ACETALS
IN
POLYURETHANE FOAMS

Vento Co. - Lambiotte meeting

Ho Chi Minh City, Vietnam, January 22d, 2015

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LAMBIOTTE'S ACETALS

Acetal	Formula
Methylal	$CH_3\text{-}O\text{-}CH_2\text{-}O\text{-}CH_3$
Ethylal	$CH_3\text{-}CH_2\text{-}O\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_3$
Propylal	$CH_3\text{-}(CH_2)_2\text{-}O\text{-}CH_2\text{-}O\text{-}(CH_2)_2\text{-}CH_3$
Butylal	$CH_3\text{-}(CH_2)_3\text{-}O\text{-}CH_2\text{-}O\text{-}(CH_2)_3\text{-}CH_3$
TOU	$CH_3O\text{-}(CH_2)_2\text{-}O\text{-}CH_2\text{-}O\text{-}(CH_2)_2\text{-}OCH_3$
2-Ethylhexylal	$CH_3\text{-}(CH_2)_3\text{-}(C_2H_5)CH\text{-}CH_2\text{-}O\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH(C_2H_5)\text{-}(CH_2)_3\text{-}CH_3$

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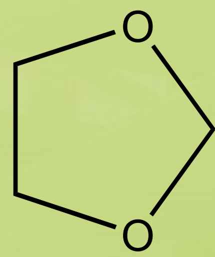
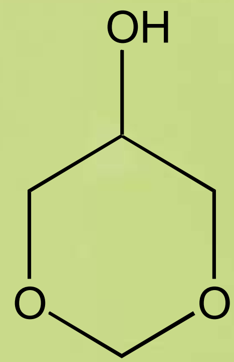
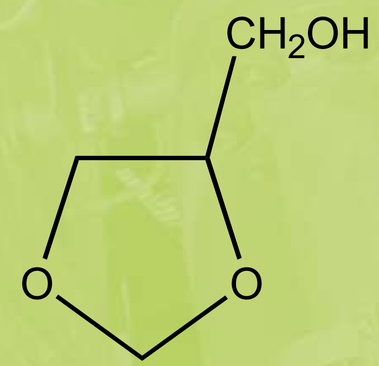
Acetal	Formula
1,3-Dioxolane	
Glycerol formal	1)  2) 

ACETALS USED IN POLYURETHANE FOAMS

Methylal as blowing agents.

Dioxolane and TOU as cleaning agents.

METHYLAL
AS
A BLOWING AGENT
FOR
POLYURETHANE FOAMS

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INTRODUCTION

The choice of physical blowing agents for polyurethane foams becomes limited.

HCFC-141b must be phased out worldwide and there are new European and American legislations to phase out HFCs

Main established options are normal Pentane and Cyclopentane.

Methylal is one of the emerging options.

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What brings Methylal ?

INTRODUCTION

Methylal is a practical and economical solution

with the safest profile for people and the environment.

INTRODUCTION

Methylal is used for :

- Rigid
- Flexible
- Integral skin
- Microcellular foams

Methylal is also an additive for One Component Foams.

Methylal is used - as sole blowing agent
- in combination with other blowing agents

DESCRIPTION of METHYLAL

Identification

$CH_3O\text{-}CH_2\text{-}OCH_3$

Also called Dimethoxymethane

Chemical class : Acetal
Neither Ether nor Diether

Raw materials

Production from natural gas which is abundant on the Earth.

No consumption of non-renewable fossil oil.

Bio-sourced Methylal

Bio-Methanol is available,

Therefore, Methylal is potentially bio-sourced.

PROPERTIES and COMPARISON with HCFC-141b and OTHER OPTIONS

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Boiling points

	Chemical structure	Boiling point (°C)
Cyclopentane	$(CH_2)_5$	49
Methylal	$CH_3O\text{-}CH_2\text{-}OCH_3$	42.3
Methylene chloride	CH_2Cl_2	40
HFC-365mfc 1,1,1,3,3-pentafluorobutane	$CF_3\text{-}CH_2\text{-}CF_2\text{-}CH_3$	40
n-Pentane	$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$	36
HFO-1336 mzz-Z (2Z)-1,1,1,4,4,4-hexafluorobut-2-ene	$CF_3\text{-}CH\text{=}CH\text{-}CF_3$ (cis)	33
HCFC-141b 1,1-dichloro-1-fluoroethane	$Cl_2FC\text{-}CH_3$	32
Methyl formate	$CH_3O\text{-}CH\text{=}O$	31.5
Isopentane	$CH_3\text{- }CH\text{-}CH_2\text{-}CH_3$ | CH_3	28
HFO-1233 zd-E trans-1-chloro-3,3,3-trifluoropropene	Cl-CH=CH-CF3 (trans)	19
HFC-245fa 1,1,1,3,3-pentafluoropropane	$CF_3\text{-}CH_2\text{-}CHF_2$	15
HFC-227ea 1,1,1,2,3,3,3-heptafluoropropane	$CF_3\text{-}CHF\text{-}CF_3$	-16.5
HFC-134a 1,1,1,2-tetrafluoroethane	$CH_2F\text{-}CF_3$	-26

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PROPERTIES Boiling points

Methylal remains a liquid up to 42.3 °C.

Therefore Methylal is more easy to handle compared to blowing agents with lower boiling point.

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Molecular weight and blowing ability

The blowing ability can be estimated from the molecular weight.

	Molecular weight	Blowing ability
Methyl formate	60	1.27
Cyclopentane	70	1.09
n-Pentane	72	1.06
Isopentane	72	1.06
Methylal	76	1
Methylene chloride	84	0.90
HFC-134a	102	0.75
HCFC-141b	117	0.65
HFO-1233 zd-E	130.5	0.58
HFC-245fa	134	0.57
HFC-365mfc	148	0.51
HFO-1336 mzz-Z	164	0.46
HFC-227ea	170	0.45

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PROPERTIES Blowing ability

Methylal has an higher blowing ability than HCFC-141b.

Methylal has a similar blowing ability than Pentanes.

Solubility in polyol

Methylal is fully miscible with all polyols.

It has no limit of solubility as other blowing agents
like Pentanes or HFCs.

Methylal is combined with blowing agents of limited solubility to increase their miscibility in polyols.

Flammability

	Flash point (°C)	GHS/CLP classification	R-phrase
Isopentane	- 51	Flammable liquid, category 1	F+ R12
n-Pentane	- 40	Flammable liquid, category 1	F+ R12
Methyl formate	- 28	Flammable liquid, category 1	F+ R12
Cyclopentane	- 40	Flammable liquid, category 2	F R11
Methylal	-30.5	Flammable liquid, category 2	F R11
HFC-365mfc	< -27	Flammable liquid, category 2	F R11
Methylene chloride	No	Non flammable	Non flammable
HFO-1336 mzz-Z	No	Non flammable	Non flammable
HFO-1233 zd-E	No	Non flammable	Non flammable
HFC-227ea	No	Non flammable	Non flammable
HFC-245fa	No	Non flammable	Non flammable
HFC-134a	No	Non flammable	Non flammable
HCFC-141b	No	Non flammable	Non flammable

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PROPERTIES Flammability

Methylal is a flammable liquid category 2.

