ASSESSMENT OF THE USE OF METHYLAL AS HCFC REPLACEMENT IN PU FOAMS

Properties and Current Use

The Ministry of Environment of Brazil and

United Nations Development Programme

Workshop

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PRESENTATION STRUCTURE

Properties of Methylal

Properties of polyols - Methylal blends

Properties of isocyanate - Methylal blends

Methylal flammability reduction

Methylal as co-blowing agent

Market

Conclusion

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PROPERTIES OF METHYLAL

Identification of methylal

Methylal is a physical blowing agent

Chemical structure : $CH_3 – O – CH_2 – O – CH_3$
also called Dimethoxymethane

Chemical class : acetals
not ethers nor diethers

Reach registered in 2010 :
Lambiotte Reach reference number :
01-2119664781-31-0000

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Methylal production doesn't consume non renewable oils

Methylal is produced from Methanol and Formaldehyde.
Formaldehyde itself is produced from Methanol.
Methanol finds its source in natural gas,
which is very abundant on the Earth.

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Contrarily to other blowing agents like Pentanes,
Methylal production doesn’t consume non-renewable oils

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Bio-sourcing of Methylal

Methylal is potentially bio-sourced,
if produced from bio-sourced Methanol

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Physical-chemical properties

Boiling point (760 torr) : 42.3°C

Ideal boiling point to be a blowing agent

Vapour pressure :	44.0 kPa	at 20°C
	126.3 kPa	at 50°C

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Insulation properties

Thermal conductivities in gaseous phase

Product	λ (10^{-2}.W/m.K)	T (°C)	λ (10^{-2}.W/m.K)	T (°C)
Methylal	1.4530	41.85	2.0390	109.85
n-Pentane	1.5829	37.78	2.2542	104.44
Isopentane	1.6736	50	2.1757	100
Cyclopentane	1.5158	49.25	2.2722	117.01

Lower (=better) thermal conductivity than Pentanes
including Cyclopentane

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Flammability

Methylal is flammable.

In Europe, it belongs to the middle class of flammability.

It is highly flammable.

It is less flammable than n-Pentane and Isopentane which are extremely flammable.

Nevertheless, blends of polyols with useful amount of Methylal for polyurethane foams show high flash point.

Moreover, blends of polyols with high amount of Methylal, show a low combustion tendency.

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Solvent power

The solvent power of Methylal is used to increase the miscibility of blowing agents with low solvent power, like Pentanes.

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Toxicology

Methylal has a very well documented toxicological profile.

Being REACH registered in Europe, all data required for a yearly production above 1000 tons are available.

The results are very good.

The TLV or MAK value in Germany of Methylal is 1000 ppm.

This value has been reviewed by the German Authorities in 2002-2003, and

it has been confirmed at 1000 ppm.

Methylal is not labelled for toxicological reasons.

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Eco-toxicology

Methylal has a good ecotoxicological profile.

The WGK of Methylal (Wassergefährdungsklasse in Germany), which evaluates the toxicity of a chemical against water, is 1 on a scale from 0 to 3, 0 being non toxic.

Methylal is also not labelled for ecotoxicological reasons.

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Atmospheric chemistry

Photochemical Ozone Creation Potential (POCP)

The degradation of organic chemicals released in the atmosphere starts with their reaction with the hydroxyl radical.

This reaction for Methylal is slow: 4.6 +/- 0.1 10^{-12} cm^3 $molecule^{-1}$ s^{-1}.

This rate is 14 times slower than expected by calculation if Methylal was considered as an ether.

Methylal, if emitted in the atmosphere, will migrate to the upper layer before forming ozone and only make a moderate contribution to the formation of tropospheric ozone.

Therefore Methylal has a low Photochemical Ozone Creation Potential (POCP).

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Maximum Incremental Reactivity (MIR)

The POCP of Methylal is confirmed by its Californian Maximum Incremental Reactivity (MIR) of 0,89.

Blowing agent	MIR	% increase
Methylal	0.89	
n-Pentane	1.23	+ 38 %
Isopentane	1.36	+ 53%
Cyclopentane	2.25	+ 153 %

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Global Warming Potential (GWP)

The Global Warming Potential (GWP) of Methylal is negligible.

