METHYL FORMATE AS BLOWING AGENT IN THE MANUFACTURE OF POLYURETHANE FOAM SYSTEMS

AN ASSESSMENT FOR THE APPLICATION IN MLF PROJECTS

OCTOBER 2010

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EXECUTIVE SUMMARY

The Executive Committee of the Multilateral Fund for the Implementation of the Montreal Protocol, through Decision 55/43, acknowledged the need to assess HCFC free technologies for use in developing countries and invited its implementing agencies, as a matter of urgency, to prepare and submit specific project proposals for the assessment of chemical systems for use with non-HCFC blowing agents. In response to this mandate UNDP formulated a number of pilot projects to investigate newly introduced HCFC free alternative technologies. This report describes the outcome of an assessment on the safe use of methyl formate (ecomate® or MF) to replace HCFC-141b in PU foams.

The use of MF based systems in PU foams has been evaluated at Purcom Quimica Ltda in Barueri/SP, Brazil and Quimiuretanos Zadro SA de CV in San Francisco del Rincon/GTO, Mexico with the objective of assessing its performance compared with HCFC-141b based systems and establishing the feasibility of its use in MLF projects.

UNDP wishes to state herewith that:

The use of MF in PU foams constitutes proprietary technology;
UNDP has refrained from any investigation or disclosure that would infringe on said property rights but limited itself to evaluation and assessment;

While UNDP has made arrangements with the owner of the technology for technology disclosure and the offering of non-exclusive (sub-)licenses to prospective MLF project beneficiaries, the negotiation of such (sub-)licenses will be the responsibility of the beneficiaries;

Any findings and/or recommendations by UNDP are based on the assumption that beneficiaries will follow health and safety procedures as outlined by the Agency in this document and its attachment and/or recommended by the technology owner.

The technology using MF in PU foam is owned and marketed by Foam Supplies, Inc. (FSI) in the USA. While still small compared to HCFC-141b, its use has been growing substantially in the last few years as the following table shows:

Table 1

YEAR	AMOUNT (metric tons)		
	Methyl Formate	Polyol System	HCFC-141b Equivalent
2005	40	850	100
2006	75	1,500	180
2007	160	3,200	385
2008	360	7,200	864
2009	365	7,300	875
2010	910*	18,000	2,200

* Estimate based on January thru August

Source: Foam Supplies Inc. (FSI)

Purcom was at time of project initiation the only A5 licensee and, for that reason, was selected as the recipient for this project. Because Purcom does not market shoesole systems, this application has been separately assessed through Zadro. To avoid the perception that MLF funds would cause any preferential treatment, it was agreed from the onset with FSI and relevant licensees that they would grant non-exclusive (sub-) licenses to any interested party that applies for MLF-supported HCFC phase-out projects.

The project identified 17 PU applications. After project approval, November 2008, a slightly modified action program was prepared based on:

- A thorough evaluation and incorporation in the assessment of previous work by FSI and its licensees;
- Elimination of applications requiring direct injection (mostly continuous operations);

Acceptability, for the purpose of this project, was defined as follows:

- Determining the safe use of the technology based on health, safety and environmental (HSE) data;
- Determining the applicability of the technology based on its processability;
- Determining the applicability of the technology by measuring relevant physical properties before and after replacing HCFC-141b. ,
- Collecting complementary information, views from enterprises that have tested MF formulations in their production;

The summary outcome of the assessment is as follows:

Table 2

Foam Type	Application	Acceptability			
		Health, Safety and Environment (HSE)	Processability	Physical Properties	Assessment
Flexible and Integral Skin Foams	Hyper-soft molded	+	+	+	+
	Hyper-soft blocks	+	+	+	+
	Viscoelastic molded	+	+	+	+
	Viscoelastic blocks	+	+	+	+
	Steering wheels	+	+*	+	+
	Structural (rigid)	+	+*	+	+
	Semi-flexible	+	+	+	+
	Shoesoles	+	+*	+	+
Rigid Foams	Residential Appliances	+	-	-	-
	Other Appliances	+	+	+	+/-
	Panels, Transportation, Reefers	+	+	+	+
	Spray	+	+	+	+
	Blocks	+	+*	+	+
	Pipe-in-pipe	+	+	+	+
	Buoyancies	+	+	+	+

* = separate injection of MF recommended

+ Acceptable, - unacceptable; +/- acceptable with conditions

Analysis of the outcome of the assessment led to the following conclusions:

- The use of methyl formate as an alternative blowing agent to HCFC-141b in PU foam applications can be considered as an alternative in developing countries in flexible/integral skin foam applications and in a number of rigid foam applications. It is important to consider that for certain applications on rigid foam the technology could not be recommended at this stage and on others the application of the technology should be analyzed on a case by case basis and could be subject to further optimization.

- To minimize safety risks at downstream users, such projects should preferably be implemented through their system suppliers as fully formulated systems;

- Project designers should ensure that:

  - Chemical compatibility is verified;
  - Minimum packed density is observed;
  - Health, safety and environmental recommendations are incorporated;
  - Implications related to acidity are taken into account.

Costs

Conversion costs were to be determined in Phase-II of the MF assessment. A request for funding of this project at Purcom/Brazil, which would be treated as an investment project, was to be submitted jointly with this report. However, for the following reasons it is suggested to forego such a phase in Brazil:

- The price structure for PU chemicals in Brazil is not typical. The offering of locally produced polyols is limited and imported polyols are subject to significant import duties. HCFC-141b, on the other side, is lower in cost than in most other countries. The result is that MF systems currently are more than10% higher priced than HCFC-141b systems (in Mexico this is less than 5%).

In this context, UNDP has developed generally applicable cost templates to calculate the incremental cost of conversion from HCFC-141b to MF-based foams (4.5.1, 4.5.2). It should be pointed out that capital and chemical cost can differ significantly from country to country and are also subject to economy of scale considerations.

1. Introduction

The Executive Committee of the Multilateral Fund for the Implementation of the Montreal Protocol, through Decision 55/43 acknowledged the need to assess selected HCFC-free technologies for use in developing countries and invited implementing agencies as a matter of urgency to prepare and submit a limited number of time-specific project proposals for the development, optimization and validation of chemical systems for use with non-HCFC blowing agents. In response to this mandate, UNDP formulated a number of pilot projects to evaluate technology issues that it deemed unresolved. These issues ranged from determination of related global warming effects to validation of technologies that had been not, or only sporadic, been used in an Article-5 context. From these projects, six have been approved and one of these, the assessment of the use of methyl formate (MF) in non-continuous PU applications, has been technically completed. This particular pilot project has been designed around Purcom Quimica LTDA ("Purcom"), the largest independent system house in Brazil and specialized in tailor-made PU systems covering most PU applications. A notable exception is the application of PU foam in shoesoles, which has been validated through a pilot project executed by Quimiuretanos Zadro, a system house in Mexico that is specialized in PU shoesole systems.

MF as blowing agent in PU foams was first introduced by Foam Supplies, Inc. (FSI). The company filed December 18, 2001 for a US patent which was awarded June 22, 2004. By now, FSI has filed for, or has been awarded, patents in most major countries. The use of MF in PU foams has developed as follows (information from FSI):

Table 3

YEAR	AMOUNT (metric tons)		
	Methyl Formate	Polyol System	HCFC-141b Equivalent
2005	40	850	100
2006	75	1,500	180
2007	160	3,200	385
2008	360	7,200	864
2009	365	7,300	875
2010	910*	18,000	2,200

* Estimate based on January thru August

The development of ecomate® has taken a life of its own and market share has grown as shown in the table above. Marketed under the name ecomate®, MF is currently licensed to the following enterprises:

- Australian Urethane Systems — Asia Pacific
- British Oxygen Corporation — Selected European Countries
- Purcom Quimica — South America
- Expanded Incorporation — India
- Resichem — South Africa

FSI has agreed to non-exclusive (sub) licensing in the future to system houses that are beneficiaries of MLF-funded HCFC phase-out projects. While the Brazilian part of the assessment was concluded in February 2010, the shoesole part took until August 2010. A first draft—excluding shoesoles—was presented during a workshop March 23/24 held in Curitiba, Brazil, with the participation of system houses, government officers, end users, regional experts, National Ozone Officers from the region and

representatives from several implementing agencies as well as other providers of competing technologies. The completed assessment will be presented to interested parties at a workshop in Leon, Mexico (19th Oct 2010). The complete assessment addresses comments/suggestions from the first workshop participants, Foam Technical Options Committee (FTOC) individual experts consulted, as well as from a peer reviewer.

Technology is ever evolving and there could be future improvements in the use of MF as auxiliary blowing agent that may reduce or eliminate current performance limits. It is believed that the mandate of UNEP's Foams Technical Options Committee is to monitor and to report to the Montreal Protocol parties on such evolutions. UNDP believes that the current assessment is sufficient to draw conclusions on its potential use in MLF projects.

2. Project Design

Approved Design

The project in its approved version was designed to develop, optimize and assess the use of MF as replacement technology for HCFC-141b in 17 PU applications and would cover acquisition of the necessary testing/prototyping equipment; development of formulations for all pertinent applications; optimization and assessment of these formulations, as well as dissemination of the experience gained through workshops. It also included the determination of incremental changes and related costs (ICCs and IOCs) deemed necessary at both system houses and downstream users to use the technology safely.

Modified Design

- **Peer Review:** projects normally do include a peer review of the proposed design. However, in this case a peer as review was not required as part of the submission. UNDP felt it prudent to add such a review to the completion procedure of the project (**Attachment-I**).

- **Limitations**: it is emphasized that this assessment serves a very practical purpose which is ***to determine the extent to which MF can be satisfactorily used in MLF-funded HCFC phase-out projects and, in this way, avoid unexpected setbacks in project implementations***

  This does not include an exhaustive investigation into the way the technology works. It does include back-to-back testing with the technology it replaces but also review of existing data, specifically on health, safety and environment. The term ***"evaluation"*** **or** ***"assessment"*** therefore better describes the task at hand than the more formal/legal term ***"validation"***.

- **Applications:** The applications for which the assessment was carried out are listed in the table under Section 3.
- **Optimization:** UNDP decided that optimization together with customers is more effective than prototyping at the system house only and would avoid some of the need for "phase-II" projects.
- **Collaborators:** While the project design remained centered around Purcom and Zadro, results have been shared and assistance was provided by other system houses using methyl formate, such as

Australian Urethane Systems:	Australia	Licensee
Resichem:	South Africa	Licensee
Foam Supplies, Inc.:	USA	Owner of the technology

  Together these system houses cover significant geographical areas. These companies have also shared their customer's views and information on their experience with MF (available upon request).

In recent HPMP related technical presentations the outcome of this assessment has been shared with PU system providers as well as downstream users. As a result, five system houses have already signed non-disclosure agreements and are testing MF systems in their own laboratories. Five others have contacted the technology owner of its licensees for the same purpose. Users in The Dominican Republic, Mexico, Nigeria and Uruguay have voiced their intention to convert to MF.

3. Project Implementation

The project was approved at the 56th ExCom meeting in November 2008. Funding was received in February 2009. The original list of applications was modified and reviewed on work already completed (to save time, Purcom started immediately after project conception). By late August 2009, formulation development was completed and by 8th October 2009 an action plan for the assessment was ready . By December 18, all optimization except shoesoles work was completed. In August, 2010 the optimization of shoesole formulations, which suffered initially from complications related to compatibility issues was finalized.