It belongs to the same class as HFC-365mfc
(unblended with HFC-227ea).

It is less flammable than commonly used blowing agents like normal Pentane and Isopentane.

Which are flammable liquid category 1.

NEVERTHELESS,

Flammability concerns are overcome once Methylal is blended with polyols.

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PROPERTIES Flammability

Low percentages of Methylal (up to 2-3 %) in polyols give a high closed cup flash point.

Blend % (w/w)		Flash point (closed cup) (°C) with				
Polyol	Methylal	Polyol (viscosity at 22°C : 930 mPa.s)	Sorbitol propoxylated polyol (OH number 456, viscosity at 25°C: 14500 mPa.s)	Aromatic polyester polyol (OH number 289, viscosity at 25°C : 6410 mPa.s)	Aromatic polyester polyol (Functionality 2, OH number 235, viscosity at 25°C : 3850 mPa.s)	Aromatic polyester polyol (Functionality 2, OH number 242, viscosity at 25°C : 3670 mPa.s)
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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PROPERTIES Flammability

Higher percentages of Methylal (up to 7-8 %) in polyols give a high open cup flash point.

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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Even higher percentages of Methylal (up to 8-9 %) in polyols give non-combustible blends.

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

Blends of polyols with up to 12 % of Methylal ignite in the presence of a source of ignition, but is still self-extinguishing.

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- The non-combustibility of blends is very important for the labeling in Europe because Annex VI to Consolitated Version of Directive 1999/45/EC says that a preparation having a flash point equal to or greater than 21°C and less than or equal to 55°C need not be classified as flammable if the preparation could not in any way support combustion.

- Regulation (EC) 1272/2008 on Classification, Labelling and Packaging, based on GHS, which will be in force on June 1st 2015, says, at chapter 2.6.4.5., that liquids with a flash point of more than 35°C need not be classified in Category 3 if negative results have been obtained in the sustained combustibility test L.2, Part III, section 32 of the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria.

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PROPERTIES Flammability

This flammability abatement behavior is not observed with other flammable blowing agents of category 1 or 2

(like normal Pentane and Cyclopentane).

Blend % (w/w)		**Flash point (closed cup) (°C) with**	
Polyol (visco 930 mPa.s)	**Blowing agent**	**Methylal**	**n-Pentane**
100	**0**	**–**	**–**
98	**2**	**25.5**	**7.0**
96	**4**	**9.0**	**< -18**
94	**6**	**2.0**	**< -18**
92	**8**	**-3.0**	**< -18**
90	**10**	**-10.0**	**< -18**

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PROPERTIES Flammability

Even if non-flammable, HCFC-141b has explosion limits, as well as Methylal.

	Lower explosion limit, % (vol.)	**Upper explosion limit, % (vol.)**
Methylal	**2,2**	**19,9**
HCFC-141b	**5,6**	**17,7**

Vapors of HCFC-141b or Methylal may form explosive mixture with air.

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Insulation properties

Product	λ (mW/m.K) at 25°C
HFO-1233 zd-E	9.94 – 10.2 (20° C)
HCFC-141b	10
HFC-365mfc	10.6
HFO-1336 mzz-Z	10.7
Methyl Formate	10.7
Methylal	11
Cyclopentane	12 - 13
HFC-245fa	12.5 (24°c)
HFC-227ea	13.3
Isopentane	13.8
HFC-134a	14.5
n-Pentane	14.6

Methylal has among the lowest thermal conductivity.

In partial replacement of normal Pentane, Cyclopentane or HCFC-365mfc, Methylal improves the foam insulation.

Vapor pressure

	hPa	Measurement temperature
Cyclopentane	362	21°C
Methylal	400	20°C
HFC-365mfc	433	20°C
Methylene chloride	584	25°C
n-Pentane	585.9	21°C
HFO-1336 mzz-Z	604	20°C
HCFC-141b	763	20°C
Methyl formate	781	25°C
Isopentane	1000	27.5°C
HFO-1233 zd-E	1065	20°C
HFC-245fa	1227	20°C
HFC-227ea	4040	21°C
HFC-134a	5740	20°C

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PROPERTIES Vapor pressure

The flash point of a blend depends on

the vapor pressure and
the lower flammability limit of its constituents.

High vapor pressure of flammable blowing agents increases the flammability of their blends with polyols.

Toxicology

	GHS/CLP classification	R phrases
Methylal	-	-
Cyclopentane	-	-
HFC-365mfc	-	-
HFC-245fa	-	-
HFC-134a	-	-
HCFC-141b	-	-
n-Pentane	Aspiration Toxicity Cat. 1; Specific target organ toxicity — single exposure Cat. 3	Xn R65; R66, R67
Isopentane	Aspiration Toxicity Cat. 1; Specific target organ toxicity — single exposure Cat. 3	Xn R65; R66, R67
Methyl formate	Acute Toxicity (oral/inhalation) Cat. 4; Serious eye damage/eye irritation: Cat. 2 Specific target organ toxicity following single exposure: Cat. 2 Specific target organ toxicity following single exposure: Cat. 3 (irritating to respiratory system)	Xn R20/21/22, R68/20/21/22; Xi R36/37
Methylene chloride	Carcinogenic Cat. 2	Xn R40

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PROPERTIES Toxicology

According to GHS/CLP classification
(Globally Harmonised System/Classification, Labelling and Packaging),

Methylal,
Cyclopentane
HFCs
HCFC-141b

are not labeled for toxicological concerns.

HCFC-141b is not Reach registered because its use has been stopped in Europe before the Reach legislation.

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PROPERTIES Toxicology

Methylal is the blowing agent with the highest official occupational exposure limits.

	Austria (ppm)	Belgium (ppm)	Denmark (ppm)	Finland (ppm)	France (ppm)	Germany (ppm)	Ireland (ppm)	Italy (ppm)	Netherlands (ppm)	Spain (ppm)	Sweden (ppm)	Switzerland (ppm)	UK (ppm)	US (ppm)
Methylal	1000	1000	1000	1000	1000	1000	1000	1000		1000		1000	1000	1000
Isopentane	600	600	500	500	1000	1000	667		1800 mg/m3	1000	600	600	600	600
n-pentane	600	600	500	500		1000					600	600		600
Cyclopentane		600	300		600		600	600		600		600		600
HFC–365mfc	Supplier recommended OEL: 1000 ppm													
HFC-227ea	Supplier recommended OEL: 1000 ppm													
HFO-1233zd-E	Supplier recommended OEL: 800 ppm													
HFO-1336mzz-Z	Supplier recommended OEL: 500 ppm													
HFC–134a														1000
HCFC-141b														500
HFC–245fa														300
Methyl formate	50	100	50	50	100	50	100	100		100	100	50		100
Methylene chloride	50	50	35	100	50	75	50	50		50	35	50	100	25

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Eco-toxicology

	GHS/CLP classification	R phrases	WGK
Methylal	-	-	1
HFC-365mfc	-	-	1
HFC-227ea	-	-	1
HFC-245fa	-	-	1
HFC-134a	-	-	1
Methyl formate	-	-	1
Methylene chloride	-	-	2
HFO-1336mzz	-	-	Not available
Cyclopentane	Chronic Aquatic Toxicity Cat.3	R52/53	1
HFO-1233 zd-E	Chronic Aquatic Toxicity Cat.3	R52/53	Not available
n-Pentane	Chronic Aquatic Toxicity Cat.2	N R51/53	2
Isopentane	Chronic Aquatic Toxicity Cat.2	N R51/53	2
HCFC-141b	Chronic Aquatic Toxicity Cat.3 Harms public health and the environment by destroying ozone in the upper atmosphere	R52/53, N R59	1

PROPERTIES Ecotoxicology

Methylal
HFCs
HFO-1336mzz-Z

are not labeled for eco-toxicological concerns, as well as

Methyl formate
Methylene chloride

But these two last blowing agents have toxicological concerns

Atmospheric chemistry

Ozone Depletion Potential

Methylal has no ozone depletion potential (ODP).