Nevertheless, its GWP is only 3/5 of the GWP of Pentanes because Methylal only contains 3 carbons and 2 oxygens.

Ozone Depletion Potential (ODP)

By definition, the Ozone Depletion Potential (ODP) of Methylal is zero because Methylal doesn't contain any halogen atom.

Stability

Thermal stability

Stable for 7 days at 200°C

Stability against peroxide formation

Methylal does not form any peroxides

Without blanketing, there is no formation of peroxides after 1143 days.

Hydrolysis studies

Acetals are stable in neutral and basic conditions, and may hydrolyse in aqueous acidic conditions.

Nevertheless, Methylal shows a very slow rate of hydrolysis : there were no traces of hydrolysis of Methylal after 1 year at a pH level above 4.

At lower pH, rates remain slow.

Grades available

	Pure quality	Anhydrous quality
Methylal	99.5 % min.	99.9 % min.
Methanol	< 0.05 %	< 0.05 %
Formaldehyde	< 0.0005 %	< 0.005 %
Water	< 0.5 %	< 0.03 %

Sales specifications

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PROPERTIES OF POLYOLS – METHYLAL BLENDS

Miscibility

Methylal is fully miscible with all polyols, including aromatic polyester polyols

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Viscosity

Methylal is a strong viscosity reducer.

The reduction depends on the viscosity of the polyol itself : the higher the viscosity, the higher the reduction.

Composition % w/w		Viscosity (mPa.s)	
Polyol	Methylal	Tercarol 8092 (at 20°C)	Polyol (visco at 22°C : 930 mPa.s)
100	0	21840	930
98	2	8740	700
96	4	4566	500
94	6	3183	380
92	8	1416	300
90	10	448	235
85	15	361	140

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Flammability

Blends of polyols with Methylal can show high closed cup flash point.

The flash point depends on the viscosity and /or the nature of the polyol : polyols of higher viscosities give higher flash points.

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Blend % (w/w)		Flash point (closed cup) (°C) with				
Polyol	**Methylal**	**Polyol (visco at 22°C : 930 mPa.s)**	**Tercarol 8092 (viscosity at 25°C : 14500 mPa.s)**	**Terate 2033**	**Terate 2541**	**Terate 7541**
100	0					
99.5	0.5	> 70.0				
99	1	48.0		> 70.0	> 70.0	70.0
98.5	1.5	39.0		58.0	56.0	47.0
98	2	25.5	45.0	53.0	37.0	35.5
96	4	9.0	31.5			
94	6	2.0	22.0			
92	8	-3.0	12.5			
90	10	-10.0	7.5			

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Open cup flash points show much higher values than closed cup flash points.

Blend polyol/methylal 92.5 / 7.5 w/w %	Cleveland open cup flash point (°C)
With a polyol for spray foam	64
With a polyol for panels	68

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Combustibility

Blends of polyols with high amounts of Methylal show a low tendency to combustion.

Blend % (w/w)		Combustion description (in the presence of a flame)
Polyol (visco 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 vapours ; no further ignition in presence of a flame
88	12	Ignition of the vapours ; can be repeated, but is self extinguishing
86	14	Continuous burning

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Labeling (European)

European legislation says that,
if the flash point of a blend is between 21°C and 55°C
but the blend doesn't contribute to the combustion,
it doesn't need to be labelled as flammable

PROPERTIES OF ISOCYANATE – METHYLAL BLENDS

Methylal is also miscible with isocyanates.

Closed cup flash points of blends of isocyanate with a low percentage of Methylal are high.

Suprasec 5025	Methylal	Closed cup flash point (°C)
99.5	0.5	>70.0
99.0	1.0	46.0
98.5	1.5	29.0
98.0	2.0	23.0
97.5	2.5	18.0
97.0	3.0	12.0
96.5	3.5	8.0
96.0	4.0	4.0

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METHYLAL FLAMMABILITY REDUCTION

In systems, Methylal can be shared between the polyol and the isocyanate.