Following is a final list of applications that have been evaluated:

Table 4

Foam Type	Application	Milestones		
		Development	Optimization	Assessment
Flexible and Integral Skin Foams (FPF, ISF)	Hyper-soft molded	Completed	Completed	+
	Hyper-soft blocks	Completed	Completed	+
	Viscoelastic blocks	Completed	Completed	+
	Viscoelastic blocks	Completed	Completed	+
	Steering wheels	Completed	Completed	+
	Structural (rigid)	Completed	Completed	+
	Semi-flexible	Completed	Completed	+
	Shoesoles	Completed	Completed	+
Rigid Foams (RPF)	Domestic refrigeration	Completed	Discontinued*	-
	Other Appliances	Completed	Completed	+/-
	Transportation, Reefers	Completed	Completed	+
	Panels-discontinuous	Completed	Completed	+
	Spray	Completed	Completed	+
	Blocks	Completed	Completed	+
	Pipe-in-pipe	Completed	Completed	+

+ Acceptable, - unacceptable; +/- acceptable with conditions

***** The results did not justify continuation of trials

Notes: Methyl formate in continuous panels, boardstock and marine applications have been already proven in the USA, the UK and Australia on equipment and process conditions comparable to those in A5 countries. Other appliances include (apart from bottle coolers, display cabinets, etc) water heaters and thermoware which were previously separately listed but are very similar in formulations

4. Project Outcomes

Methyl-formate or methyl-methanoate is the methyl ester of formic acid. It belongs to the family of oxygenated hydrocarbons (hydrocarbons with one or more oxygenated functional groups). It has a relatively low molecular weight and is commonly used in the manufacture of formamides, formic acid, pharmaceuticals, insecticides and, more recently, as a blowing agent for foams. There has been also use as a refrigerant. A Material Safety Data Sheet (MSDS) prepared by the International Programme on Chemical Safety (IPCS) is attached (**Attachment-II**). There are also MSDSs from a number of suppliers and users.

Following data on physical properties have been taken from this MSDS and the 2006 FTOC report and compared with HCFC-141b, as it is targeted as an alternative to this substance:

Table 5

Property	Methyl Formate	HCFC-141b
Appearance	Clear liquid	Clear liquid
Boiling point	31.3°C	32°C
LEL/UEL	5-23%	7.6-17.7%
Vapor pressure	586 mm Hg @ 25°C	593 mm Hg @ 25°C
Lambda, gas	10.7 mW/mk @ 25°C	10.0 mW/mk @ 25°C
Auto ignition	>450°C	>200°C
Specific gravity	0.982	1.24
Molecular weight	60	117
GWP	Negligible	630
ODP	0	0.11

Sources: IPCS and FTOC

4.1 Health, Safety and Environment (HSE)

4.1.1 Health

Following data are taken from the Pesticide Action Network (PAN[1]) Registry:

Acute Hazard:	Not listed
Carcinogen:	Not listed
Endocrine Disruption:	Not listed
Reproductive and Development Toxicity:	Not listed

MF is transformed in the body very rapidly (with a half-life of several seconds) into formic acid and methanol. The MSDS mentions 'R20/22' (harmful by inhalation and if swallowed) and 'R36/37' (irritating to eyes and respiratory system). OSHA assigned the substance a 100 ppm TWA and 150 ppm STEL. In the USA, MF is recognized as "GRAS" (**G**enerally **R**ecognized **A**s **S**afe) and therefore exempt from premarket approval requirements of the Federal Food, Drug and Cosmetic Act. In the EU, it is pre-registered under REACH with no further action required u/t 2018.

[1] www.pan-international.org

Based on studies conducted on behalf of FSI by certified industrial hygienists (**Attachment-III**), process emissions from MF in an indoor sprayfoam application—a worst case emission scenario—were determined to be <10.00 ppm at operator samples and <23.00 ppm from area samples. These values are well under the OSHA PEL. For injection applications they were significantly lower.

Conclusion: *Based on the before mentioned evidence the use of MF as a blowing agent in PU foams appears not to create health concerns up and above those with HCFC-141b. It is highly recommended that applicable safe handling guidelines are followed.*

4.1.2 Safety

Methyl Formate's MSDS mentions that methyl formate is "*extremely flammable"* and "*vapor/air mixtures are explosive"*. Based on this, one of the main arguments voiced against the use of methyl formate as blowing agent in PU foams is its perceived explosiveness. The term explosiveness, however, should be used with care and properly defined. Explosion is defined as" the bursting, or rupture, of an enclosure or container due to the development of internal pressure from a deflagration or detonation as defined in NFPA 69". Essential elements required to trigger an explosion are fuel, air, an ignition source, and containment.

Please note that the fuel can be pure MF or an MF-based fully formulated systems. To bring the latter to explosion is virtually impossible. Apart from the problem to get the polyol mixture ignited, the heat of combustion is so low that the necessary pressure built-up in containment will just not be achieved.

Attachment IV deals with flammability issues in more detail. It concludes that:

- Methyl formate as a pure liquid is very flammable and requires proper safeguards. The risk of explosion is, however, remote because its low heat of combustion;
- A PU system base on methyl formate can be formulated as a low combustible liquid and will not reach the LFL even in the drum's head space; and
- There is no reason to treat methyl formate fully formulated systems differently from HCFC-141b fully formulated systems.

Flammability is therefore not an issue for downstream users that apply fully formulated systems. The situation is different for system houses that purchase "pure" (97.5%) methyl formate, blend this with polyol and other components and then package the fully formulated systems into drums for shipment. While measurements show that even then it is difficult to reach the lower flammable limit, it still exists and it is therefore advised to follow recommendations for handling flammable liquids, as below:

- Proper personal protective equipment;
- Closed blending containers, with a dry nitrogen blanket;
- Explosion proof equipment (pump, agitator, light, heating/cooling,);
- Electrically grounded equipment and drums (grounding clip);
- A stationary sensor with alarm function set on 20% LEL;
- Adequate ventilation
- Meter MF under the level of the liquid to which it is being added (to avoid static electricity)
- Use closed blenders to avoid human exposure to isocyanate vapors, in case methyl formate is blended in isocyanate

Conclusion: *There are fire safety risks associated with blending MF at system house level. They can be managed by following established standards and procedures. For preblended systems, no incremental fire risk exists.*

4.1.3 Environment

Methyl Formate is not registered as a hazardous air pollutant, groundwater contaminant or persistent organic pollutant (POP). Ecotoxicity data are not available. In the USA, methyl formate is not treated as a volatile organic compound (not a smog generator) and is SNAP approved. In Europe it is compliant with the RoHS and WEEE directives[2]. Its ODP is zero and its GWP insignificant (USEPA/Federal Register 69.190SNAP). In the EU it is preliminary permitted under REACH regulations.

Conclusion: *MF fully formulated systems do not pose an environmental hazard based on current regulations*

4.2 System Processability

4.2.1 Shipping & Storage

Shipment of MF can be carried out in carbon steel vessels or containers. No special material is required. Carbon steel is also acceptable for storage and piping. Under high moisture conditions (>80% RH) it is suggested to use stainless steel. Potential for moisture contamination can be avoided with a simple nitrogen blanket. MF has a very low viscosity (10% of that of water). This causes the need to recalibrate viscosity sensitive metering equipment (such as low-pressure pumps) but also allows for gravity or low pressure transfer (around 0.7 bar). Pump transfer is more suitable. Shipping, storage, and handling considerations are the same as for HCFC-141b. Transportation and storage labeling has to follow applicable regulations in the countries of use.

Conclusion: *No special considerations are required for shipment and storage of MF fully formulated systems*

4.2.2 Stability

Manufacturers typically offer shelf lives of 6 months for their systems after date of manufacturing if stored in original, unopened containers at temperatures typically between 10°C and 30°C. MF based rigid foam made from two year old samples did still match the reactivity of freshly blended product. Industrial trials showed that MF blended polyols for ISF applications are limited in stability and loose catalytic activity after about one month. Blending MF in isocyanate solved the problem.

Conclusion: *MF fully formulated polyol systems for all applications, except integral skin foams are sufficiently stable. MF blended isocyanate systems are stable*

[2] RoHS: Restriction of Hazardous Substances (EU directive), WEEE: Waste Electric and Electronic Equipment (EU directive)

4.2.3 Hydrolysis and Corrosion

With only small amounts of water in the polyol and none in isocyanates, hydrolysis is not expected to be a major issue. The measured pH (typically 6.25) indicates the same. The slight acidity raises, however, concern of potential corrosiveness. The manufacturers emphasize that, provided stabilized systems are used, no special considerations are needed for equipment. They claim that MF systems are used in all types of equipment, and that equipment used for processing HCFC-141b can be used with MF systems.

There are however two known cases where customers claimed corrosion issues. Investigation of the complaints showed that in one case the user was using un-stabilized systems while in the other case the age of the equipment (20+ years) may have played a role. The relationship of corrosion to the use of MF was not established in both cases. Nevertheless, caution is recommended.

Conclusion: *Equipment and components that come in contact with MF fully formulated systems should be preferably corrosion resistant*

4.2.4 Compatibility

Any auxiliary blowing agent requires compatible polyols and MF is not an exception. FSI states that it uses the same polyols, surfactants, catalysts and other additives as it did before (using HCFC-141b, HCFC-22 and HFC-134a). Purcom changed polyols in several cases, but this was part of an optimization process and would have been recommended for the same systems blown with HCFC-141b. For instance, Purcom's spray foam was not very successful in the market and needed stabilization by introducing additional polyols that are elsewhere common in spray foam applications. Their use improved Purcom's systems with both HCFC-141b and MF.

It should be emphasized that compatibility issues when changing blowing agents are normal. Cyclopentane-based systems required at their introduction sometimes significant polyol adjustments to overcome solubility issues and early HCFC-141b-based systems showed severe shrinkage and it took time to conclude that the potent solvent character of this substance limits it use in a system.

Conclusion: *There are no specific compatibility issues of MF with polyols and/or additives. However, it is recommended that in designing conversion projects, baseline polyols used need to be carefully checked and any required changes to polyols and related costs should be identified.*

4.3 Foam Properties

Determining the acceptability and applicability of an HCFC-141b replacement technology includes measuring of relevant physical properties before and after replacing HCFC-141b. The technology is deemed acceptable for a particular application if the physical properties are within a predetermined range (generally 10%) from the original properties using HCFC-141b. Testing has been conducted at following locations:

- Flexible and integral skin foams at Purcom;
- Shoesole foams at Zadro (Mexico) and CETEC (certified laboratory for shoe testing in Mexico);
- Rigid foams at FSI(USA);

- Steering wheels at Takata-Petri (Brazil). The company was not prepared to disclose testing details but confirmed compliance with relevant Volkswagen requirements and provided positive assessment. Domestic refrigerators at Mabe(Mexico).