Ozone depletion potential	
	ODP
Methylal	**0**
HCFC-141b	**0.11**

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Global Warming Potential

Methylal has a negligible GWP

	GWP 100-yr
Methylal	Negligible
n-Pentane	Negligible
Isopentane	Negligible
Methyl formate	Negligible
Carbon dioxide	1
HFO-1233 zd-E	1
HFO-1336 mzz-Z	2
Methylene chloride	9
Cyclopentane	11
HCFC-141b	782
HFC-365mfc	804
HFC-245fa	858
HFC-134a	1300
HFC-227ea	3350

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PROPERTIES   Atmospheric chemistry

Atmospheric lifetime

	Time
Methylal	2.3 days
HCFC-141b	9.2 years

PROPERTIES Atmospheric chemistry

Maximum Incremental Reactivity

The Maximum Incremental Reactivity of Methylal is low, confirming that emissions of Methylal will only moderately contribute to the formation of ozone.

Blowing agent	MIR	% increase
Methylal	0.94	
n-Pentane	1.31	+ 39 %
Isopentane	1.45	+ 54%
Cyclopentane	2.39	+ 154 %

The MIR of Methylal is much lower than the one of all Pentanes.

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Labelling summary

Summarizing the GHS/CLP classification of blowing agents,

ONLY Methylal and HFO-1336 mzz-Z don't have any classification for

Toxicology

Eco-toxicology

Atmospheric chemistry

PROPERTIES Labelling summary

Labelling			
Blowing agent	Toxicolgy	Eco-toxicology	Atmospheric chemistry
Methylal	+	+	+
HFO-1336 mzz-Z	+	+	+
Methyl formate	-	+	+
Methylene chloride	-	+	+
Cyclopentane	+	-	+
HFO-1233 zd-E	+	-	+
HFC-365mfc	+	+	-
HFC-245fa	+	+	-
HFC-134a	+	+	-
HCFC-141b	+	-	-
n-Pentane	-	-	+
Isopentane	-	-	+

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Stability in systems

Methylal is an Acetal.

Acetals are stable in neutral and alkaline conditions.

Polyurethane systems are usually alkaline

Therefore there are no concerns of hydrolysis of Methylal in water-based systems.

Acetals may hydrolyze in aqueous acidic conditions,
but it has been shown there are no traces of hydrolysis of Methylal after one year at pH 4.

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PROPERTIES Stability

pH	ppm of formaldehyde detected	
	initially	after 1 year
4	0.29	0.58
3.5	3.57	403

Methylal / water 30/70, H_2SO4, 20°C

At lower pH, rates remain slow.

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PROPERTIES Stability

Methyl formate, being an ester, may hydrolyze in alkaline conditions, which are the conditions of the polyol side of polyurethane systems.

Half-life at 25°C:

pH 4: 257.8 h.
pH 7: 28.6 h.
pH 9: 0.7 h.

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Solvent power – Foam dimensional stability

The solvent power of a blowing agent makes that it is easily miscible with polyols.

It also helps the solubilization of poorly miscible blowing agents.

Nevertheless high solvent power is an issue for dimensional stability.

Methylal has a solvent power higher, but relatively closer compared to other commonly used blowing agents.

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Solubility parameters

	δT (MPa½)	δD	δP	δH
Methyl formate	20,9	15,3	8,4	10,2
Methylene chloride	20,2	13,4	11,7	9,6
Methylal	18,24	14,83	6,01	8,76
Cyclopentane	16,5	16,1	3,9	0,6
HFC–365mfc	16,4	16,4	0	0
HCFC-141b	15,7	15,7	4	1
HFC–245fa	15,7	15,7	0	0
n-pentane	14,4	14,4	0	0
Isopentane	13,7	13,7	0	0
HFC–134a	13,5			

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Heat of combustion

Lower heat of combustion of blowing agent reduces the flammability of the foam.

	kJ/g
Methylene chloride	2.1
HFC-227ea	3.3
HFC-134a	4.2
HFC-245fa	6.1
HCFC-141b	7.94
Methyl formate	16.8
HFO-1233 zd-E	< 19
HFO-1336 mzz-Z	< 19 expected
Methylal	25.44
n-Pentane	41.9
Cyclopentane	44.2
Isopentane	46
HFC-365mfc	?

Methylal has a lower heat of combustion than Pentanes.

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PROPERTIES OF POLYOLS-METHYLAL BLENDS

POLYOLS – METHYLAL BLENDS

Methylal is fully miscible with all polyols, for which it is a viscosity reducer.

Composition % w/w		Viscosity (mPa.s)	
Polyol	Methylal	Sorbitol propoxylated polyol (OH number 456) (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

The reduction depends on the viscosity of the polyol itself :

the higher the viscosity, the higher the reduction.

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POLYOLS – METHYLAL BLENDS

Blends of polyols with Methylal have a reduced flammability.

The flash point of blends depends on the nature and the viscosity of the polyol.

Blends with polyols of higher viscosities have higher flash points.

Blends of polyols with up to 8-9 % of Methylal are non-combustible.

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PROPERTIES OF ISOCYANATES-METHYLAL BLENDS

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.

Standard polymeric MDI (% NCO : 31.0, viscosity at 25°C 210 mPa.s, average functionality : 2.7)	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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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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GRADES AVAILABLE

For polyurethane formulations

Pure quality suggested

Anhydrous quality suggested when blended with isocyanate.

For One Component Foams

Anhydrous quality

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EXAMPLES
OF
POLYURETHANE FORMULATIONS
WITH METHYLAL
AS ONLY BLOWING AGENT

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Types

Rigid foams

- Truck
- Water heater
- Thermoware
- Appliance (Rigid injection)
- PIR Foams
- Non-continuous rigid block
- Spray
- Pour in place

FORMULATIONS Types

Semi-rigid foams

Packaging

Flexible foams

Viscoelastic blocks (non-continuous)

Viscoelastic moulded

High resilience moulded

Viscoelastic blocks

Integral skin foams

Structural

Furniture

Steering wheels

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Example

Methylal is used in a wide variety of rigid foams.

In flexible foams, only low percentages of Methylal are used. Therefore these formulations are non-flammable.

In integral skin foams, Methylal is a very good blowing agent for non-water-based and water-based formulations.
In water-based formulations Methylal strongly improves the quality of the skin.

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Methylal in rigid foams

TRUCK

	Methylal		HCFC-141b	
	%	pph	%	pph
Voranol 466	61,60	80,00	55,70	80,00
Voranol 2110b	15,40	20,00	13,92	20,00
Glycerine	3,31	4,30	2,99	4,30
TCPP	10,01	13,00	9,05	13,00
Niax L-6900 (silicone)	1,15	1,50	1,04	1,50
Niax C-5 (amine A)	0,08	0,10	0,10	0,14
Niax A-107 (amine B)	0,69	0,90	0,97	1,40
Water	1,60	2,08	0,91	1,30
Methylal	6,16	8,00	-	-
HCFC-141 b	-	-	15,32	22,00
Total	100,00	129,88	100,00	143,64

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Methylal in rigid foams

TRUCK

Properties	Unit	Methylal	HCFC-141b
Density	Kg/m^3	41,3	39,8
K factor	mW/mK	24,6	22,5
Compression set 10% (Pa)	kPa	172,1	174,4
Compression set 10% (Pe)	kPa	210,3	213,2
Dim. stability (+70 °C)			
side 1 max	%	-0,64	-0,58
side 1 min	%	-0,18	-0,16
side 2 max	%	-0,67	-0,56
side 2 min	%	-0,22	-0,19
thickness max	%	-2,24	-4,11
thickness min	%	1,82	2,32
Dim. Stability (-20 °C)			
side 1 max	%	0,04	0,03
side 1 min	%	-0,02	-0,01
side 2 max	%	0,04	0,03
side 2 min	%	-0,03	0,01
thickness max	%	0,12	0,09
thickness min	%	0,04	0,01

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WATER HEATER

Methylal in rigid foams
WATER HEATER

	Methylal		HCFC-141b	
	%	pph	%	pph
Voracor CD	79,00	95,00	72,15	100,00
Voranol CP 450	4,15	5,00	-	-
Glycernie	-	-	2,89	4,00
TCPP	6,64	8,00	9,38	13,00
Niax L-6900 (silicone)	1,50	1,90	0,87	1,20
Niax A-300 (catalyst)	0,66	0,80	0,29	0,40
Niax C-8 (catalyst)	-	-	0,43	0,60
Water	1,41	1,70	1,01	1,40
Methylal	6,64	8,00	-	-
HCFC-141b	-	-	12,98	18,00
Total	100,00	120,40	100,00	138,60

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Methylal in rigid foams

WATER HEATER

Properties	Unit	Methylal	HCFC-141b
Density	Kg/m^3	39,4	36,9
K factor	mW/mK	24.5	22,6
Compression set 10% (Pa)	kPa	236,8	249,9
Compression set 10% (Pe)	kPa	-	217,7
Dim. stability (+70 °C)			
side 1 max	%	-0,31	0,85
side 1 min	%	-0,29	-0,11
side 2 max	%	-0,41	-0,35
side 2 min	%	-0,28	0,03
thickness max	%	-0,57	-4,53
thickness min	%	-0,55	-0,18
Dim. stability (-20 °C)			
side 1 max	%	-0,10	0,25
side 1 min	%	-0,06	0,06
side 2 max	%	-0,07	0,10
side 2 min	%	-0,04	0,03
thickness max	%	-0,27	0,21
thickness min	%	-0,23	0,04

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Methylal in rigid foams

THERMOWARE

Methylal in rigid foams
THERMOWARE

	Methylal		HCFC-141b	
	%	pph	%	pph
Voranol 466	77,28	100,00	69,33	100,00
TCPP	10,05	13,00	9,01	13,00
Niax L-6900 (silicone)	1,31	1,70	0,55	0,80
DMEA (catalyst A)	0,46	0,60	0,55	0,80
Niax A-300 (catalyst B)	0,85	1,10	0,76	1,10
Niax C-8 (catalyst C)	-	-	0,19	0,27
Water	2,32	3,00	1,59	2,30
Methylal	7,73	10,00	-	-
HCFC-141b	-	-	18,02	26,00
Total	100,00	129,40	100,00	144,27

Lambiotte &Cie

Methylal in rigid foams
THERMOWARE

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

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Methylal in rigid foams

APPLIANCE (RIGID INJECTION)

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Methylal in rigid foams
APPLIANCE (RIGID INJECTION)

	Methylal		HCFC-141b	
	%	pph	%	pph
Polyol A (sucrose based)	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

Comments
- New Silicone
- Polyol
- Water

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Methylal in rigid foams
APPLIANCE (RIGID INJECTION)

Properties	Unit	Methylal	HCFC-141b
Density	Kg/m^3	40,6	38,2
K factor	mW/mK	23,7	22,7
Compression set 10% (Pa)	kPa	183,5	197,7
Compression set 10% (Pe)	kPa	182,6	195,3
Dim. stability (+70 °C)			
side 1 max	%	1,67	6,97
side 1 min	%	-0,81	-0,24
side 2 max	%	-0,90	-0,81
side 2 min	%	0,05	-0,31
thickness max	%	4,78	0,73
thickness min	%	0,13	-0,25
Dim. stability (-20 °C)			
side 1 max	%	0,41	-0,16
side 1 min	%	-0,01	-0,01
side 2 max	%	0,28	-0,59
side 2 min	%	-0,03	-0,14
thickness max	%	-0,92	-5,87
thickness min	%	-0,28	-0,52

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Comments

- Decrease K factor and compression set

Methylal in rigid foams

PIR

	Methylal	
	%	pph
Voranol 466	39,23	50,00
Plex 1400	39,23	50,00
TCPP	8,20	10,45
Niax L-6900 (silicone)	1,10	1,40
C-32	1,18	1,50
DMEA (catalyst)	0,78	1,00
Water	1,10	1,40
Methylal	9,18	11,70
Total	100,00	127,45

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Methylal in rigid foams

NON CONTINUOUS BLOCKS

	Methylal		HCFC-141b	
	%	pph	%	pph
Voranol 466	60,61	79,00	55,27	85,00
Plex 1400	8,44	11,00	-	-
Desmophen 4050	7,67	10,00	-	-
Voranol 2110b	-	-	6,50	10,00
Voranol CP 450	-	-	3,25	5,00
Glycerine	-	-	2,60	4,00
TCPP	11,51	15,00	8,45	13,00
Niax L-6900 (silicone)	0,81	1,05	1,30	2,00
DMEA (catalyst)	0,23	0,30	-	-
Niax A-300 (catalyst)	-	-	0,44	0,67
Niax C-8 (catalyst)	-	-	0,12	0,18
Water	1,53	2,00	1,26	1,93
Methylal	9,20	12,00	-	-
HCFC-141b	-	-	20,81	32,00
Total	100,00	130,35	100,00	153,78

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73

Methylal in rigid foams

NON CONTINUOUS BLOCKS

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

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Methylal in rigid foams

SPRAY

Methylal in rigid foams
SPRAY

	Methylal		HCFC-141b	
	%	pph	%	pph
Desmophen 4050N	52,47	70,00	43,03	69,97
Voranol CP 450	22,49	30,00	18,47	30,03
TCPP	12,19	16,27	9,98	16,23
Niax L-6900 (silicone)	1,21	1,62	-	-
DMEA (catalyst A)	0,61	0,81	0,50	0,81
Lead octoate (catalyst B)	0,07	0,09	0,06	0,10
Water	1,22	1,63	1,00	1,62
Methylal	9,74	13,00	-	-
HCFC-141b	-	-	26,96	43,83
Total	100,00	133,42	100,00	162,59

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Methylal in rigid foams
SPRAY

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

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Methylal in rigid foams

POUR IN PLACE

	Methylal		HCFC-141b	
	%	pph	%	pph
Voracor CD	83,16	100,00	82,08	100,00
Glycerine	0,92	1,11	0,90	1,10
Niax L-5770(silicone)	0,27	0,32	-	-
Niax L-6900(silicone)	-	-	0,11	0,13
PC-32 (additive)	2,08	2,50	-	-
Niax C-8 (catalyst A)	0,83	1,00	0,52	0,63
DMEA (catalyst B)	1,00	1,20	0,56	0,68
Water	1,24	1,49	1,22	1,48
Methylal	10,50	12,63	-	-
HCFC-141b	-	-	14,61	17,80
Total	100,00	120,25	100,00	121,82

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Analysis of typical pour in place systems

COMPOSITON

Component (php)		A	B	C	D
Water		2,38	2,38	2,90	2,90
Fomulated Polyol		97,62	97,62	97,1	97,1
Sub Total		100,00	100,00	100,00	100,00
Methylal		8	6	6	8
Total		108,0	106,0	106,0	108,0
Polymeric MDI		145,0	145,0	145,0	145,0

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Analysis of typical pour in place systems

TEST CONDITIONS

Test Condition		A	B	C	D
Proc. Condition	blown	21,07	18,34	21,42	23,57
Pol/Iso ratio		0,745	0,731	0,731	0,745
Pol/Iso temperature	celsius	22	22	22	22
Pol/Iso pressure	bar	130	130	130	130
Reactivity	seconds				
Cream		4	4	4	3
Gel		43	35	30	30
Tack		51	53	45	46
Free Rise Density	kg/m3	27,7	28,6	27,1	24,7

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Analysis of typical pour in place systems

RESULTS

Brett Mould		A	B	C	D
MFD	kg/m3	36,9	37,1	34,4	32,2
Flow Index		1,332	1,298	1,268	1,302
Mould Temperature	Celsius	45	45	45	45
Moulded Density	kg/m3	42,2	42,4	39,6	37
4 min expansion	mm	0,89	0,84	0,88	0,9
OP	%	14,57	14,18	15,01	15,01
Compressive Strength	Kpa	206	189	208	160
CS corrected @32kg/m3	Kpa	130	118	145	124
Lambda Laser @24C	mW/mK	22,83	22,87	22,43	23,12

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Methylal in semi-rigid foams

PACKAGING

	Methylal		HCFC-141b	
	%	pph	%	pph
Voranol 4701	29,65	70,00	26,56	70,00
Enviropol 101	12,71	30,00	11,38	30,00
Niax L5770(silicone)	1,10	2,60	0,99	2,60
Niax C-8 (catalyst)	3,81	9,00	3,41	9,00
Water	17,79	42,00	15,93	42,00
Methylal	34,94	82,50	-	-
HCFC-141b	-	-	41,73	110,00
Total	100,00	236,10	100,00	263,60

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Methylal in flexible foams

FLEXIBLE BLOCK

Components	Parts by weight		
	Example 1 (comparison)	Example 2	Example 3
SYStol T 151	100.00	100.00	100.00
Water	4.50	4.50	4.50
Tegostab BF 2370	1.20	1.40	1.50
Dabco 33 LV	0.30	0.33	0.60
Tin octanoate	0.24	0.38	0.80
Methylal	0	5.00	10.00
TDI (isomer distribution 2,4 : 2,6 = 80 : 20)	110	110	110

Source : Elastogran GmbH, Germany

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PHYSICAL PROPERTIES	STANDARD	EXAMPLE 1	EXAMPLE 2	EXAMPLE 3
BULK DENSITY [KG/M³]	DIN 53 420	21.3	17.8	15.7
COMPRESSIVE STRENGTH [KPA]	DIN 53 577	3.5	2.5	1.7
ELONGATION AT BREAK [%]	DIN 53 571	138	137	149
TENSILE STRENGTH [KPA]	DIN 53 571	82	65	58
REBOUND ELASTICITY [%]	DIN 53 573	45.9	44.9	44.5
COMPRESSION SET [%] 50%/70°C/22H	DIN 53 572	2.2	3	4.5
IMPRESSION HARDNESS B 40% [N]	DIN 53 576	199	145	102

Source: Elastogran GmbH, Germany

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Methylal in flexible foams

Methylal replaces methylene chloride

	Enthalpy of vaporization at saturation pressure (10^7 J/kmol)
Methylal	2.8886 (at 298.00 K)
Methylene chloride	2.8451(at 298.15 K)

Methylal reduces scorching.

Methylal gives a soft touch to the foam.

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Methylal in flexible foams

VISCOELASTIC BLOCK (non continuous)

	Methylal		HCFC-141b	
	%	pph	%	pph
Multranol 9199T	22,88	24,23	22,88	24,38
Voranol CP-1421	22,87	24,22	22,87	24,37
Voranol 2120	17,44	18,47	17,44	18,58
Softcel VE 1100	19,16	20,29	19,16	20,41
Desmophen 4050	3,83	4,06	3,83	4,08
Voranol 4701	8,24	8,73	7,68	8,18
Niax L-5440 (silicone A)	0,48	0,51	0,48	0,51
Tegostab B 8409 (silicone B)	0,58	0,61	0,58	0,62
Niax A-1 (catalyst A)	0,09	0,09	0,09	0,09
AA 303 (catalyst B)	0,38	0,40	0,38	0,40
Water	2,25	2,38	2,25	2,39
Methylal	1,80	1,91	-	-
HCFC-141b	-	-	2,36	2,51
Total	100,00	105,90	100,00	106,52

Methylal in flexible foams

VISCOELASTIC BLOCK

	Methylal		HCFC-141b	
	%	pph	%	pph
Multranol 9199T	13,61	15,00	13,45	15,00
Voranol CP-1421	52,59	58,00	52,03	58,00
Voranol 2120	16,33	18,00	16,14	18,00
Voranol CP 450	3,63	4,00	3,59	4,00
DWL 4066 polyol	4,54	5,00	4,48	5,00
1,4-Butanediol	0,54	0,60	0,54	0,60
Niax L-5440 (silicone A)	1,00	1,10	0,99	1,10
Tegostab B 8409 (silicone B)	0,91	1,00	0,90	1,00
Niax A-1 (catalyst A)	0,14	0,15	0,13	0,15
AA 303 (catalyst B)	0,27	0,30	0,27	0,30
Water	3,04	3,35	3,00	3,35
Methylal	3,40	3,75	-	-
HCFC-141b	-	-	4,48	5,00
Total	100,00	110,25	100,00	111,50

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FLEXIBLE MOLDED FOAM

Methylal in flexible foams

FLEXIBLE MOLDED

Component	Example 1 (comparison)	Example 2
Lupranol 2045	85.55	84.25
Pluracol 973	10.00	10.00
Dimethylamino-propylamine	0.40	0.40
Dabco 33LV	0.20	0.20
Tegostab B 8631 (silicone stabilizer)	0.15	0.15
Water	3.70	3.00
Methylal	0	2.00
Polyisocyanate*	72	60

Source : Elastogran GmbH, Germany

*prepolymer based on diphenylmethane diisocyanate and polyphenyl polymethylene polyisocyanates having an NCO content of 27.5% by weight

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Methylal in flexible foams

FLEXIBLE MOLDED

Physical properties	Example 1	Example 2
Bulk density [kg/m³]	40	40
Compressive strength [kPa]	4.8	3.4
Indentation hardness [N]	320	210
Compression set (50%/70°C/22h) [%]	6.5	5.1
Hysteresis [%]	26.9	22.2

Source : Elastogran GmbH, Germany

It is possible to lower the bulk density, or to produce a more flexible foam of the same bulk density, by the use of methylal.

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Methylal in flexible foams

VISCOELASTIC MOLDED

	Methylal		HCFC-141b	
	%	pph	%	pph
Multranol 9199T	75,00	80,50	74,30	80,50
Voranol 2120	16,15	17,30	16,00	17,33
Voranol 4701	2,02	2,20	2,00	2,17
Niax L-5440 (silicone A)	0,25	0,27	0,25	0,27
Tagostab B 8409 (silicone B)	1,01	1,08	1,00	1,08
Niax A-1 (catalyst A)	0,15	0,16	0,15	0,16
AA 303 (catalyst B)	0,30	0,32	0,30	0,32
Water	3,00	3,22	3,00	3,25
Methylal	2,12	2,27	-	-
HCFC-141b	-	-	3,00	3,25
Total	100,00	107,32	100,00	108,33

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Methylal in flexible foams
VISCOELASTIC MOLDED

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

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Methylal in flexible foams

HIGH RESILIENCE MOLDED

	Methylal		HCFC-141b	
	%	pph	%	pph
Voranol 4701	73,09	79,22	73,09	80,00
NC 701 copolymer	19,18	20,78	18,27	20,00
Niax L-3001 (silicone)	0,46	0,50	0,46	0,50
AA 303 (catalyst A)	0,73	0,79	0,73	0,80
Niax A-4 (catalyst B)	0,34	0,37	0,34	0,35
Water	3,46	3,75	3,46	3,79
Methylal	2,74	2,97	-	-
HCFC-141b	-	-	3,65	4,00
Total	100,00	108,38	100,00	109,44

Comments

- Few modifications
- Small increase in the copolymer

Lambiotte &Cie

Methylal in flexible foams
HIGH RESILIENCE MOLDED

Properties	Unit	Methylal	HCFC-141b
Density (foam)	Kg/m^3	40,1	38,3
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
ILD 25%	N	151	150
ILD 40%	N	233	236
ILD 65%	N	527	536

Comment

- Similar properties
- Open cells
- Improved Compression Set

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Flexible molded foam

- Reduce the amount of water in water based formulation
- Improves the flowability
- Reduces the temperature during foaming
- Improves cell opening
- Improves the compression set

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Methylal in integral skin foams

STRUCTURAL

	Methylal		HCFC-141b	
	%	pph	%	pph
Voracor CD 947	57,62	70,00	-	-
Voracor 466 (rigid polyol)	-	-	56,00	70,00
Voranol 4701	24,70	30,00	24,00	30,00
Glycerine	5,14	6,24	5,00	6,25
Glycol	5,14	6,24	5,00	6,25
Niax L-6900 (silicone)	1,54	1,87	1,50	1,87
A 303 (catalyst)	1,54	1,87	1,50	1,87
Water	0,21	0,25	0,20	0,25
Methylal	4,11	5,00	-	-
HCFC-141b	-	-	6,80	8,50
Total	100,00	121,47	100,00	124,99

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INTEGRAL SKIN FOAM

Methylal in integral skin foams
INTEGRAL SKIN FOAM

Components	Parts by weight		
	Example 1 (comparison)	Example 2	Example 3
Lupranol 2045	67.40	66.40	63.40
Lupranol 2043	11.65	11.00	11.20
Pluracol 973	13.00	13.00	13.00
Ethylene glycol	6.00	6.00	6.00
Lupragen N 201 (amine catalyst)	1.10	1.10	1.10
Water	0.85	0.60	0.40
Methylal	0	1.90	4.90
Polyisocyanate*	56.9	52.3	48.4

Source : Elastogran GmbH, Germany

*prepolymer based on diphenylmethane diisocyanate, carbodiimide modified diphenylmethane diisocyanate and polyphenyl polymethylene polyisocyanates having NCO content of 26.3% by weigh

Methylal in integral skin foams

INTEGRAL SKIN FOAM

Example	Shore hardness (DIN 53505)	Bulk density, core zone [kg/m³] (DIN 53420)	Bulk density, peripheral zone [kg/m³] (DIN 53420)	Surface (microscopic analysis)
1	A78	400	750	Irregular, holes
2	A76	410	920	Smooth, closed
3	A74	390	960	Smooth, closed

Source : Elastogran GmbH, Germany

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Methylal in integral skin foams

INTEGRAL SKIN FOAM

Components	Parts by weight	
	Example 4 (comparison)	Example 5
Lupranol 2043	65.9	65.9
Lupranol 2042	16.3	15.0
Lupranol 2045	3.1	3.1
1,4-butanediol	10.7	10.7
Ethylene glycol	2.0	2.0
Lupragen N 201	1.1	1.1
Water	0.9	0.6
Methylal	0	1.6
Polyisocyanate*	73.6	68.3

Source: Elastogran GmbH, Germany

*prepolymer based on diphenylmethane diisocyanate, carbodiimide modified diphenylmethane diisocyanate and polyphenyl polymethylene polyisocyanates having NCO content of 26.3% by weight

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Methylal in integral skin foams
INTEGRAL SKIN FOAM

Example	Shore hardness (DIN 53505)	Bulk density, core zone [kg/m³] (DIN 53420)	Bulk density, peripheral zone [kg/m³] (DIN 53420)	Surface (microscopic analysis)
4	A50	455	780	Irregular, holes
5	A53	483	920	Smooth, closed

Source: Elastogran GmbH, Germany

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Methylal in integral skin foams

FURNITURE

	Methylal		HCFC-141b	
	%	pph	%	pph
Voranol 4701	87,11	100,00	83,88	100,00
Glycol	7,26	8,34	7,25	8,64
Niax L-3001 (silicone)	0,24	0,28	0,24	0,29
AA 303 (amine)	0,64	0,73	0,63	0,75
Methylal	4,75	5,45	-	-
HCFC-141b	-	-	8,00	9,54
Total	100,00	114,80	100,00	119,22

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Methylal in integral skin foams

STEERING WHEELS

	Methylal		HCFC-141b	
	%	pph	%	pph
Voranol 4701	79,48	100,00	78,48	100,00
Glycol	6,70	8,54	6,70	8,54
Niax L-3001 (silicone)	0,22	0,28	0,22	0,28
Colorant	3,00	3,82	3,00	3,82
AA 303 (amine)	0,60	0,76	0,60	0,76
Methylal	10,00	12,74	-	-
HCFC-141b	-	-	11,00	14,02
Total	100,00	126,14	100,00	127,42

Comments

- modification just in the blowing agent

Methylal in integral skin foams
STEERING WHEELS

Properties	**Unit**	**Methylal**	**HCFC-141b**
Entire sample			
Moulded density	Kg/m^3	356,7	**348,6**
Hardness	Shore A	50	**52**
Resilience	%	35	**34**
Foam core			
Internal density	Kg/m^3	265,3	**244,2**
Tensile strength	kPa	241	**238**
Elongation	%	63	**66**
Tear strength	N/mm	1,090	**1,150**
Compression set (50%)	%	21	**19**
Skin only			
Tensile strength	kPa	980	**975**
Elongation	%	78	**77**
Tear strength	N/mm	3810	**3780**

Comments

- Similar properties

Methylal in integral skin foams

Processing

- Miscible in all raw materials
- Good flowability
- In water based system provides better processability
- Good skin formation

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Methylal in shoe soles and micro-cellular

Methylal is used industrially as blowing agent for shoe soles.

Flammability reduction of Methylal based polyurethane formulations

Share Methylal between the polyol and the isocyanate.

Increase the quantity of water.

Combine Methylal with non flammable blowing agents or blowing agents with moderate flammability.

- HFC-245fa
- HFC-365mfc/HFC-227ea
- HFC-134a
- HFOs

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Dimensional stability control of rigid foams with Methylal

The following tools improve the dimensional stability

- use of branched polyols,
- use of aminic polyols,
- use of crosslinkers,
- choice of the silicone,
- increase of the percentage of water in the formulation,
- increase of the index,
- slight increase of the density.

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Emissions during production and use of Methylal based formulations

Flammability limits of Methylal are:

- LFL = 1.6 % vol = 5700 ppm
- UFL = 17.6 % vol

Exposure limits of Methylal are:

- STEL = 1250 ppm = 22 % of LFL
- TLV = 1000 ppm = 17 % of LFL

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FORMULATIONS

Worker exposure evaluation
(according to Brazilian legal standard as published in Directive 3214/78 of the Ministry of Labor in its NR-9)

Production of a rigid system for pour-in-place formulation
(1.6% Methylal)

Personal Sampling (production area operators)
= 3.4 – 17.3 ppm = 0.3 -1.7 % of TLV
Area Sampling (blending and weighing area)
= 2.6 – 6.5 ppm = 0.2 – 1.4 % of STEL

Workers' exposure to Methylal emissions is limited.

Recommendations for 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 and local guidelines

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RECOMMENDATIONS

Methylal emissions detector 0 – 2000 ppm

Recommendations for 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 or certified third party
- Adequate ventilation
- Adherence to MSDS and local guidelines

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METHYLAL
AS
CO-BLOWING AGENT

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METHYLAL AS CO-BLOWING AGENT

Methylal is combined with

normal Pentane
Cyclopentane
HFC-245fa
HFC-365mfc/HFC-227ea
HFC-134a
and also HCFC-141b

for various reasons.

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METHYLAL AS CO-BLOWING AGENT

Better miscibility of the blowing agent,

Better flow,

Influence on the vapor pressure of the blowing agent,

Better foam uniformity,

Reduction of the cells size,

Reduction of the thermal conductivity,

Better adhesion to metallic surfaces

Reduction of costs.

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Methylal combined with normal Pentane

Methylal improves the miscibility of normal Pentane,

once blended to n-pentane,

or blended to polyol

as shown in an example with Tercarol 8092.

n-pentane is not soluble in Tercarol 8092.

Methylal is fully miscible with Tercarol 8092.

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Methylal combined with normal Pentane

Increasing the amount of methylal in Tercarol 8092 increases the limit of miscibility of n-pentane.

Tercarol 8092 (weight in g)	Methylal (w. in g)	Solubility of n-pentane (w. in g)
20	0	Not soluble
20	2	0.87
20	4	2.93

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Methylal combined with normal Pentane

Increasing the amount of methylal in n-pentane – methylal blends increases the miscibility of the blend.

Blend % w/w		Solubility in g in 20g of Tercarol 8092
n-Pentane	Methylal	
100	0	Not miscible
50	50	5.3
40	60	Fully miscible
0	100	Fully miscible

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Methylal combined with 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.

Methylal combined with normal Pentane

Methylal in combination with n-Pentane improves the flow.

This is very impressive on machine trials.

In hand-mix trials, results are more modest.

The length of free foaming in an inclined open tube is measured.

Flowability depending on methylal content	
Methylal content (php)	Relative flowability
0	100%
5	106%
10	107%
15	107%

Methylal combined with normal Pentane

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 normal Pentane

A partial replacement of pentane by methylal in a blend with polyol raises the flash point

Blend % (w/w)			Flash point (closed cup) (°C)
Polyol (visco 930 mPa.s)	n-Pentane	Methylal	
96	4	0	< - 18
96	2	2	- 3.0
96	0	4	9.0

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Methylal combined with normal Pentane

More surprisingly, the addition of methylal to a blend of polyol with pentane raises the flash point

Blend % (w/w)			Flash point (closed cup) (°C)
Polyol (visco 930 mPa.s)	n-Pentane	Methylal	
96	4	0	< -18
94	4	2	- 17

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Methylal combined with Cyclopentane

Cyclopentane has a higher boiling point than methylal.

It is generally used in combination with normal or 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.

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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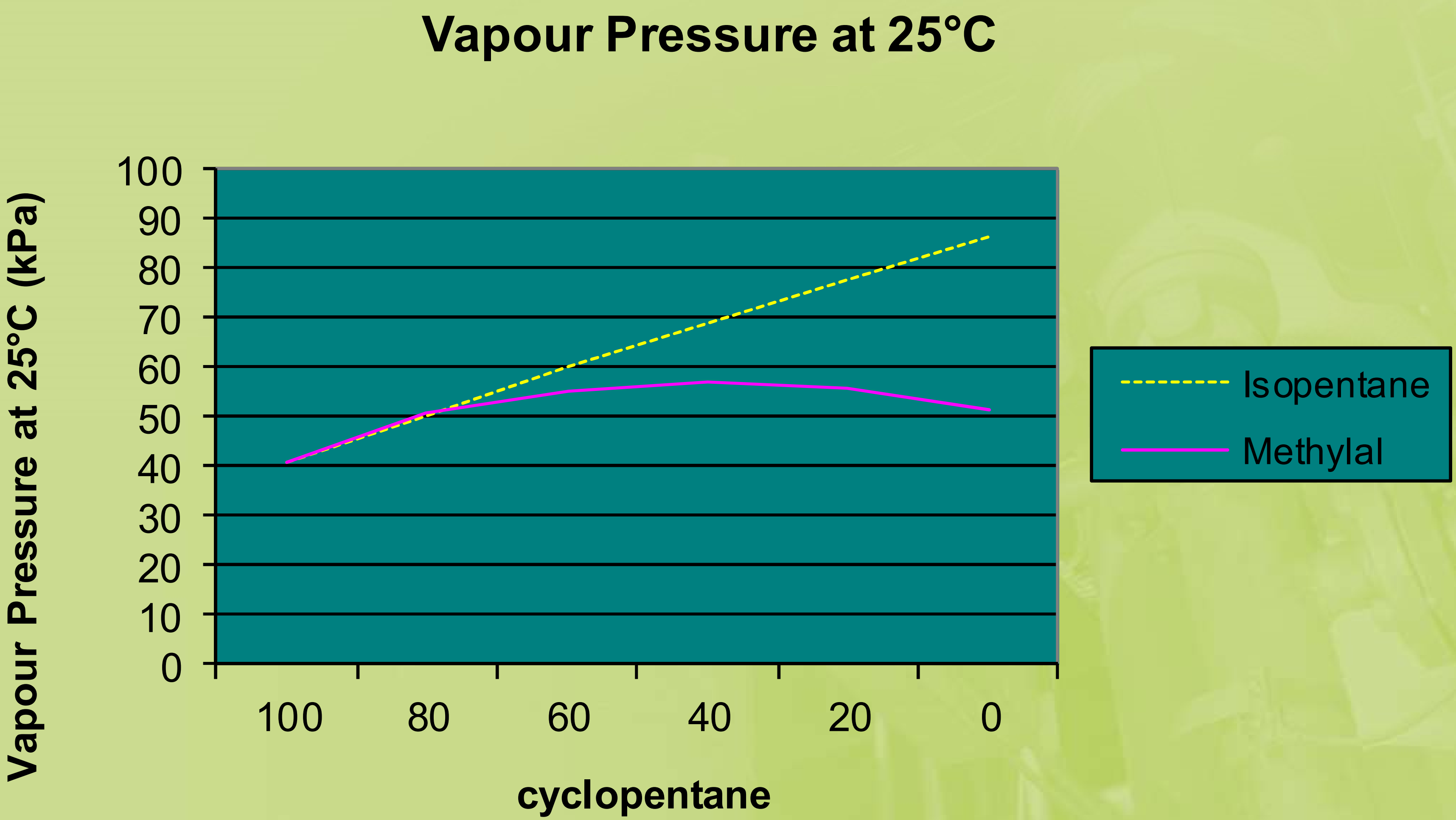
Methylal combined with Cyclopentane



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.

Methylal combined with HFC-365mfc

Methylal has interesting properties once combined with HFC-365mfc.

HFC-365mfc has a boiling point of 40°C.

HFC-365mfc is promoted in combination with HFC-227ea as a non-flammable blend.

HFC-227ea is used as a flame extinguisher for HFC-365mfc.

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Methylal combined with HFC-365mfc

Blends of polyols with HFC-365mfc and methylal show surprising open cup flash points.

With a constant amount of blowing agents, the open cup flash point is higher with higher amount of methylal.

Blends			Cleveland open cup flash point (°C)	
Polyol	HFC-365mfc	Methylal	Polyol for spray foam	Polyol for panel
87.5	12.5	0	38	38
85.31	12.19	2.5	34	38
85.5	9.5	5	40	40
85.56	6.94	7.5	42	40
92.5	0	7.5	64	68

% are in weight

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Methylal combined with HFC-365mfc

Open cup flash points are very similar with HFC-365mfc alone and with blends HFC-365mfc and methylal.

With 7.5% of methylal in the blends, HFC-365mfc seems to drop the open cup flash point of the blend :

64 or 68 °C without HFC-365mfc

against

42 or 40 °C with HFC-365mfc.

These measurements have not been made with blends HFC-365mfc - HFC-227ea, but with HFC-365mfc alone.

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Methylal combined with HFC-365mfc

Closed cup flash points are only high with low percentage of methylal.

Blends			Abel closed cup flash point (°C)	
Polyol	HFC-365mfc	Methylal	Polyol for spray foam	Polyol for panel
87.5	12.5	0	24.5	22.0
85.31	12.19	2.5	11.5	21.0

% are in weight

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Methylal combined with HFC-365mfc

In combination in low volumes with HFC-365mfc, methylal decreases the condensation at low temperature in rigid foam cells, thus improving the thermal insulation.

Thermal conductivity at 10°C (initial)

Blend (wt %)		λ with	
HFC-365mfc	Methylal	Terate	Stepan
100	0	23.4	23.3
85	15	23.0	22.3
75	25	22.8	22.9

PIR foams index 250

Source : Solvay, Brussels, Belgium

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Methylal combined with HFC-365mfc

Fire performance is not affected by low percentage of methylal

Methylal decreases the cost of HFC-365mfc.

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Methylal combined with HFC-245fa

HFC-245fa is very expensive.
It is used to avoid manipulation of flammable products
provide non-flammability to the produced foam.

Methylal, even being flammable, can partially substitute HFC-245fa
keeping an acceptable flash point of the preblend with polyol, and
not affecting 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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Methylal combined with HFC-134a

HFC-134a has a boiling point of –27°C

It is poorly miscible in polyols.

So important losses occur during the preparation of the pre-blend

Preparation is also very long due to the poor miscibility.

Phase separation is also often observed.

Methylal combined with HFC-134a

Methylal improves the miscibility of HFC-134a in the polyol,

thus reducing the mixing time

which will reduce the losses

and keep a single phase after blending.

This avoids formulation composition modification during the use of the system.

The miscibility increase improves the foam uniformity and the aesthetic aspect of the product.

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Methylal combined with HFC-134a

Methylal also decreases the pressure generated by HFC-134a, which will also decrease the losses.

Composition (w%)		Pressure at 20°C (bar)
HFC-134a	Methylal	
100	/	6.2
95	5	5.4
90	10	5
85	15	4.6
80	20	4.3
60	40	3

Pressure of HFC-134a –Methylal blends

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Methylal combined with HFC-134a

Methylal also improves the adhesion on metallic surfaces

Blends with up to 15% of methylal in HFC-134a remain non-flammable according to the ‘aerosol definition’ of flammability.

Their use does not affect the fire performance of the foam.

Methylal being cheaper than HFC-134a also reduces the cost.

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Methylal combined with HCFC-141b

HCFC-141b can be partially substituted by methylal keeping, with low level of methylal, the non-flammability of the blend.

Methylal is mainly used to reduce the cost.

Nevertheless, it’s use is beneficial for the environment.

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CONCLUSIONS ABOUT METHYLAL AS BLOWING AGENT

What brings METHYLAL :

Practically useable

Cost-effective

Lower environmental, health and safety profile

A blowing agent for the future

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1,3-DIOXOLANE AND TOU (2,5,7,10-TETRAOXAUNDECANE) AS CLEANING AGENTS

Properties

	1,3-Dioxolane	TOU
Boiling point (°C) (760 torr)	74-75	210
Kauri-butanol index	> 207	> 200
Solubility parameters δ_t	22,07	18,74
δ_d (dispersion)	16,95	15,16
δp (polarity)	7,85	6,09
δh (hydrogen bonding)	11,76	9,19

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Labeling

1,3-Dioxolane :

Flammable class 2

Eye irritant

TOU :

No labeling

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Compatibility with polyurethanes

Sheets of material are immersed in acetal during 1 day at 25°C.

The measure of the weight change is a measure of compatibility.

A high weight increase means there is a non-compatibility

Compatibility with polyurethanes

	1,3-Dioxolane	TOU
Fabeltan 85C (Fabelta)	> 1000	> 107,76

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Cleaning

1,3-Dioxolane and TOU are used to clean :

- injection heads
- tools
- molds

THANK YOU

Lambiotte &Cie