METHYLAL AS BLOWING AGENT IN THE MANUFACTURE OF POLYURETHANE FOAM SYSTEMS

AN ASSESSMENT FOR APPLICATION IN MLF PROJECTS

MARCH 2012

-FINAL DRAFT-

TABLE OF CONTENTS

EXECUTIVE SUMMARY

Common technologies for replacing HCFC-141b include water/isocyanate, hydrocarbons and HFCs. Water may have limitations in thermal insulation applications; HFCs usually have high GWP values and hydrocarbons high in investment costs. There is therefore a need to assess other potential alternatives and, therefore, to investigate emerging/emerged technologies on their properties, costs, availability, sustainability and environmental performance. Decision 55/43 by the Executive Committee of the Multilateral Fund for the Implementation of the Montreal Protocol ("MLF") reflects this by promoting pilot projects aimed at validating technologies in a developing country ("A5") context.

This particular pilot project—the use of methylal ("ML")—has been designed around Arinos Quimica Ltda ("Arinos") in Sao Paulo, Brazil, a large independent system house producing PU systems that cover most PU applications, with input from Lambiotte & Cie/Belgium, a major supplier of methylal and a proponent for its use in PU foams and assistance from Dow-Brazil for product testing. To assure that methylal technology would be available world-wide, UNDP has first assessed the supply scenario. It has found that methylal is offered by manufacturers in Belgium, England, India, Korea and China. While methylal has been patented for a multitude of narrow PU applications, none of these patents cover broad use and/or have resulted in attempts to license its use and Lambiotte is of the understanding that none of these patents can claim effective and comprehensive intellectual rights on the use of methylal in PU foams. Therefore it can be concluded that methylal is commonly available and free to use in foam applications. The assessment addresses in sequence

- Health, safety and environmental considerations,
- Processability, including stability, compatibility shipping and storage
- System composition information
- Overview of physical properties obtained from trials for different applications
- Indicative conversion costs
- Conclusions and recommendations

Sixteen different PU foam applications have been identified that use currently HCFC-141b and these have been evaluated on the potential use of methylal as blowing agent with HCFC-141b as baseline technology to compare with. The different activities included:

- Acquisition of the necessary testing/prototyping equipment;
- Optimization and validation of all 16 formulations on prototyping equipment;
- Development of safe practices meeting national and international standards for the transportation, storage and use of methylal in system houses and of methylal-containing systems at SMEs;
- Dissemination of the experience gained through a workshop.

It is emphasized that this assessment serves a very practical purpose which is to

Determine the extent to which methylal 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, however, include back-to-back testing with the technology it replaces as well as a review of existing data, specifically on health, safety and environment. Some limited industrial hygienic testing has been conducted as well.

Implementation started with a review of the 18 originally earmarked applications to assess the possibility to combine applications based on same or very similar formulations, determination of the assessment parameters and critical issues for acceptability. The applications template was then functionally rearranged and reduced as follows:

Foam type	Application		Critical Properties	Developed and tested
Non Insulating Foams	Integral skin foams	Flexible	Friability, surface	√
		Shoe soles	Surface	√
		Structural (rigid)	Surface	√
		Semi-flexible	Surface	√
	Flexible foams	Flexible molded	Appearance, touch	√
		Hyper-soft block	Appearance, touch	√
		Viscoelastic molded	Slow mechanical recovery	√
		Viscoelastic block	Slow mechanical recovery	√
	Semi-rigid foams	Packaging foam	Shock absorption	√
Insulating foams	Rigid PU/PIR foams	Refrigeration	Insulation, adhesion, dimensional stability, (lack of) water permeability	√
		Water heaters		
		Trucks		
		Blocks, Panels		
		Spray		
		Thermoware		
		PIR Blocks		

Acceptability, for the purpose of this project, is defined as:

- Determining the safe use of the technology based on health, safety and environmental (HSE) data;
- Determining the applicability of the technology based on processability and relevant physical properties;
- Collecting complementary information, views from enterprises that have tested ML formulations.

Based on the information presented in this report and its attachments It can be concluded that methylal:

- Does not create incremental health concerns;
- While on downstream level mitigated through preblending, still requires safety measures as outlined;
- Does not pose an environmental hazard;
- Shipments and storage in its pure form must comply with its flammability status (GHS);
- In fully formulated systems <2% methylal (polyols) or <2% methylal (isocyanates) requires no special safety considerations. Systems containing 2-5 php need individual consideration and above that level, compliance with GHS category 2 or 3 is required. Local regulations are also to be complied with;
- In fully formulated systems for all applications are stable.
- In blends are not corrosive;
- In blends with polyols and/or additives do not pose compatibility issues. However, it is recommended that when designing conversion projects, the compatibility of baseline polyols will be carefully checked and the impact on flammability characteristics determined;
- Has in systems a shelf life of at least 6 months under standardized conditions;
- In non-insulation foams, regardless of application ML matches, in a narrow margin, HCFC-141b foams. With more optimization, even better results can be expected;
- In thermal insulation foams match HCFC-141b foams within an acceptable range (+/- 5%) in stability and density but carry a penalty in insulation value.

Also:

- No data on long-term performance are as of yet available;
- Customers selected for performance trials—one per application—all expressed their agreement with the performance of methylal-based PU systems.
- Conversion cost estimates show relatively low capital and operating costs:

Incremental Capital Costs

ENTITY	ACTION	CALCULATION	Comment
System House	Explosion proofing of blending tanks	AA x 30,000	As for methyl formate
System House	Nitrogen dispenser	BB x 8,000	
System house	ML vapor monitors	2 x 2,500	To monitor IH compliance
System House	Spray/PIP safety package	CC x 7,500	Exhaust, grounding
System House	LPD/HPD safety package	DD x 15,000	Exhaust, grounding
System House	Pycnometer (closed cell tester)	10,000	As FSPOP project template
System House	Portable K-factor tester	10,000	
System House	Refractometer (test chemical purity)	10,000	
System House	Small rent-out dispenser	EE x 25,000	
System House	Project Management	FF clients @ 1,000	
System House	Monitoring & technology transfer	30,000	
System House	Contingencies	10% of capital costs	
Customers	ML vapor monitor	FF x 2,500	To monitor IH compliance*
Customers	Spray/PIP retrofit packages	GG x 7,500	Exhaust, grounding
Customers	LPD/HPD retrofit package	HH x 15,000	Exhaust, grounding
Customers	New Dispensers	II x 35,000	Include safety packages
Customers	Trials, testing, training,	KK machines @ 3,000	As in approved projects
Customers	Contingencies	10% of capital costs	

Incremental Operating Costs (based on 10/2011 pricing)

CHEMICAL	PRICE (US$/kg)	BASELINE		Expert A		Expert B		Expert C		Cost Base	
		%	Cost	%	Cost	%	Cost	%	Cost	%	Cost
Polyol	3.20	38	1.22	40	1.28	40	1.28	42	1.34	42	1.34
Isocyanate	3,00	50	1.50	52	1.56	54	1.62	50	1.50	50	1.50
HCFC-141b	2.40	12	0.29	--	--	--	--	--	--	--	--
Methylal	4.00	--	--	8	0.32	6	0.24	8	0.32	8	0.32
Cost			3.01		3.16		3.14		3.16		3.16
Difference			**Base**		**0.15**		**0.13**		**0.15**		**0.15**

It should be pointed out that these costs can differ significantly over time, from country to country and based on comparative size.

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

Foam Type	Application	Assessment				
		HSE	Processing	Flamma/ Bility*	Physical Properties	Results
Non insulation foams	Flexible	+	+	+	+	+
	Shoe soles	+	+	+	+	+
	Structural (rigid)	+	+	+	+	+
	Semi-flexible	+	+	+	+	+
	Flexible molded	+	+	+	+	+
	Hyper-soft block	+	+	+	+	+
	Viscoelastic molded	+	+	+	+	+
	Viscoelastic block	+	+	+	+	+
	Packaging foam	+	+	+	+	+
Insulation Foams	Refrigeration	+	+	+/-	+/-	+/-
	Water heaters	+	+	+/-	+/-	+/-
	Trucks	+	+	+/-	+/-	+/-
	Blocks, Panels	+	+	+/-	+/-	+/-
	Spray	+	+	+/-	+/-	+/-
	Thermoware	+	+	+/-	+/-	+/-
	PIR	+	+	+/-	+/-	+/-

HSE + Good (compliance with international standards)
Processing: + Good (agreement as per customer who carried out the qualifying trials);
Flammability: + Non flammable (Cleveland closed cup test; as per formulations in attachment VII)
+/- May be flammable (Cleveland closed cup test)
Phys. Properties: + Good (agreement as per customer who carried out the qualifying trials based on +/- 5% range of results)
+/- Fair (acceptance is subject to company´s willingness to adopt a somewhat less favorable insulation value).
Note*: Source Lambiotte / Arinos

Note on flammability tests – the tests typically used to determine flammability (open and closed cup tests) are typically designed for transportation purposes and do not reflect very well danger in the workplace. For that reason, the EU has for processing purposes different tests, emphasizing the sustainability of a fire from emissions. Lambiotte reported that ML-based systems with less that 8 php ML do pass such tests. UNDP intends to commission a review of the flammability of all HCFC-141b replacements to be conducted by a recognized flammability expert.

Based on this assessment, the use of methylal as an alternative blowing agent to replace HCFC-141b in PU foam applications in MLF projects is considered feasible. The results indicate, however, that it is better suited for non-insulation foams than for insulation foams. Taking into consideration that the baseline is the comparison between optimized HCFC-141b based systems and recently developed methylal-based systems, the results for rigid (insulation) foams applications carries a penalty in insulation value of up to 10 %. However, there is room for further optimization such as cell size reduction and choice of surfactants and catalysts. This should be individually evaluated by system houses and other suppliers.

The adoption of methylal should be subject to the following conditions:

1. Projects should preferably be implemented through local system houses;
2. Project designers should ensure that:
   a. Chemical compatibility is verified,
   b. Implications related to the flammable character of the substance are addressed as recommended.

This pilot project included a workshop to disseminate the results of the project. This workshop was held in Brazil, at 6th and 7th of December 2011, with the 108 attending from 12 system houses from Brazil; 13 foam manufacturers from Brazil, Jamaica and Trinidad/Tobago; other representatives from five Article 5 countries (*Colombia, Panamá, Paraguay, Peru and Jamaica*); representatives from UNDP, UNEP and GIZ; three Brazilian industry associations (*Abripur, Abiquim and Abrava*), eight blowing agent manufacturers/distributors (*from Brazil, Belgium and United States*) and six foam injection equipment manufacturers. Invitations were sent to FTOC members, with three of them attending. The workshop's duration was two days with the first day focusing on the pilot project itself and the second day presenting a broad technology discussion with presentations made by major national/international system houses and blowing agent manufacturers.

1. Introduction

Common technologies for replacing HCFC-141b in PU foams have been limited to water/isocyanate (sometimes combined with enhancements such as super-critical CO_2, formic acid, etc.), hydrocarbons and HFCs. Water has limitations in thermal insulation applications; HFCs usually have high GWP values and hydrocarbons are high in investment costs. There is therefore need to assess other potential alternatives and, therefore, to investigate emerging technologies on their technical merits, cost, availability, sustainability and environmental performance. Decision 55/43 of the Executive Committee of the Multilateral Fund for the Implementation of the Montreal Protocol ("MLF") reflects this by promoting pilot projects aimed at validating technologies in a developing country ("A5") context. The detailed objectives of such projects would be to:

- Develop, optimize and validate the use of alternative blowing agents or technologies in polyurethane foam applications meeting local and international safety standards;
- Demonstrate these technologies in a limited amount of downstream operations;
- Transfer the technologies to interested stakeholders, such as system houses and individual downstream users through workshops and investment projects.

UNDP has prepared six pilot projects which may cover substantially all current commercially available products that have potential or have been proven as blowing agent in foams but have not yet been assessed in an A5 context or that could be improved upon. These technologies are:

Substance	Sub-Sector	Country	Status	Justification
Supercritical CO_2	SPF	COL	Implementing *	Evaluation in thermal insulation applications
Hydrocarbons	RPF, ISF	EGY	Completing	Evaluation of cost saving options
Methyl Formate	RPF ISF FPF	BRA/MEX	Completing	Validation of a commercial available product
Methylal	RPF ISF FPF	BRA	Completed	Validation of a commercial available product
HFO-1234ze	XPS	TUR	Implementing	Validation of a commercial available product
CO_2/Methyl Formate co-blowing	XPS	CHI	Recently approved	Evaluation of performance for XPS Foam Boards and validating XPS extrusion equipment redesign

**Project approved as part of Japan Bilateral Cooperation. UNDP is implementing this project in behalf of Japan. There is also a World Bank Demonstration Project for sprayfoam in China with undefined technology choice*

There are other emerging HCFC replacements that are not yet commercially available. Most of these are based on unsaturated HFCs, also called hydrofluoroolefins or HFO's and mainly geared towards replacement of (saturated) HFCs in developed countries. They share low/no flammability, zero or insignificant ODP and insignificant GWPs as the following overview shows:

	HBA-2[1]	FEA-1100[2]	AFA-L1[3]
Chemical Formula	n/k	n/k	n/k
Molecular Weight	<134	161-165 (est.)	<134
Boiling point (^{0}C)	>15 <32	>33	>15 <30
Gas Conductivity (mWm^{0}K at 10 ^{0}C)	n/k	10.7	10
Flammable limits in Air (vol. %)	None	None	None
TLV or OEL (ppm; USA)	n/k	n/k	n/k
GWP (100 y)	<15	5	<15
ODP	0	0	0

[1]Honeywell [2]DuPont [3]Arkema

These chemicals may not be commercially available in the A5 markets within the next 2-3 years and that will be too late for application in projects for compliance with the HPMP Stage-I targets. From the mentioned pilot projects, the assessment of the use of methyl formate (MF) in non-continuous PU applications has been technically completed while the assessment of cost-effective HC technologies, the use of methylal and the use of HFO-1234ze are in the final stages with the experimental work done.

This particular pilot project—the use of methylal ("ML")—has been designed around Arinos Quimica Ltda ("Arinos")/Brazil, a large independent system house producing PU systems covering most PU applications, with input from Lambiotte & Cie/Belgium, a major supplier of methylal and a proponent for its use in PU foams as well as Dow-Brazil, which conducted most product testing. The application of methylal is shoesoles has been undertaken by Zadro, a system house in Mexico, specialized in this application.

To assure that methylal technology would be commercially available world-wide, UNDP has assessed its supply scenario as well as other potential barriers such as application patents.

Supply scenario – methylal is offered by manufacturers in Belgium, England, India, Korea and China. From these manufacturers, the only one that researched its use in PU foam applications and is actively marketing this is Lambiotte & Cie. These efforts have resulted in its use in around 20 European countries. In most cases its use is as a co-blowing agent in conjunction with other HCFC replacement such as hydrocarbons (HCs) and hydrofluorocarbons (HFCs). While this demonstration project undertaken in two large Latin American countries had been successful, the application of methylal technology should be carefully evaluated in the context of the local situation prevailing in each country.

Application patents – methylal has been patented for a multitude of narrowly defined PU applications, going back as far as 1995. None of these patents can claim effective and comprehensive intellectual rights on the use of methylal in PU foams and therefore the technology is considered free to use (source Lambiotte).

This assessment addresses in sequence

- Health, safety and environmental considerations,
- Processability, including stability, compatibility shipping and storage
- System composition information
- Overview of physical properties obtained from trials for different applications
- Indicative conversion costs
- Conclusions and recommendations

UNDP acknowledges with appreciation the cooperation extended by the project partners: Arinos, Lambiotte, Zadro and Dow do Brasil.

2. Design

PU foams are used in applications with different formulations. The original 18 applications as mentioned in the approved version of the project document have been narrowed down to 16 applications that use currently HCFC-141b. Under this project, these applications have been evaluated on the potential use of methylal as blowing agent with HCFC-141b as baseline technology to compare with. The different activities consisted of:

- Acquisition of the necessary testing/prototyping equipment;
- Optimization and validation of all 16 formulations on prototyping equipment;
- Development of safe practices meeting national and international standards for the transportation, storage and use of methylal in system houses and of methylal-containing systems at SMEs;
- Dissemination of the experience gained through a workshop.

Changing blowing agents, which are essential components in foam formulations, requires determination of baseline values for critical properties. Some are general in nature but others are specific as the following list shows:

Foam type	Application	Critical Properties	Relevant Tests
Integral Skin and Microcellular Foams	Flexible	Friability, surface	Visual (pinhole count) Abrasion, tear resistance
	Shoe soles		
	Structural (rigid)		
	Semi-flexible		
Rigid Foams	C/D refrigeration	Insulation, adhesion, dimensional stability, water permeability resistance	K-Value/peel strength (sometimes(heat loss, dimensional stability, closed cell content
	Water heaters		
	Trucks		
	Blocks/panels		
	Spray		
	Thermoware		
	PIR		
Semi-Rigid Foams	Packaging foam	Shock absorption	Drop test (hand)
Flexible Foams	Flexible molded	Appearance, touch	ILD/CLD (mostly by hand)
	Hyper-soft slabstock		
	Viscoelastic molded	Slow recovery	Recovery modulus (mostly by hand)
	Viscoelastic slabstock	Slow recovery	

Many companies and their suppliers do not conduct testing on properties of their foams on a regular base—or not at all--nor do they set standards. In such cases, rather than testing on meaningless properties, it has been deemed more important that the user expresses its agreement (in writing) with the quality and performance of the methylal-containing foam. These letters are compiled in **Attachment VIII**.

However, it is generally preferred to determine baseline data on critical properties against which the new foams can be objectively compared. It is emphasized that this assessment serves a very practical purpose which is to

Determine the extent to which methylal can be satisfactorily used in MLF-funded HCFC phase-out projects and, in this way, avoid unexpected setbacks in project implementations

This assessment does not include an exhaustive investigation into the way the technology works. It does, however, include back-to-back testing with the technology it replaces as well as 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"***.

Every application started with the development of laboratory formulations using methylal as auxiliary blowing agent (ABA). When these formulations were deemed acceptable, they were applied in machine trials. While initial trials were done as the system house, UNDP and Arinos decided that optimization together with customers would be more effective than prototyping at the system house only. Accordingly, formulations developed by Arinos and initially optimized at their facilities have been further optimized at customer level. The customers confirmed in writing if and when the formulation met their minimum requirements.

