Flammability Investigation of Different Refrigerants using an operating MAC system in a simulated front end collision situation

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OBRIST Engineering

Introduction

A flammability investigation of three different refrigerants for Mobile Air Conditioning was carried out. In a first step the actual safety level of R134a was investigated. The results were put in relation to the two possible alternatives R744 and 2,3,3,3-Tetrafluoroprop-1-ene (also called HFO-1234yf).

Test Setup – First Phase

A VW Lupo system was used to do the testing (Figures 1-2). The system was charged with refrigerant (500gr for R134a and HFO-1234yf) and operated under real operating conditions (Pd ~15bar). As lubrication medium PAG oil ND8 (135ml for all tests) was used. A possible leak of the refrigerant caused by a front end collision was simulated by a release of refrigerant through a manually operated valve onto a hot surface. Such a front end collision can rupture a refrigerant line and release the refrigerant-oil mixture into the engine compartment. The released refrigerant-oil mixture was directed to a hot surface simulating a turbo charger or hot exhaust manifold. The surface temperature was measured and the temperature was adjusted through a controller of the electrical powered heat source (Figures 3-4).

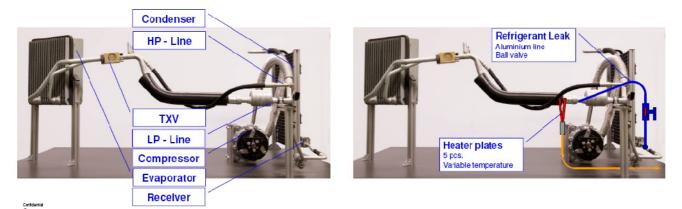


Figure 1 R134a A/C system (VW Lupo)

Figure 2 Test adaptations to R134a A/C system (VW Lupo)

The base line test with R134a (ignition temperature >743degC) and ND8 (flash point 204degC) was carried out to define the existing safety level in the vehicle. A surface temperature of 970degC was chosen. Under this condition it was possible to show that the mixture could not be ignited.

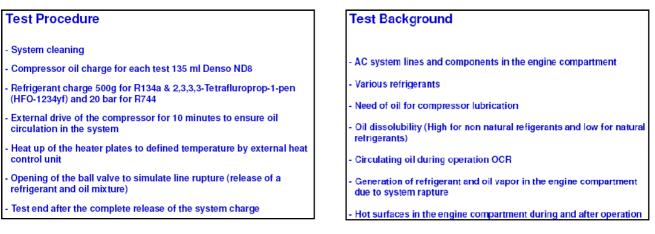


Figure 3 Test Procedure

Figure 4 Test Background

R134a prevents the mist of oil and refrigerant vapor from ignition. During this test no flame propagation was observed. It could be concluded that the use of R134a and ND8 oil is safe up to surface temperatures of 970degC.

In a second test, R134a was replaced by R744 (charge of 50gr and additional R744 container of 20kg was connected to the system) and the test was repeated at the same surface temperature of 970degC. Since the oil circulation rate in a R134a system is higher (~4%) and more refrigerant is solved in the circulating oil than in an R744 system, the risk of mist ignition and the causing of a pilot fire is reduced with the inflammable refrigerant R744. In a normal operating, R744 system pressures are higher than in the one used during the test. However, the lower-than-normal pressures of the R744 system are considered to increase the risk of ignition since a higher pressure would cause also higher release speeds and therefore reduce the probability to ignite the mixture. In the test the release pressure was stabilized to 20bar. No misting was observed and no ignition was observed.

The third test was carried out with 2,3,3,3-Tetrafluroprop-1-ene (also called HFO-1234yf and having a flash point of ~400degC). Miscibility and solubility characteristics with ND8 are considered to be similar to R134a. During the testing an ignition was observed and the flame propagation and the flammability envelop was judged to be substantial.

Conclusion First Phase

R134, having an A1 rating (not flammable according to ASHRAE safety standard), cannot be ignited during an accident simulation (vehicle front end) and under realistic operating conditions including circulating oil. R744, having also an A1 rating, behaves similar to R134a and the risk of ignition can be judged to be lower than with R134a. R744 is therefore generating an improved safety level. The HFO-1234yf, with a probable ASHRAE safety rating of A2 or an even lower safety level in terms of flammability and toxicity (toxicity testing not completed) clearly increases the risk of a pilot fire after a front end collision.

Test Setup – Second Phase

In a second level testing the release of HFO-1234yf oil mist onto a surface with lower temperatures was investigated. The temperature was reduced to 800degC in order to simulate an operating turbo charger hit by a mixture of tetrafluoro-1-propene and PAG oil ND8. In this scenario the mixture was again ignited. The flame propagation and the flammability envelope lead to the conclusion that this pilot fire had caused a secondary fire in the engine compartments. It could be concluded that by using HFO-1234yf, today's high safety level in terms of flammability would be significantly reduced, causing an increased vehicle damage after moderate front end collisions and putting human life at risk.

In a next step, the temperature was reduced to 600degC (simulating a hot exhaust manifold). Also in this setup the refrigerant oil mixture was ignited. The flame propagation was substantial and even so the flammability envelope was reduced, it could still be judged to be sufficient to cause a secondary fire.

