METHYLAL AS ECOLOGICAL BLOWING AGENT

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PRESENTATION STRUCTURE

Properties of Methylal

Properties of polyols - Methylal blends

Methylal as co-blowing agent

Methylal as a single blowing agent or combined with water

Conclusion

PROPERTIES OF METHYLAL

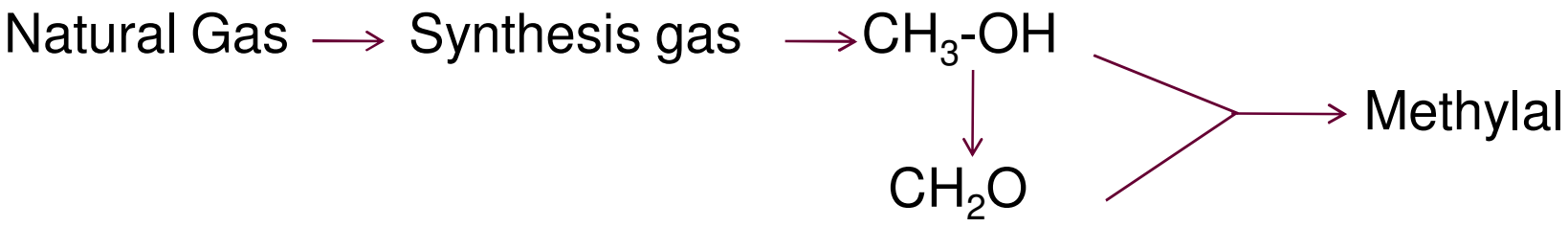
Identification of Methylal

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

Methylal production doesn't consume non renewable oils



The source of Methylal is 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

Bio-sourcing of Methylal

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

Physical-chemical properties

Boiling point (760 torr) : 42.3℃

Ideal boiling point to be a blowing agent

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 thermal conductivity than Pentanes including Cyclopentane

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.

Flammability

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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.

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.

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.

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).

Atmospheric chemistry

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 %

Atmospheric chemistry

Global Warming Potential (GWP)

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

But, only 3/5 of the GWP of Pentane.

Atmospheric chemistry

Ozone Depletion Potential (ODP)

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

Stability against peroxide formation

Methylal does not form any peroxides

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

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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.

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PROPERTIES OF POLYOLS – METHYLAL BLENDS

Miscibility

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

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

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			

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

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

METHYLAL AS CO-BLOWING AGENT

Methylal is combined with :

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

General advantages of these combinations

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

METHYLAL IN POLYURETHANE FORMULATION

Integral Skin Foam

Rigid Foam

Flexible Molded Foam

GENERAL ASPECTS

- ✓ **Miscibility**
- ✓ **Flowability**
- ✓ **Vapor pressure**
- ✓ **Cell uniformity**
- ✓ **Adhesion**
- ✓ **Cost**

INTEGRAL SKIN

FORMULATION

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol	79,48	100,00	78,48	100,00
Glycol	6,70	8,54	6,70	8,54
Silicone	0,22	0,28	0,22	0,28
Colorante	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

Comments

- modification just in the blowing agent

PROPERTIES

Results		Methylal	Standard HCFC 141b
Whole Sample			
Molded density	Kg/m³	356,7	348,6
Hardness	Shore A	50	52
Resilience	%	35	34
Core zone			
Internal Density	Kg/m³	265,3	244,2
Tensile Strength	kPa	241	238
Elongation	%	63	66
Tear Strength	N/mm	1090	1150
Compression Set (50%)	%	21	19
Skin zone			
Tensile Strength	kPa	980	975
Elongation	%	78	77
Tear Strength	N/mm	3810	3780

The trials were in integral skin for furniture

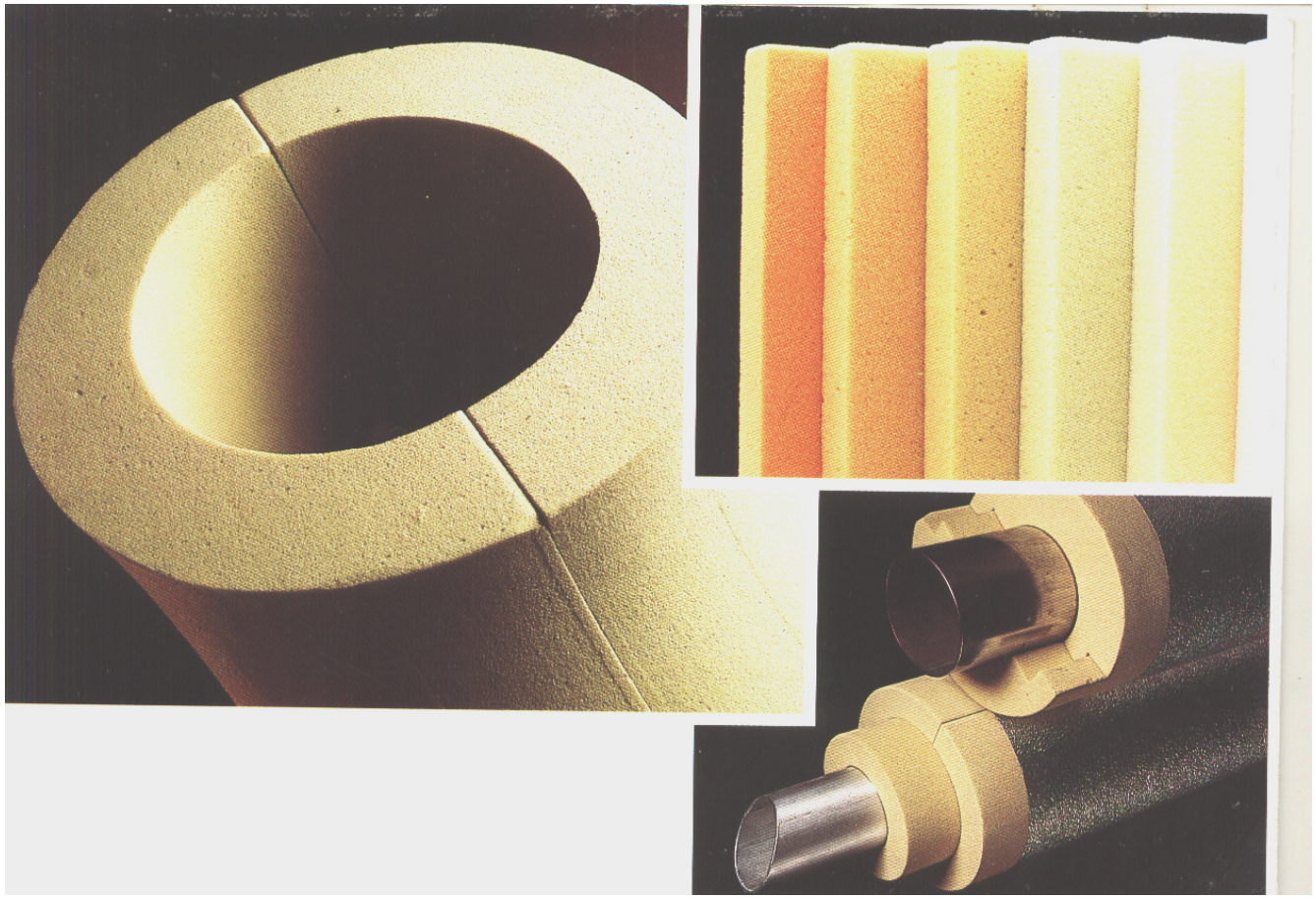
Comment

- Similar Properties

PROCESSING

- ✓ **Miscible in all Raw Materials**
- ✓ **Good Skin formation**
- ✓ **Good flowability**
- ✓ **In water based system provide better processability**

RIGID FOAM



FORMULATION

Comments
- New Silicone
- Polyol
- Water

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol A (based sucrose)	76,80	86,98	81,57	100,00
Polyol B (glycerine propoxylated polyether triol)	7,50	8,49	---	---
Polyol C (Aminic tetrafunctional polyether polyol)	4,00	4,53	---	---
Crosslinker	0,90	1,02	0,90	1,10
Silicone A	---	---	0,74	0,90
Silicone B	1,00	1,13	---	---
Catalyst A	0,25	0,28	0,51	0,63
Catalyst B	0,25	0,28	0,55	0,68
Water	1,30	1,47	1,21	1,48
Methylal	8	9,06	0,00	0,00
HCFC-141b	0,00	0,00	14,52	17,80
Total	100,00	112,96	100,00	122,59

PROPERTIES

Results		Methylal	Standard HCFC 141b
Core density	kg/m3	40,6	38,2
Compression set 10% Transverse / Parallel	kPa	182,6 / 183,5	195,3 / 197,7
Dim. Stability +70°C (side1 max. / side1 min.)	%	+1,67 / -0,81	+6,97 / -0,24
Dim. Stability -20°C (side1 max. / side1 min.)	%	+0,41 / -0,01	-0,16 / -0,01
Dim. Stability +70°C (side 2 max. / side 2 min.)	%	-0,90 / +0,05	-0,81 / -0,31
Dim. Stability -20°C (side 2 max. / side 2 min.)	%	+0,28 / -0,03	-0,59 / -0,14
thickness max. +70°C / -20°C	%	+4,78 / -0,92	+0,73 / -5,87
thickness min. +70°C / -20°C	%	+0,13 / -0,28	-0,25 / -0,52
K Factor	mW/mK	23,66	22,70

The trials were in commercial refrigerator

Comments

- Decrease K factor and compression set

PROCESSING

- ✓ Improves the Miscibility of pentanes in polyol
- ✓ Safer than hydrocarbons
- ✓ Improves the adhesion
- ✓ Can be used in combination with others blowing agents
- ✓ Cost

FLEXIBLE MOLDED FOAM

FLEXIBLE MOLDED FOAM

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol Polyether	73,09	79,22	73,09	80,00
Copolymer Polyol	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

Comments

- Few modifications
- Small increase in the copolymer

PROPERTIES

Results		Metilal	Standard HCFC 141b
Density	kg/m3	38,3	40,1
Resilience	%	46	46
Tensile Strength at break	kPa	126,8	130,9
Tear Propagation	N/mm	575,5	614,5
Elongation at break	%	128,6	123,8
Compression set 50%	%	9,83	11,0
IDL 25 %	N	151	150
IDL 40 %	N	233	236
IDL 65 %	N	527	536

The trials were in flexible molded for furniture

Comment

- Similar properties
- Open cells
- Improved Compression Set

FLEXIBLE MOLDED FOAM

- ✓ Improve cell open
- ✓ Reduces the temperature during foaming
- ✓ Improve the flowability
- ✓ Reduce the amount of water in water based formulation
- ✓ Improve compression set

CONCLUSIONS

- ✓ Methylal showed good performance in the field
- ✓ Methylal offers similar or better properties than others ecologic blowing agent
- ✓ Methylal combined with other blowing agents can show advantages
- ✓ Safe for human health
- ✓ Ecological blowing agent
- ✓ Excellent stability in polyurethane systems
- ✓ Flammability can be controlled
- ✓ Immediate availability