Test protocols are on file. Test results have been categorized as follows:

- Flexible and Integral Skin Foams
  - Hypersoft Foams (molded, blocks)
  - Viscoelastic Foams (molded, blocks)
  - Semi flexible
  - Structural (rigid)
  - Steering Wheels
  - Shoesoles
- Rigid Foams
  - Domestic refrigeration
  - Other Appliances (including water heaters and thermoware)
  - Panels, Blocks and Transportation
  - Spray foams

4.3.1 Flexible and Integral Skin Foams

4.3.1.1 Hypersoft Foams

The tests were conducted at Purcom. Test results are as below:

Table 6

PROPERTY	TEST PROCEDURE		UNITS	HCFC-141b	MF
	NBR*	ASTM			
Density	8537	D-3574	Kg/m^3	19.4	19.2
ILD 25%	9176	D-3574	N	11	10
ILD 40%	9176	D-3574	N	13	13
ILD 65%	9176	D-3574	N	24	23
Comfort Factor	9176	D-3574	n/a	2.2	2.3
Resilience	8619	D-3574	%	42	40
Compression Set 90%	8797	D-3574	%	3	3
Tensile strength	8515	D-3574	kPa	80	88
Elongation	8515	D-3574	%	460	470
Tear Strength	8516	D-3574	N/m	456	460

*National Brazilian Standard

Conclusion: *The test results with MF are within an acceptable margin from the ones with HCFC-141b*

4.3.1.2 Viscoelastic Foams

The tests were conducted at Purcom. Test results are as below:

Table 7

PROPERTY	TEST PROCEDURE		UNITS	HCFC-141b	MF
	NBR	ASTM			
Density	8537	D-3574	Kg/m^3	34.2	34.8
ILD 25%	9176	D-3574	N	28	31
ILD 40%	9176	D-3574	N	36	39
ILD 65%	9176	D-3574	N	60	61
Comfort Factor	9176	D-3574	n/a	2.1	2
Resilience	8619	D-3574	%	6	5.5
Compression Set 90%	8797	D-3574	%	5	5
Tensile strength	8515	D-3574	kPa	60	65
Elongation	8515	D-3574	%	230	222
Tear Strength	8516	D-3574	N/m	270	301

Conclusion: *The test results with MF are within an acceptable margin from the ones with HCFC-141b or better*

4.3.1.3 (Semi) Flexible Integral Skin Foams

Tests were conducted at Purcom. Two different grades of hardness were tested:

Table 8
Black (softer)

PROPERTY	TEST PROCEDURE		UNITS	HCFC-141b	MF
	ASTM	DIN			
Product					
Molded Density	D-3574		kg/m3	288	285
Hardness	D-2240	53505	Shore A	35	35
Resilience	D-3574		%	45	45
Foam Core					
Internal Density	D-3574		Kg/m3	233	230
Tensile strength		53571	kPa	229	235
Elongation		53571	%	98	95
Tear Strength		53575	N/m	1,280	1,300
Compression set (50%)	D-3574		%	28	30
Skin Only					
Tensile strength		53504	kPa	1,000	1,000
Elongation		53504	%	96	95
Tear Strength		53515	N/m	4,380	4,375

Table 9
White (firmer)

PROPERTY	TEST PROCEDURE		UNITS	HCFC-141b	MF
	ASTM	DIN			
Product					
Molded Density	D-3574		kg/m3	300	298
Hardness	D-2240	53505	Shore A	44	44
Resilience	D-3574		%	45	45
Foam Core					
Internal Density	D-3574		Kg/m3	215	205
Tensile strength		53571	kPa	215	210
Elongation		53571	%	63	60
Tear Strength		53575	N/m	880	860
Compression set (50%)	D-3574		%	5	3
Skin Only					
Tensile strength		53504	kPa	1,720	1,700
Elongation		53504	%	79	77
Tear Strength		53515	N/m	4,700	4,680

Conclusion: *The test results with MF are within an acceptable margin from the ones with HCFC-141b*

4.3.1.4 Rigid Integral Skin Foams

There are no formal specifications for rigid integral skin foams in Brazil. The customer judges the surface, which needs to be free of pinholes. In very few exceptions, drop tests or bending tests are performed. The structural strength, however, is much larger than for comparable materials and generally no compliance tests are conducted. While most manufacturers use water-based systems, some insist on HCFC-141b because the skin is thicker (water-based products only provide densification towards the outside rather than a skin) and can be better polished. There is also a large use of rigid structural foam in shoesole applications (platform shoes). Test results on these are mentioned under "shoesoles" and in this case there are stringent requirements. In all rigid structural foam applications MF functioned as well as HCFC-141b.

Conclusion: *MF provides a comparable performance to HCFC-141b*

4.3.1.5 Steering Wheels

Takata-Petri in Brazil supplies steering wheels to almost all (international) car manufacturers in this country. They use exclusively MF systems which they blend in-house in the isocyanate site. This avoids system degradation of the polyol side which is observed when blending MF with ISF-specific catalysts and stabilizers. Takata-Petri confirms that the product meets the requirements of all their customers but declined to provide specifics claiming confidentiality. It was, however, willing to provide a written statement(available upon request) **(**Other, non-OEM suppliers of steering wheels use preblended ISF formulations with good results, however blended in the isocyanate side.

Conclusion: *MF provided a comparable performance to HCFC-141b as per the assessment of one company that supplies to international car manufacturers*

4.3.1.6 Shoesoles

Zadro's specifications are based on HCFC-141b-blown foams. It produces 8 main formulations that have been consolidated into four main ones—others being derivatives for special customers. All foam samples have been prepared in Zadro's laboratory using a low-pressure prototype dispenser. Densities have been determined by Zadro, other tests were performed by CIATEC, a federally owned and operated testing facility for the shoe industry. CIATEC is ISO-9001/2000 certified. The results are as follows:

Table 10

Property	**All types**	**R-095**	**R-096**	**R-099**	**QZCT15**	**Test Method**
Type		**SPORT**	**TRAVEL**	**RIGID**	**SEMI-RIGID**	
Blowing Agent	**141b**	**MF**	**MF**	**MF**	**MF**	
Density (kg/m^3)	<450	400	440	420	400	DIN 53420 ASTM D-792
Tear resistance (kgf/cm)	>6*	38.9	41.5	n/a	n/a	DIN 53507 ASTM D-624
Abrasion Resistance (mg, maximum)	<350	337.2	140.3	147.0	146.9	DIN 42516 ASTM D-1044
Flex Resistance (%, 30,000 cycles)	<200*	0	0	n/a	n/a	DIN 53543 ASTM D-1052

* Only applicable for flexible shoesoles

Tests protocols for all tests are on file.

Please note that formulation R-099 is rigid integral skin foam and the outcome support previous conclusions for this application. An important aspect of ISF foams in general is a smooth, pinhole-free surface. Methyl formate performed very well on this.

Conclusion: *MF perform equally or better compared to standards derived from HCFC-141b*

4.3.2 Rigid Insulation Foams

Test samples were prepared and tests were performed by FSI based on formulations prepared by, and chemicals from Purcom. This procedure was selected because Purcom did not have test facilities to perform full testing for these applications and no independent test facilities could be sourced in Brazil. On the other side, sending foam samples abroad compromised the samples so that local foaming was required. Test results were as follows:

4.3.2.1 Domestic Appliances

As part of an assessment of HCFC replacement technologies, Mabe, an international manufacturer of domestic refrigerators tested in its corporate technology center in Queretaro/Mexico a fully formulated, MF-based system from Purcom for domestic refrigeration insulation. A Lanzen panel ("Brett Mold") was used for these trials along with a Cannon high-pressure dispenser. Several samples were injected with minimal fills and over-packs of 10, 15 and 20%. A square mold was used in order to prepare test specimens for K-Factor, Compression and Dimensional Stability testing. Results were as follows:

Processing showed a slow reaction profile was compared with the current system. This would result in a dramatic cycle time extension on both cabinets and doors.

Free Density was recorded at 21 kg/m^3, which is a low density for Queretaro´s altitude, a 24 kg/m^3 is recommended.

Minimal Filling Density (MFD) was recorded at 33 kg/m^3 which is relatively high. Recommended MFD for domestic refrigeration is in the range of 27-28 kg/m^3. A low flow was observed, which predicts bad filling in narrow areas or complex geometries such as liners ribs, fridge mullion, etc.
Density Profile was calculated from an over-packed specimen which was 36 kg/m^3 at average but some sections shown densities as low as 28 kg/m^3. The average density/cut density ratio for this measurement must be in the range of 90-95%. In this case we found a ratio of 28/36x100 = **77%**.
When this parameter is below 90%, more PU is needed to achieve the minimal density which should be in the range of 30-31 kg/m^3. Purcom recommends a density of >35 kg/m^3 in order to get optimal results of this system, but this density could not be reached at this altitude because it would require over-pack exceeding 30%, which is too high and unsafe.

The K-Factor observed (0.18 BTU-in/ft^2.ºF.hr) was too high for time zero recording. Current values are around 0.135 BTU-in/ft^2.ºF.hr. This means a 33% difference and a potential increase in energy consumption of roughly 15%, which is detrimental for energy consumption standards.

Compression Set and Dimensional Stability were suitable and within specifications.

It was concluded that the system would need extensive optimization to meet the requirements of domestic appliance manufacturers in general and Mabe's relatively high altitude requirements specifically.
FSI as well as Purcom claim that through such optimization much better results can be obtained and, at a minimum, insulation and densities matching cyclopentane can be obtained. However, the aim of this assessment is comparison with HCFC-141b and the prevailing density for this application is 32 kg/m^3, which cannot be reached by MF at the current level of technology. It was decided therefore that continuing optimization of formulations for this sub-sector would serve no purpose for the MLF at this

point. FSI and Purcom may pursue this directly for their own benefit. Mabe's information is part of the testimonies.

Conclusion: *MF fully formulated systems in domestic appliances did not perform well. They showed higher densities and much lower insulation performance compared to HCFC-141b systems*

4.3.2.2 Other Appliances

The same system as used at Mabe was tested at Metalfrio/Celaya, Mexico and produced acceptable results for commercial refrigeration (bottle coolers) with densities around 36 kg/m^3 and improved k-factors. Metalfrio's baseline formulation, however, was water-based foam and therefore do not fit the assessment criteria.

Following tests were conducted on a generic fully formulated commercial refrigeration system and have significance for all other appliance foams:

Table 11

TESTS	UNITS	HCFC-141b UNDP-A*	HCFC-141b UNDP-B*	MF UNDP-C*	MF UNDP-D*
Closed Cell	%	98.20%	97.08%	98.76%	97.68%
Density,	pcf	1.72	1.67	1.69	2.10
Density, Cold Age, -80°F (-62.2°C)	pcf	1.72	2.08	1.88	2.00
Dimensional Stability 1-Day	Δ V, %	-21.99	-3.35	-0.62	-0.14
	Δ M, %	-2.08	0.27	0.52	0.94
Dimensional Stability 7-Day	Δ V, %	-22.60	-4.35	-1.12	-0.21
	Δ M, %	-2.56	-0.23	0.52	0.28
Density, Heat Age, 200°F (93.3°C)	pcf	1.69	2.03	1.91	1.99
Dimensional Stability 1-Day	Δ V, %	0.08	12.49	-6.43	-1.35
	Δ M, %	-1.03	-0.71	-1.51	-1.45
Dimensional Stability 7-Day	Δ V, %	2.86	2.62	-5.26	-1.20
	Δ M, %	-0.37	-0.04	-0.75	-0.98
Density, Humid Age, 158°F, 100% RH (70°C)	pcf	1.72	2.07	1.91	2.01
Dimensional Stability 1-Day	Δ V, %	7.50	5.75	-5.24	-2.73
	Δ M, %	0.99	0.94	-0.07	0.35
Dimensional Stability 7-Day	Δ V, %	8.18	6.23	-8.91	-2.61
	Δ M, %	4.10	1.45	3.55	7.09
Density, Compression, Parallel	pcf	1.71	2.10	1.95	2.02
	CS, psi	20.61	25.50	27.36	23.00
Density, Compression, Perpendicular	pcf	1.70	2.07	1.88	2.00
	CS, psi	12.12	18.29	13.81	20.30

TESTS	UNITS	HCFC-141b UNDP-A*	HCFC-141b UNDP-B*	MF UNDP-C*	MF UNDP-D*
Thermal Conductivity at 55°F midpoint Blowing Agent λ	mW/m-°K	10	10	10.7	10.7
k-factor	BTU-in/ft2-hr-°F	0.138	0.140	0.145	0.145
λ value	mW/m-°K	19.9	20.1	20.9	20.9

* refers to different foam sample batches

Test results are reported in the imperial system which is customary in the US. As the purpose of the tests is comparison, no conversion has been performed.