Conclusion Second Phase

It can be concluded that 2,3,3,3-Tetrafluoroprop-1-ene (HFO-1234yf) used as a refrigerant in a vehicle application reduces significantly today's safety level in terms of flammability. Possible implications are increased insurance premiums since the cost for repair will be increased. Further investigation is necessary on the implications for persons being present in confined spaces, e.g. during accidents in tunnel or garages, when such a fire happens (due to the low LC50 values of the thermal decomposition products). The risk of a pilot fire caused by a front end collision in a vehicle using HFO-1234yf is significantly increased. A risk that the pilot fire causes a secondary fire became clearly visible during testing and is highly possible (the flames consumed the polycarbonate indicator panels and the operational wire harness).

Background

Pure ND8 oil was released without refrigerant to the 600degC surface. The oil was ignited. The flame propagation and the flammability envelope were judged to be moderate but the burning oil will provide the MIE (minimum ignition energy) for the ignition of HFO-1234yf.

An additional flammability test of pure HFO-1234yf was conducted using a cigarette lighter. The refrigerant was ignited and flame propagation was observed. The person handling the test was equipped with an active carbon filter mask and fire protective gear. The reason for the mask and protective gear was that the thermal decomposition products of HFO-1234yf are Hydrogen fluoride (HF) and Carbonyl fluoride (COF2). These substances have a LC50 (lethal concentration) value at 1h of 966 ppm and Carbonyl fluoride (COF2) is

having a LC50 value at 1h of only 360 ppm. LC50: 50% of an animal population dies within 1h if the atmosphere contains the indicated amount of the substance in ppm.

Technical Development Direction

When compared to R152a (A2), the HFO-1234yf flammability envelope is slightly reduced. However, the flammability envelope of HFO-1234yf requires either an oil free circuit or a secondary loop for the front end heat exchanger.

Outlook

In a next phase, side impact collision will be investigated during which refrigerant lines inside the passenger compartment are ruptured.

Annex

- 1) Material certificate for 2,3,3,3-Tetrafluoroprop-1-ene CAS No 754-12-1
- 2) MSDS for 2,3,3,3-Tetrafluoroprop-1-ene Chemical Formula C₃H₂F₄
- 3) MSDS for PAG oil ND8
- 4) MSDS for R744
- 5) MSDS for R134a
- 6) 2,3,3,3-Tetrafluoroprop-1-ene Container Sticker pictures

1) Material certificate for 2,3,3,3-Tetrafluoroprop-1-ene CAS No 754-12-1

	CERTIFICATE OF ANALYSIS	
Product:	2,3,3,3-Tetrafluoroprop-1-ene	
Code No:	PC0987	
CAS No:	754-12-1	
Formula:	$C_3H_2F_4$	
Batch No:	Q14B-40	
Purity:	99%	
Identity:	Conforms to reference	
Date:	08 th February 2008	

2) MSDS for 2,3,3,3-Tetrafluoroprop-1-ene Chemical Formula $C_3H_2F_4$

SAFETY DATA SHEET

2,3,3,3-TETRAFLUOROPROP-1-ENE

Page 1 Issued: 25/09/2007 Revision No: 3

1. IDENTIFICATION OF T	THE SUBSTANCE / PREPARATION AND OF THE COMPANY / UNDERTAKING	
Product name:	2,3,3,3-TETRAFLUOROPROP-1-ENE	
CAS number:		
Product code:	PC0987	
Company name:	Apollo Scientific Ltd	
	Bredbury, Stockport, SK6 2QR, Tel 0161 406 0505	
2. HAZARDS IDENTIFICA	ATION	
Main hazards:	Flammable. Irritating to eyes, respiratory system and skin.	
3. COMPOSITION / INFO	RMATION ON INGREDIENTS	
Hazardous ingredients:	2,3,3,3-TETRAFLUOROPROP-1-ENE >90%	
4. FIRST AID MEASURE	S (SYMPTOMS)	
Skin contact:	There may be irritation and redness at the site of contact.	
Eye contact:	There may be irritation and redness. The eyes may water profusely.	
Ingestion:	There may be soreness and redness of the mouth and throat.	
Inhalation:	There may be irritation of the throat with a feeling of tightness in the chest. Exposure may cause	
	coughing or wheezing.	
4. FIRST AID MEASURE	S (ACTION)	
Skin contact:	Remove all contaminated clothes and footwear immediately unless stuck to skin. Wash	
	immediately with plenty of soap and water.	
Eye contact:	Bathe the eye with running water for 15 minutes. Consult a doctor.	
Ingestion:	Wash out mouth with water. Consult a doctor.	
Inhalation:	Remove casualty from exposure ensuring one's own safety whilst doing so. Consult a doctor.	
5. FIRE-FIGHTING MEAS	URES	
Extinguishing media:	Suitable extinguishing media for the surrounding fire should be used. Carbon dioxide. Dry	
	chemical powder.	
Exposure hazards:	In combustion emits toxic fumes.	
Protection of fire-fighters:	Wear self-contained breathing apparatus. Wear protective clothing to prevent contact with skin	
	and eyes.	
6. ACCIDENTAL RELEAS	SE MEASURES	
Personal precautions:	Refer to section 8 of SDS for personal protection details. If outside do not approach from	
	downwind. If outside keep bystanders upwind and away from danger point. Mark out the	
	contaminated area with signs and prevent access to unauthorised personnel. Turn leaking	
	containers leak-side up to prevent the escape of liquid.	
Environmental precautions:	Do not discharge into drains or rivers. Contain the spillage using bunding.	
Clean-up procedures:	Absorb into dry earth or sand. Transfer to a closable, labelled salvage container for disposal by	
	an appropriate method. [cont]