Two blends of limited flammability are obtained

instead of one blend with higher and one blend with lower flammability.

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METHYLAL IN COMBINATION WITH OTHER BLOWING AGENTS

- normal Pentane
- Cyclopentane
- HFC-365mfc
- HFC-245fa

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General advantages to use Methylal

- Miscibility
- Flow
- Pressure
- Foam uniformity
- Size of the cells
- Thermal conductivity
- Adhesion
- Cost

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Methylal combined with normal Pentane

Methylal improves the miscibility of normal Pentane.

Methylal improves the foaming uniformity.

The number of voids, pinholes, craters, lakes etc. is reduced.

Methylal reduces the size of the cells.

In partial replacement of n-pentane, methylal makes the mixing of polyol, isocyanate and blowing agent easier at the mixing head.

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Methylal combined with normal Pentane

Methylal in combination with n-Pentane improves the flow.

Methylal improves the adhesion on metallic surfaces.

Methylal decreases the thermal conductivity of the foam.

Methylal combined with n-Pentane provides a foam thermal conductivity close to that of Cyclopentane.

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Methylal combined with normal Pentane

In blends with n-pentane, methylal increases the pressure generated by n-pentane.

This is observed even if the vapour pressure of methylal is lower than that of n-pentane.

Blends (%w/w)		Vapour pressure [kPa] (ASTM D 323-modified)	
n-pentane	Methylal	at 25°C	at 50°C
100	0	66.5	156.5
80	20	72.5	168.5
75	25	73.0	170.5
65	35	73.5	173.0
60	40	73.5	173.0
0	100	51.0	128.2

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Methylal combined with Cyclopentane

Cyclopentane has a higher boiling point than methylal.

It is generally used in combination with isopentane to get more pressure in the blowing.

Methylal, with its higher vapour pressure, also gives more pressure in replacement of cyclopentane.

Nevertheless, contrarily to isopentane, the increase is not linear.

At low percentage, methylal gives as much pressure as isopentane.

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Methylal combined with Cyclopentane

Blends cyclopentane - co-blowing agent (% w/w)	Vapour pressure of the blend with the co-blowing agent (kPa) (ASTM D-323-modified)			
	at 25°C		at 50°C	
	Isopentane	Methylal	Isopentane	Methylal
100/0	40,8	40,8	100,2	100,2
80/20	50,5	50,8	119,6	120,9
60/40	60,4	55,2	138,4	131,4
40/60	69	57,2	157,3	136,1
20/80	77,8	56,1	175,8	135,4
0/100	86,6	51,8	195,1	126,3