A more accurate thermal efficiency evaluation would be using products in side-by-side (reverse heat flow) testing). **Attachment–V** describes the outcome and conditions of such a test for a refrigerator and a freezer. With only 0.75 ^{0}C lower temperature increase compared with HCFC-141b, the results are better than expected from the difference in the λ factor of the blowing agents and appear to indicate that MF performs better in a laminated product than in a non-laminated sample.

Also important would be to assess long term performance of the foam. An evaluation of physical properties over an extended period of time is provided in **Attachment-VI**. The outcome shows that MF-based foams perform well over time with minimal degradation of foam properties.

4.3.2.2.1 Water heaters

While a sub-application for other appliance foams, the density of water heater foams are generally lower and over-pack is less.

Following results were measured with a Purcom system, foamed and tested at FSI:

Table 12

PHYSICAL PROPERTIES		TEST METHOD	UNITS	HCFC-141b SYSTEM	MF SYSTEM
Density	Core	D-1622	Pcf	2.07	2.12
Closed Cell Content		In-house	%	98.20	98.76
Perpendicular Compression	Density	D-1621	Pcf	2.23	2.35
	Strength	D-1621	Psi	29.40	29.57
Cold age	Density	D-1622	Pcf	2.23	2.32
	ΔV	D-6226	%	0.67	-0.57
	ΔM	D1622	%	-1.05	-0.79
Heat Age	Density	D-1622	Pcf	2.25	2.32
	ΔV	D-6226	%	1.35	-0.65
	ΔM	D1622	%	-1.10	-1.98
Humid Age	Density	D-1622	Pcf	2.20	2.29
	ΔV	D-6226	%	6.04	-8.84
	ΔM	D1622	%	1.69	-0.23

PHYSICAL PROPERTIES		TEST METHOD	UNITS	HCFC-141b SYSTEM	MF SYSTEM
Thermal Conductivity @ 55°F Midpoint	λ		mW/m-hr-°K	22.4	24.6
	K-factor	C-518	BTU-in/hr-ft^{-}F	0.155	0.171

4.3.2.2.2 Thermoware

This is also a sub-application of other appliance foams (FTOC classification) but with even lower densities than water heaters and less over-pack. Insulation values are also less critical and a more dimensional flexibility allows mitigation through design changes.

Following results were measured with a Purcom system, foamed and tested at FSI:

Table 13

PHYSICAL PROPERTIES		TEST METHOD	UNITS	HCFC-141b SYSTEM	MF SYSTEM
Density	Core	D-1622	Pcf	1.56	1.66
Closed Cell Content		In-house	%	97.08	97.68
Perpendicular Compression	Density	D-1621	Pcf	1.54	1.66
	Strength	D-1621	Psi	18.41	18.08
Cold age	Density	D-1622	Pcf	1.65	1,87
	ΔV	D-6226	%	1.34	-1.47
	ΔM	D1622	%	-0,50	-1.11
Heat Age	Density	D-1622	Pcf	1.67	1.95
	ΔV	D-6226	%	1.34	-1.47
	ΔM	D1622	%	-0,87	-2.04
Humid Age	Density	D-1622	Pcf	1.62	1.94
	ΔV	D-6226	%	5.32	-12.03
	ΔM	D1622	%	1.63	4.82
Thermal Conductivity @ 55°F Midpoint	λ		mW/m-hr-°K	20.8	24.0
	K-factor	C-518	BTU-in/hr-ft^{-}F	0.144	0.155

Conclusion: *The test results on essential properties with MF fully formulated systems in "Other Appliances" were within an acceptable margin from the ones with HCFC-141b*

4.3.2.3 Panels/Blocks/Transportation

Back to back commercial production of panels with HCFC-141b and with MF has been witnessed at Coldair in Curitiba/Brazil[3] with no difference in appearance and density except a significantly improved metal/foam adhesion. A visit of the company was included in the referenced workshop program in March 2010. Densities in these applications are typically 38-41 kg/m^3—sometimes higher. Following are the results of comparative testing of a formulation from Purcom, foamed and tested at FSI for this kind of application:

[3] **ColdAir** Indústria e Comércio de Sistemas de Refrigeração Estrada da Graciosa, 5823, Curitiba - PR, 83412-460, Brazil. (0xx)41 3675-9545.The company can also be contacted through Purcom

Table 14

PHYSICAL PROPERTIES		TEST METHOD	UNITS	HCFC-141b SYSTEM	MF SYSTEM
Density	Core	D-1622	Pcf	1.88	1.96
Closed Cell Content		In-house	%	98.20	98.76
Perpendicular Compression	Density	D-1621	Pcf	1.78	2.03
	Strength	D-1621	Psi	20.54	26.72
Cold age	Density	D-1622	Pcf	1.82	2.08
	ΔV	D-6226	%	-2.44	0.37
	ΔM	D1622	%	-1.75	-1.08
Heat Age	Density	D-1622	Pcf	1.83	2.14
	ΔV	D-6226	%	1.40	0.10
	ΔM	D1622	%	-1.23	-1.02
Humid Age	Density	D-1622	Pcf	1.82	2.10
	ΔV	D-6226	%	6.15	3.96
	ΔM	D1622	%	0.12	0.11
Thermal Conductivity @ 55ºF Midpoint	ʎ		mW/m-hr-ºK	20.2	26.8
	K-factor	C-518	BTU-in/hr-ft-F	01.40	0.151

Conclusion: *The testified use of MF in current commercial production of rigid foam for panels/blocks/transportation applications indicates that there are no specific issues with MF as compared to HCFC-141b and product tests back this up.*

4.3.2.4 Spray foam

Purcom's HCFC-141b-based sprayfoam systems did not perform well in stability. The systems were based on locally produced Mannich (polyether) polyols only, while most sprayfoam systems include in addition a mix of aromatic amine and polyester polyols. The system was converted to MF, optimized with the mentioned different polyols and then shipped to the USA for foaming and testing**.** The results are as follows:

Table 15

PHYSICAL PROPERTIES		TEST METHOD	UNITS	HCFC-141b SYSTEM	MF SYSTEM
Density	Core	D-1622	Pcf	1.90	1.94
Closed Cell Content		In-house	%	97.08	97.68
Perpendicular Compression	Density	D-1621	Pcf	2.66	1.86
	Strength	D-1621	Psi	14.88	27.92
Cold age	Density	D-1622	Pcf	1.94	3.00
	ΔV	D-6226	%	-0.48	-0.90
	ΔM	D1622	%	0.00	0.37
Heat Age	Density	D-1622	Pcf	1.84	3.07
	ΔV	D-6226	%	-2.04	-7.84
	ΔM	D1622	%	-7.84	-0.61
Humid Age	Density	D-1622	Pcf	1.91	2.84
	ΔV	D-6226	%	-1.53	-2.89

PHYSICAL PROPERTIES		TEST METHOD	UNITS	HCFC-141b SYSTEM	MF SYSTEM
	ΔM	D1622	%	10.37	9.89
Thermal Conductivity @ 55^{o}F Midpoint	λ		mW/m-hr-^{o}K	19.9	24.5
	K-factor	C-518	BTU-in/hr-ft^{-}F	0.138	0.170

All physical properties compare well except the thermal conductivity. It has to be kept in mind, however, that this is a completely new system for Purcom and some further optimization will be needed.
FSI sells MF sprayfoam systems in the US market along with HFC-134a-based sprayfoam systems. These compare as follows:

Table 16

PHYSICAL PROPERTIES		ASTM TEST METHOD	UNITS	ECOMATE SYSTEM	HFC-134a SYSTEM
Density	Free Rise		Pcf	1.9-2.1	1.9-2.1
	Core	D-1622	Pcf	2	2
Compressive Strength	Perpendicular	D-1621	Psi	24	20
Water Absorption	Weight	D-2127	lbs/ft^2	0.01	0.02
	Volume	D-6226	%	>92	>92
Thermal Efficiency	Initial K factor	C-518	BTU-in/hr-ft^{-}F	0.14-0.16	0.15-0.16
	BA λ		mW/m.k	10.7	14
Dimensial Stability	Wet	D-2126	% Vol change	<1	-1
	Dry		% Vol change	n/d	n/d
	Cold		% Vol change	0	0
Fire Resistance		UL94 HF1		Yes	Yes

Conclusion: *The mechanical properties of MF-based spray foams are equivalent to commercial HCFC-141b systems or better but the thermal efficiency needs further optimization*

4.4 Additional information from companies which are MF users

UNDP solicited and received views/information from companies where MF has been trialed. In addition, system houses that sell ecomate® systems were asked to collect the same from companies that currently use MF systems in their commercial operations.

Following table shows the answers received (actual letters are on file):

Table 17

Foam Type	Application	Company	Country	Acceptability Assessment
Flexible and Integral Skin Foams	Hyper-soft molded	Kumar	Brazil	+
	Hyper-soft blocks	Aumar	Brazil	+
	Viscoelastic molded	Aumar	Brazil	+
	Viscoelastic blocks	Tropical	Brazil	+
	Steering wheels	Takata Petri	Brazil	+
	Structural (rigid)	Injefox Poliuretane	Brazil Brazil	+ +
	Semi-flexible	Injefox Rallyspeed	Brazil Australia	+ +
Rigid Foams	Domestic refrigeration	Mabe	Mexico	-
	Commercial refrigeration	Gelopar Zero Chill Flow Fabristeel Perlick H&K Dallas Cooke	Brazil South Africa Australia China USA USA New Zealand	+ + + + + + +
	Water heaters	Prosol	Brazil	+
	Transportation, Reefers	Termosul	Brazil	+
	Panels continuous	Paneltech	Australia	+
	Panels-discontinuous	Danica	Brazil	+
	Spray	Somma Isar Global Polyair	Brazil Brazil Australia Australia	+ + + +
	Blocks	Coldair	Brazil	+
	Thermoware	Plastitalia Evakool	Brazil Australia	+ +
	Pipe-in-pipe	Somma	Brazil	+
	Buoyancies	Sealite	Australia	+

+ Acceptable, - unacceptable; +/- acceptable with conditions

Some of the customers purchase MF-based systems already 3-5 years.

4.5 Conversion Costs

UNDP has developed a generally applicable cost template to calculate incremental cost of conversion from HCFC-141b to MF-based foams. It should be pointed out that capital and chemical cost can differ significantly from country to country and are also subject to economy of scale considerations.

4.5.1 Incremental Capital Costs

Table 18

ENTITY	ACTION	CALCULATION	COSTS (US$)
System House	Explosion proofing of blending tanks	AA x 30,000	
System House	Nitrogen dispenser	BB x 8,000	
System House	Spray/PIP retrofit package	CC x 5,000	
System House	LPD retrofit package	DD x 10,000	
System House	Pycnometer (closed cell tester)	1 x 5,000	
System House	Portable K-factor tester	1 x 10,000	
System House	Refractometer (test chemical purity)	1 x 10,000	
System House	Small rent-out dispenser	EE x 10,000	
System House	Project Management	FF customers @ 1,000	
System House	Monitoring & technology transfer		
System House	Contingencies	10% capital costs	
System house	**Sub-Total**		
Customers	Spray/PIP retrofit packages	GG x 5,000	
Customers	LPD/HPD retrofit package	HH x 10,000	
Customers	New Dispensers	II x 20,000	
Customers	Trials, testing, training,	KK customers @ 3,000	
Customers	Contingencies	10% of 202,000	
Customers	**Sub-Total**		
		GRAND TOTAL	
		C/E (US$/kg/ODS)	

4.5.2 Incremental Operating Costs

Following is an example of an incremental cost template for IOCs. Prices are for illustration only. Four system houses/experts were asked to convert a given HCFC-based formulation to MF. The results are quite similar. The last two formulations leave the chemical ration the same, which is required for sprayfoams.