SAFETY DATA SHEET 2,3,3,3-TETRAFLUOROPROP-1-ENE

Page 2

7. HANDLING AND STOP	AGE
Handling requirements:	Avoid direct contact with the substance. Ensure there is sufficient ventilation of the area. Do
	not handle in a confined space. Avoid the formation or spread of mists in the air. Only use in
	fume hood.
Storage conditions:	Store in cool, well ventilated area. Keep container tightly closed.
Suffable packaging:	Must only be kept in original packaging.
8. EXPOSURE CONTROL	L8 / PERSONAL PROTECTION
Engineering measures:	Ensure there is sufficient ventilation of the area.
Respiratory protection:	Self-contained breathing apparatus must be available in case of emergency.
Hand protection:	Protective gloves.
Eye protection:	Safety glasses. Ensure eye bath is to hand.
Skin protection:	Protective clothing.
9. PHYSICAL AND CHEM	IICAL PROPERTIES
State:	Gas
Colour:	Colouriess
Bolling point/range ^a C:	-28.3C@76DmmHg
Melting point/range*C:	-152.24C
10. STABILITY AND REA	CTIVITY
Stability:	Stable under normal conditions.
Conditions to avoid:	Store protected from moisture and heat Direct sunlight.
Materials to avoid:	Strong exidising agents. Strong acids.
Haz, decomp. products:	In combustion emits toxic fumes.
11. TOXICOLOGICAL INF	ORMATION
Chronic texicity:	MAY BE HARMFUL BY INHALATION, INGESTION, OR SKIN ABSORPTION.
Routes of exposure:	Refer to section 4 of SDS for routes of exposure and corresponding symptoms.
12. ECOLOGICAL INFOR	MATION
Mobility:	Volatie.
Percistence and degradability:	No data available.
Bloaccumulative potential:	No data available.
Cther adverse effects:	Etgén (confidence)
	Data not known
13. DISPOSAL CONSIDE	
13. DISPOSAL CONSIDE	
13. DISPOSAL CONSIDE	RATIONS
13. DISPOSAL CONSIDE Disposal operations:	MATERIAL SHOULD BE DISPOSED OF IN ACCORDANCE WITH LOCAL, STATE AND

[cont...]

Issued: 25/09/2007

SAFETY DATA SHEET 2,3,3,3-TETRAFLUOROPROP-1-ENE

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NB: The user's attention is drawn to the possible existence of regional or national regulations regarding disposal.

14. TRANSPORT INFORM			
14. TRANSPORT INFORM	IA LION		
ADR / RID			
UN no:	1954 ADR Class	: 2	
Classification code:	1F		
Shipping name:	COMPRESSED GAS, FLAMMABLE, N.O.S.		
Labelling:	2.1 Hazard ID no	23	
	+		
IMDG / IMO			
UN no:	1954 Class	: 2.1	
Em8:	F-0,S-U Marine pollutant		
Labelling:	2.1		
IATA / ICAO			
UN no:	1954 Class	: 2	
Packing instructions:	FORBIDDEN(P&CA); 200		
Labelling:	2.1		
15. REGULATORY INFOR	MATION		
Hazard symbols:	Initant.		
	Flammabile.		
	×		
Risk phraces:	R10: Flannmable.		
	R36/37/38: Initating to eyes, respiratory system and skin.		
Safety phraces:	\$15: Keep away from sources of Ignition - No smoking.		
	836/37/39: Wear suitable protective clothing, gloves and eye / face protection.		
	845: In case of accident or if you feel unwell, seek medical advice immediately (show the label		
	where possible).		
Note:	The regulatory information given above only indicates the principal		
	applicable to the product described in the safety data sheet. The us		
	the possible existence of additional provisions which complete thes	-	
	applicable national, international and local regulations or provisions	-	
		[cont]	

SAFETY DATA SHEET 2,3,3,3-TETRAFLUOROPROP-1-ENE

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18. OTHER INFORMATION

Legal disolalmer: The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. This company shall not be held liable for any damage resulting from handling or from contact with the above product.

3) MSDS for PAG oil ND8

.2001 16:11	DENISO	NR.576 S.2	/6
-	IDEMITSU KOSAN CÔ.	.,LTD. 1/5 First issue : JUN 17, 1999 Reviaed :	e
	Material Safety Dat	ta Sheet	
1. CHEMICAL P	RODUCT AND COMPANY IDETIF	ICATION.	
Product name	: ND-OIL8		
Product code :	32450338		
Company name	e :IDEMITSU KOSAN CO., LTD		
Address : No.	1-1,3-chome, Marunouchi, Chiyoda-k	u,Tokyo,Japan	
Telephone num	aber : +81-3-3213-3142		
	r : +81-3-3213-9415		
	ON / INFORMATION ON INGREDIE	ENTS.	
Substance / Mi	xture : Mixture		-
	Contraction of the second of		

Component	Chemical name	Wt %	CAS No.
Synthetic Oil	Polyether	> 95	24991-61-5
Additives		< 5	

Composition comment

This components are included U.S. TSCA and EINCS Inventory.

3. HAZARDS IDENTIFICATION.

Emergency averview :

Potential Health effects

Eye : Not expected to cause prolonged or significant eye irritation.

Skin: There is likely to be a mild irritation when there is contact for long periods of time or repeated contact.