Arinos was not able to source an independent physical testing laboratory in Brazil. It found Dow Chemical do Brasil, which has in Brazil a new, fully equipped and ISO-9001 certified PU testing center, willing to perform the testing.

For more details, it is referred to the approved version of the project document (**Attachment I**).

3. Implementation

The project was approved at the 58th ExCom meeting in July 2009. Funding was received in October 2009 and the project started in earnest January 2010. The list of applications was first reviewed on work already completed (to save time, Arinos started immediately after project conception) and on the potential to combine applications based on same or very similar formulations.

Safety, health and environmental information on methylal are abundant. However, there are no industrial hygienic data that relates specifically to its use in PU foams. Therefore, emission monitoring data have been included in the assessment program. Based on methylal's relatively inert behavior it would not be likely that its use impacts structural foam properties. Critical issues to be addressed would therefore be

- Flammability,
- Workplace emissions and
- (Thermal) insulation value.

As the latter is not an issue with non-insulating foams, and these also use generally low levels of auxiliary blowing agents—decreasing the likelihood of adverse flammability and emission conditions—the applications template was functionally rearranged as follows:

Foam type	Application		Critical Properties	Developed/tested
Non Insulating Foams	Integral skin foams	Flexible	Friability, surface	√
		Shoe soles	Surface	√
		Structural (rigid)	Surface	√
		Semi-flexible	Surface	√
	Flexible foams	Flexible molded	Appearance, touch	√
		Hyper-soft block	Appearance, touch	√
		Viscoelastic molded	Slow mechanical recovery	√
		Viscoelastic block	Slow mechanical recovery	√
	Semi-rigid foams	Packaging foam	Shock absorption	√
Insulating foams	Rigid PU/PIR foams	Refrigeration	Insulation, adhesion, dimensional stability, water permeability	√
		Water heaters		
		Trucks		
		Blocks, Panels		
		Spray		
		Thermoware		
		PIR Blocks		

As soon as an application development was completed, samples were forwarded for physical testing. By early 2011, formulation development and optimization was completed and by August 2011 testing was finalized. However, due to relocation of Dow's laboratory, some samples were up to 10 months old when finally tested and retesting on fresh samples was required. This was completed mid-November. Arinos commissioned an industrial hygienic survey to assess methylal emission concentration during system blending. UNDP requested system processing to be included but this was not followed up on. The same data can also be used to assess the flammability of process emissions.

Methylal is also recommended in combinations with other blowing agents, such as HFC-365mfc and cyclopentane. This aspect has not been assessed in this project as its application concerns more developed countries than developing ones—the target of this assessment.

The pilot project for the evaluation/assessment of methylal as approved by the Executive Committee included a workshop to disseminate the results of the project. In conformity, a workshop was held in Sao Paulo, Brazil at the 6th and 7th of December 2011, with the participation of 108 attendants from 12 system houses from Brazil (being eight A5 owned: *Amino, Arinos, Ariston, M.Cassab, Polisystem, Polyurethane, Purcom and Utech*; and four non-A5: *Bayer, BASF, Dow and Huntsman*); from 13 foam manufacturing enterprises from Brazil and from Jamaica and Trinidad & Tobago; representatives from five Article 5 countries (*Colombia, Panamá, Paraguay, Peru and Jamaica*); representatives from UNDP, UNEP and GIZ ; three Brazilian industry associations (*Abripur, Abiquim and Abrava*), eight blowing agent manufacturers/distributors (*from Brazil, Belgium and United States*) and six foam dispenser manufacturers. Also, invitations were sent to FTOC members, with attendance of three of them. The workshop consisted of two days where the first day was focused in the pilot project itself, and its findings. The second day involved a broad technology discussion with presentations made by the major national and international system houses and blowing agent manufacturers.
*The Agenda and the presentation given in the workshop can be downloaded at:

http://www.protocolodemontreal.org.br/eficiente/sites/protocolodemontreal.org.br/pt-br/site.php?secao=eventos&pub=224

[1]

[1] *The Agenda and the presentation given in the workshop can be downloaded at:
http://www.protocolodemontreal.org.br/eficiente/sites/protocolodemontreal.org.br/pt-br/site.php?secao=eventos&pub=224

4. Outcomes

Methylal, also called dimethoxymethane, belongs to the acetal family. It is a clear, colorless, flammable liquid with a relatively low boiling point and a sweet odor. Its primary use is as a solvent in the manufacture of perfumes, resins, adhesives, paint strippers and protective coatings. It is moderately soluble in water (33 % by weight) and miscible with most common organic solvents. A Material Safety Data Sheet (MSDS) prepared by Lambiotte & Cie and OSHA's Occupational Health Guideline for methylal are attached (**Attachment II**). There are many MSDS available from other suppliers, traders and independent institutions, which provide essentially the same information but Lambiotte follows the Global Harmonization System (GHS)—which will be the future standard for OSHA as well. Following data on physical properties are compared with HCFC-141b, which it seeks to replace:

Property	Methylal	HCFC-141b
Appearance	Clear liquid	Clear liquid
Boiling point	42 °C	32 °C
LFL/UFL	2.2-19.9 %	7.6-17.7
Vapor pressure	400 mm Hg @ 20 °C	593 mm Hg @ 25 °C
Lambda, gas	14.5 mW/m.k@ 42 °C*	10.0 mW/m.k @ 25 °C
Auto ignition	235 °C	>200 °C
Specific gravity	0.821 @ 20 °C	1.24
Molecular weight	76.09	117
ODP	0	0.11
GWP	Negligible	630

*Extrapolation at 25 °C would be ~ 11

Below is a comparison with other, common, foam blowing agents on the most relevant properties:

Property	HCFC-141b	Methylal	Cyclo Pentane	HFC-245fa	Methyl Formate
LFL/UFL (%)	7.3-16.0	1.6/17.6	1.4-8.0	None	5.0-23.0
Molecular Weight	117	76	70	134	60
Gas Conductivity (mW/m°K)	10 (25°C)	14.5 (42°C)*	11 (10°C)**	12.5 (24°C)	10.7 (25°C)
TLV/OEL (ppm)	500 (TLV)	1,000 (TLV)	600 (TLV)	300 (WHEEL)	100 (TLV)
Global warming potential (100 y; IPCC-1996)	630	Negligible	11	820	Negligible
ODP	0.11	0	0	0	0
Photochemical Ozone Creation Potential (MIR)	<0.01	0.89	2.39	0.00	0.06

*Extrapolation at 25 °C would be ~ 11; **extrapolation at 25 °C would be ~13.9

Methylal is offered in different purities. It is recommended (Lambiotte) that the pure grade suits its use as blowing agent best:

Compound	Cosmetic Grade	Anhydrous Grade	Pure Grade	Technical Grade
Methylal	**99.5 % min.**	**99.9 % min.**	**99.5 % min.**	**93 % min.**
Methanol	< 1 ppm	< 0.05 %	< 0.05 %	6.5 % max
Formaldehyde	< 1 ppm	< 0.005 %	< 0.0005 %	< 0.02 %
Water	< 0.5 %	< 0.03 %	< 0.5 %	< 0.25 %

4.1 Health, Safety and Environment (HSE)

4.1.1 Health

Methylal's toxicity profile compares as follows with HCFC-141b:

	Methylal	HCFC-141b
• TLV (TWA)	1000 ppm	500 ppm
• TLV (STEL)	1250 ppm	500 ppm
• Acute toxicity (oral)	LD50 5.6 g/kg (rat)	LD50 5 g/kg (rat)
• Sub-acute inhalation	NOEL = 4,000 ppm (8 x 6 h)	20,000 ppm
• Sub-chronic inhalation:	NOEL = 2,000 ppm	20,000 ppm
• Eye irritation:	minor to moderate	minor to moderate
• Skin irritation:	none to slight	none to slight
• Dermal sensitization:	not allergenic	non allergenic
• Ames test:	no mutagenic activity	no mutagenic activity

To assess actual emissions compared to the applicable TWA and STEL, a workers exposure evaluation has been commissioned. This evaluation was conducted by Environ/San Bernardo-SP at the Arinos facility, following the Brazilian legal standard as published in Directive 3214/78 of the Ministry of Labor in its NR-9. The values measured show the following range:

- Personal Sampling (production area operators) 3.4 – 17.3 ppm
- Area Sampling (blending and weighing area) 2.6 – 6.5 ppm

This is between 0.3 - 1.7 % of the TLV (TWA) and between 0.2 – 1.4 % of the TLV (STEL). The evaluation, which in its full text is attached (**Attachment-III**) concludes that:

The Occupational Quantitative Assessment of Methylal in the atmospheric air at Arinos showed that all samples are lower than the action level from TLV-TWA (ACGIH)

Although the evaluation indicates that no IH or flammability issues are to be expected when preparing ML-based systems—the only operation that processes pure ML—an application specific audit for downstream users needs to confirm this. Methylal users can for relatively moderate costs (around US$ 2,500/unit) conduct their own compliance testing with an electronic monitor made by new Cosmos/Japan:

METHYYLAL EMISSONS DETECTOR 0-2,000 ppm

An extensive toxicological profile is attached (**Attachment-IV**).

4.1.2 Safety

Methylal is classified as highly flammable (R11) and an eye irritant (R19). Some MSDS mention also R36 (might form explosive peroxides). However, Lambiotte reports from its tests that methylal does **not** form any peroxides (*0 ppm of peroxides after 1143 days under air or under nitrogen*) so that this statement, while tentative, appears incorrect. Following flammability related data are available:

• flash point (open cup):	-18°C (-0.4°F)
• auto-ignition temperature:	237°C (458.6°F)
• lower/upper flammability limits:	1.6 % vol (LFL)/17.6 % vol (UFL)

Methylal used as proposed will reduce the related risk at downstream users by preblending at supplier level (system houses). Meeting applicable industrial hygienic thresholds will keep emissions well under the LFL (STEL = 1250 ppm = 22 % of LFL). Moreover, in view of the outcome of the Environ industrial hygiene evaluation, it is not expected that at any time a methylal concentration of 17.3 ppm would be exceeded. This translates into expected airborne methylal concentrations to be less than 0.03% of the LFL.

As mentioned, there are no data on explosion risks. Essential elements required to trigger an explosion are fuel, air, an ignition source and containment. Fuel could be pure methylal or a methylal-based fully formulated system. To bring the latter to explosion at downstream user level is not possible as long as, as mentioned before, industrial hygienic thresholds are respected—but the margin at TLV level—while unlikely to be reached—Is not a very comfortable one as it is common standard to set LFL alarm levels on 20-35%. Aside from the challenge to ignite the polyol mixture, the heat of combustion is very low so that the necessary pressure built-up in containment will not easily be achieved. **Attachment V** addresses flammability issues more in detail.

Notwithstanding the very remote likelihood of a sustainable flammable situation—much less even an explosion risk—it is advised to follow recommendations for the handling of flammable liquids as, regardless of the likelihood of explosion risk, fully blended methylal-based systems exceeding 2-7.5 php in polyol and/or isocyanate are flammable and might require compliance with applicable local regulations.

4.1.3 Environment

Methylal has a relatively good eco-toxicological profile:

	Methylal	HCFC-141b
• Daphnids, fish (Brachydanio Rerio)	no effect	31.2 – 126 mg/L
• Biodegradability (ISO/DIS 8192)	biodegradable	not biodegradable

Its atmospheric chemistry is also favorable, with a relatively low photochemical ozone creation potential (POCP), a short atmospheric residence period of 2-5 days, a negligible global warming potential (GWP) and—because there are no halogens incorporated in the molecule—zero stratospheric ozone depletion potential (ODP).

Lambiotte commissioned an eco-toxicological profile, which is attached (**Attachment VI**).

4.2 System Processability

4.2.1 Shipping, Handling and Storage

The proper shipping name for methylal is UN1234 METHYLAL, 3, II. It is highly flammable and needs to be labeled accordingly:

Signal Word: **Danger**
Hazard Statement: **Highly flammable liquid and vapor**

The label as shown belongs to the labeling elements of the "Global Harmonization System (GHS) for Flammable and Combustible Liquids", an international hazard classification system proposed under the guidance of the United Nations Subcommittee for GHS, and adopted—or in the process of adoption—by an ever-growing group of countries, including Brazil, the EU and the USA. Methylal users should, however, also check—and comply with—local regulations as they may have different requirements and the most stringent should be applied.

Shipment and storage of methylal can be carried out in carbon steel vessels or containers. No special material is required. Carbon steel is also acceptable for storage and piping. Methylal has a very low viscosity which 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, however, considered more suitable.

4.2.2 Stability

Following stability data have been provided by Arinos and Lambiotte:

- Thermal stability - Stable for 7 days at 200 ^{0}C
- Peroxide building - No formation of peroxides has been detected
- Hydrolysis - Stable under neutral/alkaline conditions (polyols are slightly alkaline)
  - The pH of ML systems matches approximately those of HCFC-141b
  - Very slow (>1 year) hydrolysis under acid condition
- Corrosion - No corrosivity determined

Manufacturers typically offer shelf lives of 6 months after date of manufacturing for their systems, if stored in original, unopened containers at temperatures typically between 10^{o}C and 30^{o}C. Methylal-based systems as offered by Arinos are meeting this shelf life standard.

Moreover, internal tests at Arinos show no change in activity of retained formulation samples stored for at least twelve months under standard conditions.

4.2.3 Compatibility

Methylal is miscible with all types of polyols commonly used in PU foam applications. This is an advantage compared to hydrocarbons which require sometimes significant polyol adjustments to overcome solubility issues and mix rather as dispersions than being truly dissolved. HCFC-141b-based systems are completely miscible but show some instability when blended in large concentrations. It took the industry time to conclude that the potent solvent character of this substance limits its use in a system. Liquid HFCs show limited miscibility in some polyols.

All application trials at Arinos have been conducted using the same chemicals as with HCFC-141b. From this, it can be concluded that the replacement of HCFC-141b with methylal does not require qualitative changes in chemicals. However, different polyols and/or additives could impact the flammability of the systems. This is not entirely negative as it also creates an option for optimization. Preliminary studies show that polyols of higher viscosity give systems with higher flashpoints. Also, because methylal is miscible in polyols as well as isocyanates, the option exists to reduce flammability by blending in both system components. These potential options for optimization in fire behavior, while highly recommended, need to be conducted by individual system houses and are beyond the scope of this assessment.

Methylal also acts as a potent viscosity reducer, typically cutting polyol viscosities in half or even less. This accommodates processing of higher viscosity blends such as in shoesoles.

4.3 System Composition

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

- Equimolar replacement would require 1 kg methylal to replace 1.54 kg HCFC-141b;
- Because of the strong solvent effect of HCFC-141b this ratio can, however, change for high-ABA formulations to 1:1.7 or even 1:1.9. In other words, ML is more effective in high ABA formulations;
- If the objective would be to keep the methylal system non flammable, the maximum amount of methylal would be between 2 and 5 php—depending on the choice of polyol—which is equivalent to 3.5—8.5 php HCFC-141b. Increased water levels or blending of ML in isocyanate could provide additional blowing;
- If flammability is accepted—and accounted for in safety measures—any amount of HCFC-141b in a commercial formulation can be replaced by the equivalent amount of ML without significant other formulation changes;
- Blends of polyols with a high amount of methylal still may be exempt from flammability labelling because they show low combustion tendencies. In the EU, as well in countries with similar applicable regulations, no flammable labelling is needed if the flash point of a blend is between 21°C and 55°C but the blend doesn't contribute to the combustion.

Attachment VII contains sample formulations for different applications. These formulations should be considered guidelines as each commercial application needs its own optimization.

4.4 Foam Properties

Determining the acceptability of an HCFC-141b replacement technology includes measuring of relevant physical properties before and after replacing HCFC-141b. A technology is deemed acceptable for a particular application if the physical properties are within a predetermined range (generally 10%, but the downstream user has the last word) from the original properties using HCFC-141b. For subjective issues such as appearance and for applications not requiring testing, the downstream user's determination of the quality is the ultimate criterion of acceptability.

As final trials have been conducted at customer level, these customers have been requested—and complied with—providing a declaration stating agreement with the methylal-base foams in their particular application. For all applications, such declarations have been received and are on file.

All development and initial optimization trials have been conducted at Arinos' Development Center. Final optimization and validation took place at selected downstream users. Physical testing has been conducted at the Arinos and Dow Brazil facilities. The development and testing of PU shoesoles has been performed through Zadro/Mexico. Individual test protocols are on file.

Test results/discussions have been categorized as follows:

- Non Insulation Foams
    1. Hypersoft Foams (blocks)
    2. Viscoelastic Foams (molded)
    3. Viscoelastic Foams (blocks)
    4. Flexible Foams (molded)
    5. Integral Skin Foams (flexible)
    6. Integral skin Foams (semi-rigid)
    7. Integral Skin Foams (rigid/structural)
    8. Microcellular foams (shoesoles)
    9. Packaging foams (semi-rigid)

- Insulation Foams
    1. Appliance Foams (rigid injection)
    2. Water Heaters
    3. Panels, Blocks
    4. Transportation
    5. Thermoware
    6. Polyisocyanurate Foams (PIR)
    7. Spray foams

In many cases the ML densities did not quite match the ones for HCFC-141b. The delay in testing, based on Dow's laboratory relocation caused a time crunch that did not allow further optimization. However, this is not an issue inherent to the use of ML but just misjudging of the impact of converting from laboratory (hand-mixed) foams to machine trials.