Table 19

CHEMICAL	PRICE (US$/kg)	BASELINE		Company A		Company B		Company C		Company D	
		%	Cost	%	Cost	%	Cost	%	Cost	%	Cost
Polyol	3.20	38	1.22	40	1.28	40.6	1.30	42.5	1.36	44	1.41
Isocyanate	3,00	50	1.50	53	1.59	53.4	1.60	50	1.50	50	1.50
HCFC-141b	2.40	12	0.29	--	--	--	--	--	--	--	--
MF	4.00	--	--	7	0.28	6	0.24	7.5	0.30	6	0.24
Cost			3.01		3.15		3.14		3.16		3.15
Difference			**Base**		**0.14**		**0.13**		**0.15**		**0.14**

4.6 System Details

With proprietary technology involved, formulation disclosure is a complex issue. While UNDP has been involved with and has financially supported adjustments of MF-containing formulations for applications that were not already commercial and/or optimizing such formulations in an A5 context, it has not ventured into the underlying technology partly due to intellectual property issues.

Following general rules apply when changing from HCFC-141b to MF as auxiliary blowing agent (ABA):

- Equimolar replacement would require 1 kg HCFC-141b to be replaced by 0.51 kg MF;
- Because of the strong solvent effect of MF, this ration can change at lower MF loads;
- However, the objective to keep the system non flammable, limits the maximum amount of MF to 8 php; equivalent to 16 php HCFC-141b. Increased water levels make up for additional blowing;
- In practice, 1 kg HCFC-141b can be replaced by anywhere from 0.35 kg (spray foam) to 1kg (high-density ISF);
- An MF system has to be stabilized to work well, with minimal hydrolysis and related corrosion and potential silicon/catalyst attack. This stabilization is proprietary technology.

To support MLF recipients, UNDP has arranged with FSI and its licensees that any interested (potential) MLF recipient will be offered, on request:

- Product Information Sheets (PIS) for specific applications;
- Samples and use instructions subject to signature of a non-disclosure/non-analysis agreement;
- A non-exclusive use (sub-) license.

5. Conclusions

Based on the information presented in this Report it is concluded that:

5.1 Health, Safety, Environment

- The use of MF does not create health concerns up and above those with HCFC-141b. Both substances have flammable limits but in fully formulated systems will not reach these even remotely under process conditions;
- Flammability of MF is an inherent safety risk. However, this risk is sharply mitigated—even virtually eliminated—at downstream user level when using fully formulated systems;
- MF-based systems do not pose an environmental hazard based on current knowledge/regulations;
- MF-based systems are approved by the US EPA for use in **all** foam applications (SNAP approval).

5.2 System Processability

- Special considerations are required for the shipment and storage of pure MF.
- No special considerations are required for fully formulated systems with less than 6% MF (polyols) or less than 2% MF (MDI) following USDOT regulations. Local regulations have to be consulted.
- MF-blended polyol systems for all applications except for integral skin foams are stable. MF-blended isocyanate systems are always stable. UNDP does not support blending in isocyanate and proposes instead separate injection through a third stream as developed by Zadro for shoesoles;
- Although there is no conclusive evidence of corrosive effects, it is recommended that components that come in contact with MF or MF blends should be corrosion resistant;
- There are no identified compatibility issues of MF with polyols and/or additives. However, it is recommended that when designing conversion projects, the compatibility of baseline polyols will be carefully checked and any required changes to polyols and related costs should be identified.

5.3 Foam Properties

- MF based hypersoft foams match HCFC-141b foams;
- MF based viscoelastic foams match HCFC-141b foams;
- MF based flexible/semi-/rigid/rigid ISF foams match HCFC-141b within an acceptable range;
- MF-based shoesole systems match or exceed HCFC-141b foams;
- MF based rigid foams for other appliances match HCFC-141b foams within an acceptable range;
- MF based spray foams match HCFC-141b systems within an acceptable range and outperform HCFC-134a and HCFC-22-based systems;
- MF based rigid foams for discontinuous panels and transportation match HCFC-141b foams within an acceptable range;
- Product and long-term performance (reversed heat flow and 5 year performance) is acceptable.

It is concluded from customer testing that:

- MF based foams for steering wheels match HCFC-141b foams within an acceptable range;
- MF based foams for domestic refrigerators and freezers do not sufficiently match HCFC-141b foams based on density and insulation.

Information provided by companies that are MF users indicates that:

Integral Skin:

- One company that supplies products to international car manufacturers informed that MF based rigid integral skin foams match HCFC-141b foams within an acceptable range. Other companies that manufacture steering wheels use standard ISF systems
  MF based foams for buoyancies match HCFC-141b foams within an acceptable range
- One company that produces continuous panels informed that it uses MF without any problem and that MF based foams match HCFC-141b foams within an acceptable range

5.4 Conversion Costs

UNDP has developed a cost template to calculate the incremental cost of conversion from HCFC-141b- to MF-based foams. It should be pointed out, however, that capital and operating (chemical) costs can differ significantly from country to country and that these are also subject to economy of scale operations and location of the supplier.

5.5 Overall Assessment

Following is a consolidated overview of the findings of this report:

Table 20

Foam Type	Application	Assessment			
		HSE	Processability	Physical Properties	Results
Flexible and Integral Skin Foams	Hyper-soft molded	+	+	+	+
	Hyper-soft blocks	+	+	+	+
	Viscoelastic molded	+	+	+	+
	Viscoelastic blocks	+	+	+	+
	Steering wheels	+	+*	+	+
	Structural (rigid)	+	+*	+	+
	Semi-flexible	+	+	+	+
	Shoesoles	+	+*	+	+
Rigid Foams	Residential Appliances	+	-	-	-
	Other Appliances	+	+	+/-	+/-
	Panels, Transportation, Reefers	+	+	+	+
	Spray	+	+	+	+
	Blocks	+	+*	+	+
	Pipe-in-pipe	+	+	+	+
	Buoyancies	+	+	+	+

* = separate injection of MF recommended
+ Acceptable, - unacceptable; +/- acceptable with conditions

Based on this assessment, UNDP believes that the use of Methyl Formate as an alternative blowing agent to replace HCFC-141b in PU foam applications in MLF projects would have to be subject to the following conditions:

1. Projects should preferably be implemented through local system houses to minimize safety risks at downstream users ;
2. Project designers should ensure that:
    a. Chemical compatibility is verified,
    b Minimum density is observed,
    c. Health, safety and environmental recommendations are incorporated,
    d. Implications related to the flammable and corrosive character of the substance are addressed,
    e. A compliance monitoring proposal is included.
    f. Local availability and costs of polyols and other elements should be considered to determine operational costs.

Attachments

1. ATTACHMENT Ia: METHYL FORMATE ASSESSMENT: RESPONSE TO PEER REVIEW
2. ATTACHMENT Ib: PEER REVIEW ON THE ASSESSMENT OF METHYL FORMATE AS A POLYURETHANE FOAM BLOWING AGENT WITH COMMENTS
3. ATTACHMENT II: METHYL FORMATE - MATERIAL SAFETY DATA SHEET
4. ATTACHMENT III: METHYL FORMATE EMISSIONS
5. ATTACHMENT IV: COMBUSTIBILITY OF METHYL FORMATE
6. ATTACHMENT V: REVERSE HEAT FLOW STUDY
7. ATTACHMENT VI: LONG TERM PERFORMANCE

ATTACHMENT Ia: METHYL FORMATE ASSESSMENT: RESPONSE TO PEER REVIEW

Decision 55/43 requires Agencies to inform the ExCom on pilot projects through *"a progress report after each of the two implementation phases…".* UNDP suggested **in addition,** the following alternative supervision arrangements:

1. By the Secretariat through an independent, qualified foam expert.
2. ExCom to consider requesting Parties to have the supervision of the validation through the UNEP Foams Technical Options Committee (FTOC).

UNDP felt that such a peer review, which could be extended to a preview of intended individual validation programs and preview/endorsement before transferring to Phase-II sub-projects, would increase project quality and general acceptability. However, the FTOC felt that its participation in such a review process would fall outside its mandate and declared itself unable to provide a formal opinion on the report. UNDP then resorted to the usual peer review process for proposed ODS phaseout projects and requested a review by Dr. Mike Jeffs, formerly employed by Huntsman, former Secretary General of ISOPA and standing member of the FTOC. The full review is shown below, with comments provided on UNDP's request by Mr. Bert Veenendaal, UNDP Senior Expert Foams (in "review' mode).

A first draft of this assessment was completed and presented to the FTOC May 18 as part of the FTOC's general technology review process. Comments and suggestions from individual FTOC members were taken into account in a new draft dated June 1, 2010 which was forwarded to the peer reviewer June 3. Present version of the report addresses the comments provided by the independent technical report (Attachment Ib). Below is a summary of UNDP answers to some of the points in the review. The reviewer mentions following required characteristics for a foam blowing agent with the following characteristics:

1. *An established use base, preferably over some years, such that its use can be stated as "well proven" in all the target applications*
2. *Very low GWP and hence no environmental pressures to curtail its use; also the toxicology should not require any special measures to protect personnel in the manufacturing areas*
3. *Economical to use in terms of both the costs per kg of foam made and the safety (flammability) engineering requirements*
4. *Safe to use without the precautions required for pentane and safe to use in the application of spray foams*
5. *Suitable for a broad range of applications in terms of the various aspects of processability*

UNDP does not necessarily disagree with these required characteristics but would like to point out that in the case of methyl formate there was in 2007 no established use base in A2 countries and exactly for that reason it was deemed necessary to prepare an assessment for a substance that, at least from available literature, promised to fit all other requirements mentioned by the reviewer. UNDP does remark in its report on the—rather dramatic—increase of the use of methyl formate after that date, but just to indicate a trend that started after the decision for an assessment was made. For the same reason, testimonies for each application have been collected from companies that use MF in their commercial operations. If there would have been an established use base in A2 countries at the time of project preparation, no assessment would have been needed.

All other requirements have been addressed albeit in another format, i.c.:

- Health, Safety, Environment (HSE)
- System Processability
- Physical Properties
- Conversion Costs

Health, Safety, Environment – while health and environment related data are accepted by the reviewer, a desire for more emission testing is voiced. In response, UNDP has commissioned two additional industrial hygiene

studies (one in Brazil and one in South Africa) that will be submitted separately to the ExCom. However, UNDP does not really see the need, as the studies incorporated in the assessment show consistently a very large safety margin in operator exposure as well compared to the flammability potential under operation conditions (<0.2% of the LFL. It can indeed be stated that it has been impossible in trials to create conditions in which the lower flammable limit could even be approached. In view of flammability risk MF gases are comparable with HCFC-141b. UNDP is, however, not adverse to the idea of a post-implementation HSE review by a qualified person and has already sourced affordable equipment for that purpose (~ US$ 2,000 per monitor). There are also monitoring badges available from at least two suppliers and these may also be considered.

System Processability – reviewer correctly voices exposure concerns when remarking on the stability of polyol blends for integral skin foams and the proposed solution (by Purcom) to blend MF in the isocyanate. UNDP mentions in its report (section 5.5: Overall Validation) that *"based on the need to blend MF with the isocyanate this is not recommended from an HSE point of view"*. However, in the mean time, as part of the evaluation of MF in shoesole applications, an alternative procedure has been developed that avoids the need of blending in isocyanate.