Not expected to be harmful to interval organs if absorbed through the skin.

Ingestion: No data available.

Inhalation: No data available.

12.JUL.2001 16:11 DENS0

NR.576 S.3/6

IDEMITSU KOSAN CO., LTD.

2/5First issue : JUN 17,1999

Revised : 32450338

MSDS No . : 4. FIRST AID MEASURES. Eye contact : Flush eyes with fresh water for at least 15 minutes, then seek medical attention. Skin contact : Wash contact areas thoroughly with soap and water Inhalation : Remove to fresh air. Cover the victim's body with blanket, rest in keeping warm, and seek medical attention immediately Ingestion : If swallowed, do not induce vomiting. Seek medical attention immediately. If contaminated in mouth, flush thoroughly with water 5. FIRE-FIGHTING MEASURES. _____ FLAMMABLE PROPERTIES Flash point and Method : 204°C (COC) Flammable Limits : No data available. Extinguishing media : CO2, Dry Chemical, Form and Water Fog. Fire fighting instructions : For fires involving this material, do not enter any enclosed or confined fire space without proper protective equipment, including self-contained breathing apparatus. Combustion products : Normal combustion forms carbon dioxide and water. Incomplete combustion can produce carbon monoxide. 6. ACCIDENTAL RELEASE MEASURES. Eliminate all open flame in vicinity of spill or released vapor. Stop the source of the leak or release. Clean up releases as soon as possible, observing precaution in Exposure Controls/Personal Protection. Contain liquid to prevent further contamination of soil, surface water or groundwater. Clean up small spills using appropriate techniques such as absorbent materials or pumping. Where feasible and appropriate, remove contaminated soil. Follow prescribed procedures for reporting and responding to larger releases.

IDEMITSU KOSAN CO.,LTD		JUN 17,199 32450338
7. HANDLING AND STORAGE		
Do not weld, heat drill container . Residue may ignite with heated sufficiently CAUTION : Do not use pressure to empty drum or may force.	-	
8. EXPOSURE CONTROLS / PERSONAL PROTECTION.		
Engineering Controls :	-**	
Use adequate ventilation to keep the airborne con	centrations of	this mater
below the recommended exposure standard.		Control and the state of the state
Personal protective equipment :		
Eye/ Face Protection :		
No special eye protection is usually necessary.	Where splashing	ng is possib
wear safety glasses with side shields as a good safe	sty practice.	
Skin protection :		
No special protective clothing is normally required	d. Avoid pr	olonged or
frequently repeated skin contact with this materia	L	
Skin contact can be minimized by wearing protect	tive clothing.	
Respiratory protection :		
No respiratory protection is usually necessary.		
conditions create high airborne concentrations , th respirator is required.	e use of an ap	proved
9. PHYSICAL AND CHEMICAL PROPERTIES.		
Physical description :		
Light yellow liquid with characteristic order.		
Vapor pressure : < 5 mmHg (@20 °C)		
Boiling point : > 250°C (IBP)		
Pour point : -45.0		
Solubility : Insoluble in water		
Density : 1.00 g/cm ³ (@15°C)		
Viscosity : 43.3 mm ² /s (@40°C)		

4/5

IDEMITSU KOSAN CO., LTD. First issue : JUN 17,1999 Revised : MSDS No .: 32450338 10. STABILITY AND REACTIVITY. Hazardous decomposition products : No data available Chemical stability : Stable Condition to avoid : No data available Incompatibility with other materials : May react with strong oxidizing agent, such as chlorates, nitrates, peroxides, etc. Hazardous polymerization : Polymerization will not occur.

11. TOXICOLOGICAL INFORMATION.

Eye effects : No product toxicology data available.

The hazard evaluation was based on data from similar materials. Skin effects : Very mild irritant to the skin.

The skin irritation hazard is bases on data for a similar materials.

Acute oral effects : The acute oral toxicity is based on data for a similar materials. Acute inhalation effects : The acute inhalation is based on data for a similar materials. Additional toxicology information :

None of the oils requires a cancer warning under the OSHA Hazard Communication Standard(29 CFR 1910.1200). These oils have not been listed in the National Toxicology Program(NTP)Annual Report and the International Agency for Research on Cancer(IARC)

12. ECOLOGICAL INFORMATION.

Ecotoxicity : No data available.

Environmental fate : This material is not expected to be readily biodegradable.

13. DISPORSAL CONSIDERATIONS.

Place contaminated material in disposable containers and dispose of in a manner consistent with applicable regulations. Contact local environmental or health authorities for approved disposal of this materials.

VINTRE CTRUCKTY TZ (N)	0 A 3 T (0 ()	TIM
IDEMITSU KO	SAND	1.1.1.1

IDEMITSU KOSAN CO.,LTD.	First issue : Revised : MSDS No . :	5/5 JUN 17,1999 32450338
14. TRANSPORT INFORMATION.		
The description shown may not apply to all shipping situation Dangerous Goods Regulations, for additional description req (e,g., tochnical name) and mode-specific or quantity-specific to UN No. : Not applicable	uirements	
15. REGULATORY INFORMATION. None of the listed components of this material are found on t		
indicates. 16OTHER INFORMATION.		
NFPA RATINGS : Health 1 ; Flammability 1 ; Reactivity HMIS RATINGS : Health 1 ; Flammability 1 ; Reactivity	0;	
These values are obtained using the guidelines or publish by the National Fire Protection Association (NFPA) or the Coating Association (for HMIS ratings).		
The Safety Data Sheet for Chemical Products is provided to	companies.	That handle

dangerous and toxic as reference information for safe handling. We recommend the companies to utilize the data upon understanding that the product handling requires appropriate treatment according to and conditions, and should be done on your own responsibility. Therefore the data sheet itself constitute a guarantee of safety.

