamic properties for a defined set of condenser and evaporator conditions. Thus, we have determined that the theoretical COP of 134a ranges from 96 to 98% that of 12 under the condenser and evaporator temperatures shown in Fig. 1. The same COP relationship should be achievable in actual test cycles.

We also estimate that the capacity of 134a and 12 should be very similar.

In this area, as in foams, the outlook is encouraging. On a performance basis, 134a meets almost all of the criteria necessary to merit serious consideration as a replacement for CFC-12. Of course, development of 134a compatible lubricants is very important.

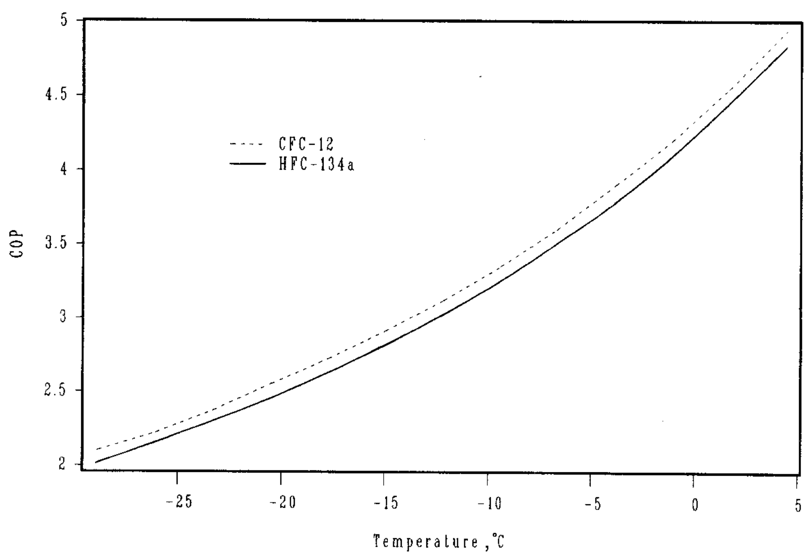

Fig. 1. Comparison of theoretical COP of Rankine refrigeration cycle using CFC-12 and HFC-1343a with the condenser at 48.9°C (120°F) and varying the evaporator temperature between −28.9°C (−20°F) and 4.4°C (40°F).

4. CHLOROFLUOROCARBON SUBSTITUTES: TOXICITY TEST STATUS

It might be worthwhile to summarize some of the information available on the toxicity testing of the leading CFC substitutes. To date, subacute inhalation studies have been completed on 134a, and so far it is judged to have a low order of toxicity. Also, preliminary work indicates that 134a is not teratogenic, mutagenic, or embryotoxic at concentrations up to 50,000 ppm. However, to be confident of its suitability for large-scale commercial use, full teratology and chronic tests will have to be completed. My colleagues in toxicology tell me that these kinds of tests involve literally hundreds of animals, which means that they will be examining thousands of organs for damage and comparing tens of thousands of tissue slides. All in all, it would be difficult to compress the additional time required for 134a toxicity work to less than about 5 years.

Results of subchronic tests on HCFC-123 reveal no serious side effects at concentrations up to 0.1 %. Short-term exposure shows no mutagenic or teratogenic activity. However, this work is about 10 years old and we believe that it must be verified before chronic tests begin. Here again, we are looking at an elapsed time of about 5 years for a complete toxicological evaluation of 123.

HCFC-141b testing is not quite as far along as either 123 or 134a. However, based on a 6-h exposure, its inhalation toxicity is lower than that of 11. It does give a weakly positive test for mutagenicity. Complete testing for 141b will probably take 5–6 years.

A toxicology committee representing 14 leading fluorocarbon suppliers worldwide is sponsoring testing on 134a and 123—to start during the second quarter of 1988—so we are certainly under way. HCFC-141b will be sponsored separately.

5. CHLOROFLUOROCARBON SUBSTITUTES: COMMERCIALIZATION

As a final point, some of the factors involved in commercializing a CFC substitute are discussed. Here we can use 134a as an example to compare a normal commercialization sequence with our accelerated schedule. Normally, there are several distinct steps or phases of activity leading to the commercialization of a new product. The laboratory phase defines process chemistry. Several alternate routes to 134a are possible. All are complex, multistep syntheses and it is the job of the project team to identify and demonstrate on a laboratory scale the most practical route with the best economic potential. These activities could take 2–3 years.

The pilot plant is usually built when the laboratory process is well understood. Here the objective is to demonstrate the process on a multiton per year level in anticipation of a further scaleup to commercial levels. From start to finish, pilot plant work could take 2–3 years.

The same logic applies to the commercial phase. Plant construction usually begins after the operability of the pilot plant has been demonstrated and after toxicity testing is complete. Plant startup can be extremely burdensome and time-consuming. This phase usually takes 2–3 years.

Overall it could take 7–10 years to get into production in normal circumstances. At Allied-Signal, work is under way on an accelerated schedule, which telescopes all of these steps. Here plant construction begins before we are confident of our ability to scale the process to commercial reality and long before chronic inhalation tests are complete. This schedule leaves little room for error. Both the technical and the financial risks increase significantly compared to the normal timetable for commercialization. Nevertheless, we seek to initiate commercial production of CFC substitutes in as short a time as 5 years—a time frame consistent with the completion of toxicity testing on the new compounds. This timing is also coincident with the 20% cutback in chlorofluorocarbon production proposed by the EPA. Thus, developing shortages of 11 and 12 might well be eased.

Overall, we are optimistic about the prospects for environmentally acceptable products. We are working diligently to make available a family of stratospherically safe fluorocarbons which meet end users' requirements and reduce consumption of 11 and 12.