Physical Properties – The reviewer states his preference to test from machine samples rather than from laboratory ones. This opinion is generally shared but for integral skin, which features commonly metal inserts and relatively small, complicated shaped parts, this is not always possible and praxis has shown good correlation between hand-mix and machine samples in physical properties. Apart from ISF/FMF applications, all samples originate from machine-made foams which is essential of insulation and shoesole applications. The mentioned lack of information on rigid ISF foams is recognized and remediated in the final assessment. The observation that insufficient testing on rigid foams is conducted is related to the fact that the reviewer based his report on an outdated version of the assessment. The newer version UNDP sent well before the peer review report includes complete test results for all applications.

Conversion Costs – This section is misunderstood. MF containing systems can be handled without specific safety precautions related to flammability or explosion risk. This is not the case for system houses but one system house supplies at average 30 customers. In other words, safety related costs are reduced to 1/30 of those of hydrocarbon projects. The cost threshold in Mexican projects pending approval (less than US$ 5.00/kg ODS) shows this impressively. Actual operating costs differ greatly per country. To facilitate fair comparison, UNDP has developed a cost template that offers standardization in costing approaches. The template is included in the final report.

Editorial Comments – UNDP agrees with the suggestions but wants to point out that most of these were already implemented in the June version of the assessment.

Conclusions – the reviewer observes that global polyurethane system houses have not taken a lead in optimizing MF technology. This is indeed the case and is the very reason that the MLF needed to take the lead on this or forgo a technology that shows potential in cost containment as well in foam properties. Recently though, changes in attitude are becoming apparent and two of these global players have now signed evaluation agreements for MF. Also, the explosive growth in the use of MF—albeit still a minor technology compared with HCFCs or HCFs—shows growing acceptance.

In all this, the limited scope of this assessment should be emphasized. The MLF does not want project failures and wants to make sure that recipients know the pros and cons of a technology that is as of yet not, or not well, known in most A5 countries. The aim is not to conduct or fund research and development. UNDP feels that this assessment provides a clear picture of the potential of methyl; formate to replace HCFC-141b and will avoid adverse surprises during project implementation—as has been, for instance, the case with LCD technology.

ATTACHMENT Ib: PEER REVIEW ON THE ASSESSMENT OF METHYL FORMATE AS A POLYURETHANE FOAM BLOWING AGENT WITH COMMENTS

Dr Mike Jeffs
14/07/2010

1. INTRODUCTORY COMMENTS

Several novel blowing agent technologies have been introduced since the beginning of the MLF process and most have played significant roles in ODS replacement in both A2 and A5 countries. In general, most of these technologies were developed by the major polyurethane formulation suppliers, who operate in both A2 and A5 countries. In many cases they worked with fluorocarbon or hydrocarbon suppliers. This approach has been very successful and a full palette of technologies has been successfully delivered. Additional technological refinements have often been developed by smaller system houses for niche applications in both A2 and A5 countries. A key-blowing agent has been HCFC-141b, which is well proven, and in large-scale use for polyurethane insulation foams plus integral skin foams for shoe soles and automotive/furniture applications.

However, the acceleration of the phase-down of HCFC-141b availability under Decision XIX/6 has emphasized the critical role that this blowing agent has carried out. It has been economical to use, flammability precautions are minor and inexpensive and the physical properties of foams based on it, particularly insulation values, closely match those of CFC-11, which it replaced. It should be remembered that, when first introduced in the early 1990s, HCFC-141b-based foams had major dimensional instability problems leading to large insurance payouts (for shrunken roofs).

Hydrocarbon (pentane)-based foam technologies were introduced at the same time as HCFC-141b and have been very successful but are only economical to apply at medium to large blowing agent-consuming enterprises and, so far, have been considered to be unsafe to use for the important spray foam application.

The later HFCs, such as HFC-245fa and HFC-365mfc, have been successfully introduced in several applications but their in-use costs (operating costs) are much (30 to 100%) higher than for HCFC-141b. Additionally, because of their comparatively high GWPs, their use may be controlled by legislation in both A2 and A5 countries.

Thus, Decision XIX/6 forces on the foam industry the very urgent requirement for a blowing agent with the following characteristics:

6. An established use base, preferably over some years, such that its use can be stated as “well proven” in all the target applications
7. Very low GWP and hence no environmental pressures to curtail its use; also the toxicology should not require any special measures to protect personnel in the manufacturing areas
8. Economical to use in terms of both the costs per kg of foam made and the safety (flammability) engineering requirements
9. Safe to use without the precautions required for pentane and safe to use in the application of spray foams
10. Suitable for a broad range of applications in terms of the various aspects of processability
11. Suitable for a broad range of applications in terms of foam physical properties including dimensional stability and insulation values (for insulating foams)

This report has been commissioned by the UNDP and funded by the MLF to ascertain whether or not technology based on Methyl Formate (MF) meets these criteria. The technology owner is Foam Supplies, Inc (FSI) which sells and licenses MF technology as ecomate®

2. KEY COMMENTS

The report reviewed is dated 25/05/2010 and includes an Attachment (Appendix) on a study of Reverse Heat-Flow. Additional information from FSI on 5-year ageing of foam articles and on “Safe Handling Recommendations for ecomate® spray foam systems” has also been taken into consideration by the reviewer ***(see comment under Editorial Comments).***

In addressing the six criteria listed at the end of Section 1 the following can be stated:

1. The total usage of MF for foam blowing has built up over 5 years and 365 tons were used in 2009. In considering that up to 16 separate applications targeted this usage of MF in 2009 the usage is just less than 23 tons per application. ***There may be some applications where there has been above average usage, which could bring use experience in that application up to the cusp of the “well proven” status. If this is the case there is no relevant information in the report for such a judgment to be made.***

   Another consideration is with regard to the experience cited by various enterprises in their testimonies (Section 4.4). A total of 30 enterprises have submitted these testimonies and their average usage of MF must have been only about 12 tons per user. ***This cannot be interpreted as sufficient use to be characterised as “well proven”.*** It is also noted that the evaluation in shoe soling application will be evaluated in an additional programme to take place in Mexico.

   In determining the relevance of the reported use of MF it would be illuminating to identify those applications where usage per enterprise exceeded, for example 50 tons in 2009. It would also be very useful to cite the use per sub-sector.

2. It is clear that the GWP of MF is very low and there should not be any environmental/climate issue with this. In addition, there is no evidence of any other environmental issue.

   The toxicology data do not raise significant concerns but it should be noted that all training activities are opportunities to remind staff that there should be no exposure to diisocyanates (MDI or TDI). It is the reviewer’s understanding that MF will be registered for the European Union’s REACH Regulation by BASF (due by 11/2010) and that this registration will include the application of foam blowing. The data in this registration submission should be incorporated in revisions of the MSDS. The rather limited industrial hygiene data (only two applications) show emissions are below OSHA limits.

3. The costs per kg of foam made are understood to be broadly similar to those for HCFC-141b. However, most usage of MF-based technologies is expected to be by small to medium-sized foam manufacturers who buy pre-blended formulations from system houses. It is clear that the equipment and procedures required for the safe preparation of formulations are similar to those for pentane. The capital costs associated with the storage and pre-blending operations for pentane are about 50% of the overall costs for a complete foaming plant. Presumably, the MLF will meet these very significant capital costs.

4. In considering the question of safety in foaming operations there are several factors to consider – see table for the main combustibility parameters for MF.

   The data indicate that MF’s combustibility performance is in-between those of HCFC-141b and pentane. Whilst this is not a precise scientific statement it indicates that concern is considerably higher than for HCFC-141b. The report contains data on airborne concentrations of MF in two processing/applications. ***As an intermediate measure it is advisable to measure concentrations of MF for each foaming operation to ascertain proximity or otherwise to the LEL.***

	Methyl Formate	HCFC-141b	Cyclopentane
Flash Point C	-19°C	None	-49°C
Flame Limits (v%)			
Lower (LEL)	4	7.6	1.5
Upper (UEL)	23	17.7	7.8
Auto Ignition Temperature	449	550	260
DOT Shipping Classification	Class III Flammable	Not regulated	Class III Flammable

The reviewer has more concern with respect to spray foam operations, particularly in confined situations. The FSI document "Safe Handling Recommendations for ecomate® spray foam systems" referred to above gives guidance and a clear set of recommendations should be developed for each (processing) application and, especially, for spray foaming. These recommendations should include a requirement, until a further review, for MLF projects to include the measurement of concentrations and the provision for detectors and enhanced ventilation.

See also comments on the combustibility of foams in section VI below.

5. The report contains information on shipping and storage, stability, hydrolysis/ corrosion and compatibility with polyols. One issue raised is the stability in integral skin formulations and the apparent solution of blending in the diisocyanate (typically MDI) stream rather than in the polyol. This should be approached with care because of the hazards of handling diisocyanates. It is also mentioned that this stability issue may be associated with the limited range of polyols available to Purcom.

   In the discussion on hydrolysis and corrosion it is noted that equipment and components should be preferably corrosion resistant. This conservative approach is supported.

   As stated in the report, questions of polyol compatibility arise whenever a chemical component is changed in formulations. Purcom has been active in this area, including on spray foam systems in collaboration with UNDP. Unfortunately, circumstances prevented the evaluation of the foams resulting from this process. The recommendation that potential users optimise their formulations around MF is, of course, fully supported.

6. Foam property information is provided for 10 applications using either flexible or rigid products. The latter include several insulation foam applications. The test sample preparation methods are given in Attachment-VI. It is noted that flexible and integral skin samples were prepared by hand mixing. ***It would be preferable and more representative of production techniques to have machine-made samples.*** Samples for rigid foams (pour and spray foams) were prepared using dispensing machines. Comments per application are as follows:

- **Hyper Soft Foams:** Purcom carried out a range of tests (ASTM and National Brazilian Standard) and results are essentially the same as for the HCFC-141b-based control.

- **Viscoelastic Foams:** Purcom carried out a range of tests (ASTM and National Brazilian Standard) and results are essentially the same as for the HCFC-141b-based control.

- **Flexible Integral Skin Foams (Including Steering Wheels):** Purcom carried out a range of tests (ASTM and DIN) on two hardness grades (ca. 35 and 44 hardness by Shore A) and results are similar to those obtained for the HCFC-141b-based control. There is no data for Steering Wheels as the testing was carried out by

the enterprise Takata-Petri who has not shared their data except to state that the MF-based material met VW requirements (Specification #?). ***The reviewer recommends that data be obtained by additional testing to verify the suitability of MF in this application***. (Note that shoe-soling testing will be carried out at a later date (in Mexico).

- Rigid Integral Skin Foams: There is no information on who performed the evaluation (Purcom?) and no data. One criterion is that the surface is free of pinholes. ***It is claimed that foams based on MF give a comparable performance to those based on HCFC-141b but further information would be helpful.***

- Rigid Insulation Foams: It is clear that the evaluation of the properties of rigid insulating foams based on MF is incomplete. This is due to limited testing facilities being available at Purcom plus the nature of test data required to verify insulating foams, which should include medium-long terms ageing tests on thermal conductivity and dimensional stability. The latter are partially covered by the additional paper on "Ecomate After Five Years" and by the Reverse Heat Leakage Tests (Attachment 4). The former has several illustrations of parts stored for 5 years. Changes in dimensions are stated to be less than 3.5% in all cases.

1. **Domestic Appliances:** Mabe carried out the testing with formulations developed by Purcom. The foam system required higher densities than those that are normal in this application, poor flow and cure time plus thermal conductivities much higher than for HCFC-141b-based foams. It is accepted that the foam system was not optimised around MF and improved results are likely as a result. Given the position achieved by cyclopentane and pentane blends it was decided not to pursue optimisation in this sub-sector.

2. **Other Appliances:** The formulations used in the previous section were tested by another enterprise (Matalfrio/Celaya) and compared to HCFC-141b-based controls. Based on the results displayed, the MF-based foams showed more shrinkage, on average, in the dimensional stability testing up to 7 days. No longer-term data is displayed. . There was also a small increase (4.5%) in initial thermal conductivity. It is noted that reverse heat leakage tests by FSI on unspecified formulations showed slightly less heat leakage for MF compared to HCFC-141b-based foamed cabinets. The data in the "Ecomate After Five years" for a drinks dispenser a slightly higher loss in insulation efficiency after 5 years compared to a HFC-134a-based control. Tests on display cabinets showed losses in insulation efficiency that were less than for the HFC-134a-based controls.

3. **Water Heaters:** A Purcom system was foamed and tested by FSI in comparison to a HCFC-141b-based control. The cold, hot and humid ageing data do not show the ageing period involved and so no comments are possible beyond the point that there is little difference in properties compared to the control. The initial thermal conductivity is about 10% higher for MF compared to HCFC-141b-based foams.

4. **Thermoware:** Again, a Purcom system was foamed and tested by FSI in comparison to an HCFC-141b-based control. The densities in this application are lower than in the previous appliance applications. However, it is noted that shrinkage is higher than for the controls, particularly under hot and humid conditions. Again, the test time is not specified. The initial thermal conductivity is over 7% higher for MF compared to HCFC-141b-based foams.

5. **Panels/Blocks/Transportation:** Again, a Purcom system was foamed and tested by FSI in comparison to an HCFC-141b-based control. At the higher densities in these applications here is no significant difference in dimensional stability test data shown. Again, the test time is not specified. The initial thermal conductivity is about 8% higher for MF compared to HCFC-141b-based foams. The data in the "Ecomate After Five years" for an insulated shipping container showed a small loss in insulation efficiency after 5 years. ***An additional point is the combustibility of the finished articles, particularly if they are subject to building codes/regulations in the end use such as part of a building – this is the case in many A5 countries. This information should be obtained where applicable.***

6. **Spray Foams:** It would appear that only data from FSI is included and then in comparison with a control based on HFC-134a that is generally not used in A5 countries. The data show, not altogether surprisingly, better properties for MF than for the control. ***Further testing is necessary and will be carried out with an optimised formulation to be developed by Purcom and foamed and tested by FSI. It is necessary to include controls based on HCFC-141b in this extension of the testing programme. An additional point is the combustibility of the foam in use. Spray foams are normally subject to building codes/regulations in the end use such as part of a building – this is the case in many A5 countries. This information should be obtained where applicable.***

3. EDITORIAL COMMENTS

There are a small number of editorial comments to be made. These include:

- All pages to be numbered and correlated with the Contents (page 2)
- Consideration to be given to inclusion of the additional papers from FSI on 5-year ageing of foam articles and on “Safe Handling Recommendations for ecomate® spray foam systems” into the report (as attachments?)
- There are additional style/language/grammar points which should be clear after a Word spell check.

4. CONCLUSIONS

The report and attachments are key parts of a comprehensive review of the suitability of MF for a range of applications as a replacement for HCFC-141b. The challenge is particularly sever as HCFC141b is used in a large number of A5 countries in almost all polyurethane foam applications. It must also be remembered that Decision XIX/6 imposes tight and global deadlines that were rarely encountered by “emerging” blowing agents in the past. Many of the apparent shortfalls in MF’s performance are very likely to be addressed by formulation optimisation but, in the present case, this optimisation process has not, so far, been led by the global polyurethanes systems houses – as was the case with earlier blowing agents.

However, this review highlights several points that require further data/attention. These are included in the text of this review in ***blue italic font***. They are in the following areas:

- Information on experience and MF usage per application (sub-sector)
- Combustibility safety during foam processing – need for concentration measurements and ventilation
- Combustibility of the end product/foam in some cases
- Data on spray foams and shoe soling elastomer applications
- Further and longer-term dimensional stability test data, particularly for rigid insulating foams. As a temporary measure the density of foams which are normally near 32 kg/m^3 could be increased by 2-3 kg/m^3 to safeguard dimensional stability until more experience is gained
- Similarly, longer term thermal conductivity testing using accelerated ageing methods such as the slicing method or ageing at 70°C

ATTACHMENT II: METHYL FORMATE - MATERIAL SAFETY DATA SHEET

METHYL FORMATE 0664 April 1997			
CAS No: 107-31-3 RTECS No: LQ8925000 UN No: 1243 EC No: 607-014-00-1 Formic acid methyl ester Methyl methanoate C2H4O2 / HCOOCH3 Molecular mass: 60.1			
TYPES OF HAZARD/ EXPOSURE	**ACUTE HAZARDS/SYMPTOMS**	**PREVENTION**	**FIRST AID/FIRE FIGHTING**
FIRE	Extremely flammable.	NO open flames, NO sparks, and NO smoking.	Powder, alcohol-resistant foam, water spray, carbon dioxide.
EXPLOSION	Vapor/air mixtures are explosive.	Closed system, ventilation, explosion-proof electrical equipment and lighting. Prevent build-up of electrostatic charges (e.g., by grounding). Do NOT use compressed air for filling, discharging, or handling.	In case of fire: keep drums, etc., cool by spraying with water.
EXPOSURE			
Inhalation	Cough. Dizziness. Dullness. Headache. Labored breathing. Shortness of breath. Unconsciousness.	Ventilation, local exhaust, or breathing protection.	Fresh air, rest. Artificial respiration may be needed. Refer for medical attention.
Skin	Redness.	Protective gloves.	Remove contaminated clothes. Rinse skin with plenty of water or shower. Refer for medical attention.
Eyes	Redness.	Safety goggles.	First rinse with plenty of water for several minutes (remove contact lenses if easily possible), then take to a doctor.
Ingestion	(Further see Inhalation).	Do not eat, drink, or smoke during work.	Rinse mouth. Give a slurry of activated charcoal in water to drink. Induce vomiting (ONLY IN CONSCIOUS PERSONS!). Rest. Refer for medical attention.

SPILLAGE DISPOSAL	**PACKAGING & LABELLING**
Evacuate danger area! Collect leaking liquid in sealable containers. Absorb remaining liquid in sand or inert absorbent and remove to safe place. Do NOT wash away into sewer. Personal protection: self-contained breathing apparatus.	F+ Symbol Xn Symbol R: 12-20/22-36/37 S: (2-)9-16-24-26-33 UN Hazard Class: 3 UN Pack Group: I
EMERGENCY RESPONSE	**SAFE STORAGE**
Transport Emergency Card: TEC (R)-30S1243 NFPA Code: H 2; F 4; R 0	Fireproof. Separated from strong oxidants. Cool.

Prepared in the context of cooperation between the International Programme on Chemical Safety and the European Commission © IPCS 2005 **SEE IMPORTANT INFORMATION ON THE BACK. IPCS** International Programme on Chemical Safety

0664 METHYL FORMATE	
IMPORTANT DATA	
Physical State; Appearance COLOURLESS LIQUID, WITH CHARACTERISTIC ODOUR. **Physical dangers** The vapor is heavier than air and may travel along the ground; distant ignition possible. The vapor mixes well with air, explosive mixtures are easily formed. **Chemical dangers** Reacts vigorously with oxidants. **Occupational exposure limits** TLV: 100 ppm as TWA, 150 ppm as STEL; (ACGIH 2004). MAK: 50 ppm, 120 mg/m3; Peak limitation category: II(4); skin absorption (H); Pregnancy risk group: C; (DFG 2004).	**Routes of exposure** The substance can be absorbed into the body by inhalation of its vapor and by ingestion. **Inhalation risk** A harmful contamination of the air can be reached very quickly on evaporation of this substance at 20/C. **Effects of short-term exposure** The substance is irritating to the eyes and the skin. The vapor is irritating to the eyes and the respiratory tract. The substance may cause effects on the central nervous system. Medical observation is indicated.
PHYSICAL PROPERTIES	
Boiling point: 32/C Melting point: -100/C Relative density (water = 1): 0.98 Solubility in water, g/100 ml at 20/C: 30 Vapor pressure, kPa at 20/C: 64 Relative vapor density (air = 1): 2.07 Relative density of the vapor/air-mixture at 20/C (air = 1): 1.7 Flash point: -19/C Auto-ignition temperature: 449/C Explosive limits, vol% in air: 5-23 Octanol/water partition coefficient as log Pow: -0.21	
ENVIRONMENTAL DATA	
NOTES	
The odor warning when the exposure limit value is exceeded is insufficient. Card has been partly updated in October 2004 and 2005. See sections Occupational Exposure Limits, EU classification, Emergency Response.	
ADDITIONAL INFORMATION	
LEGAL NOTICE	Neither the EC nor the IPCS nor any person acting on behalf of the EC or the IPCS is responsible for the use which might be made of this information
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ATTACHMENT III: METHYL FORMATE EMISSIONS

1. Occupational Exposure

Methyl formate has been assessed by OSHA (the US Occupational Safety and Health Administration), resulting in an Occupational Guideline September 1978, which is still valid. This information has been incorporated in all available MSDSs. OSHA and the American Conference of governmental Industrial Hygienists (ACGIH) have both instituted applicable exposure limits as follows:

OSHA PEL (ppm)	ACGIH TLV (ppm)	ACGIH STEL (ppm)
100	100	150

PEL = permissible emission limit (8 hr average)
TLV = threshold value limit (8 hr average)
STEL = short term exposure limit (15 min average)

FSI commissioned three industrial hygienic (IH) surveys, two by "Safe Day Consulting" (Missouri) and one by ICU (Texas). These surveys covered sprayfoam (1) and refrigerated vending machines applications (2-this survey was repeated to determine the effect on emissions of a low and high production rate). Both contractors are certified, used AIHA accredited laboratories and maintained chain of custody logs. Full individual results cannot be published because of pertinent US laws that regulate such disclosure to safeguard medical records (HIPAA and AAEMR). UNDP has confidentially reviewed the chains of custody and has de-personalized detailed records of the outcome on file. The outcomes were as follows:

Application	Survey Date	Concentration Range	Average Concentration
Sprayfoam	02-18-2004	1.3 – 23 ppm	8.2 ppm
Vending Machines	03-13-2003	0.0 – 4.5 ppm	2.2 ppm
Vending Machines	02-18 2004	0.5 – 23 ppm	0.9 ppm

Under no circumstance the permissible emission level was even approached and, so even less the lower flammability level (50,000 ppm).

2. Other Exposure

The ICU survey also including sampling around drums with polyol blend with the following results

- 6" above open container 0 ppm
- Immediately above open container: 0 ppm
- 2" above liquid: < 500 ppm (<1% LFL)
- 6" above liquid: 0 ppm
- Immediately above fresh foam: 0 ppm
- Immediately above 1hour old foam: 0 ppm

These tests were done with an electronic monitor programmed in % LFL and therefore not able to make precise differentiation at very low LFLs.

Conclusion: no specific exposure control limits are needed for methyl formate system operations

ATTACHMENT IV: COMBUSTIBILITY OF METHYL FORMATE

One of the arguments voiced against the use of methyl formate as blowing agent in PU foams is its perceived explosiveness. This has been initially the case with HCFC-141b as well—first projects included explosion proofing—but praxis showed this concern was not justified. It may be useful to look into the phenomenon of combustibility.

1. BACKGROUND

Properties commonly used to define flammable substances are [4]:

- **flash point**: the lowest temperature at which vapors above the liquid will "flash" when exposed to a flame in a standard test apparatus
- **auto-ignition temperature**: the temperature at which a flammable substance will burn spontaneously (without an external ignition source)
- **flammable limits**: concentrations range where a flame will propagate away from an ignition source
- **maximum explosion pressure**: highest buildup of pressure after ignition in a closed vessel
- **maximum rate of pressure rise**: maximum slope of the plot of pressure versus time, after ignition, up to maximum pressure
- **minimum ignition energy**: smallest amount of energy in an electric spark which will ignite a flammable mixture
- **heat of combustion**: the energy released as heat when a compound undergoes complete combustion with oxygen under standard conditions

2. APPLICATION TO EXPANSION AGENTS

Combustibility - a blowing agent is commonly stored and processed as a liquid but then turns due to an exothermic reaction between water and isocyanate (and to a lesser extent polyol and isocyanate) into a gas, expanding the still liquid reaction mixture and filling the generated foam cells. Addressing the combustibility of a blowing agent as a liquid is therefore equally important as of MF as a gas. For instance, HCFC-141b is not flammable as a liquid but its vapors may still burn. As it easily generates vapors at ambient conditions it should therefore also be tested for gaseous flammable properties. HCFC-141b is therefore often listed as “moderately” flammable or simply “yes”[5]. Methyl formate, on the other side, is, even as a liquid flammable—which does not necessarily imply explosive. I t has a burning profile very much like alcohol, i.e. it burns with a low energy, blue flame and its energy of combustion is very low—much more like HCFC-141b than like pentanes. Following data show this:

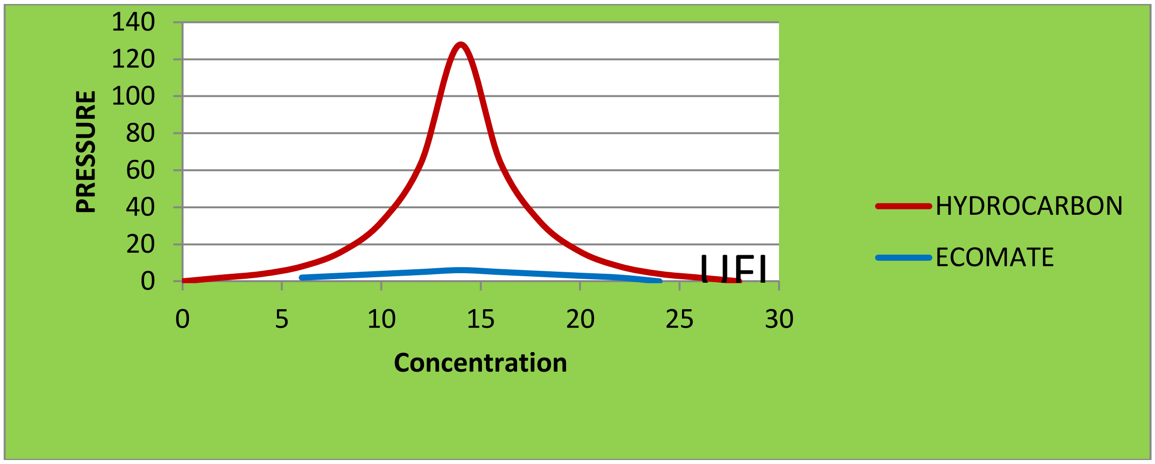
Substance	Heat of Combustion (kcal/g)	Comments
HCFC-141b	1.88	
Methyl Formate	3.88	
Pentane (commercial mix)	11.5	Cyclopentane estimated ~10% lower

The low heat of combustion is also the reason that neither HCFC-141b nor MF adds to the fire load of foams the way HCs do. HCFC-containing polyol systems generally are non flammable and the same is the case for MF—**within certain limits.**

Finally, a low heat of combustion decreases the **explosion pressure** and the **maximum rate of pressure rise** as the following picture shows (courtesy FSI):

[4] Panov, G.E. and Polozkov, V. T.. “Flammable Substances”, Encyclopedia of Occupational Health and Safety, 3rd Edition, International Labor Office Geneva, pp. 881-883 (1983)

[5] Lavelle, J. P., “Flammability Characteristics of HCFC 141b and HCFC-142b”, Journal of Fire Sciences 1989 7; pp 426-439



Flash Point is commonly the primary property to describe the fire hazard of a **liquid**. Pure MF, with its flashpoint of -32^0 C certainly needs proper safeguarding but this changes after blending with a product of no or low combustibility. Tests have shown such systems to be meeting non-flammability labeling criteria by the US-DOT—non-sustained burning at 120^0 F (ASTM D4206-96)—at MF concentrations <6% for polyols and <2% for isocyanates. Such concentrations suffice to reformulate almost all HCFC-based systems. FSI has this certified through sustained burning tests in September 2005 by the St. Louis testing Laboratories.

Flammable, Flammability, or **Explosive** limits are the primary property describing the fire hazard of **gases**. They indicate the proportion of combustible gases in a mixture, between which limits this mixture is flammable. The lower flammable limit (LFL) describes the leanest mixture that is still flammable, i.e. the mixture with the smallest fraction of combustible gas, while the upper flammable limit (UFL) identifies the richest flammable mixture. A **deflagration** is a propagation of a combustion zone at a speed less than the speed of sound in the un-reacted medium. A **detonation** is a propagation of a combustion zone at a velocity greater than the speed of sound in the un-reacted medium. An **explosion** is the bursting, or rupture, of an enclosure or container due to the development of internal pressure from a deflagration or detonation as defined in NFPA 69.

The three essential items for burning a material are fuel, air (or another oxidizing agent), and an ignition source. If there is not enough fuel, the mixture is considered below the lower flammability limit and it will not burn. Once the fuel-air mixture is within the flammable range, there still must be an ignition source present for it to burn (assuming the temperature is less than the auto-ignition temperature). Given a substance has a flammability range, there are several potential scenarios:

Scenario	Mitigating Action
The LFL will not be approached	No action required
The LFL can be approached or exceeded	Exhaust will keep the space under LFL
The LFL will be exceeded	Spark arrestors will keep the space free of ignition sources

The mitigation actions for the latter two scenarios are frequently combined and completed with an early warning system (sensors with alarm function).

3. APPLICATION TO METHYL FORMATE

For neither HCFC-141b nor methyl formate the LFL will be even remotely be approached under standard process conditions (ambient temperatures 15-40 ^{0}C; substance emissions under legal exposure limits) as the following calculations show:

Methyl Formate

- LEL = 5% in air by volume = 125 g/m^3 = 50,000 ppm
- Maximum concentration allowed by OSHA.NIOSH/ACGIH:
    - TWA = 100 ppm = 250 mg/m^3 = **0.20% of LFL**
    - STEL = 150 ppm = 375 mg/m^3 = **0.30% of LFL**

HCFC-141b

- LEL = 7.4% in air by volume = 925 g/m^3 = 193,000 ppm
- Maximum concentration allowed (WEEL):
    - TWA = 500 ppm = 2,4 g/m^3 = **0.26% of LFL**
    - STEL = 3,000 ppm = 14.4 g/m^3 = **1.56% of LFL**

4. CONCLUSIONS

- Methyl formate as a pure liquid is very flammable and requires proper safeguards. The risk of explosion is, however, remote because its low heat of combustion;
- A PU system base on methyl formate can be formulated as a low combustible liquid and will not reach the LFL even in the drum's head space; and
- There is no reason to treat methyl formate differently from HCFC-141b.

ATTACHMENT V: REVERSE HEAT FLOW TESTS (SUMMARY, DETAILED VERSION IN SEPARATED FILE)

INTRODUCTION

Reverse heat flow testing can be used to determine the heat flowing through the product which must be removed by the cooling system. This testing provides a measurement of the comparative efficiency of a cooling system in which insulation foam is one of the components. By keeping all other parameters the same, the comparative insulation performance of one insulation component can be measured. In this case this is applied to comparing different foam types.

Foam Supplies, Inc. (FSI commissioned this test in March 2008 as part of a program to support customers in achieving Energy Star performance for their appliance products. The test, however, also provides a comparison between the insulation performance of HCFC-141b and methyl formate.

TEST METHOD

Two identical freezer chest were used, one with methyl formate blown foam and one with HCFC141b foam. Each chest was heated by one light bulb of 40W at an ambient temperature of 4.40^0 C. The chests were fed from one energy source (= same voltage) for 24 hours. The temperature at that point was

89.890 F for the HCFC-141b foam
88.6640 F for the methyl formate foam

Difference 1.25^0 F or 0.7^0 C

The test was repeated with a 100W lamp at an ambient temperature of -17.8^0 C. Tis time the temperatures were

86.01^0 F for the HCFC-141b foam
84.73^0 F for the methyl formate foam

Difference 1.27^0 F or 0.7^0 C

The differences are deemed by the industry as negligible

CONCLUSION

HCFC-141b and methyl formate blown foams perform virtually identical in energy loss.

Details of the tests are on file.

ATTACHMENT VI: LONG TERM PERFORMANCE (SUMMARY, DETAILED VERSION IN SEPARATED FILE)

INTRODUCTION

The purpose of this study is to evaluate the long-term performance of MF-blown foams. A number of parts of various types from a variety of industries were stored in a warehouse at ambient conditions for a minimum of 5 years. Similar parts were foamed and tested when initially trialed and the results of those tests were used as the baseline for this study.

INSULATION VALUE

An insulated shipping container manufactured on July 12, 2002 was after 5 years retested in accordance with the original test method. A block of dry ice was placed into the container and the lid closed and sealed with shipping tape. Ambient temperature was 70·F. The temperature inside the box was measured with a thermocouple and allowed to stabilize for 1 hour before reaching stasis. This initial temperature was measured and the test began from there. The interior temperature was then measured and recorded every 24 hours. The results are as follows:

Inside Temperature	Initial Testing July 13-15, 2002	Retesting November 10-12, 2008
24 hours	No change	1^0 F increase
48 hours	4^0 F increase	6^0 F increase
72 hours	6^0 F increase	8^0 F increase

In another test, Individual samples were taken from three commercial refrigerators to compare insulation values from when they were originally foamed and five years later. The refrigerators were stored under ambient conditions in a warehouse. Samples were tested at different temperatures relating to their particular end-use but all follow-up testing was run at the same temperatures as the original test. Sample were tested In following ASTM-C 518: "Standard Test Method for Steady-State Thermal Transmission Properties by Means of the Heat Flow Meter Apparatus". The results are as follows:

Application	Test temperature (^{0}F)	Δ k Factor
Cold Vending Machine	75	+1.2%
Cold Vending Machine	77	+2.4%
Glass front reach-in Cabinet	55	+12.5%

THERMAL STABILITY

Soft drink dispensers with exposed foam skins were tested using the "Ice Melt" method according to industry standards. One gallon plastic jugs were filled with equal amounts of tap water and then frozen. Lids for the units were constructed from identical pieces of e>.1:ruded polystyrene to make the test consistent between units. A jug of ice was placed into each unit and the lid placed on top. At 24 hour intervals the water was poured off each jug and the jug was then reweighed to calculate the melt. All units were tested at 75 'F ambient to simulate a convenience store atmosphere. Test -Identical units were constructed and tested using foam systems blown with different blowing agents. The test units were foamed with an ecomate system and the control units were foamed with the manufacturer's current HFC-134a system. The test was designed to measure both the difference in insulation value when it is made and after multiple years in the field. The results were that after more than five years storage, the unit foamed with MF showed 0.5% more loss in insulation value over time than the HFC-134a control. Neither unit exhibited a change in physical dimensions greater than 1%.

DIMENSIONAL STABILITY

More than 20 foam parts were stored under ambient conditions in a warehouse for 5 years. The parts included exposed skin soft drink dispensers, ice bins, rotomolded food service carriers, doors and walk-in cooler panels. All parts remained stable after 5 years. The worst part exhibited less than 3.5% change in any direction.