4) MSDS for R744

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SAFETY DATA SHEET	Revised edition no : 1
	Date : 15/7/2005
	Supersedes : 0/0/0
Carbon dioxide	AL018A

1 IDENTIFICATION OF THE SUBSTANCE / PREPARATION AND OF THE COMPANY / UNDERTAKING



Trade name	: Carbon dloxide		
MSDS No	: AL018A		
Chemical formula	: CO2		
Company identification	: AIR LIQUIDE SA		
	France		
-	See paragraph 16 "OTHER INFORMATION"		
Emergency phone nr	: See paragraph 16 "OTHER INFORMATION"		
2 COMPOSITION / INFORMATION C			
Substance / Preparation	. Substance.		
Substance name Carbon dioxide	Contents CAS No EC No Index No Classification		
	urities which will influence the classification of the product.		
3 HAZARDS IDENTIFICATION			
Hazards identification	: Liquefied gas.		
Hazard's identification	In high concentrations may cause asphyxiation.		
4 FIRST AID MEASURES			
First aid measures			
- Inhalation	: In high concentrations may cause asphyxiation. Symptoms may include loss of		
- Innalation	mobility/consciousness. Victim may not be aware of asphyxiation.		
	Low concentrations of CO2 cause increased respiration and headache.		
	Remove victim to uncontaminated area wearing self contained breathing apparatus. Keep victim warm and rested. Call a doctor. Apply artificial respiration if		
	breathing stopped.		
- Skin/eye contact	. Immediately flush eves thoroughly with water for at least 15 minutes.		
	In case of frostbite spray with water for at least 15 minutes. Apply a sterile dressing.		
	Obtain medical assistance.		
- Ingestion	: Ingestion is not considered a potential route of exposure.		
5 FIRE-FIGHTING MEASURES			
Flammable class	: Non flammable. : Eveneurs to fra may source containers to sunture/evelopie.		
Specific hazards	: Exposure to fire may cause containers to rupture/explode.		
Hazardous combustion products	: None.		
Extinguishing media			
- Suitable extinguishing media	: All known extinguishants can be used.		
Specific methods	If possible, stop flow of product. Move away from the container and cool with water from a protected position.		
	more smay non-the container and coor with water non-a protected position.		

AIR LIQUIDE SA France

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SAFETY DATA SHEET	Revised edition no : 1
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Carbon dioxide	AL018A

5 FIRE-FIGHTING MEASURES (continued)

Special protective equipment for fire : In confined space use self-contained breathing apparatus. fighters

Personal precautions	: Evacuate area. Wear self-contained breathing apparatus when entering area unless atmosphere i proved to be safe. Ensure adequate air ventilation.			
Environmental precautions	 Try to stop release. Prevent from entering sewers, basements and workpits, or any place where its accumulation can be dangerous. 			
Clean up methods	: Ventilate area.			
clean up metrous	. Therefore we writed.			
HANDLING AND STORAGE				
	: Keep container below 50°C in a well ventilated place.			

8 EXPOSURE CONTROLS / PERSONAL PROTECTION

Personal protection	: Ensure adequate ventilation.
Occupational Exposure Limits	: Carbon dioxide : TLV© -TW A [ppm] : 5000
	Carbon dioxide : TLV© -STEL [ppm] : 30000
	Carbon dioxide : OEL (UK)-LTEL [ppm] : 5000
	Carbon dioxide : OEL (UK)-STEL [ppm] : 15000
	Carbon dioxide : MAK - Germany [ppm] : 5000

9 PHYSICAL AND CHEMICAL PROPERTIES

Physical state at 20 °C	: Liquefied gas.			
Colour	: Colourless.			
Odo(u)r	: No odour warning properties.			
Molecular weight	: 44			
Melting point [°C]	: -58.6			
Boiling point [°C]	: -78.5 (s)			
Critical temperature [°C]	: 30			
Vapour pressure, 20°C	: 57.3 bar			
Relative density, gas (air=1)	: 1.52			
Relative density, liquid (water=1)	: 0.82			
Solubility in water [mg/l]	: 2000			
Flammability range [vol% in air]	: Non flammable.			
Other data	: Gas/vapour heavier than air. May accumulate in confined spaces, particularly at or below ground level.			