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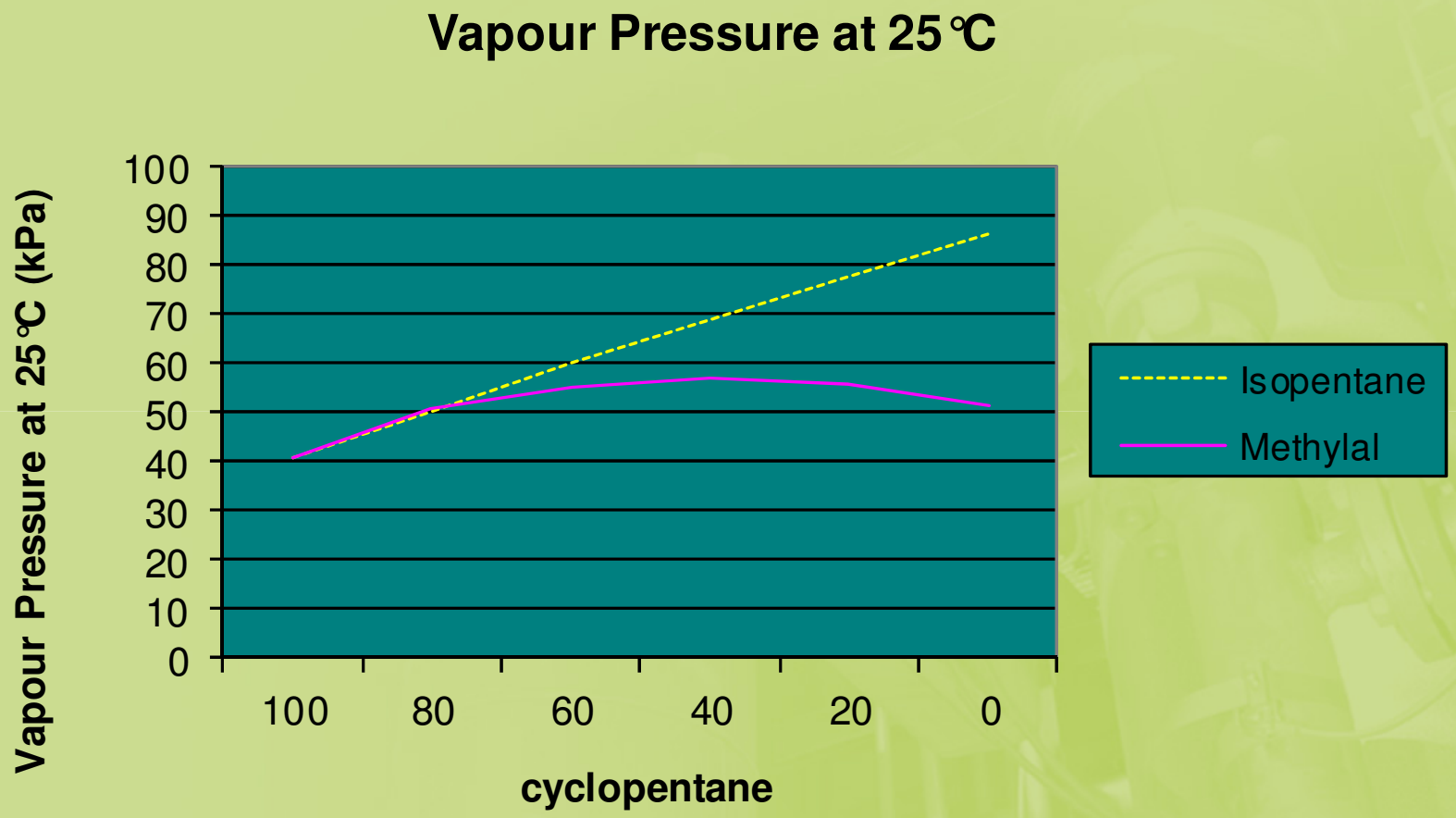
Methylal combined with Cyclopentane



Methylal combined with Cyclopentane

Methylal decreases the thermal conductivity of the foam.

Methylal increases the blowing rate of the foam.

Methylal increases the compressive strength of the foam.

Methylal brings the same advantages described with normal Pentane.

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Methylal combined with HFC-365mfc

Blends polyol-HFC-365mfc (without HFC-227ea) and blends polyol-Methylal have similar flammability.

Methylal improves the thermal insulation.

Fire performance of the foam is not affected by low percentage of Methylal.

Methylal reduces the cost.

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Methylal combined with HFC-245fa

HFC-245fa is non-flammable

Low percentage of Methylal in replacement of HFC-245fa keeps an acceptable flash point of the preblend with polyol, and does not affect the fire performance of the final foam.

Blends polyol-methylal-HFC-245fa show an optimum flash point, which is not at the lowest level of methylal.

Combined with HFC-245fa, the main function of methylal is the reduction of cost.

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MARKET

Used in Europe in about 20 countries.

Used alone, or combined with

- water
- HFC-365mfc
- HFC-245fa
- Cyclopentane
- n-Pentane
- HCFC-141b (in countries where it is allowed)

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Market

Applications cover a wide range of products:

- blocks
- panels
- refrigeration
- boilers
- trucks
- sprays
- pipe insulation
- flexible moulded foams
- integral skin foams
- one component foams.

A significant part of the volume is used by system houses.

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CONCLUSION

Ecological

Safe for people

Economical

Good technical performance

Controled flammability

Used alone or as co-blowing agent

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