4.4.1 Non Insulating Foams

4.4.1.1 Hypersoft Foams (blocks)

- Assessment Letter: Techfoam
- Machine: Boxfoam
- Test results:

Properties	Unit	HCFC 141b	Methylal
Density (foam)	Kg/m3	25,3	25,7
Resilience	%	38	37
Tensile Strength at break	kPa	127,6	139,5
Tear Propagation	N/mm	526,3	530,6
Elongation at break	%	504,3	483,4
Compression set 50%	%	5,4	5,6

ILD 25%	N	9,7	8,3
ILD 40%	N	13,7	10,9
ILD 65%	N	22,4	19,6

4.4.1.2 Viscoelastic Foams (molded)

- Assessment letter: Vittaflex
- Machine Low Pressure
- Test results:

Properties	Unit	HCFC 141b	Methylal
Density (foam)	Kg/m^3	48,6	46,7
Resilience	%	12	10
Tensile Strength at break	kPa	101,4	109,2
Tear Propagation	N/mm	518,2	545,3
Elongation at break	%	494,8	461
Compression set 50%	%	3.7	3.6
ILD 25%	N	36	31
ILD 40%	N	46	43
ILD 65%	N	73	72

4.4.1.3 Viscoelastic Foams (block)

- Assessment letter: Techfoam
- Machine: Boxfoam
- Test results:

Medium Density

1) Properties	Unit	HCFC 141b	Methylal
Density (foam)	Kg/m^3	36	42,5
Resilience	%	6	6
Tensile Strength at break	kPa	77,7	63,6
Tear Propagation	N/mm	378	267,9
Elongation at break	%	234,3	284,3
Compression set 50%	%	0,94	0,61
ILD 25%	N	41	35
ILD 40%	N	58	49
ILD 65%	N	105	92

Low Density

2) Properties	Unit	HCFC 141b	Methylal
Density (foam)	Kg/m^3	27,7	26
Resilience	%	4	4
Tensile Strength at break	kPa	55,3	58,1
Tear Propagation	N/mm	296,4	260,5
Elongation at break	%	278,1	314

Compression set 50%	%	1,6	2,1
ILD 25%	N	6	6
ILD 40%	N	14	13
ILD 65%	N	36	31

4.4.1.4 Flexible Foams (molded)

- Assessment letter: Brastec Florense
- Dispenser: Low Pressure
- Test results:

Properties	Unit	HCFC 141b	Methylal
Density (foam)	Kg/m^3	38,3	40,1
Resilience	%	46	46
Tensile Strength at break	kPa	130,9	126,8
Tear Propagation	N/mm	614,5	575,5
Elongation at break	%	123,8	128,6
Compression set 50%	%	11	9,83
ILD 25%	N	150	151
ILD 40%	N	236	233
ILD 65%	N	536	527

4.4.1.5 Integral Skin Foams (flexible)

- Assessment Letter: Blitz
- Machine: High Pressure
- Test results:

Properties	Unit	HCFC 141b	Methylal
Entire Sample			
Molded Density	Kg/m3	348,6	356,7
Hardness	Shore A	52	50
Resilience	%	34	35
Foam Core			
Internal Density	Kg/m^3	244,2	265,3
Tensile Strength	kPa	238	241
Elongation	%	66	63
Tear Strength	N/mm	1,150	1,090
Compression Set (50%)	%	19	21
Skin Only			
Tensile Strength	kPa	975	980
Elongation	%	77	78
Tear Strength	N/mm	3780	3810

4.4.1.6 Integral Skin Foams (semi-rigid)

- Assessment Letter: Blitz
- Machine: High Pressure
- Test results: No tests are required in Brazil

4.4.1.7 Integral Skin Foams (rigid/structural)

- Assessment Letter: Blitz
- Machine: High Pressure
- Test results: No tests are required in Brazil.

4.4.1.8 Microcellular Foams (shoesoles)

- Assessment Letter: Test report Zadro/Ciatec (accredited test center)
- Machine: Low-pressure
- Test results:

Property	All	R-095	R-096	R-099	QZCT15	Test Method
Type	types	SPORT	TRAVEL	RIGID	SEMI-RIGID	
Blowing Agent	**141b**	**ML**	**ML**	**ML**	**ML**	
Density (kg/m^3)	<450	450	450	400	400	DIN 53420 ASTM D-792
Tear resistance (kgf/cm)	>6*	25.4	41.6	n/a	n/a	DIN 53507 ASTM D-624
Abrasion Resistance (mg, maximum)	<350	161.3	242.3	96.5	232.8	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

4.4.1.9 Packaging Foams (semi-rigid)

- Assessment Letter: Poliuretanos do Brasil
- Machine: Low Pressure
- Test results: No tests are required in Brazil.

4.4.2 Insulation Foams

4.4.2.1 Appliance Foams (rigid injection)

- Assessment Letter: MF Cozinhas
- Machine: High Pressure
- Test results:

Properties	Unit	HCFC 141b	Methylal
Density	Kg/m^3	38,2	40,6
K factor	mW/mK	22,7	23.7

Compression set 10%	kPa	197,7	183,5
Compression set 10%	kPa	195,3	182,6
Dim. Stability (+70 C)			
side 1 max	*%*	6,97	1,67
side 1 min	*%*	-0,24	-0,81
side 2 max	*%*	-0,81	-0,90
side 2 min	*%*	-0,31	0,05
thickness max	*%*	0,73	4,78
thickness min	*%*	-0,25	0,13
Dim. Stability (-20 C)			
side 1 max	*%*	-0,16	0,41
side 1 min	*%*	-0,01	-0,01
side 2 max	*%*	-0,59	0,28
side 2 min	*%*	-0,14	-0,03
thickness max	*%*	-5,87	-0,92
thickness min	*%*	-0,52	-0,28

4.4.2.2 Water Heaters

- Assessment Letter: Heliotek
- Machine: High Pressure
- Test results:

Properties	Unit	HCFC 141b	Methylal
Density	Kg/m^3	36.9	39.4
K factor	mW/mK	22,6	24.5
Compression set 10% (Pa)	kPa	249,9	236,8
Compression set 10% (Pe)	kPa	217,7	-
Dim. Stability (+70 C)			
side 1 max	*%*	0,85	-0,31
side 1 min	*%*	-0,11	-0,29
side 2 max	*%*	-0,35	-0,41
side 2 min	*%*	0,03	-0,28
thickness max	*%*	-4,53	-0,57
thickness min	*%*	-0,18	-0,55
Dim. Stability (-20 C)			
side 1 max	*%*	0,25	-0,10
side 1 min	*%*	0,06	-0,06
side 2 max	*%*	0,10	-0,07
side 2 min	*%*	0,03	-0,04
thickness max	*%*	0,21	-0,27
thickness min	*%*	0,04	-0,23

4.4.2.3 Panels, Blocks

- Assessment Letter: Politech
- Machine: Boxfoam
- Test results:

Properties	Unit	HCFC 141b	Methylal
Density	Kg/m^3	43,7	43,0
K factor	mW/mK	22,2	25.1
Compression set 10% (Pa)	kPa	243,1	211,8
Compression set 10% (Pe)	kPa	276,5	262,9
Dim. Stability (+70 C)			
side 1 max	%	-1,19	-0,9
side 1 min	%	-0,09	-0,04
side 2 max	%	-0,44	-1,11
side 2 min	%	-0,01	-0,52
thickness max	%	-6,31	-2,85
thickness min	%	-0,91	1,18
Dim. Stability (-20 C)			
side 1 max	%	0,53	-0,08
side 1 min	%	-0,11	-0,02
side 2 max	%	-0,32	-0,32
side 2 min	%	0,05	-0,06
thickness max	%	6,21	-6,26
thickness min	%	0,05	-0,12

4.4.2.4 Transportation

- Assessment Letter: Furgões Roma
- Machine: High Pressure
- Test results:

Properties	Unit	HCFC 141b	Methylal
Density	Kg/m^3	39,8	41.3
K factor	mW/mK	22,5	24.6
Compression set 10% (Pa)	kPa	174,4	172.1
Compression set 10% (Pe)	kPa	213,2	210.3
Dim. Stability (+70 C)			
side 1 max	%	-0,58	-0.64
side 1 min	%	-0,16	-0.18
side 2 max	%	-0,56	-0.67
side 2 min	%	-0,19	-0.22
thickness max	%	-4,11	-2.24
thickness min	%	2,32	1.82

Dim. Stability (-20 C)			
side 1 max	%	0,03	0.04
side 1 min	%	-0,01	-0.02
side 2 max	%	0,03	0.04
side 2 min	%	0,01	-.03
thickness max	%	0,09	0.12
thickness min	%	0,01	0.04

4.4.2.5 Thermoware

- Assessment letter: Soprano
- Machine: High Pressure
- Foam Tests:

Properties	Unit	HCFC 141b	Methylal
Density	Kg/m^3	36,9	39,4
K factor	mW/mK	22,8	24,2
Compression set 10% (Pa)	kPa	203,6	184,3
Compression set 10% (Pe)	kPa	189	158,9
Dim. Stability (+70 C)			
side 1 max	%	0,43	1,08
side 1 min	%	0,09	0,01
side 2 max	%	0,70	1,94
side 2 min	%	-0,02	0,06
thickness max	%	-1,25	-2,35
thickness min	%	-0,70	-0,63
Dim. Stability (-20 C)			
side 1 max	%	0,20	-0,15
side 1 min	%	0,02	-0,02
side 2 max	%	0,16	0,13
side 2 min	%	-0,02	-0,02
thickness max	%	-6,88	-1,33
thickness min	%	0,41	-0,07

4.4.2.6 Polyisocyanurate Foams (Blocks)

- Assessment Letter: Politech
- Machine: Boxfoam
- Test results:

Properties	Unit	HCFC 141b	Methylal
Density	Kg/m^3	41,5	42,5
K factor	mW/mK	25,1	27.2
Compression set 10% (Pa)	kPa	312,8	169,8

Compression set 10%	kPa	321,1	148,4
Dim. Stability (+70 C)			
side 1 max	%	-0,89	0,43
side 1 min	%	-0,08	0,02
side 2 max	%	-1,47	1,65
side 2 min	%	-0,84	0,36
thickness max	%	-3,00	-3,55
thickness min	%	-0,59	0,25
Dim. Stability (-20 C)			
side 1 max	%	-0,05	0,15
side 1 min	%	0,03	-0,01
side 2 max	%	0,04	0,10
side 2 min	%	0,02	0,02
thickness max	%	-0,38	7,39
thickness min	%	-0,13	0,01

4.4.2.7 Spray Foams

- Assessment Letter: Isar
- Machine: High Pressure
- Test results:

Properties	Unit	HCFC 141b	Methylal
Density	Kg/m3	28,6	31,5
K factor	mW/mK	21,03	23,15
Compression set 10% (Pa)	kPa	198,6	194,3
Compression set 10% (Pe)	kPa	183,5	181,9
Dim. Stability (+70 C)			
side 1 max	%	-0,56	-0,62
side 1 min	%	-0,15	-0,17
side 2 max	%	-0,54	-0,65
side 2 min	%	-0,18	-0,21
thickness max	%	-3,98	-2,17
thickness min	%	2,25	1,76
Dim. Stability (-20 C)			
side 1 max	%	0,04	0,05
side 1 min	%	-0,01	-0,03
side 2 max	%	0,04	0,05
side 2 min	%	0,01	0,04
thickness max	%	0,12	0,16
thickness min	%	0,01	0,05

Note: because of shortness in time, this application, a minor application in Brazil, was not completely optimized.

5. Conversion Costs

Following are tentative cost templates to calculate incremental cost of conversion from HCFC-141b to methylal-based foams. It should be pointed out that equipment and chemical cost can differ significantly from country to country, from time to time, and are also subject to economy of scale considerations.

5.1 Incremental Capital Costs

ENTITY	ACTION	CALCULATION	Comment
System House	Explosion proofing of blending tanks	AA x 30,000	As for methyl formate
System House	Nitrogen dispenser	BB x 8,000	
System house	ML vapor monitors	2 x 2,500	To monitor IH compliance
System House	Spray/PIP safety package	CC x 7,500	Exhaust, grounding
System House	LPD/HPD safety package	DD x 15,000	Exhaust, grounding
System House	Pycnometer (closed cell tester)	10,000	As FSPOP project template
System House	Portable K-factor tester	10,000	
System House	Refractometer (test chemical purity)	10,000	
System House	Small rent-out dispenser	EE x 25,000	
System House	Project Management	FF clients @ 1,000	
System House	Monitoring & technology transfer	30,000	
System House	Contingencies	10% of capital costs	
Customers	ML vapor monitor	FF x 2,500	To monitor IH compliance*
Customers	Spray/PIP safety packages	GG x 7,500	Exhaust, grounding
Customers	LPD/HPD safety package	HH x 15,000	Exhaust, grounding
Customers	New Dispensers	II x 35,000	Include safety packages
Customers	Trials, testing, training,	KK machines @ 3,000	As in approved projects
Customers	Contingencies	10% of capital costs	

* This monitor could be deleted in case the supplier or a certified third party conducts an industrial hygiene survey that proves the TLV under production conditions to be less than 20% of the TLV. The cost of such a survey, however, might exceed to cost of a monitor

5.2 Incremental Operating Costs

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

CHEMICAL	PRICE (US$/kg)	BASELINE		Expert A		Expert B		Expert C		Cost Base	
		%	Cost	%	Cost	%	Cost	%	Cost	%	Cost
Polyol	3.20	38	1.22	40	1.28	40	1.28	42	1.34	42	1.34
Isocyanate	3,00	50	1.50	52	1.56	54	1.62	50	1.50	50	1.50
HCFC-141b	2.40	12	0.29	--	--	--	--	--	--	--	--
Methylal	4.00	--	--	8	0.32	6	0.24	8	0.32	8	0.32
Cost			3.01		3.16		3.14		3.16		3.16
Difference			**Base**		**0.15**		**0.15**		**0.15**		**0.15**

6. Conclusions

Based on the information presented in this report and its attachments it is concluded that:

6.1 Health, Safety, Environment

- The use of methylal does not create incremental health concerns;
- Flammability is an inherent safety risk and, although on downstream user level drastically mitigated through the use of preblended systems, requires safety measures as outlined in **Attachment V**;
- Methylal-based systems do not pose an environmental hazard based on current knowledge.

6.2 System Processability

- Shipment and storage of pure methylal must comply with its flammability status (GHS Category 2—highly flammable liquid and vapor);
- No special considerations are required for fully formulated systems with less than 2% methylal (polyols) or less than 2% methylal (isocyanates). Systems containing 2-5 php methylal need individual consideration and above that level, compliance with GHS category 2 or 3 is required. Local regulations have to be consulted in addition;
- Methylal-based systems for all applications are stable;
- Methylal and methylal blends are not corrosive;
- There are no compatibility issues of methylal with polyols and/or additives. However, it is recommended that when designing conversion projects, the compatibility of baseline polyols will be carefully checked and the impact on flammability characteristics determined;
- The shelf life for methylal meets the commercial requirement of at least 6 months under standardized conditions

6.3 Foam Properties

- Methylal-based non-insulation foams, regardless of application, match HCFC-141b foams;
- Methylal-based thermal insulation foams match HCFC-141b foams within a determined variation range in stability and density but carry a penalty in insulation value of up to 10 %. This is comparable with methyl formate while better than HCs and water-based systems;
- No data on long-term performance are as of yet available;
- Customers selected for performance trials—one per application—all expressed agreement with the performance of methylal-based PU systems.

6.4 Conversion Costs

Indicative conversion cost estimates by UNDP show modest capital and operating costs increases compared to other conversions from HCFC-141b.

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

7. Overall Assessment

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

Foam Type	Application	HSE	Assessment			
			Processing	Flamma/ bility	Physical Properties	Results
Non insulation foams	Flexible	+	+	+	+	+
	Shoe soles	+	+	+	+	+
	Structural (rigid)	+	+	+	+	+
	Semi-flexible	+	+	+	+	+
	Flexible molded	+	+	+	+	+
	Hyper-soft block	+	+	+	+	+
	Viscoelastic molded	+	+	+	+	+
	Viscoelastic block	+	+	+	+	+
	Packaging foam	+	+	+	+	+
Insulation Foams	Refrigeration	+	+	+/-	+/-	+/-
	Water heaters	+	+	+/-	+/-	+/-
	Trucks	+	+	+/-	+/-	+/-
	Blocks, Panels	+	+	+/-	+/-	+/-
	Spray	+	+	+/-	+/-	+/-
	Thermoware	+	+	+/-	+/-	+/-
	PIR	+	+	+/-	+/-	+/-

HSE + Good (Compliance with international standards)
Processing + Good (agreement as per customer who carried out the qualifying trials);
Flammability + Non flammable (Cleveland closed cup test; as per formulations in Annex VII)
+/- May be flammable (Cleveland closed cup test)
Phys. Properties + Good (agreement as per customer who carried out the qualifying trials based on +/- 5% range of results)
+/- Fair (acceptance is subject to company´s willingness to adopt a somewhat less favorable insulation value).
Source: Lambiotte / Arinos

Note on flammability tests – the tests typically used to determine flammability (open and closed cup tests0 are typically designed for transportation purposes and do not reflect very well danger in the workplace. For that reason, the EU has for processing purposes different tests, emphasizing the sustainability of a fire from emissions. ML-based systems with less that 8 php ML do pass such tests.

Based on this assessment, the results indicate that ML-based systems are an excellent HCFC-141b substitute for non-insulation PU foams.

They are less suited for the replacement of HCFC-141b in (thermal) insulation PU foams as they carry a penalty in insulation value of up to 10 %. Further optimization may reduce this—but unlikely will eliminate this penalty entirely.

Safe use of methylal 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:

- Projects should preferably be implemented through local system houses to minimize safety risks at downstream users ;
- Project designers should ensure that:
  - Chemical compatibility is verified,

- Implications related to the flammable character of the substance are addressed as recommended in **Attachment V**:

SYSTEM HOUSES

- 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 methylal vapor sensor with alarm function set on 20% (= ~TLV)
- Adequate ventilation
- Meter Methylal under the level of the liquid to which it is being added
- Adherence to MSDS, OSHA and local guidelines

DOWNSTREAM USERS

- Proper personal protective equipment
- Electrically grounded equipment and drums (grounding clip)
- A methylal vapor sensor with alarm function set on 20% LFL (= ~TLV) LFL OR an industrial hygiene survey by supplier/certified third party
- Adequate ventilation
- Adherence to MSDS and local guidelines

ATTACHMENT I:
PROJECT DOCUMENT (APPROVED VERSION)

COUNTRY:	**Brazil**	**IMPLEMENTING AGENCY:**	**UNDP**
PROJECT TITLE:	**Pilot project to Validate Methylal as Blowing Agent in the Manufacture of Polyurethane Foams (Phase-I)**		
PROJECT IN CURRENT BUSINESS PLAN:		**Based on ExCom Decision 55/43(e i-iii)**	
SECTOR:		**Foams**	
ODS USE IN SECTOR			
Baseline:		**N/A**	
BASELINE ODS USE:		**N/A**	
PROJECT IMPACT (ODP targeted):		**N/A**	
PROJECT DURATION:		**9 months (Phase-I only)**	
PROJECT COSTS:		**US$ 464,200 (Phase-I only)**	
LOCAL OWNERSHIP:		**100 %**	
EXPORT COMPONENT:		**0 %**	
REQUESTED MLF GRANT:		**US$ 464,200**	
IMPLEMENTING AGENCY SUPPORT COST:		**US$ 34,815 (7.5 %)**	
TOTAL COST OF PROJECT TO MLF:		**US$ 499,015**	
COST-EFFECTIVENESS:	**N/A**		
PROJECT MONITORING MILESTONES:		**Included**	
NATIONAL COORDINATING AGENCY:		**Ministry of Environment - MMA/PROZON**	

Project Summary

Brazil became a Party to the Vienna Convention and Montreal Protocol on 19 March, 1990. Brazil also ratified the London, Copenhagen, Montreal and Beijing Amendments. The country is fully committed to the phaseout of HCFCs and willing to take the lead in assessing new HCFC phaseout technologies, particularly in the foam sector. It has a vibrant local PU system house system that caters to SMEs while all international PU chemical manufacturers are represented which concentrate on the larger users

The objective of this project is to develop, optimize, validate and disseminate the use of methylal in PU foam applications. Validating now can save a multiple of the validation costs in subsequent projects.

The project is divided in two distinct phases:

Phase-I: development, optimization, validation and technology dissemination
Phase-II: implementation in 15 downstream enterprises covering all relevant applications

At this stage funding only for Phase-I is requested. The costs Phase-II are included as a preliminary indicative estimate. The Phase-II costs will be updated after completion of Phase-I and submitted for approval in 2009. It is the intent that the UNEP Foams Technical Options Committee will be involved in the validation.

IMPACT OF PROJECT ON COUNTRY'S MONTREAL PROTOCOL OBLIGATIONS

This project is a pilot project aimed to validate a new HCFC phase-out technology and will contribute indirectly to the fulfillment of Brazil's Montreal Protocol obligations. If successfully validated, the technology will contribute to availability of cost-effective options that are urgently needed to implement HCFC phase-out, particularly at SMEs.

Prepared by: Rappa, Inc. **Date: May 2009**

PROJECT OF THE GOVERNMENT OF BRAZIL
PILOT PROJECT TO VALIDATE METHYLAL AS BLOWING AGENT IN THE MANUFACTURE OF POLYURETHANE FOAM (PHASE-I)

1. PROJECT BACKGOUND

This project has been prepared as response to the Executive Committee Decision 55/43 and it is part of a limited group of pilot validation projects being implemented by UNDP with the objective to develop, optimize and validate chemical systems for use with non-HCFC blowing agents. At its 56th meeting, November 2008, the Executive Committee approved the first two pilot projects (one in Brazil) that will address the validation of one of these technologies (methyl formate) in all relevant PU applications. The present project aims to undertake a similar process in Brazil with another technology (methylal). The other technologies that make part of this limited group of pilot validation initiatives are listed in Table 1 below and will be tested in other countries.

2. PROJECT OBJECTIVES

The objectives of this project are to:

1. Develop, optimize and validate the use of methylal as auxiliary blowing agent in polyurethane foam applications meeting local and international safety standards;
2. Demonstrate the technology in a limited amount of downstream operations;
3. Transfer the technology to interested stake holders, such as system houses and individual HCFC users, anywhere in the world.

3. INTRODUCTION

Current validated technologies for replacing HCFC-141b in foams are restricted to water/isocyanate, hydrocarbons and HFCs. With water non-performing in thermal insulation applications, HFCs being high in global warming potential and hydrocarbons high in investment costs, it is important to validate other options. ExCom Decision 55/43 reflects this by promoting pilot projects aimed to validate technologies. UNDP has followed recent developments in this industry very closely. Its evaluation also covered potential improvements on validated technologies that raise environmental concerns or are high in cost. Based on its findings it has prepared a total of five (5) pilot projects which may cover all commercially available products that have potential as blowing agent in foams but have not yet been validated in an A5 context. These technologies are:

SUBSTANCE	STATUS	COMMENTS
Hydrocarbons	To be submitted to the 58th ExCom	Evaluation of cost saving options
Methyl formate	Approved at the 56th ExCom	Technical validation of a commercial available product
Methylal	To be submitted to 58th ExCom	Technical validation of a commercial available product
Supercritical CO_2	Under development	Technical validation of a commercial available product
HFO-1234ze*	To be submitted to 57th ExCom	Technical validation of a commercial available product

* A Hydro-Fluoro-Olefin. Full name: trans-1,3,3,3-tetra fluoro propene; $CHF=CHCF_3$

This project covers the validation of methylal in all relevant foam applications. Methylal is a commercially available product that is used mainly for solvent applications and, to a lesser extent, in aerosols. It has no ODP and a negligible GWP. It is in limited use in Europe as a co-blowing agent to enhance HC and HFC systems. However, it has also potential as a sole auxiliary blowing agent in situations where HFCs are not welcomed or HCs are too expensive in investment related to the size of a particular operation. The first is an issue relevant to MOP decision XIX-6 which, under others, stipulates the need to include environmental concerns and the latter is a recurring issue in Article 5 countries where 80% of the enterprises qualify as SME.

Technology validation is a global task. However, it has to be executed in a particular country and UNDP is therefore preparing the proposals in consultation and with the consent of the relevant countries, and requested endorsement letters from the countries are included. However, because of the global impact, deduction of the first phase, which deals with development, optimization and validation from the national aggregate HCFC consumption, would not be fair and it is requested to treat phase-1 this way.

4. INFORMATION ON PARTICIPATING COMPANIES

This pilot project is designed around Arinos Quimica Ltda ("Arinos"), a Brazilian system house. Contact information is as follows:

Company:	Arinos Quimica Ltda
Contact:	Mr. Henrique Bavoso, Commercial Director
Address:	Rua Arinos, 15 – Pq Industrial Agua Vermelha, Osasco, SP CEP 06276-032, Brazil
Ph/Fx/EM:	+5511-3602-7254/+5511-3602-7215/henrique.bavoso@arinos.com.br

Arinos is the successor of Flexquim which was founded in 1993 by Mateos Raduan Dias. The company initially focused on the distribution of chemicals to the flexible PU foam industry. As business evolved into other distribution products and PU systems, it was decided in 1997, along with the relocation to a new, enlarged plant, to rename the business into Arinos because the original name did not match the products anymore. The company is 100 % Brazilian owned. Combined annual sales are US$ 100 million (2008). In addition to its main plant and headquarters in Sao Paulo, it has two branches in the north and the south and three regional sales offices. It employs about 130. Annual sales for the PU system house part have developed as follows (rounded):

2005 US$ 2,300,000 2006 US$ 4,300,000 2007: US$ 7,000,000 2008: US$ 10, 500,000

Arinos has a customer base of about 250 PU companies that purchase systems. Its distribution operation is much larger with 3,500 customers that include non-PU areas such as foodstuff, solvents, pharmaceuticals, etc. From the 250 registered PU system buyers, 50 are regular customers. Arinos also counts with the conditions required to undertake this assignment: knowledge and access to the technology, research and development capacity and interest to undertake the testing.
There is no export to other countries. Base PU chemicals are purchased from Dow, Bayer, Solvay and Momentive (former OSI, the successor of Union Carbide's Silicones Division). The company processes the following auxiliary blowing agents (2007/2008):

Substance	2007	2008	Remarks
HCFC-141b	120 t	180 t	all rigid and integral skin applications
Methylene Chloride	40 t	60 t	packaging foams
Methylal	n/a	n/a	at this time only sample amounts

Methylal is purchased from Lambiotte, Belgium. Lambiotte has developed methylal in Europe as a co-blowing agent in rigid PU foams. Arinos intends to pursue its use as a sole or auxiliary blowing agent as it sees a large potential market in Latin America, which consists in majority of small users that cannot handle pure hydrocarbons and methylal offers the possibility to address flammability issues at the system house only rather than at user level. For this purpose, Arinos has entered into an exclusive distributorship for methylal with Lambiotte. Arinos has preliminary identified 15 companies covering 18 applications that address all major HCFC-consuming PU applications in Brazil.

5. PROJECT DESCRIPTION

The project is divided into two phases:

- Phase-I: development, optimization, validation, technology dissemination
- Phase-II: implementation at recipients covering all applications

5.1 PHASE-I

PU foams are used in applications with different formulations. 18 applications have been identified that use currently HCFC-141b. The first phase, which includes development, optimization and validation of methylal as replacement technology for HCFC-141b will involve the systems house only. Arinos has already developed the technology for one application (packaging foams) but this still will need validation. Phase-I of this project will consist of:

- Acquisition of the necessary testing/prototyping equipment;
- Development of the remaining 17 applications;
- Optimization and validation of all 18 formulations on prototyping equipment;
- Development of safe practices meeting national and international standards for the transportation, storage and use of methylal in system houses and of methylal-containing systems at SMEs;
- Dissemination of the experience gained through a workshop.

Changing blowing agents, essential components in formulations, require determination of baseline values for critical properties. Some, are general in nature but others are specific as the following list shows:

Foam type	Application	Status	Critical Properties	Action
Integral Skin	Steering wheels	Not developed	Friability, surface	Development, Optimization, Validation
	Shoe soles	Not developed	Surface	Development, Optimization, Validation
	Structural (rigid)	Not developed	Surface	Development, Optimization, Validation
	Semi-flexible	Not developed	Surface	Development, Optimization, Validation
Rigid Insulation	Domestic refrigeration	Not developed	Insulation, adhesion	Development, Optimization, Validation
	Commercial refrigeration	Not developed	Insulation, adhesion	Development, Optimization, Validation
	Water heaters	Not developed	Insulation, adhesion	Development, Optimization, Validation
	Trucks	Not developed	Insulation, adhesion	Development, Optimization, Validation
	Panels-continuous	Not developed	Insulation, adhesion	Development, Optimization, Validation
	Panels-discontinuous	Not developed	Insulation, adhesion	Development, Optimization, Validation
	Spray	Not developed	Insulation, adhesion	Development, Optimization, Validation
	Blocks	Not developed	Insulation	Development, Optimization, Validation
	Thermoware	Not developed	Insulation, adhesion	Development, Optimization, Validation
	Pipe-in-pipe	Not developed	Insulation, adhesion	Development, Optimization, Validation
Semi-Rigid	Packaging foam	Developed	Shock absorption	Development, Optimization, Validation
Flexible Foams	Hyper-soft molded	Not developed	Appearance, touch	Development, Optimization, Validation
	Hyper-soft slabstock	Developed	Appearance, touch	Development, Optimization, Validation
	Low resilience	Developed	Resilience curve	Development, Optimization, Validation

Companies and their suppliers do not conduct regular testing on properties of their foams, nor do they set standards. Therefore the acquisition of suitable testing equipment and the determination of baseline data on critical properties is a precondition for a successful validation program. In addition, prototyping equipment is required to limit burdensome and costly downstream production testing to a minimum. The outcome of this part of the project will be a list of application-specific product requirements and tests to measure these. After this, optimization and validation can start in earnest.

Based on the outcome of these programs, the technology will then be technically cleared for industrial application under Phase-II as well for dissemination to other interested system houses world-wide. Past experience has shown how important it is to assure commercial availability and local technical support. In this project, following action is proposed to achieve this goal to the extent possible:

- UNDP has stipulated—and Arinos has agreed to—offering the technology to all system houses in good standing, meeting in this way eligibility criteria (everything that is developed during the project implementation using MLF funds will be public knowledge and will be disclosed).
- Technology dissemination workshops will be conducted for interested systems houses as soon as the technology is deemed transferable.

5.2 PHASE-II

After the formulation for a particular application has successfully passed its evaluation, UNDP will apply for approval of the second project phase, which is application in manufacturing contexts. 15 companies, covering all 18 applications, will apply the technology in their operations. Product and process testing will be conducted by the system house. UNDP will conduct safety audits. Process adaptations will be made as needed to meet requirements as indicated in the previous table. This phase is not part of the present submission, which is focused in validation of the technology.

5.3 SUPERVISION ARRANGEMENTS

Decision 55/43 requires Agencies to report accurate project cost data as well as other data relevant to the application of the technologies through *"a progress report after each of the two implementation phases"*. UNDP suggests in addition supervision of the validation by the UNEP Foams Technical Options Committee. The FTOC has, in its September 2008 meeting, in principle agreed to such an assignment.

6. TECHNICAL OPTIONS FOR HCFC REPLACEMENT IN PU FOAMS

6.1 GENERAL OVERVIEW

Annex-1 provides an overview of all HCFC-141b replacement technologies that are currently available, proposed or under development. Based on these data, it appears that

- Straight conversion of HCFCs to HFCs will always increase the GWP;
- HCs, CO_2 (liquefied or derived from water), methylal and methyl formate will be options in PU foams that decrease—virtually eliminate—GWP in PU foams;
- Emerging technologies such as HBA-2, AFA-L1 and FEA 1100 will require at least two more years before (potential) commercialization;
- PU validation may therefore include cost-optimized hydrocarbons, methyl formate, methylal and environmentally optimized HFC formulations.

6.2 METHYLAL AS REPLACEMENT TECHNOLOGY FOR HCFC-141b

Methylal, also called dimethoxymethane, belongs to the acetyl family. It is a clear colorless, chloroform-like odor, flammable liquid with a relatively low boiling point. Its primary uses are as a solvent and in the manufacture of perfumes, resins, adhesives, paint strippers and protective coatings. It is soluble in three parts water and miscible with the most common organic solvents.

Property	Methylal	HCFC-141b
Appearance	Clear liquid	Clear liquid
Boiling point	42 °C	32 °C
LEL/UEL	2.2-19.9 %	7.6-17.7
Vapor pressure	400 mm Hg @ 20 °C	593 mm Hg @ 25 °C
Lambda, gas	14.5 mW/m.k@ 42 °C	10.0 mW/m.k @ 25 °C
Auto ignition	235 °C	>200 °C
Specific gravity	0.821 @ 20 °C	1.24
Molecular weight	76.09	117
GWP	Negligible	630
TLV (USA)	1000 ppm TWA	500 ppm TWA/500 ppm STEL

Methylal has a very low toxicity while HCFC-141b classifies as moderately toxic:

	Methylal	**HCFC-141b**
• TLV (MAK):	1000 ppm	500 ppm
• Acute toxicity:	LD50 > 7 g/kg	8,000 ppm
• Acute inhalation toxicity (LC50)	15,000 ppm	10,000 ppm
• LC50	18,354 ppm	92,000 ppm
• Sub-acute inhalation	NOEL = 4,000 ppm (8 x 6 h)	20,000 ppm
• Sub-chronic inhalation:	NOEL = 2,000 ppm	20,000 ppm
• Eye irritation:	minor to moderate	minor to moderate
• Skin irritation:	none to slight	none to slight
• Dermal sensitization:	not allergenic	non allergenic
• Ames test:	no mutagenic activity	no mutagenic activity

Methylal has also lower eco-toxicity than HCFC 141b:

	Methylal	**HCFC-141b**
• Daphnids, fish (Brachydanio Rerio)	no effect	31.2 – 126 mg/L
• Biodegradability (ISO/DIS 8192)	biodegradable	not biodegradable

Methylal is, however flammable:

- flash point (open cup): -18°C (-0.4°F)
- auto-ignition temperature: 237°C (458.6°F)
- explosion limits: 1.6 % vol (LEL)/17.6 % vol (UEL)

Methylal as proposed, however, will reduce—or even eliminate—the related risk by premixing at the system house. Consequently, safety precautions will be less than for current HC applications.

Following is a list comparing methylal with other, common foam blowing agents on the most relevant properties:

	HCFC-141b	Methylal	Cyclo Pentane	HFC-245fa
LEL/UEL (%)	7.3-16.0	1.6/17.6	1.4-8.0	none
Molecular Weight	117	76	70	134
Gas Conductivity (mW/m°K)	10 (25°C)	14.5 (42°C)*	11 (10°C)	12.5 (24°C)
TLV/OEL (ppm)	500 (TLV)	1,000 (TLV)	600 (TLV)	300 (WHEEL)
GWP (100 y; IPCC-1996)	630	Negligible	11	820
ODP	0.11	0	0	0

*Extrapolation at 25 °C would be ~ 11

In summary, methylal compares very well to other, commercially available, HCFC replacement alternatives. UNDP's conclusion is that the chemical is worth a thorough validation.

Apart from the use of methylal as sole auxiliary blowing agent, its use as a co-blowing agent in conjunction with hydrocarbons and HFCs for rigid foam applications has been described in the literature. It is claimed that in continuous panels methylal improves the miscibility of pentane, promotes blending in the mixing head, foam uniformity, flow, adhesion to metal surfaces and insulation properties, reducing simultaneously the size of the cells. In discontinuous panels, where most producers use non-flammable agents, the addition of a low percentage of Methylal to HFCs (245fa, 365mfc or 134a) makes it possible to prepare pre-blends with polyols of low flammability with no detrimental effect on the fire performance of the foam. Methylal reduces the cost, improves the miscibility, the foam uniformity and flow and the adhesion to metal surfaces. Co-blown with HFC-365mfc, it also improves the thermal insulation. In domestic refrigeration compared to cyclopentane alone Methylal increases blowing rate and compressive strength. In sprayfoam it reduces the cost of HFC-245fa/-365mfc. There is no known use of methylal as sole auxiliary blowing agent.

Finally, it would be interesting to apply methylal in natural polyol systems—such as castor or soy oil based polyols. Such systems have generated high interest in Brazil and world-wide.

Despite all literature references, public knowledge of methylal's industrial performance as blowing agent is quite limited. To validate its use as a possible replacement of HCFCs for MLF projects in developing countries, peer reviewed evaluations should be carried out to assess its performance in integral skin and rigid insulating foams. Following parameters should be carefully monitored:

- Fire performance in actual operating conditions (considering flammability of the pure chemical)
- Polyol miscibility, an advantage claimed in the literature
- Foam flow (taking into account the relatively high -compared to other blowing agents- boiling point)
- Foam thermal conductivity (Gas conductivity value is not reported)
- Skin formation. (A cited US patent suggests a clear benefit)
- Diffusion rate in the polyurethane matrix (in view of its high solvent power)

One could ask if future use of methylal in an additional application—foams—would not stress the supply and therefore would have price implications. However, the potential use in foams is just a fraction of the current use in other applications and no supply issue is therefore expected. Methylal is offered in different purities. It is recommended that the pure grade suits its use as blowing agent best:

Compound	Cosmetic Grade	Anhydrous Grade	Pure Grade	Technical Grade
Methylal	**99.5 % min.**	**99.9 % min.**	**99.5 % min.**	**93 % min.**
Methanol	< 1 ppm	< 0.05 %	< 0.05 %	6.5 % max
Formaldehyde	< 1 ppm	< 0.005 %	< 0.0005 %	< 0.02 %
Water	< 0.5 %	< 0.03 %	< 0.5 %	< 0.25 %

7. PROJECT COSTS

Making cost forecasts for pilot projects is difficult as they are by nature unpredictable. UNDP has used to the extent possible guidance provided by the Secretariat in Doc 55/47 Annex III, Appendix II. One uncertainty is the flammability. The Material Safety Data Sheet (MSDS) mentions methylal to be "highly flammable". On the other side, it can be expected that emissions from PU systems containing methylal and from the actual foam process will be much lower—likely even below applicable explosion limits. UNDP considers the process at the system house (prototyping, blending) hazardous and requiring adequate safeguards but the use of pre-blended systems may be non-flammable. That implies that from the 18 applications most likely only 3 (all continuous operations that directly meter the blowing agent) are deemed to require safeguards. Consequently, the Secretariat's template for flammable blowing agents has been used in 4 cases (three users and the system house) and the template for non-flammable substances 12 cases. This has a beneficial impact on the expected budget. The price of methylal in Brazil is US$ 3.00/kg while HCFC-141b is US$ 2.40. However, the molecular weight of methylal is lower so that a better blowing efficiency can be expected. This may be partially offset by solubility and diffusion so that an actual prediction is difficult and the calculation of IOCs should await the results of the system development. Following are the summarized cost expectations:

#	ACTIVITY	COSTS (US$)		
		INDIVIDUAL	SUB-TOTAL	TOTAL
	PHASE-I – DEVELOPMENT/OPTIMIZATION/VALIDATION/DISSEMINATION			
1	Preparative work Project Preparation Technology Transfer, Training	 30,000 25,000	55,000	**464,200**
2	System Preparation Development (17 applications) @ 5,000 Optimization (17 applications) @ 3,000 Validation (18 applications) @ 2,000	 85,000 51,000 36,000	172,000	
3	Laboratory Equipment K-factor tester US$ 10,000 Refractometer 5,000 Brett mold 5,000 HP laboratory dispenser 50,000 Sprayfoam/PIP dispenser 20,000 pH tester 5,000 Abrasion tester 25,000 Cell gas analyzer 20,000 Laboratory Safety	 10,000 5,000 5,000 50,000 20,000 5,000 25,000 20,000 10,000	150,000	
4	Peer review/preparation of next phase		20,000	
5	Technology Dissemination Workshops		25,000	
6	Contingencies (10%)		42,200	

	PHASE-II – HCFC PILOT PHASEOUT PROJECT COVERING ALL APPLICATIONS (tentative and not part of the current funding request)			
1	System House adaptations 1 Blender 1 Tank for Methylal Safety measures Contingencies (10%)	 50,000 20,000 25,000 9,500	104,500	**629,700 + IOCs**
2	Discontinuous Operations (12) 14 Retrofits @ 15,000 14 Trial Programs @ 3,000 Contingencies (10%)	 210,000 42,000 25,200	277,200	
3	Continuous Operations (3) 3 ex proof metering systems @ 15,000 3 ventilation units @ 25,000 3 sensor systems @ 15,000 3 grounding programs @ 5,000 Contingencies	 45,000 75,000 45,000 15,000 18,000	198,000	
4	Peer review/safety audits		50,000	
5	Incremental Operating Costs		Not determined	

UNDP requests at this stage a grant for the first phase of this project amounting to **US$ 464,200.**

8. IMPLEMENTATION/MONITORING

TASKS	2009				2010			
	1Q	2Q	3Q	4Q	1Q	2Q	3Q	4Q
Project Start-up								
MF Project Approval	X							
Receipt of Funds		X						
Grant Signature		X						
Management activities								
-Monitoring/oversight activities in place		X						
-Progress Reports to NOU and Excom			X		X	X	X	
Phase-I								
-Procurement		X						
-Installation			X					
-System development		XX	X					
-System optimization		X	XX					
-System validation at system house			XXX					
-Peer review/detailed design of phase- II			X					
-Approval phase-II				X				
- Technology Dissemination Workshop(s)				X				
Phase-II								
-Prepare individual Implementation plans				X				
-Procurement					X			
-Installation/start-up						XX		
-Trials						XX		
-Certificates of Technical Completion (COCs)						XX		
-Handover Protocols (HOPs)						X	X	
-Completion Report (PCR)							X	

MILESTONES FOR PROJECT MONITORING

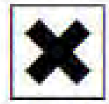
TASK	MONTH*
(a) Project document submitted to beneficiaries	2
(b) Project document signatures	3
(c) Bids prepared and requested	3, 9
(d) Contracts Awarded	3, 9
(e) Equipment Delivered	4, 11
(f) Training Testing and Trial Runs	4, 12
(g) Commissioning (COC)	14
(h) HOP signatures	15
(1) Compliance Monitoring	17

* As measured from project approval

ATTACHMENT II:
MATERIAL SAFETY DATA SHEET/OSHA GUIDELINES

MATERIAL SAFETY DATA SHEET	Page : 1
	Revision nr : 5
	Date : 30/9/2005
METHYLAL TECHNICAL GRADE	Supersedes : 20/2/2004
	L-9307


Highly flammable


Harmful

Producer
Lambiotte & Cie s.a.
Grand' Rue, 79
B-6724 Marbehan Belgique-Belgie
Tel. +32 (0)63 41 00 80
EMERGENCY : +32 (0)70 245 245

1. Identification of the product and the company

Company identification	: See distributor.
Trade name	: METHYLAL TECHNICAL GRADE.
Chemical family	: Acetal.
Type of product	: Liquid.
Use	: Industrial.

2. Information on ingredients

This product is considered to be hazardous and contains hazardous components.

Substance name		Value(s)	CAS nr / EINECS nr / EC Index	Symbol(s)	R-Phrase(s)
Methylal	:	> 93 %	000109-87-5 / 203-714-2 / -----	F	11
Methanol	:	<= 6.5 %	000067-56-1 / 200-659-6 / 603-001-00-X	F T	11-23/24/25-39/ 23/24/25

3. Hazards identification

Risk Phrases	: Harmful by inhalation, in contact with skin and if swallowed.
Dangerous substances	: Highly flammable.
Primary route of exposure	: Vapours inhalation. Skin contact.
Symptoms relating to use	
- Inhalation	: Symptoms of overexposure to vapours include : Headache. Dizziness. Drowsiness. Nausea.
- Skin contact	: Absorbed through the skin. Redness.
- Eye contact	: Direct contact with the eyes is likely irritating.
- Ingestion	: Abdominal pain, nausea. Swallowing a small quantity of this material presents some health hazard. Must not come into contact with food or be consumed.

4. First aid measures

First aid	
- Inhalation	: If overcome by exposure, remove victim to fresh air immediately. Obtain medical attention if breathing difficulty persists.
- Skin contact	: Remove affected clothing and wash all exposed skin area with mild soap and water, followed by warm water rinse.
- Eye contact	: Rinse immediately with plenty of water. Obtain medical attention if pain, blinking or redness persist.
- Ingestion	: If swallowed, immediately administer water (1/2 liter) only if victim is completely conscious/alert and induce immediately vomiting. Seek medical attention immediately.

MATERIAL SAFETY DATA SHEET	Page : 2
	Revision nr : 5
	Date : 30/9/2005
METHYLAL TECHNICAL GRADE	Supersedes : 20/2/2004
	L-9307

5. Fire - fighting measures

Flammable class	: This product is flammable.
Prevention	: No smoking. Keep away from sources of ignition.
Extinguishing media	: Foam. Dry chemical. Carbon dioxide. Large quantity of water.
Surrounding fires	: Use water spray or fog for cooling exposed containers.
Special exposure hazards	: Vapor mixes readily with air, forming explosive mixtures.
Protection against fire	: All fire-fighting personnel must wear safety suits. Use self-contained breathing apparatus when in close proximity to fire.
Special procedures	: Exercise caution when fighting any chemical fire.

6. Accidental release measures

Personal precautions	: Equip cleanup crew with proper protection.
Environmental precautions	: Prevent entry to sewers and public waters. Notify authorities if liquid enters sewers or public waters.
After spillage and/or leakage	: Clean up any spills as soon as possible, using an absorbent material to collect it. Use suitable disposal containers.

7. Handling and storage

General	: No naked lights. No smoking.
Precautions in handling and storage	: Do not use compressed air to either agitate or transfer the contents of storage containers (tanks) / shipping drums containing this material.
Technical protective measures	: Ground well. Use only non-sparking tools. Use special care to avoid static electric charges.
Storage	: Keep container closed when not in use. Store in dry, cool, well-ventilated area.
Storage - away from	: Heat sources.
Handling	: Handle in accordance with good industrial hygiene and safety procedures. Wash hands and other exposed areas with mild soap and water before eat, drink or smoke and when leaving work.

8. Exposure controls / personal protection

Personal protection	
- Respiratory protection	: Approved dust or mist respirator should be used if airborne particles are generated when handling this material.
- Skin protection	: Wear suitable gloves resistant to chemical penetration.
- Eye protection	: Even though no specific eye irritation data is available, wear eye protection appropriate to conditions of use when handling this material.
- Ingestion	: When using, do not eat, drink or smoke.
Industrial hygiene	: Provide local exhaust or general room ventilation to minimize dust and/or vapour concentrations.

9. Physical and chemical properties

Physical state	: Volatile liquid.
Colour	: Colourless.
Odour	: Ethereal.
pH value	: No data available.
Molecular weight	: 76.08
Melting point [°C]	: -104.8
Initial boiling point [°C]	: 42.3
Density	: .861
Viscosity	: cP (30°C) .325

MATERIAL SAFETY DATA SHEET	Page : 3
	Revision nr : 5
	Date : 30/9/2005
METHYLAL TECHNICAL GRADE	Supersedes : 20/2/2004
	L-9307 www.lbum.com

9. Physical and chemical properties (continued)

Solubility in water [% weight]	: 32.3
Flash point [°C]	: -18
Auto-ignition temperature [°C]	: 237
Explosion limits - lower [%]	: 1.6
Explosion limits - upper [%]	: 38.5

10. Stability and reactivity

Hazardous decomposition products	: Thermal decomposition generates : Carbon dioxide.
Hazardous reactions	: Reacts with : Strong acids.
Hazardous properties	: Vapor mixes readily with air, forming explosive mixtures.
Conditions to avoid	: Heat. Sparks. Open flame.

11. Toxicological information

Rat oral LD50 [mg/kg]	: 5620
Rabbit dermal LD50 [mg/kg]	: No data available.
Rat inhalation LC50 [mg/kg]	: No data available.

12. Ecological information

48 H-CE50 - Daphnia magna [mg/l]	: No data available.
Persistence and degradability	: Biodegradable

13. Disposal considerations

Disposal	: Dispose in a safe manner in accordance with local/national regulations. Dispose of this material and its container at hazardous or special waste collection point.

14. Transport information

Hazard Label(s)

: Flammable. Harmful.

- Proper shipping name	: UN 1234 METHYLAL, 3, II
- UN No.	: 1234
- H.I. nr :	: 33
- ADR/RID	: Group : II Class : 3
- IMO-IMDG code	: Class 3
- EMS-Nr	: F-E S-D
UN Packing group	: II

15. Regulatory information

Symbol(s)	: Harmful.
R Phrase(s)	: R11 - Highly flammable. R20/21/22 - Harmful by inhalation, in contact with skin and if swallowed. R68/20/21/22 - Harmful : possible risk of irreversible effects through inhalation, in contact with skin and if swallowed.
S Phrase(s)	: S03 - Keep in a cool place.

MATERIAL SAFETY DATA SHEET	Page : 4
	Revision nr : 5
	Date : 30/9/2005
METHYLAL TECHNICAL GRADE	Supersedes : 20/2/2004
	L-9307 www.lisam.com

15. Regulatory Information (continued)

S09 - Keep container in a well-ventilated place.
S16 - Keep away from sources of ignition - No smoking.
S24 - Avoid contact with skin.
S33 - Take precautionary measures against static discharges.
S35 - This material and its container must be disposed of in a safe way.
S36/37 - Wear suitable protective clothing and gloves.
S53 - Avoid exposure - obtain special instructions before use.
S59 - Refer to manufacturer/supplier for information on recovery/recycling.

16. Other information

Further information : None.

The contents and format of this MSDS are in accordance with EEC Commission Directive 2001/58/EEC.

DISCLAIMER OF LIABILITY The information in this MSDS was obtained from sources which we believe are reliable. However, the information is provided without any warranty, express or implied, regarding its correctness. The conditions or methods of handling, storage, use or disposal of the product are beyond our control and may be beyond our knowledge. For this and other reasons, we do not assume responsibility and expressly disclaim liability for loss, damage or expense arising out of or in any way connected with the handling, storage, use or disposal or the product. This MSDS was prepared and is to be used only for this product. If the product is used as a component in another product, this MSDS information may not be applicable.

End of document

Occupational Health Guideline for Methylal

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3OCH_2OCH_3$
- Synonyms: Dimethoxymethane; methyl formal; formal; dimethylacetal formaldehyde
- Appearance and odor: Colorless liquid with a pungent odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylal is 1000 parts of methylal per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 3100 milligrams of methylal per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methylal can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. *Short-term Exposure:* Overexposure to methylal may cause irritation of the eyes, nose, and throat, lightheadedness, incoordination, and unconsciousness.

2. *Long-term Exposure:* Prolonged overexposure to methylal may cause irritation of the skin.

3. *Reporting Signs and Symptoms:* A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methylal.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylal at potentially hazardous levels:

1. *Initial Medical Screening:* Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methylal exposure.

—Skin disease: Methylal is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although methylal is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although methylal is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methylal might cause exacerbation of symptoms due to its irritant properties.

2. *Periodic Medical Examination:* Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Methylal vapor is a mild respiratory irritant with anesthetic properties. Mice exposed at 11,000 ppm showed mild irritation of the eyes and respiratory tract, as well as incoordination; recovery was rapid after single exposures. At 14,000 ppm, mice showed more respiratory irritation, occasional pulmonary edema, and a greater degree of anesthesia. At the LC50 level of approximately 18,000 ppm, animals died of bronchopneumonia with fatty changes in the liver, kidney, and heart. At 4000 ppm rats were unaffected by daily 6-hour exposures.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

September 1978

Skin irritation may be expected due to defatting action by the solvent, and eye irritation if splashing occurs. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 76
2. Boiling point (760 mm Hg): 44 C (111 F)
3. Specific gravity (water = 1): 0.86
4. Vapor density (air = 1 at boiling point of methylal): 2.6
5. Melting point: −105 C (−157 F)
6. Vapor pressure at 20 C (68 F): 330 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 33
8. Evaporation rate (butyl acetate = 1): 23.1

• **Reactivity**

1. Conditions contributing to instability: Heat, presence of acids
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Contact with acids causes decomposition to methyl alcohol and formaldehyde.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide, formaldehyde, and methyl alcohol) may be released in a fire involving methylal.
4. Special precautions: Methylal will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: −18 C (−4 F) (closed cup)
2. Autoignition temperature: 237 C (459 F)
3. Flammable limits in air, % by volume: Lower: 1.6; Upper: 17.6
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

• **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold, but Browning notes that it has a slightly pungent odor.
2. Eye Irritation Level: Grant states that "exposures of mice and guinea pigs to much higher concentrations of methylal vapor than would be encountered industrially were found to cause . . . occasional irritation of the eyes but no histologically demonstrable abnormality of the optic nerve or retina."

Patty reports that mice which had received 15 7-hour exposures at 11,000 ppm experienced only mild irritation.

No quantitative information is available, however, concerning the threshold of eye irritation.

3. Evaluation of Warning Properties: Since there is no useful quantitative information relating warning properties to air concentrations of methylal, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

Sampling and analyses may be performed by collection of methylal vapors using an adsorption tube with subsequent desorption with hexane and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methylal may be used. An analytical method for methylal is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methylal.

• Clothing wet with liquid methylal should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylal from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the methylal, the person performing the operation should be informed of methylal's hazardous properties.

• Any clothing which becomes wet with liquid methylal should be removed immediately and not reworn until the methylal is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid methylal may contact the eyes.

SANITATION

• Skin that becomes wet with liquid methylal should be promptly washed or showered to remove any methylal.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methylal may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent for adhesives, resins, gums, waxes, and protective coatings; use as a solvent for extraction of alkaloids, barbituates, organic acids, and hydroxy-acids	General dilution ventilation; process enclosure; personal protective equipment
Use in manufacture of artificial resins; use as a gasoline and diesel fuel additive; use as a special fuel for rocket and jet engines	General dilution ventilation; process enclosure; personal protective equipment
Use as a reaction solvent with acetylene or in Grignard and Reppe reaction; use as a source of formaldehyde and methanol	General dilution ventilation; process enclosure; personal protective equipment
Use as a methylating agent or chemical intermediate	General dilution ventilation; process enclosure; personal protective equipment
Use in manufacture of perfume	General dilution ventilation; process enclosure; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If methylal gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If methylal gets on the skin, promptly wash the contaminated skin with water, if the methylal has not already evaporated. If methylal soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention. If there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of methylal, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When methylal has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If methylal is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected, dissolved in alcohol of greater molecular weight than butyl alcohol, and atomized in a suitable combustion chamber. Methylal should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:
Methylal may be disposed of by dissolving in alcohol of greater molecular weight than butyl alcohol and atomizing in a suitable combustion chamber.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Methylal," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.
• Browning, E.: *Toxicity and Metabolism of Industrial Solvents*, Elsevier, New York, 1965.
• Celanese Corporation: *Product Bulletin – Methylal*, New York.
• Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.
• Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.
• Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.
• Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.
• Weaver, F. L., et al.: "Toxicity of Methylal," *British Journal of Industrial Medicine*, 8:279-283, 1951.

RESPIRATORY PROTECTION FOR METHYLAL

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Vapor Concentration	
10,000 ppm or less	Any supplied-air respirator.
	Any self-contained breathing apparatus.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
	A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors.
	Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

ATTACHMENT III: PROCESS EMISSIONS

ATTACHMENT IV
TOXICOLOGICAL PROFILE

Lambiotte & Cie S.A.

METHYLAL

(DIMETHOXYMETHANE)

TOXICOLOGICAL PROFILE

18, avenue des Aubépines
B - 1180 Brussels
BELGIUM
Tel. : +32-2-374 44 65
Fax : +32-2-375 31 55

October 19th, 1998

ACUTE TOXICITY STUDIES

Ref #	Species/ strain	Initial Group	Route of administration	Dose mg/kg bw*	Dilution	Document ID	LD 50 mg/kg bw *	Comments	Date	Laboratory
1	Mouse NA	NA	Oral (gavage ?)	NA	Undiluted	1	6,950	NA	May 1983	Municipal Public Health Department, Moscow USSR
2	Rat NA	NA	Oral (gavage ?)	NA	Undiluted	1	9,070	NA	May 1983	Municipal Public Health Department, Moscow USSR
3	Rat NA	Total : 8 F 2 F per dose	Oral (gavage ?)	1,000 2,000 3,980 7,950	Undiluted	2	> 7,950	No mortality up to 7,950 mg/kg	Dec. 1968	Dow Chemical Company USA
4	Rat Wistar	Total : 50 5 M + 5 F per dose	Oral (gavage)	1 ml/kg bw 2 « » 4 « » 8 « » 16 « »	Undiluted	3	7.46 ml/kg bw = 6.415 mg/kg bw	No mortality up to 4 ml/kg bw. Sluggishness at all doses No gross pathology changes up to 8 (males) or 2 (females) ml/kg bw	Dec. 1982	Bushy Run Research Center, PA USA
5	Rabbit NA	NA	Oral (gavage)	4560 5700	Diluted in water	4	5,700	Mortality : 1/5 at 4560 mg/kg bw 4/7 at 5700 mg/kg bw	1932	University of California Medical School, San Francisco USA

*** Unless otherwise stated**
NA : Information not available

ACUTE TOXICITY STUDIES (continued)

Ref #	Species/ strain	Initial Group	Route of administration	Dose mg/kg bw*	Dilution	Document ID	LD 50 mg/kg bw *	Comments	Date	Laboratory
6	Rabbit New Zealand	Total : 10 5 M + 5 F	Topical covered for 24 h	5,000	Undiluted	5	> 5,000	No mortality No treatment related clinical signs nor gross pathology changes	Nov. 1989	Springborn Laboratories, Ohio **USA**
7	Rabbit New Zealand	Total : 20 10 M + 10 F	Topical covered for 24 h	- 1 ml/kg bw (4 M + 4 F) - 4 ml/kg bw (2 M + 2 F) -16ml/kg bw (4 M + 4 F)	Undiluted	3	> 16 ml/kg bw = 13,760 mg/kg bw	No mortality. Clinical signs at 4 and 16 ml/kg bw Local irritation at 16ml/kg bw Gross pathology changes at 1 and 16 ml/kg bw	Dec. 1982	Bushy Run Research Center, PA **USA**
8	Mouse ICR	Total : 30 3 M + 3 F per dose	Intraperitoneal	500 1,625 2,750 3,875 5,000	Diluted with 0.9% aqueous sodium chloride	6	> 3,875 < 5,000	Mortality 5 out of 6 mice at 5,000 mg/kg bw Clinical signs at 2,750 and above	June 1990	Hazleton Laboratories, MD **USA**
9	Guinea Pig NA	NA	Subcutaneous	3.0 ml/kg bw 3.5 5.0	NA	7	> 5 ml/kg bw = 4,300 mg/kg bw	No mortality up to 5 ml/kg bw Local reaction at injection sites	1951	NIH **USA**
10	Mouse Swiss	(?) groups of 10 animals	Inhalation	NA 7 h exposure		7	LC 50 = 18,354 ppm	Nervous signs preceeding death	1951	NIH **USA**

*** Unless otherwise stated**
NA : Information not available

ACUTE TOXICITY STUDIES (continued)

Ref #	Species/ strain	Initial Group	Route of administration	Dose mg/kg bw*	Dilution	Document ID	LD 50 mg/kg bw *	Comments	Date	laboratory
11	Rat NA	NA	Inhalation	NA		8	LC 50 = 15,000 ppm	NA	NA	NA
12	Rat Wistar	Total : 30 5 M + 5 F per dose	Inhalation	Saturated vapor 23° C Exposure for 14, 27 or 51 min (males) or 18, 35 or 64 min (females)		3	NA	Death occurred between 14 to 27 min (males) or 18 to 35 min (females) Nervous signs observed	Dec. 1982	Bushy Run Research Center, PA **USA**
13	Guinea Pig NA	NA	Inhalation	NA		7	NA	Clinical signs and deaths at concentrations around 150,000 ppm in one and a half to two and a half hours.	1951	NIH **USA**

*** Unless otherwise stated**
NA : Information not available

LOCAL TOLERANCE STUDIES

Ref #	Species/ Strain	Initial group	Route of administration	Number of applications	Dilution/dose	Document ID	Comments	Date	Laboratory
14	Rabbit NA	NA	Topical (ocular instillation)	1	Undiluted	2	Unwashed : moderate to severe conjonctival irritation washed : moderate conjonctival irritation	Dec. 1968	Dow Chemical Company **USA**
15	Rabbit New Zealand	Total : 12 6 females per dose	Topical (ocular instillation)	1	Undiluted 0.01 ml/eye 0.1 ml/eye	3	0.01 ml : minor irritation of conjunctivae 0.1 ml : minor corneal and iridal injury. Minor to moderate conjunctival irritation	Dec. 1982	Bushy Run Research Center, PA **USA**
16	Rabbit New Zealand	Total : 6 3 M + 3 F	Topical	1	Undiluted 0.5 ml 4 hour exposure	3	No cutaneous reaction	Dec. 1982	Bushy Run Research Center, PA **USA**
17	Rabbit New Zealand	Total : 6 2 M + 4 F	Topical	1	Undiluted 0.5 ml 4 hour period	9	Slight transient erythema Primary irritation index (PII) = 0.42/8	Nov. 1989	Springborn Laboratories, Ohio **USA**
18	Rabbit NA	NA	Topical	10 on intact skin 3 on abraded skin	Undiluted	2	Intact skin : none to slight exfoliation Abraded skin : slight hyperemia and exfoliation	Dec. 1968	Dow Chemical Company **USA**
				10 on intact skin 3 on abraded skin	10 % solution in Dowanol DPM	2	Intact skin : none to moderate exfoliation Abraded skin : slight hyperemia and exfoliation	Dec. 1968	Dow Chemical Company **USA**

NA : Information not available

MULTIDOSE TOXICITY STUDIES

Ref #	Test/type	Species/ strain	Initial group	Route of administration	Dose	Docu-ment ID	Results	Date	Laboratory
19	Subacute (17-22 days) inhalation toxicity study in mice	Mice NA	50 mice (lowest concentration) 20 mice (mid concentration) 45 mice (highest concentration)	Inhalation (whole body) 7 h/day 13 to 15 exposures for 17 to 22 days	35.1, 42 or 58 mg/l	7	Nervous signs and mortality with a dose/response relationship	1951	NIH **USA**
20	Subacute (8 days) inhalation toxicity study in rats	Rats NA	One group of 4 F	Inhalation	4000 ppm, 6 hr daily, exposure for 8 days	10	No clinical nor hematological changes. No abnormalities at necropsy	1970	Imperial Chemical Industries **UK**
21	Subchronic (13 weeks) inhalation toxicity study in rats	Rats Wistar	Total : 80 10 M + 10 F per dose	Inhalation (nose only) 6 h/day, 5 d/week, 13 weeks	0 (control) 400, 2000 and 10,000 ppm	11	10,000 ppm : nervous signs and slightly increased liver weight 400 and 2000 ppm : no changes in clinical signs. Hematology-biochemistry-urinalyses-ophthalmology-necropsy-microscopic examination	Sept. 1994	Hoechst AG, Frankfurt **GERMANY**

NA : Information not available

REPRODUCTION STUDIES

Ref #	Study type	Species/ Strain	Initial Group	Route of Admini-stration	Dose PPM	Treatment duration	Docu-ment ID	Maternal Toxicity	Embryo/ foetotoxicity	Comments	Date	Laboratory
22	Dose range finding study by inhalation administration in the pregnant rat	Rat Charles River	Total 40 1 control and 3 treated groups 10 mated females each	Inhalation 6 hour daily exposure	0 (control) 400 2000 10,000	From day 6 to 15 of pregnancy	12	At 400 and 2000 ppm no observable effects on the parent female At 10,000 ppm reduction in body weight gain and food intake, increase in water intake	At 400, 2000 and 10,000 ppm no observable effects on the litter para-meters or the macroscopic foetal structure	At 10,000 ppm some clinical signs	1997	Huntingdon Life Science **UK**
23	Effects on embryofoetal development by inhalation in the rat	Rat Charles River	Total 100. 1 control and 3 treated groups of 25 mated females each	Inhalation 6 hour daily exposure	0 (control) 400 2000 10,000	From day 6 to 15 of pregnancy	13	At 386 and 1954 ppm : no treatment-related findings. At 10,068 ppm : reduction in body weight gain between Days 6 and 12 of pregnancy and food intake between Days 6 and 16 of pregnancy. Water intake markedly higher than controls during Days 8 to 19 post coitum.	No changes considered to be related to exposure to methylal. Exposure of the parent female to 10,068 ppm has no effect on embryo-foetal development.	No effect exposure level : 1954 ppm.	1997	Huntingdon Life Science **UK**

MUTAGENICITY STUDIES

Ref #	Study type	Study description	Treatment	Document ID	Result	Date	Laboratory
24	Ames test	In vitro genotoxicity in S. Typhimurium strains TA 1535, TA 1537, TA 1538, TA 98 and TA 100, with and without metabolic activation in a pre incubation assay with a closed phase incubation	667, 1000, 3333, 6667 and 10,000 µg/plate	14	Mutagenic activity with TA 98 and TA 100 at 10000 µg/plate in absence of metabolic activation No activity at lower concentrations	Sept. 1989	Microbiological associates, MD **USA**
25	Ames test	In vitro genotoxicity in S. Typhimurium strains (TA 1535 - TA 1537 - TA 98 and TA 100) and E. Coli WP 2 uvr A, with and without metabolic activation	Pre-incubation assay : 312.5, 625, 1250, 2500 and 5000 µg/plate Second test : exposure to vapour in air at 5, 10, 20, 40 and 80 % (v/v)	15	No mutagenic activity both in presence or in absence of metabolic activation	July 1996	Huntingdon Life Science **UK**
26	Mutagenicity in the CHO/HGPRT forward mutation assay	Exposure of CHO cells to the test substance and selection of mutants at the HGPRT locus as able to form colonies in the presence of 6-thio-guanine	0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 mg/ml with and without metabolic activation	16	Toxicity at concentrations above 1000 µg/ml No mutagenic activity both in presence or in absence of metabolic activation	Oct. 1990	Hazleton Laboratories, MD **USA**
27	Mouse micronucleus test	Evaluation of the micronuclei in bone marrow polychromatic erythrocytes of mice. 5 M and 5 F ICR mice per dose/harvest time group. Harvest time at 24 h, 48 and 72 h	Single intraperitoneal injection at doses of 400, 1333 and 4000 mg/kg bw	17	No significant increase in micronuclei in bone marrow polychromatic erythrocytes	July 1990	Hazleton Laboratories, MD **USA**

SPECIAL TOXICITY STUDIES

Ref #	Study type	Species/ strain	Initial group	Route of administration	Treatment	Document ID	Results	Date	Laboratory
28	Delayed cutaneous sensitization maximization test	Guinea pig Dunkin-Hartley	Total 30 10 M + 10 F treated group 5 M + 5 F control group	Topical	Induction on day 1 by intradermal injection (5 %) with FCA followed on day 8 by topical application (pure). Challenge on day 22 by topical application (pure)	18	No cutaneous reactions attributable to a sensitization potential	July 1995	Centre International de Toxicologie (CIT) **FRANCE**
29	Anesthesia by intravenous route in dogs	Dogs NA	10 animals	Intravenous	40 to 100 ml of a 25 % solution in normal saline	19	No mortality Anesthesia comparable to ether but transient hematuria and prolonged recovery time	August 1949	State University, Iowa City **USA**

DOCUMENTS

1. ***Methylal : Metabolism and Hygienic Standardization in a Work Environment***

   L.A. Tomilina, Yu. S. Rotenberg, F.D. Mashbits, M.B. Komanovskaia, and L.M. Knizhnikova.

   Gig. Truda, 1984, n° 6, 27-29

2. ***Toxicological Properties and Industrial Handling Hazards of Dimethoxymethane***

   Biochemical Research Laboratory, The Dow Chemical Company

   December 16th, 1968

   EPA/OTS Doc # 86-870002205 (1987)

   NTIS/OTS 0515995

3. ***Methylal : Acute Toxicity and Primary Irritancy Studies in Rats and Rabbits***

   Bushy Run Research Center, Pennsylvania, U.S.A.

   Submitted by the Union Carbide Corporation, Danbury, Connecticut, U.S.A.

   December 7th, 1982

   EPA/OTS Doc # 88-920001329 (1992)

   NTIS/OTS 0536049

4. ***Biochemorphic Aspects of Paraldehyde and Certain Acetals***

   P.K. Knoefel, Lester Lonergan and C.D. Leake.

   Proceedings of the Society for Experimental Biology and Medicine. 29, 730-732 (1932).

5. ***Acute Dermal Toxicity Study in Rabbits with Methylal***

Springborn Laboratories Inc., Spencerville, Ohio, U.S.A.

Submitted by the Hoechst Celanese Corporation, Dallas, Texas, U.S.A.

November 22nd, 1989

EPA/OTS Doc # 86-900000034 (1989)

NTIS/OTS 0521584

6. ***Single Acute Exposure Dose Selection Study on Methylal***

Hazleton Laboratories America, Inc., Kensington, Maryland, U.S.A.

Submitted by the Hoechst Celanese Corporation, Dallas, Texas, U.S.A.

June 14th, 1990

EPA/OTS Doc. # 86-900000469 (1990)

NTIS/OTS 0524346

7. ***The Toxicity of Methylal***

F.L. Weaver, Jr., A.R. Hough, B. Highman, L.T. Fairhall

Brit. J. Industr. Med., 1951, 8, 279

8. ***NPIRI Raw Material Data Handbook***
(National Association of Printing Ink Research Institute)

V.I Organic Solvents, 1974, p. 73

9. ***Primary Skin Irritation Study in Rabbits with Methylal***

Springborn Laboratories, Inc., Spencerville, Ohio, U.S.A.

Submitted by Hoechst Celanese Corporation, Dallas, Texas, U.S.A.

November 3rd, 1989

EPA/OTS Doc # 86-900000029 (1989)

NTIS/OTS 0535051

10. ***The Subacute Inhalation Toxicity of 109 Industrial Chemicals***

J.C. Cage

Brit. J. Industr. Med., 1970, 27, 1

11. ***Testing for Subchronic (13 weeks) Inhalation Toxicity in Male and Female Wistar Rats.***

Pharma Development, Corporate Toxicology, Hoechst Aktiengesellschaft, Frankfurt am Main, Germany.

September 27th, 1994

Summary of the 491 page study.

12. ***Methylal. A Dose Range Finding Study by Inhalation Administration in the Pregnant Rat.***

Huntingdon Life Sciences, Ltd., Huntingdon, England.

13. ***Methylal. A Study for Effects on Embryofoetal Development by Inhalation Administration in the Rat.***

Huntingdon Life Sciences, Ltd., Huntingdon, England.

14. ***Salmonella / Mammalian - Microsome Preincubation Mutagenicity Assay with a Closed Phase Incubation System***

Microbiological Associates, Inc., Rockville, Maryland, U.S.A.

Submitted by the Hoechst Celanese Corporation, Dallas, Texas, U.S.A.

September 20th, 1989.

EPA/OTS Doc # 86-900000004

EPA/OTS 0521278

15. ***Methylal, Bacterial Mutation Assay***

Huntingdon Life Sciences Ltd, Huntingdon, England.

July 23rd, 1996

Study on Salmonella typhimurium (strains TA 1535, TA 1537, TA 98 and TA 100)
Escherichia coli (WP 2 uvr A)

Pre-incubation method

Methylal as a vapour in air

16. ***Mutagenicity Test on Methylal in the CHO/HGPRT Forward Mutation Assay***

Hazleton Laboratories America, Inc., Kensington, Maryland, U.S.A.

Submitted by the Hoechst Celanese Corporation, Dallas, Texas, U.S.A.

October 10th, 1990

EPA/OTS Doc # 86-910000038 (1990)

NTIS/OTS 0528332

17. ***Mutagenicity Test on Methylal In Vivo Mouse Micronucleus Assay***

Hazleton Laboratories America, Inc., Kensington, Maryland, U.S.A.

Submitted by the Hoechst Celanese Corporation, Dallas, Texas, U.S.A.

July 25th, 1990

EPA/OTS Doc # 86-900000475 (1990)

NTIS/OTS 0530014

18. ***Skin Sensitization Test in Guinea-Pigs***
(Maximization method of Magnusson, B. and Kligman, A.M.)

Centre international de toxicologie, Evreux, France

July 11th, 1995

19. ***Anesthesia with Methylal in Dogs, Mice and Rats***

Robert W. Virtue.

Anesthesiology, Vol. 12 (1951), 100-108.

ATTACHMENT V
FLAMMABILITY

Flammability properties of an auxiliary blowing agent impact prominently into assessing the conditions of its potential use in the manufacture of PU foams. Before drawing conclusions pertaining to methylal it may be useful to look into the general phenomenon of combustibility.

1. DEFINITIONS

Properties commonly used to define flammable substances are[2]:

- **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

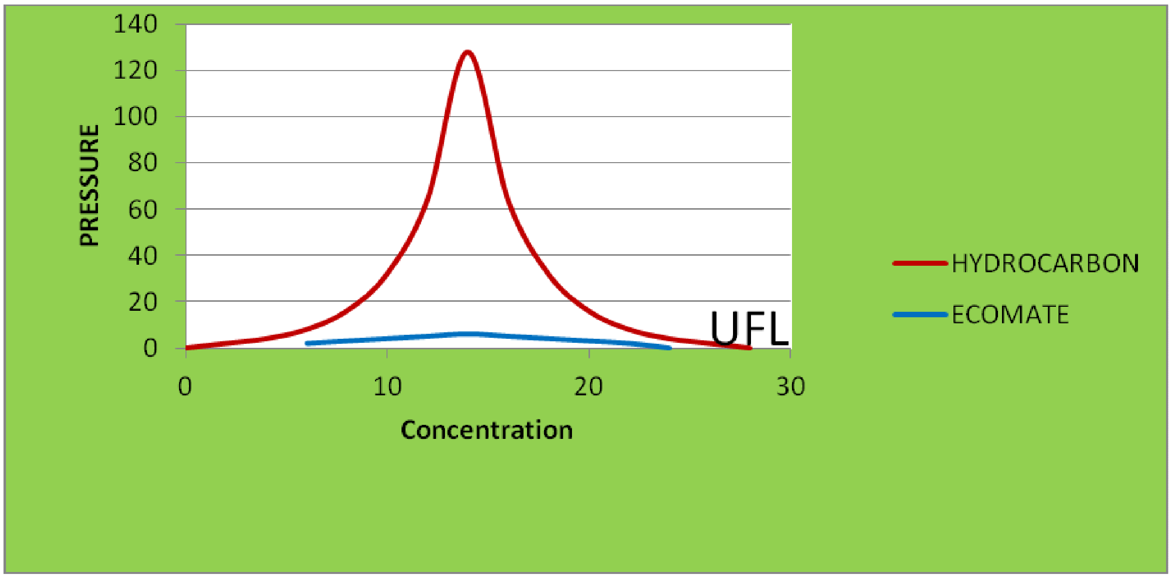
Combustibility - a blowing agent is commonly stored and processed as a liquid but turns into a gas as part of the foam expansion, due to the exothermic reaction between water and isocyanate (and to a lesser extent polyol and isocyanate), expanding the still liquid reaction mixture and filling the generated foam cells. Addressing the combustibility of a blowing agent as a liquid is equally important as of 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 frequently listed in an MSDS as "moderately" flammable or simply "yes"[3]. Methylal, on the other side, is even as a liquid flammable (which does not necessarily imply explosive). Its burning profile is 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	1.9	
Methyl Formate	3.9	
Methylal	6.1	
Ethanol	7.1	
Pentane (commercial mix)	11.5	Cyclopentane estimated ~10% lower

[2] 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)
[3] Lavelle, J. P., "Flammability Characteristics of HCFC 141b and HCFC-142b", Journal of Fire Sciences 1989 7; pp 426-439

The relatively low heat of combustion is also the reason that neither HCFC-141b nor ML 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 ML—**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; ecomate = methyl formate, the pressure line for methylal would be somewhat higher but still much lower than for hydrocarbons):



Flash Point is commonly used as the primary property to describe the fire hazard of a **liquid**. Pure ML, with its flashpoint of -18^{0}C certainly needs proper safeguarding but that change after blending with products of 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 ML concentrations <2-5% for polyols and <2% for isocyanates. Such concentrations suffice to reformulate low/medium-HCFC-based systems.

Flammable, Flammability, or **Explosive** limits are the primary property describing fire hazards of **gases**. They indicate the proportion of combustible gases in a mixture, between which limits this mixture is flammable and **CAN** be explosive. 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. Three essential items for burning a material are fuel, air (oxygen or another oxidizing agent) and an ignition source,

If, under atmospheric conditions, there is not enough fuel, a 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 or anti-spark devices such as electrical grounding etc. will eliminate an ignition source
The LFL will be exceeded	Spark arrestors will keep the space free of ignition sources

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

3. APPLICATION TO METHYLAL

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

Methylal

- LFL = 1.6% in air by volume = 220 g/m^3 = 5,700 ppm
- Maximum concentration allowed by OSHA.NIOSH/ACGIH:
  - TWA = 1,000 ppm = 220 mg/m^3 =17**% of LFL**
  - STEL = 1,250 ppm = 275 mg/m^3 = **22% 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**

The margin of 4.5-6 of the maximum allowable vapor concentration compared to the LFL is not a very comfortable one. One should, however, also take into account that blends of polyols with methylal show a low tendency to combustion (Lambiotte) as the following data show:

Blend (php)		Combustion Description (in the presence of a flame)
Polyol (viscosity 930 mPa.s)	Methylal	
98	2	No ignition
96	4	No ignition
94	6	No ignition
92	8	No ignition
90	10	Single ignition of the vapors; no further ignition in presence of a flame
88	12	Ignition of the vapors; can be repeated but is self-extinguishing
86	14	Continuous burning; no detonation

4. CONCLUSIONS/RECOMMENDATIONS

- Methylal as a pure liquid is very flammable and requires proper safeguards. The risk of detonation or explosion is, however, remote because its low heat of combustion;
- A PU system based on 1-5 php methylal in the polyol or 2-7.5 php methylal in the polyol and MDI can be formulated as a low combustible liquid and will not reach the LFL;
- PU systems with methylal exceeding that concentration are flammable liquids and need to be labeled as such. However, if applicable TWA and STEL limits are met, the emissions will not be of concern, although the safety margin of 4.5-6 is not a very comfortable one and would require close monitoring of adherence to these thresholds.

In view of the foregoing, following recommendations are offered:

1. System houses, who process pure grade methylal should have
   - 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 methylal vapor sensor with alarm function set on 20% LFL;
   - Adequate ventilation;
   - Meter Methylal under the level of the liquid to which it is being added.
2. Downstream users, who process polyol and/or Isocyanate blends should have
   - Proper personal protective equipment;
   - Electrically grounded equipment and drums (grounding clip);
   - A methylal vapor sensor with alarm function set on 20% LFL;
   - Adequate ventilation.

In all cases, the relevant MSDS and OSHA's Occupational Health Guideline for Methylal or similar applicable in the country of residence should be applied.

5.

ATTACHMENT VI
ECOTOXICOLOGICAL PROFILE

Lambiotte & Cie S.A.

METHYLAL

(DIMETHOXYMETHANE)

ECOTOXICOLOGICAL PROFILE

18, avenue des Aubépines
B - 1180 Brussels
BELGIUM
Tel. : +32-2-374 44 65
Fax : +32-2-375 31 55

April 21st, 1997

The following ecotoxicological studies have been performed : toxicity for Daphnids, toxicity for fish, growth inhibition of green algae, toxicity for bacteria, biodegradability.

Daphnids

The results of the study on the acute toxicity of methylal for Daphnia Magna are the following :

48 h LC_{50} > 1000 mg/l

48 h EC_{50} > 1000 mg/l

NOEC = 1200 mg/l

The 48-h LC_{50} and the 48-h EC_{50} of the test substance methylal cannot be calculated, there is no mortality or effect range.
The highest tested concentration which does not kill or immobilize the exposed daphnids within 48 h is 1200 $mg.l^{-1}$.

Fish

The study on the acute toxicity of methylal for fish (Brachydanio Renio) shows the following results :

96 h LC_{50} > 1000 mg/l

96 h EC_{50} > 1000 mg/l

NOEC = 1000 mg/l

The 96-h LC_{50} and the 96-h EC_{50} of the test substance methylal for Brachydanio Renio cannot be calculated, there is no mortality or effect.
The highest tested concentration which does not kill or immobilize the exposed fish within 96 h is 1000 $mg.l^{-1}$ (NOEC).

This value is based on the nominal concentration of methylal. NOEC = 700-800 $mg.l^{-1}$ (measured value).

Green algae

When diluted at 1/750 (or 0.133 %), methylal does not inhibit the growth of the green algae Chlorella vulgaris. The concentration that does inhibit 50 % of the growth can be estimated at 0.6 % (v/v). (AFNOR T 90-304 standard)

Bacteria

The acute bacterial toxicity has been studied in accordance with the DIN 38 412 standard, part 8.
Concentrations at which there is a cell propagation inhibition of 10 and 50 % have not been reached.
When diluted in water to 10 g/l, methylal inhibits 1 % of the cell propagation.

Biodegradability

At concentrations lower than 1/1000 in water, methylal shows a negative inhibition of oxygen consumption of activated sludge (in accordance with the ISO/DIS 8192 standard). It hence has a positive biodegradability.

Notes

The median lethal concentration (LC_{50}) is defined as that concentration of test substance which causes 50 % mortality in populations of test organisms within the specified exposure time.

The median effect concentration (EC_{50}) is defined as that concentration of test substance which immobilizes 50 % of the exposed organisms in the specified time period.

The No-Observed-Effect-Concentration (NOEC) is defined as the highest tested concentration which causes no mortality or immobilization among the exposed organisms after 96 h.

ATTACHMENT VII
SAMPLE FORMULATIONS

POUR IN PLACE

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol	83,16	100,00	82,08	100,00
Cross-linker	0,92	1,11	0,90	1,10
Silicone	0,27	0,32	0,11	0,13
Additive	2,08	2,50	0,00	0,00
Catalyst A	0,83	1,00	0,52	0,63
Catalyst B	1,00	1,20	0,56	0,68
Water	1,24	1,49	1,22	1,48
Methylal	10,50	12,63	0,00	0,00
HCFC-141b	0,00	0,00	14,61	17,80
Total	100,00	120,25	100,00	121,82

STRUCTURAL FOAM

	Methylal		HCFC-141b	
	%	pph	%	pph
Rigid polyol	57,62	70,00	56,00	70,00
Moulded polyol	24,70	30,00	24,00	30,00
Cross-linker	5,14	6,24	5,00	6,25
Glycol	5,14	6,24	5,00	6,25
Silicone	1,54	1,87	1,50	1,87
Catalyst	1,54	1,87	1,50	1,87
Water	0,21	0,25	0,20	0,25
Methylal	4,11	5,00	0,00	0,00
HCFC-141b	0,00	0,00	6,80	8,50
Total	100,00	121,47	100,00	124,99

NON-CONTINUOUS BLOCK

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol A	60,61	79,00	55,27	85,00
Polyol B	8,44	11,00	6,50	10,00
Polyol C	7,67	10,00	3,25	5,00
Cross-linker	0,00	0,00	2,60	4,00
TCPP	11,51	15,00	8,45	13,00
Silicone	0,81	1,05	1,30	2,00
Catalyst	0,23	0,30	0,00	0,00
Catalyst A	0,00	0,00	0,44	0,67
Catalyst B	0,00	0,00	0,12	0,18
Water	1,53	2,00	1,26	1,93
Methylal	9,20	12,00	0,00	0,00
HCFC-141b	0,00	0,00	20,81	32,00
Total	100,00	130,35	100,00	153,78

SPRAY

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol A	52,47	70,00	43,03	69,97
Polyol B	22,49	30,00	18,47	30,03
TCPP	12,19	16,27	9,98	16,23
Silicone	1,21	1,62	0,00	0,00
Catalyst A	0,61	0,81	0,50	0,81
Catalyst B	0,07	0,09	0,06	0,10
Water	1,22	1,63	1,00	1,62
Methylal	9,74	13,00	0,00	0,00
HCFC-141b	0,00	0,00	26,96	43,83
Total	100,00	133,42	100,00	162,59

TRANSPORTATION

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol A	61,60	80,00	55,70	80,00
Polyol B	15,40	20,00	13,92	20,00
Cross-linker	3,31	4,30	2,99	4,30
TCPP	10,01	13,00	9,05	13,00
Silicone	1,15	1,50	1,04	1,50
Amine A	0,08	0,10	0,10	0,14
Amine B	0,69	0,90	0,97	1,40
Water	1,60	2,08	0,91	1,30
Methylal	6,16	8,00	0,00	0,00
HCFC-141b	0,00	0,00	15,32	22,00
Total	100,00	129,88	100,00	143,64

THERMOWARE

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol	77,28	100,00	69,33	100,00
TCPP	10,05	13,00	9,01	13,00
Silicone	1,31	1,70	0,55	0,80
Catalyst A	0,46	0,60	0,19	0,27
Catalyst B	0,85	1,10	0,55	0,80
Catalyst C	0,00	0,00	0,76	1,10
Water	2,32	3,00	1,59	2,30
Methylal	7,73	10,00	0,00	0,00
HCFC-141b	0,00	0,00	18,02	26,00
Total	100,00	129,40	100,00	144,27

WATER HEATER

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol	0,00	0,00	72,15	100,00
Polyol A	79,00	95,00	0,00	0,00
Polyol B	4,15	5,00	0,00	0,00
Cross-linker	0,00	0,00	2,89	4,00
TCPP	6,64	8,00	9,38	13,00
Silicone	1,50	1,90	0,87	1,20
Catalyst	0,66	0,80	0,00	0,00
Catalyst A	0,00	0,00	0,43	0,60
Catalyst B	0,00	0,00	0,29	0,40
Water	1,41	1,70	1,01	1,40
Methylal	6,64	8,00	0,00	0,00
HCFC-141b	0,00	0,00	12,98	18,00
Total	100,00	120,40	100,00	138,60

HIGH RESILIENCE MOLDED

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol A	73,09	79,22	73,09	80,00
Copolymer	19,18	20,78	18,27	20,00
Silicone	0,46	0,50	0,46	0,50
Catalyst A	0,73	0,79	0,73	0,80
Catalyst B	0,34	0,37	0,34	0,35
Water	3,46	3,75	3,46	3,79
Methylal	2,74	2,97	0,00	0,00
HCFC-141b	0,00	0,00	3,65	4,00
Total	100,00	108,38	100,00	109,44

VISCOELASTIC

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol A	75,00	80,50	74,30	80,50
Polyol B	16,15	17,30	16,00	17,33
Polyol C	2,02	2,20	2,00	2,17
Silicone A	0,25	0,27	0,25	0,27
Silicone B	1,01	1,08	1,00	1,08
Catalyst A	0,15	0,16	0,15	0,16
Catalyst B	0,30	0,32	0,30	0,32
Water	3,00	3,22	3,00	3,25
Methylal	2,12	2,27	0,00	0,00
HCFC-141b	0,00	0,00	3,00	3,25
Total	100,00	107,32	100,00	108,33

VISCOELASTIC BLOCKS (NON CONTINOUS)

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol A	22,88	24,23	22,88	24,38
Polyol B	22,87	24,22	22,87	24,37
Polyol C	17,44	18,47	17,44	18,58
Polyol D	19,16	20,29	19,16	20,41
Polyol E	3,83	4,06	3,83	4,08
Polyol F	8,24	8,73	7,68	8,18
Silicone A	0,48	0,51	0,48	0,51
Silicone B	0,58	0,61	0,58	0,62
Catalyst A	0,09	0,09	0,09	0,09
Catalyst B	0,38	0,40	0,38	0,40
Water	2,25	2,38	2,25	2,39
Methylal	1,80	1,91	0,00	0,00
HCFC-141b	0,00	0,00	2,36	2,51
Total	100,00	105,90	100,00	106,52

STEERING WHEELS

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol	79,48	100,00	78,48	100,00
Cross-linker	6,70	8,54	6,70	8,54
Silicone	0,22	0,28	0,22	0,28
Colorant	3,00	3,82	3,00	3,82
Amine	0,60	0,76	0,60	0,76
Methylal	10,00	12,74	0,00	0,00
HCFC-141b	0,00	0,00	11,00	14,02
Total	100,00	126,14	100,00	127,42

FURNITURE

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol	87,11	100,00	83,88	100,00
Cross-linker	7,26	8,34	7,25	8,64
Silicone	0,24	0,28	0,24	0,29
Amine	0,64	0,73	0,63	0,75
Methylal	4,75	5,41	0,00	0,00
HCFC-141b	0,00	0,00	8,00	9,54
Total	100,00	114,80	100,00	119,22

ATTACHMENT VIII
PARTICIPATION LETTERSOF DOWNSTREAM USERS

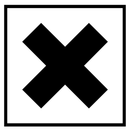
MATERIAL SAFETY DATA SHEET

METHYLAL TECHNICAL GRADE

Revision nr : 5
Date : 30/9/2005
Supersedes : 20/2/2004

L-9307
www.lisam.com

Highly flammable



Harmful

Producer
Lambiotte & Cie s.a.
Grand' Rue, 79
B-6724 Marbehan Belgique-Belgie
Tel. +32 (0)63 41 00 80
EMERGENCY : +32 (0)70 245 245

1. Identification of the product and the company

Company identification	: See distributor.
Trade name	: METHYLAL TECHNICAL GRADE.
Chemical family	: Acetal.
Type of product	: Liquid.
Use	: Industrial.

2. Information on ingredients

This product is considered to be hazardous and contains hazardous components.

Substance name		Value(s)	CAS nr / EINECS nr / EC index	Symbol(s)	R-Phrase(s)
Methylal	:	> 93 %	000109-87-5 / 203-714-2 / -----	F	11
Methanol	:	<= 6.5 %	000067-56-1 / 200-659-6 / 603-001-00-X	F T	11-23/24/25-39/ 23/24/25

3. Hazards identification

Risk Phrases	: Harmful by inhalation, in contact with skin and if swallowed.
Dangerous substances	: Highly flammable.
Primary route of exposure	: Vapours inhalation. Skin contact.
Symptoms relating to use	
- Inhalation	: Symptoms of overexposure to vapours include : Headache. Dizziness. Drowsiness. Nausea.
- Skin contact	: Absorbed through the skin. Redness.
- Eye contact	: Direct contact with the eyes is likely irritating.
- Ingestion	: Abdominal pain, nausea. Swallowing a small quantity of this material presents some health hazard. Must not come into contact with food or be consumed.

4. First aid measures

First aid	
- Inhalation	: If overcome by exposure, remove victim to fresh air immediately. Obtain medical attention if breathing difficulty persists.
- Skin contact	: Remove affected clothing and wash all exposed skin area with mild soap and water, followed by warm water rinse.
- Eye contact	: Rinse immediately with plenty of water. Obtain medical attention if pain, blinking or redness persist.
- Ingestion	: If swallowed, immediately administer water (1/2 liter) only if victim is completely conscious/alert and induce immediately vomiting. Seek medical attention immediately.

5. Fire - fighting measures

Flammable class	: This product is flammable.
Prevention	: No smoking. Keep away from sources of ignition.
Extinguishing media	: Foam. Dry chemical. Carbon dioxide. Large quantity of water.
Surrounding fires	: Use water spray or fog for cooling exposed containers.
Special exposure hazards	: Vapor mixes readily with air, forming explosive mixtures.
Protection against fire	: All fire-fighting personnel must wear safety suits. Use self-contained breathing apparatus when in close proximity to fire.
Special procedures	: Exercise caution when fighting any chemical fire.

6. Accidental release measures

Personal precautions	: Equip cleanup crew with proper protection.
Environmental precautions	: Prevent entry to sewers and public waters. Notify authorities if liquid enters sewers or public waters.
After spillage and/or leakage	: Clean up any spills as soon as possible, using an absorbent material to collect it. Use suitable disposal containers.

7. Handling and storage

General	: No naked lights. No smoking.
Precautions in handling and storage	: Do not use compressed air to either agitate or transfer the contents of storage containers (tanks) / shipping drums containing this material.
Technical protective measures	: Ground well. Use only non-sparking tools. Use special care to avoid static electric charges.
Storage	: Keep container closed when not in use. Store in dry, cool, well-ventilated area.
Storage - away from	: Heat sources.
Handling	: Handle in accordance with good industrial hygiene and safety procedures. Wash hands and other exposed areas with mild soap and water before eat, drink or smoke and when leaving work.

8. Exposure controls / personal protection

Personal protection	
- Respiratory protection	: Approved dust or mist respirator should be used if airborne particles are generated when handling this material.
- Skin protection	: Wear suitable gloves resistant to chemical penetration.
- Eye protection	: Even though no specific eye irritation data is available, wear eye protection appropriate to conditions of use when handling this material.
- Ingestion	: When using, do not eat, drink or smoke.
Industrial hygiene	: Provide local exhaust or general room ventilation to minimize dust and/or vapour concentrations.

9. Physical and chemical properties

Physical state	: Volatile liquid.
Colour	: Colourless.
Odour	: Ethereal.
pH value	: No data available.
Molecular weight	: 76.08
Melting point [°C]	: -104.8
Initial boiling point [°C]	: 42.3
Density	: .861
Viscosity	: cP (30°C) .325

9. Physical and chemical properties (continued)

Solubility in water [% weight]	: 32.3
Flash point [°C]	: -18
Auto-ignition temperature [°C]	: 237
Explosion limits - lower [%]	: 1.6
Explosion limits - upper [%]	: 38.5

10. Stability and reactivity

Hazardous decomposition products	: Thermal decomposition generates : Carbon dioxide.
Hazardous reactions	: Reacts with : Strong acids.
Hazardous properties	: Vapor mixes readily with air, forming explosive mixtures.
Conditions to avoid	: Heat. Sparks. Open flame.

11. Toxicological information

Rat oral LD50 [mg/kg]	: 5620
Rabbit dermal LD50 [mg/kg]	: No data available.
Rat inhalation LC50 [mg/kg]	: No data available.

12. Ecological information

48 H-CE50 - Daphnia magna [mg/l]	: No data available.
Persistence and degradability	: Biodegradable

13. Disposal considerations

Disposal	: Dispose in a safe manner in accordance with local/national regulations. Dispose of this material and its container at hazardous or special waste collection point.

14. Transport information

Hazard Label(s)

	: Flammable. Harmful.
- Proper shipping name	: UN 1234 METHYLAL, 3, II
- UN No.	: 1234
- H.I. nr :	: 33
- ADR/RID	: Group : II Class : 3
- IMO-IMDG code	: Class 3
- EMS-Nr	: F-E S-D
UN Packing group	: II

15. Regulatory information

Symbol(s)	: Harmful.
R Phrase(s)	: R11 - Highly flammable. R20/21/22 - Harmful by inhalation, in contact with skin and if swallowed. R68/20/21/22 - Harmful : possible risk of irreversible effects through inhalation, in contact with skin and if swallowed.
S Phrase(s)	: S03 - Keep in a cool place.

15. Regulatory information (continued)

S09 - Keep container in a well-ventilated place.
S16 - Keep away from sources of ignition - No smoking.
S24 - Avoid contact with skin.
S33 - Take precautionary measures against static discharges.
S35 - This material and its container must be disposed of in a safe way.
S36/37 - Wear suitable protective clothing and gloves.
S53 - Avoid exposure - obtain special instructions before use.
S59 - Refer to manufacturer/supplier for information on recovery/recycling.

16. Other information

Further information : None.

The contents and format of this MSDS are in accordance with EEC Commission Directive 2001/58/EEC.

End of document

Occupational Health Guideline for Methylal

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $CH_3OCH_2OCH_3$
- Synonyms: Dimethoxymethane; methyl formal; formal; dimethylacetal formaldehyde
- Appearance and odor: Colorless liquid with a pungent odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for methylal is 1000 parts of methylal per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 3100 milligrams of methylal per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Methylal can affect the body if it is inhaled, is swallowed, or comes in contact with the eyes or skin.

- **Effects of overexposure**

1. Short-term Exposure: Overexposure to methylal may cause irritation of the eyes, nose, and throat, lightheadedness, incoordination, and unconsciousness.

2. Long-term Exposure: Prolonged overexposure to methylal may cause irritation of the skin.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to methylal.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to methylal at potentially hazardous levels:

1. Initial Medical Screening: Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from methylal exposure.

—Skin disease: Methylal is a defatting agent and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of this agent.

—Liver disease: Although methylal is not known as a liver toxin in humans, the importance of this organ in the biotransformation and detoxification of foreign substances should be considered before exposing persons with impaired liver function.

—Kidney disease: Although methylal is not known as a kidney toxin in humans, the importance of this organ in the elimination of toxic substances justifies special consideration in those with impaired renal function.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of methylal might cause exacerbation of symptoms due to its irritant properties.

2. Periodic Medical Examination: Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Methylal vapor is a mild respiratory irritant with anesthetic properties. Mice exposed at 11,000 ppm showed mild irritation of the eyes and respiratory tract, as well as incoordination; recovery was rapid after single exposures. At 14,000 ppm, mice showed more respiratory irritation, occasional pulmonary edema, and a greater degree of anesthesia. At the LC50 level of approximately 18,000 ppm, animals died of bronchopneumonia with fatty changes in the liver, kidney, and heart. At 4000 ppm rats were unaffected by daily 6-hour exposures.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

Skin irritation may be expected due to defatting action by the solvent, and eye irritation if splashing occurs. No chronic systemic effects have been reported in humans.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**

1. Molecular weight: 76
2. Boiling point (760 mm Hg): 44 C (111 F)
3. Specific gravity (water = 1): 0.86
4. Vapor density (air = 1 at boiling point of methylal): 2.6
5. Melting point: −105 C (−157 F)
6. Vapor pressure at 20 C (68 F): 330 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 33
8. Evaporation rate (butyl acetate = 1): 23.1

- **Reactivity**

1. Conditions contributing to instability: Heat, presence of acids
2. Incompatibilities: Contact with strong oxidizing agents may cause fires and explosions. Contact with acids causes decomposition to methyl alcohol and formaldehyde.
3. Hazardous decomposition products: Toxic gases and vapors (such as carbon monoxide, formaldehyde, and methyl alcohol) may be released in a fire involving methylal.
4. Special precautions: Methylal will attack some forms of plastics, rubber, and coatings.

- **Flammability**

1. Flash point: −18 C (−4 F) (closed cup)
2. Autoignition temperature: 237 C (459 F)
3. Flammable limits in air, % by volume: Lower: 1.6; Upper: 17.6
4. Extinguishant: Dry chemical, alcohol foam, carbon dioxide

- **Warning properties**

1. Odor Threshold: No quantitative information is available concerning the odor threshold, but Browning notes that it has a slightly pungent odor.
2. Eye Irritation Level: Grant states that "exposures of mice and guinea pigs to much higher concentrations of methylal vapor than would be encountered industrially were found to cause . . . occasional irritation of the eyes but no histologically demonstrable abnormality of the optic nerve or retina."

Patty reports that mice which had received 15 7-hour exposures at 11,000 ppm experienced only mild irritation.

No quantitative information is available, however, concerning the threshold of eye irritation.

3. Evaluation of Warning Properties: Since there is no useful quantitative information relating warning properties to air concentrations of methylal, this substance is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

- **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

- **Method**

Sampling and analyses may be performed by collection of methylal vapors using an adsorption tube with subsequent desorption with hexane and gas chromatographic analysis. Also, detector tubes certified by NIOSH under 42 CFR Part 84 or other direct-reading devices calibrated to measure methylal may be used. An analytical method for methylal is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 2, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00260-6).

RESPIRATORS

- Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.
- In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

- Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent repeated or prolonged skin contact with liquid methylal.
- Clothing wet with liquid methylal should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of methylal from the clothing. If the clothing is to be laundered or

otherwise cleaned to remove the methylal, the person performing the operation should be informed of methylal's hazardous properties.

• Any clothing which becomes wet with liquid methylal should be removed immediately and not reworn until the methylal is removed from the clothing.

• Employees should be provided with and required to use splash-proof safety goggles where liquid methylal may contact the eyes.

SANITATION

• Skin that becomes wet with liquid methylal should be promptly washed or showered to remove any methylal.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to methylal may occur and control methods which may be effective in each case:

Operation	Controls
Use as a solvent for adhesives, resins, gums, waxes, and protective coatings; use as a solvent for extraction of alkaloids, barbituates, organic acids, and hydroxy-acids	General dilution ventilation; process enclosure; personal protective equipment
Use in manufacture of artificial resins; use as a gasoline and diesel fuel additive; use as a special fuel for rocket and jet engines	General dilution ventilation; process enclosure; personal protective equipment
Use as a reaction solvent with acetylene or in Grignard and Reppe reaction; use as a source of formaldehyde and methanol	General dilution ventilation; process enclosure; personal protective equipment
Use as a methylating agent or chemical intermediate	General dilution ventilation; process enclosure; personal protective equipment
Use in manufacture of perfume	General dilution ventilation; process enclosure; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If methylal gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If methylal gets on the skin, promptly wash the contaminated skin with water, if the methylal has not already evaporated. If methylal soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention. If there is skin irritation, get medical attention.

• **Breathing**

If a person breathes in large amounts of methylal, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When methylal has been swallowed, get medical attention immediately. If medical attention is not immediately available, get the afflicted person to vomit by having him touch the back of his throat with his finger or by giving him syrup of ipecac as directed on the package. This non-prescription drug is available at most drug stores and drug counters and should be kept with emergency medical supplies in the workplace. Do not make an unconscious person vomit.

• **Rescue**

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If methylal is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected, dissolved in alcohol of greater molecular weight than butyl alcohol, and atomized in a suitable combustion chamber. Methylal should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:
Methylal may be disposed of by dissolving in alcohol of greater molecular weight than butyl alcohol and atomizing in a suitable combustion chamber.

REFERENCES

• American Conference of Governmental Industrial Hygienists: "Methylal," *Documentation of the Threshold Limit Values for Substances in Workroom Air* (3rd ed., 2nd printing), Cincinnati, 1974.

• Browning, E.: *Toxicity and Metabolism of Industrial Solvents*, Elsevier, New York, 1965.

• Celanese Corporation: *Product Bulletin - Methylal*, New York.

• Deichmann, W. B., and Gerarde, H. W.: *Toxicology of Drugs and Chemicals*, Academic Press, New York, 1969.

• Grant, W. M.: *Toxicology of the Eye* (2nd ed.), C. C. Thomas, Springfield, Illinois, 1974.

• Patty, F. A. (ed.): *Toxicology*, Vol. II of *Industrial Hygiene and Toxicology* (2nd ed. rev.), Interscience, New York, 1963.

• Sax, N. I.: *Dangerous Properties of Industrial Materials* (3rd ed.), Van Nostrand Reinhold, New York, 1968.

• Weaver, F. L., et al.: "Toxicity of Methylal," *British Journal of Industrial Medicine*, 8:279-283, 1951.

RESPIRATORY PROTECTION FOR METHYLAL

Condition	Minimum Respiratory Protection* Required Above 1000 ppm
Vapor Concentration	
10,000 ppm or less	Any supplied-air respirator. Any self-contained breathing apparatus.
Greater than 10,000 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against organic vapors. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.

Relatório de Análise nº 107006.10.11

Cliente Contratante/Avaliado: ARINOS QUÍMICA LTDA.
Rua Arinos, 15 - Parque Industrial Água Vermelha - Osasco - SP - CEP 06276-032
CNPJ 01.722.256/0001-75
Sr. Mario Cezar da Silva

Amostra: Ar ambiental
Recebida em: 14/10/2011
Data da análise: 20/10/2011

Método: NIOSH 1611.

Amostra	Nº do Cliente	Vol./Tempo	Coleta	Resultados	
107006.1	000090109	2,28 L	13/10/2011	Metilal 6,5 ppm	---
107006.2	000077662	3,00 L	13/10/2011	Metilal <2,6 ppm	---

Notas

1 - Amostragem: realizada pela Environ Científica. O relatório de amostragem encontra-se anexado. O resultado e dados são válidos somente para a amostra analisada.
2 - BC: não apresentou massa acima do limite de quantificação.
3 - O resultado foi corrigido pelo branco de meio que não apresentou massa acima do limite de quantificação.
4 - A fase secundária das amostras não apresentou o analito acima de 10 % em relação à fase frontal. Concentrações superiores a 10 % na fase secundária indicam a possibilidade de perda.
5 - As amostras foram recebidas acondicionadas conforme previsto na metodologia.
6 - O resultado precedido de "<" significa que não foi detectado o analito acima do limite de quantificação.

Limites de Quantificação:

Metilal 20 µg.

Siglas:

BC = branco de campo; LQ = limite de quantificação; ppm = parte por milhão; ppb = parte por bilhão; mg/m^3 = miligrama por metro cúbico; mg = miligrama; µg = micrograma; NI = não informado; "<" = abaixo do LQ; f/cc = Fibra por centímetro cúbico; NE = não estabelecido.

São Bernardo do Campo, 31/10/2011

Oscar Shigueo Umemura
CRQ IV 04218265
Supervisor do Laboratório

Suzano 19 de agosto de 2011

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação para produção de espuma **VISCOELÁSTICA E HIPER SOFT.**

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

Nome: Helton Luiz de Araújo Santos

Cargo: Espumador

Empresa: Techfoam Ind.Comercio Ltda
TECHFOAM IND. E COM. LTDA

BLITZ
PROJETOS ESPECIAIS
Sempre uma idéia melhor!

Ribeirão Pires, 29 de julho de 2011.

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação para produção de espuma Integral skin, Rigido Estrutural e Semirrígido.
O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.
Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

Nome: Klaus Dieter Schnur
Cargo: Diretor Comercial
Empresa: Blitz Indústria e Comércio de Plásticos Ltd.

Blitz Indústria e Comércio de Plásticos Ltda.
Rua Dieter L. A. R. Schnur, 113 (Rod. SP 31 Km 42) – Sítio do Francês – CP 107 – CEP 09416-100 - Ribeirão Pires – S.P.
Fone: (0XX11) 4828.3444 Fax: (0XX11) 4828.3619 E-mail: sac@blitzplasticos.com.br
www.blitzplasticos.com.br

SOPRANO
Um universo de possibilidades.

Farroupilha - RS, 03 de março, 2011.

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação para produção de espuma rígida.

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

Robson C. Balbinot

Nome: ROBSON COLOMBO BALBINOT

Cargo: Analista de Processo

Empresa: Soprano

Local, data, ano

Cambé PR   01/06/2011

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do Sistema de Poliuretano, ***Aripol 514FR*** da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação, para produção de espuma rígida por injeção.

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

09.402.716/0001-90
90432582-11
EQUIPAMENTOS RODOVIÁRIOS ROMA LTDA.
Rod. Celso Garcia Cid, 2451 - PR 445
Jd. Rian - CEP 86187-000
CAMBÉ — PR

Atenciosamente,

Nome: Cl[illegible] Balsanelo

Cargo: Encarregado Produção

Empresa: Furgão Roma

POLITECH®
POLIURETANOS

Porto Alegre, Maio de 2011.

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação para produção de espuma de Bloco Rígido.

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

Nome: Sérgio José Correa

Cargo: Diretor Comercial

Politech Poliuretanos Indústria e Comércio Ltda – Rua Dona Alzira , 433 – Bairro Sarandi – Cep: 91110-010 – Porto Alegre – RS – Brasil – Fone/Fax: 00- (51)-3344-6909 e-mail: vendas@politech.ind.br

PURAPELE

MANUFATURA DE PELES FLORENSE LTDA.

VILA NOVA ROMA - 95270-000 - FLORES DA CUNHA - RS
FONE / FAX: (054) 292-2130
INSC. CGCMF Nº 89.968.390/0001-00 - INSC. ESTADUAL Nº 048/0002630

Flores da Cunha - RS, 03 de março, 2011.

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação para produção de espuma Flexível Moldado.

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como, aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

Nome: CIRIO SIGNORI

Cargo: DIRETOR

Empresa: Manufatura de Peles Florense Ltda.

MF COZINHAS INDUSTRIAIS LTDA
R: Herculano de Freitas, 99 - Fundação São Caetano do Sul S.P.
CEP 09520-280 – Fone/Fax: 0xx 11 4223-5060
E-MAIL: cookmachine@mfcozinhas.com.br
Home Page: www.mfcozinhas.com.br

São Caetano do Sul, 14 de Abril de 2011

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da ARINOS QUÍMICA LTDA contendo o agente de expansão METHYLAL incorporado na formulação para produção de espuma Rigida de Isolamento Térmico usada para fabricação de balcões refrigerados.
O resultado obtido na aplicação com o sistema incorporado com METHYLAL apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.
Portanto, o sistema com METHYLAL atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente

MF COZINHAS INDUSTRIAIS LTDA.

Silvia Maria Ap. Saltini Filleti
Diretora

isar
Isolamentos
Térmicos e Acústicos

Qualidade Certificada · isar
ISO 9001:2000

São Paulo, 07 de Abril de 2011.

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação para produção de espuma Rígida de Isolamento Térmico em aplicação por Spray.

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

Rafael Siais Furtado
Diretor Comercial
Isar Isolamentos Térmicos e Acústicos Ltda

Poliuretanos
Brasil

Santana de Parnaíba, 07 de abril de 2011.

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação para produção de espuma semi-rígida com aplicação em embalagens.

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

POLIURETANOS BRASIL LTDA
Rafael Santamaria Sarmento

vittaflex
espumas especiais

Declaração

Declaramos para os devidos fins que realizamos teste de sistema da ***Arinos Química LTDA*** Contendo o agente de expansão ***Methylal*** incorporado na formulação para produção de espuma visco elástica.
O resultado obtido na aplicação com o sistema incorporado com ***methylal*** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.
Portanto, o sistema com ***methylal*** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente

Célio Machado

Célio Machado
Químico industrial
Vittaflex

Suzano 19 de agosto de 2011

DECLARAÇÃO

Declaramos para os devidos fins que realizamos testes do sistema da **ARINOS QUÍMICA LTDA** contendo o agente de expansão **METHYLAL** incorporado na formulação para produção de espuma **VISCOELÁSTICA E HIPER SOFT.**

O resultado obtido na aplicação com o sistema incorporado com **METHYLAL** apresentou as mesmas propriedades físicas e mecânicas, bem como aspecto do sistema incorporado com o agente expansor HCFC 141b.

Portanto, o sistema com **METHYLAL** atende todas as nossas necessidades técnicas e produtivas.

Atenciosamente,

Nome: Helton Luiz de Araújo Santos

Cargo: Espumador

Empresa: Techfoam Ind.Comercio Ltda

TECHFOAM IND. E COM. LTDA