		Page : 3 / 4			
	SAFETY DATA SHEET	Revised edition no : 1			
		Date : 15/7/2005			
		Supersedes : 0/0/0			
	AL018A				
10 STABILITY AND REACTIV	ITY				
Stability and reactivity	: Stable under normal conditions.				
11 TOXICOLOGICAL INFORM	ATION				
Toxicity information	ty information : In high concentrations cause rapid circulatory insufficiency. Symptoms are headache, nausea and vomiting, which may lead to unconsciousness.				
12 ECOLOGICAL INFORMATI	ION				
Ecological effects information Global warming factor [CO2=		ute to the greenhouse effect.			
13 DISPOSAL CONSIDERATI	ONS				
General	: Do not discharge into any place where its accum To atmosphere in a well ventilated place. Discharge to atmosphere in large quantities shou Contact supplier if guidance is required.	5			
UN No.	: 1013				
H.I. nr	: 20				
ADR/RID					
- Proper shipping name	: CARBON DIOXIDE				
- ADR Class	: 2				
- ADR/RID Classification code	e :2A				
 Labelling ADR 	: Label 2.2 : Non flammable, non toxic gas.				
Other transport information	compartment. Ensure vehicle driver is aware of the potential ha to do in the event of an accident or an emergence Before transporting product containers : - Ensure that containers are firmly secured. - Ensure cylinder valve is closed and not leaking. - Ensure valve outlet cap nut or plug (where provided - Ensure valve protection device (where provided - Ensure there is adequate ventilation.	 Avoid transport on vehicles where the load space is not separated from the driver's compartment. Ensure vehicle driver is aware of the potential hazards of the load and knows what to do in the event of an accident or an emergency. Before transporting product containers : Ensure that containers are firmly secured. Ensure cylinder valve is closed and not leaking. Ensure valve outlet cap nut or plug (where provided) is correctly fitted. 			
	- Compliance with applicable regulations.				
15 REGULATORY INFORMAT					
15 REGULATORY INFORMAT EC Classification		ce.			
	FION : Not classified as dangerous preparation/substan	ce.			
EC Classification	FION : Not classified as dangerous preparation/substan- Not included in Annex I. : No EC labelling required. : None.	ce.			
EC Labelling	FION : Not classified as dangerous preparation/substan- Not included in Annex I. : No EC labelling required.	ce.			

AIR LIQUIDE	SAFETY DATA SHEET	Page : 4 / 4 Revised edition no : 1 Date : 15/7/2005
~		Supersedes : 0/0/0
	Carbon dioxide	AL018A

16 OTHER INFORMATION

Asphyxiant in high concentrations.

Keep container in a well-ventilated place.

Do not breathe the gas.

Contact with liquid may cause cold burns/frostbite. Ensure all national/local regulations are observed.

The hazard of asphyxiation is often overlooked and must be stressed during operator training.

This Safety Data Sheet has been established in accordance with the applicable European Directives and applies to all countries that have translated the Directives in their national laws.

Before using this product in any new process or experiment, a thorough material compatibility and safety study should be carried out.

Details given in this document are believed to be correct at the time of going to press. Whilst proper care has been taken in the preparation of this document, no liability for injury or damage resulting from its use can be accepted.

Recommended uses and restrictions : This SDS is for information purposes only and is subject to change without notice. [Prior to purchase of products, please contact your local AIR LIQUIDE office for a complete SDS (with Manufacturer's name and emergency phone number).]

End of document

5) MSDS for R134a



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The MSDS format adheres to the standards and regulatory requirements of the United States and may not meet regulatory requirements
                   in other countries.
                         DuPont
                                                 Page
                                                      1
                 Material Safety Data Sheet
_____
                     "SUVA" 134a AUTO
2188FR
                    Revised 18-APR-2007
     -----
                                        _____
CHEMICAL PRODUCT/COMPANY IDENTIFICATION
            Material Identification
  "SUVA" is a trademark of DuPont.
  Corporate MSDS Number : DU000693
                    : 811-97-2
: CH2FCF3
  CAS Number
  Formula
  CAS Name
                     : 1,1,1,2-TETRAFLUOROETHANE
Tradenames and Synonyms
  "SUVA" 134a
  HFC 134a
Company Identification
  MANUFACTURER/DISTRIBUTOR
              DuPont Fluoroproducts
              1007 Market Street
              Wilmington, DE 19898
  PHONE NUMBERS
    Product Information : 1-800-441-7515 (outside the U.S.
                      302-774-1000)
    Transport Emergency : CHEMTREC 1-800-424-9300(outside U.S.
                      703-527-3887)
                    : 1-800-441-3637 (outside the U.S.
    Medical Emergency
                      302-774-1000)
_____
COMPOSITION/INFORMATION ON INGREDIENTS
Components
Material
                                 CAS Number
ETHANE, 1,1,1,2-TETRAFLUORO-
(HFC-134a)
                                   811-97-2 100
                          HAZARDS IDENTIFICATION
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       . . . . . . . . . .
Fotential Health Effects
  INHALATION
  ETHANE, 1,1,1,2-TETRAFLUORO-
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(HAZARDS IDENTIFICATION - Continued)

Gross overexposure may cause: Central nervous system depression with dizziness, confusion, incoordination, drowsiness or unconsciousness. Irregular heart beat with a strange sensation in the chest, "heart thumping", apprehension, lightheadedness, feeling of fainting, dizziness, weakness, sometimes progressing to loss of consciousness and death. Suffocation, if air is displaced by vapors.

SKIN CONTACT

ETHANE, 1,1,1,2-TETRAFLUORO-Immediate effects of overexposure may include: Frostbite, if liquid or escaping vapor contacts the skin.

EYE CONTACT

ETHANE, 1,1,1,2-TETRAFLUORO-"Frostbite-like" effects may occur if the liquid or escaping vapors contact the eyes.

ADDITIONAL HEALTH EFFECTS

ETHANE, 1,1,1,2-TETRAFLUORO-Increased susceptibility to the effects of this material may be observed in persons with pre-existing disease of the: central nervous system, cardiovascular system.

Carcinogenicity Information

None of the components present in this material at concentrations equal to or greater than 0.1% are listed by IARC, NTP, OSHA or ACGIH as a carcinogen.

FIRST AID MEASURES

INHALATION

If high concentrations are inhaled, immediately remove to fresh air. Keep person calm. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Call a physician.

SKIN CONTACT

In case of contact, immediately flush skin with plenty of water for at least 15 minutes, while removing contaminated clothing and shoes. Call a physician. Wash contaminated clothing before reuse. Treat for frostbite if necessary by gently warming affected area.

EYE CONTACT

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(FIRST AID MEASURES - Continued)

In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Call a physician.

INGESTION

Ingestion is not considered a potential route of exposure.

Notes to Physicians

Because of possible disturbances of cardiac rhythm, catecholamine drugs, such as epinephrine, should only be used with special caution in situations of emergency life support.

PIRE FIGHTING MEASURES

Flammable Properties

Flash Point : No flash point

Flammable Limits	in	Air, 9	k by Volume:
LEL			None per ASTM E681
UEL		1	None per ASTM E681
Autoignition		1	>743 C(>1369 F)

Fire and Explosion Hazards:

Cylinders may rupture under fire conditions. Decomposition may occur.

Contact of welding or soldering torch flame with high concentrations of refrigerant can result in visible changes in the size and color of torch flames. This flame effect will only occur in concentrations of product well above the recommended exposure limit, therefore stop all work and ventilate to disperse refrigerant vapors from the work area before using any open flames.

HFC-134a is not flammable in air at temperatures up to 100 deg. C (212 deg. F) at atmospheric pressure. However, mixtures of HFC-134a with high concentrations of air at elevated pressure and/or temperature can become combustible in the presence of an ignition source. HFC-134a can also become combustible in an oxygen enriched environment (oxygen concentrations greater than that in air). Whether a mixture containing HFC-134a and air, or HFC-134a in an oxygen enriched atmosphere become combustible depends on the inter-relationship of 1) the temperature 2) the pressure, and 3) the proportion of oxygen in the mixture. In general, HFC-134a should not be allowed to exist with air above atmospheric pressure or at high temperatures; or in an oxygen enriched environment. For example HFC-134a should NOT be mixed with air under pressure for leak testing or other purposes.

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(FIRE FIGHTING MEASURES - Continued)

Experimental data have also been reported which indicate combustibility of HFC-134a in the presence of certain concentrations of chlorine.

Extinguishing Media

Use media appropriate for surrounding material.

Fire Fighting Instructions

Cool tank/container with water spray. Self-contained breathing apparatus (SCBA) may be required if cylinders rupture or release under fire conditions.

Water runoff should be contained and neutralized prior to release.

ACCIDENTAL RELEASE MEASURES

Safequards (Personnel)

NOTE: Review FIRE FIGHTING MEASURES and HANDLING (PERSONNEL) sections before proceeding with clean-up. Use appropriate PERSONAL PROTECTIVE EQUIPMENT during clean-up.

Ventilate area, especially low or enclosed places where heavy vapors might collect. Remove open flames. Use self-contained breathing apparatus (SCBA) if large spill or leak occurs.

HANDLING AND STORAGE Handling (Personnel)

Use with sufficient ventilation to keep employee exposure below recommended limits.

Handling (Physical Aspects)

HFC-134a should not be mixed with air for leak testing or used for any other purpose above atmospheric pressure. See Plammable Properties section. Contact with chlorine or other strong oxidizing agents should also be avoided.

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# Storage
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Store in a clean, dry place. Do not heat above 52 C (126 P).

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(HANDLING AND STORAGE - Continued)

Valve protection caps and valve cutlet threaded plugs must remain in place unless container is secured with valve outlet piped to use point. Do NOT drag, slide or roll cylinders. Use a suitable hand truck for cylinder movement. Never attempt to lift cylinder by its cap. Use a pressure reducing regulator when connecting cylinder to lower pressure (>3000 psig) piping or systems. Do NOT heat cylinder. Use a check valve or trap in the discharge line to prevent hazardous back flow into the cylinder.

Cylinders should be stored upright and firmly secured to prevent falling or being knocked over. Separate full containers from empty containers. Storage area temperatures should not exceed 125 deg P (52 deg C) and should be free of combustible materials. Avoid area where salt or other corrosive materials are present. Avoid excessive inventory and storage time. Use a first-in first-out system. Keep accurate inventory records.

EXPOSURE CONTROLS/PERSONAL PROTECTION Engineering Controls

Normal ventilation for standard manufacturing procedures is generally adequate. Local exhaust should be used when large amounts are released. Mechanical ventilation should be used in low or enclosed places. Refrigerant concentration monitors may be necessary to determine vapor concentrations in work areas prior to use of torches or other open flames, or if employees are entering enclosed areas.

Personal Protective Equipment

Impervious gloves and chemical splash goggles should be used when handling liquid.

Under normal manufacturing conditions, no respiratory protection is required when using this product.

Self-contained breathing apparatus (SCBA) is required if a large release occurs.

Exposure Guidelines

2199FR Page 6 DuPont Material Safety Data Sheet Exposure Limits "SUVA" 134a AUTO PEL (OSHA) None Established None Established TLV (ACGIE) AEL * (DuPont) WEEL (AIHA) : 1000 ppm, 8 & 12 Hr. TWA : 1000 ppm, 8 Er. TWA * AEL is DuPont's Acceptable Exposure Limit. Where governmentally imposed occupational exposure limits which are lower than the AEL are in effect, such limits shall take precedence. PHYSICAL AND CHEMICAL PROPERTIES Physical Data : -26.5 C (-15.7 F) © 736 mm Eg : 96 psia © 25 C (77 F) Boiling Point Vapor Pressure Vapor Density & Volatiles : 3.6 (Air=1.0) @ 25 C (77 F) : 100 WT% % Volatiles : 0.15 WT% @ 25 C (77 F) Solubility in Water © 14.7 psia odor: Ether (slight). Form : Liquified Gas. Color Colorless. : 1.21 g/cm3 @ 25 C (77 F) : 1.208 @ 77 F (25 C) Liquid Density Specific Gravity Evaporation Rate : (CCL4 = 1); greater than 1 STABILITY AND REACTIVITY Chemical Stability Stable. Conditions to Avoid Avoid open flames and high temperatures. Incompatibility with Other Materials Incompatible with alkali or alkaline earth metals - provdered Al, Zn, Be, etc. Decomposition Decomposition products are hazardous. This material can be decomposed by high temperatures (open flames, glowing metal surfaces, etc.) forming hydrofluoric acid and possibly carbonyl fluoride.

These materials are toxic and irritating. Contact should be avoided.

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(STABILITY AND REACTIVITY - Continued)

Polymerization

Polymerization will not occur.

TOXICOLOGICAL INFORMATION

Animal Data

ETHANE, 1,1,1,2-TETRAFLUORO-

BXE :

A short duration spray of vapor produced very slight eye irritation.

SKIN:

Animal testing indicates this material is a slight skin irritant, but not a skin sensitizer.

INHALATION:

4 hour, ALC, rat: 567,000 ppm.

Single exposure caused: Cardiac sensitization, a potentially fatal disturbance of heart rhythm associated with a heightened sensitivity to the action of epinephrine. Lowest-Observed-Adverse-Effect-Level for cardiac sensitization: 75,000 ppm. Single exposure caused: Lethargy. Narcosis. Increased respiratory rates. These effects were temporary. Single exposure to near lethal doses caused: Pulmonary edema. Repeated exposure caused: Increased adrenals, liver, spleen weight. Decreased uterine, prostate weight. Repeated dosing of higher concentrations caused: the following temporary effects -Tremors. Incoordination.

CARCINOGENIC, DEVELOPMENTAL, REPRODUCTIVE, MUTAGENIC EFFECTS:

In a two-year inhalation study, HFC-134a, at a concentration of 50,000 ppm, produced an increase in late-occurring benign testicular tumors, testicular hyperplasia and testicular weight. The no-effect-level for this study was 10,000 ppm. Animal data show slight fetotoxicity but only at exposure levels producing other toxic effects in the adult animal. Reproductive data on male mice show: No change in reproductive performance. Tests have shown that this material does not cause genetic damage in bacterial or mammalian cell cultures, or in animals. In animal testing, this material has not caused permanent genetic damage in reproductive cells of mammals (has not produced heritable genetic damage).

2199FR DuPont Page 8 Material Safety Data Sheet ECOLOGICAL INFORMATION Ecotoxicological Information AQUATIC TOXICITY: 48 hour EC50 - Daphnia magna: 980 mg/L. 96 hour LC50 - Rainbow trout: 450 mg/L DISPOSAL CONSIDERATIONS Waste Disposal Contaminated HFC-134a can be recovered by distillation or removed to a permitted waste disposal facility. Comply with Federal, State, and local regulations. TRANSPORTATION INFORMATION Shipping Information DOT/IMO Proper Shipping Name : 1, 1, 1, 2-TETRAFLUOROETHANE Hazard Class 1 2.2 : 3159 UN NO. DOT/IMO Label : NONFLAMMABLE GAS Shipping Containers Tank Cars. Tank Trucks. Ton Tanks. Cylinders. REGULATORY INFORMATION U.S. Federal Regulations TSCA Inventory Status : Reported/Included. TITLE III HAZARD CLASSIFICATIONS SECTIONS 311, 312 Acute : Yes Chronic : Yes : No Fire Reactivity : No : Yes Pressure HAZARDOUS CHEMICAL LISTS SARA Extremely Hazardous Substance: No CERCLA Hazardous Substance : No SARA Toxic Chemical : NO

2199FR DuPont Page 9 Material Safety Data Sheet OTHER INFORMATION NFPA, NPCA-HMIS NPCA-HMIS Rating Health : 1 Flammability ı 0 Reactivity : 1 Personal Protection rating to be supplied by user depending on use conditions. Additional Information MEDICAL USE: CAUTION: Do not use in medical applications involving permanent implantation in the human body. For other medical applications see DuPont CAUTION Bulletin No. H-50102. The data in this Material Safety Data Sheet relates only to the specific material designated herein and does not relate to use in combination with any other material or in any process. Responsibility for MSDS : MSDS Coordinator : DuPont Fluoroproducts : Wilmington, DE 19898 : (800) 441-7515 Address Telephone # Indicates updated section.

This information is based upon technical information believed to be reliable. It is subject to revision as additional knowledge and experience is gained.

End of MSDS



6) 2,3,3,3-Tetrafluoroprop-1-ene container sticker picture

2,3,3,3-TETRAFLUOROPROP Dary 2Kg BNO 014B-40 Flammable Irritating o eyes, respiratory system and skin. Keep away from sources of ignition-No smoking. Wear suitable protective clothing, gloves and eye / face protection. In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible).