

L A M B I O T T E & C I E S . A .



Acetals

Acetals in Aerosols


Lambiotte
& Cie



L A M B I O T T E & C I E

Lambiotte & Cie. started its activities in 1860 with forestry and sawmill exploitation, producing railway sleepers. In a desire to increase the value of its wood waste production, the company adopted an innovative carbonization process to convert wood to charcoal. One of the chemical by-products of this distillation technology was methanol. From 1901, Lambiotte's interest in chemicals grew with the production of formaldehyde from wood methanol. By 1970, Lambiotte's passion for chemistry led to the use of formaldehyde as a reagent in the production of acetals and hemicetals. Since then, the company has continued to develop its expertise in production technologies, making it a leader in the highly specialised field of acetals synthesis.

We at Lambiotte are proud to offer a wide range of industrial acetals, manufactured with state-of-the-art equipment in a continuous process reaction. Our precision and technical expertise in this specialist field guarantees the highest and most constant quality and purity of product, allowing us to respond to each specific demand for synthesis of acetals and chemical derivatives from aldehydes and/or alcohols.

A dedicated support team is available to give the customer technical advice, providing tailored formulae for many industrial sectors. In order to meet the customer's needs, we propose the services of our application laboratories in aerosols, cosmetics, coatings...to develop customised formulae. Indeed, every department in Lambiotte, be it production, quality control, sales, marketing, logistics or accounting is dedicated to customer satisfaction. A world-wide network of specialised distributors ensures fast product availability, delivery, and technical support to guarantee optimal client services.



ACETALS IN AEROSOLS

Methylal and dioxolane belong to the acetal family.

THEIR PHYSICAL AND CHEMICAL CHARACTERISTICS GIVE EXTRAORDINARY BENEFITS FOR AEROSOLS :

- I. Solubilisation of ingredients
- II. Smaller particle size
- III. Shorter drying time
- IV. Pressure reduction with
 - Liquid propellants
 - Compressed gases
 - Hydrofluoro carbone
- V. Water miscibility and VOC reduction
- VI. Flammability reduction



THOSE IMPROVEMENTS ARE CONSIDERED FOR PUMP SPRAYS AS WELL AS FOR AEROSOLS.

In aerosols, Methylal can be used with all propellants such as: Propane, Butane, Isobutane, Pentane, Dimethyl Ether, 134A, 152A and also with compressed gases such as CO₂.

Acetals find applications in the following examples:

- Cosmetic
 - ⇒ Hair Care: Hair spray
 - ⇒ Toiletries: Alcohol free deodorant
 - ⇒ Sun Care: Sun protector spray / After Sun
 - ⇒ ...
- Para pharmaceuticals
 - ⇒ Cooling spray
 - ⇒ Bandaging spray
 - ⇒ ...
- Household
 - ⇒ Insecticide
 - ⇒ Cleaner
 - ⇒ Air freshener
 - ⇒ Adhesive
 - ⇒ ...
- Technical
 - ⇒ Paint
 - ⇒ Paint Stripper / Graffiti Remover
 - ⇒ Glue
 - ⇒ Lubricant / Grease / Deblocking oil
 - ⇒ ...
- Automotive
 - ⇒ Brake / Engine / Rim cleaner
 - ⇒ Lubricant / Oil / Silicone
 - ⇒ ...

ADVANTAGES

I. SOLUBILISATION OF INGREDIENTS

Liquefied gases participate in the solvency of the liquid blend in the aerosols and decrease the solvent power of the mixture. In order to dissolve ingredients, you need to increase the solvent power and therefore you must incorporate into the blend a powerful solvent such as Methylal or Dioxolane. For example the Kauri-Butanol value of Methylal is 164 and Dioxolane is 214 while methylene chloride is 115, dimethylether is 91 and propane is 15. Dioxolane is the best solvent to solubilise PU resins, acrylic resins... with propane/butane. It is the ideal substitute for the much debated chlorinated solvents. Dioxolane is the ultimate solvent to overcome heavy solubilisation problems. Better solubility of the active ingredients leads to lower the cloud point: no precipitation in the deep tube during the propellant filling...

Comparison of Kauri-Butanol values		
Solvents		Liquid propellants
Acetals	Others	
Methylal: 164 Dioxolane: 200 Ethylal: 120 Butylal: 75	Methylene chloride: 115 n-Pentane: 27 Isoparaffins: ~ 28 Dearomatized: ~ 30 Toluene: 105 Xylene: 90 d-limonene: ~ 70	Dimethylether: 91 Propane: 15 Isobutane: 17 152 A (difluoro ethane): 11

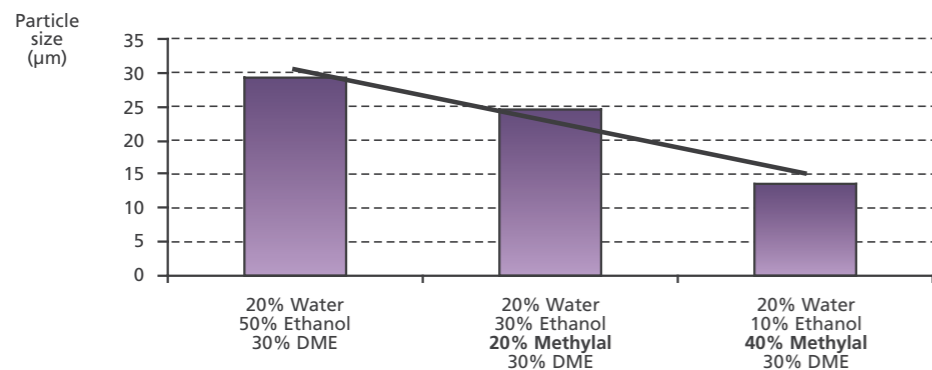
II. SMALLER PARTICLE SIZE

Thanks to its very low viscosity and surface tension, Methylal improves the spray quality and reduces the particle size.

Solvents	Viscosity 20°C (centipoises)	Surface tension (dyn/cm)
Methylal	0.335	21.12
Methylene Chloride	0.425	28.12
Ethanol	1.22	22.1

It is quite obvious to see this improvement by just adding Methylal in the referred formula, even in a water based product.

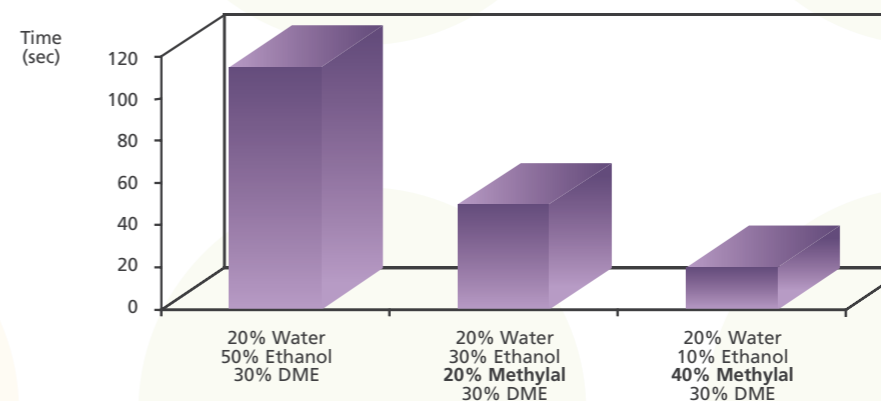
Influence of Methylal on the particles size



III. SHORTER DRYING TIME

Methylal shortens the drying time. This reduction of the drying time is much more obvious with water-based formulations with DME (low VOC). The drying time of a solvent/propellant blend sprayed on paper is dramatically reduced by the incorporation of Methylal.

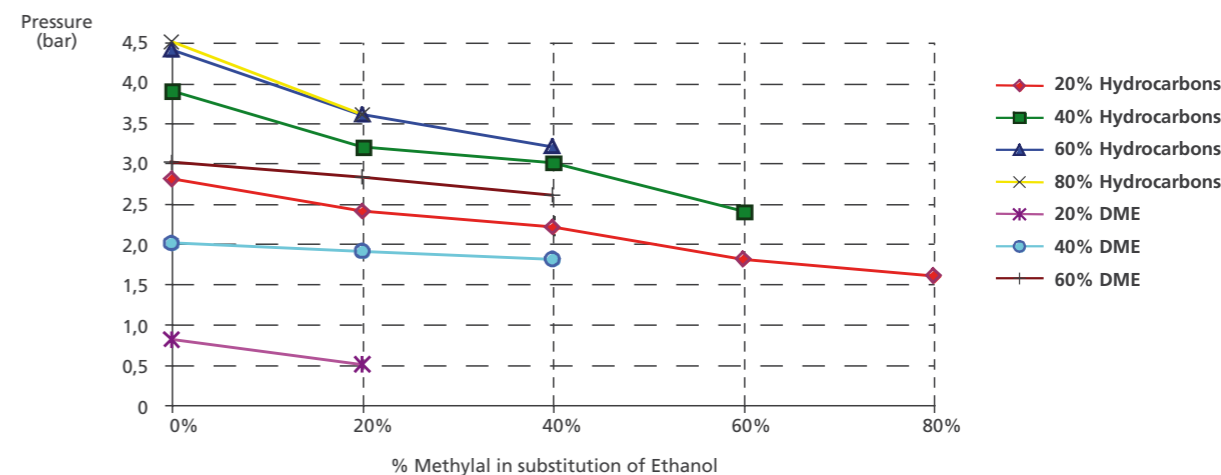
Influence of Methylal on the drying time



IV. PRESSURE REDUCTION

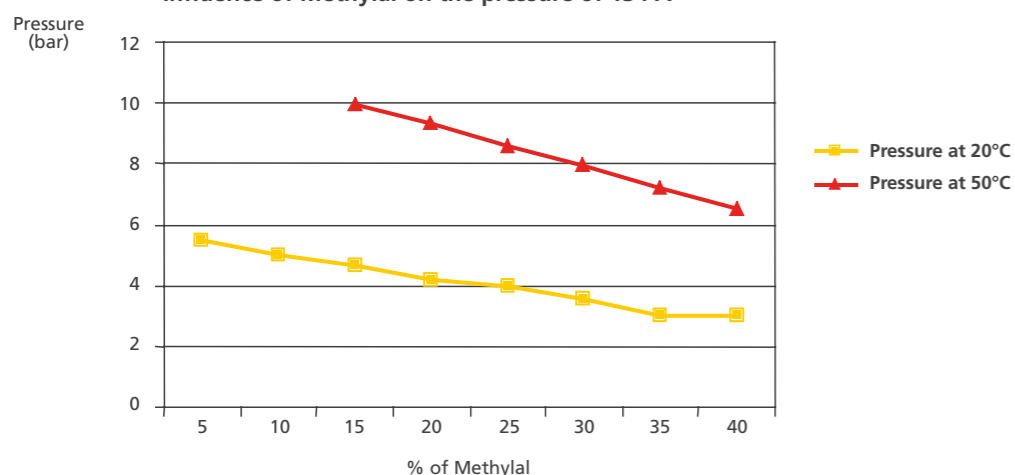
Methylal decreases the pressure generated in the can by the propellants such as Propane-butane, Dimethylether, HFA (134A and 152A) and the compressed gases CO₂ and N₂O (because of its extremely high Bunsen coefficients). For example, the fact that Methylal lowers the pressure in a can filled with propane/butane can be of interest in the case of cosmetic formulations, such as alcohol free deodorants, which have a high percentage of propellant. The pressure with DME is also reduced, which is particularly interesting in the presence of water (low VOC).

Influence of Methylal on the pressure of liquid propellants



ADVANTAGES

Influence of Methylal on the pressure of 134 A



CO₂

The acetals, Dioxolane and Methylal, show exceptional solubility properties toward carbon dioxide and nitrous oxide.

Methylal is the best solvent of CO₂, solubilising 9.5 litres of CO₂ in 1 litre of Methylal under 1 bar pressure at 20° C (versus 2.9 litres with ethyl alcohol). Thanks to its high Bunsen coefficient, Methylal helps to solubilise the actives and to increase the amount of gas in the can.

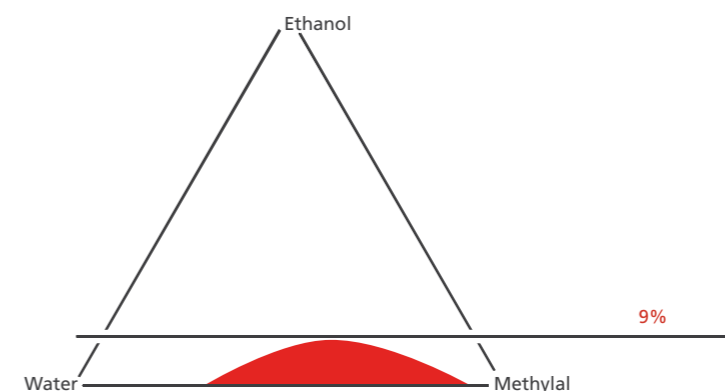
1 litre of Dioxolane dissolves more than 7 litres of CO₂. This property allows formulating at high compressed gas levels with the advantage of more constant pressure during the aerosol can life and an exceptional spray quality. The following table is showing how many litres of gas it is possible to dissolve in 1 litre of different solvents at atmospheric pressure at 20°C.

Bunsen Coefficients of CO ₂ and N ₂ O at 20°C		
Solvents	CO ₂	N ₂ O
Water	0.82	0.65
Methylal	9.50	6.80
1,3-dioxolane	7.60	5.80
Ethylal	5.65	5.85
Butylal	3.00	4.00
Methylene chloride	3.70	
Ethanol	2.60	2.80
Isopropanol	2.30	2.10
Pentane	1.94	
Dodecane	1.40	2.60
White spirit	1.65	2.60
Toluene	2.30	
Xylene	2.15	
Glycerine	0.83	
Mineral oil	0.80	
Olive oil	1.34	
Amyl acetate	4.10	4.90

V. WATER MISCIBILITY AND VOC REDUCTION

Methylal is partially miscible with water in a binary mixture: 33% Methylal in water.

But Methylal is fully miscible in ternary mixtures, by adding more than 9% of ethanol for example.



Thanks to its amphiphilic character, Methylal easily allows to formulate emulsions. Dioxolane is fully miscible with water. It boosts the solvent power of water based mixtures improving the stability of solutions and rising the cloud point. Dioxolane is compatible and miscible with all organic solvents and propellants.

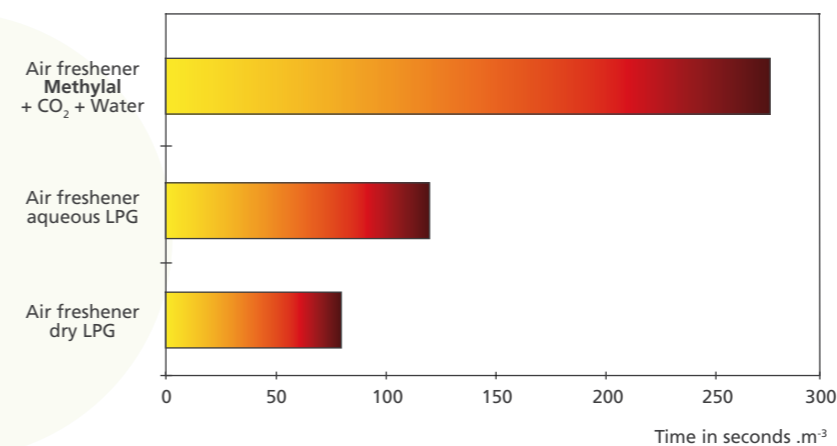
VI. FLAME REDUCTION

Methylal, when used with CO₂ and water, decreases the flammability danger of air fresheners.

Indeed, in this test, the aerosol is sprayed in a drum fitted with a lightened candle.

One measures the time before explosion.

Flammability: drum test



APPLICATIONS

COSMETICS

HAIR CARE

HAIR SPRAY

Aerosol

- ⇒ Classic
- ⇒ Low VOC
 - Anhydrous 55% VOC with 152A
 - Water based 55% VOC with DME

Pump

- ⇒ Low VOC
 - Powerful solvent for resins and actives (such as vitamins, silicones, UV filters, perfume...)
 - Fast drying
 - Reduction of the particle size
 - Low VOC - compatibility with water, with HFA

Classical Formulation of Hair spray:

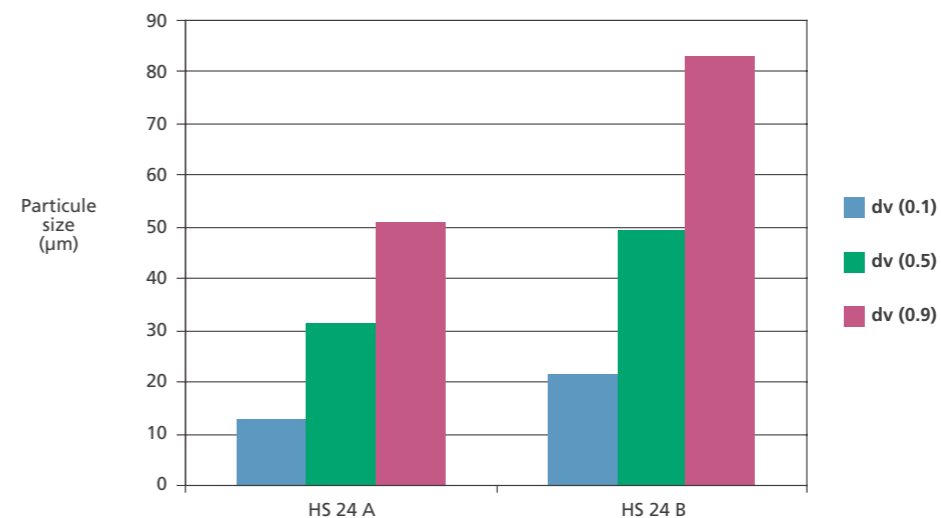
HS 24 B is a classic ethanol based formula
 HS 24 A is made with 50% ethanol and 50% Methylal.

HS 24 A % weight	Ingredients	HS 24 B % weight
6.02	Luviskol va 37 hm	6.02
0.07	Dow fluid 344	0.07
0.07	Freshlon fragrance	0.07
31.92	Ethanol	63.84
31.92	Methylal	/
30.00	Propane-butane 3.2 bar	30.00
100.00		100.00

Methylal reduces the particles size

The substitution of ethyl alcohol by Methylal improves significantly the spray quality:

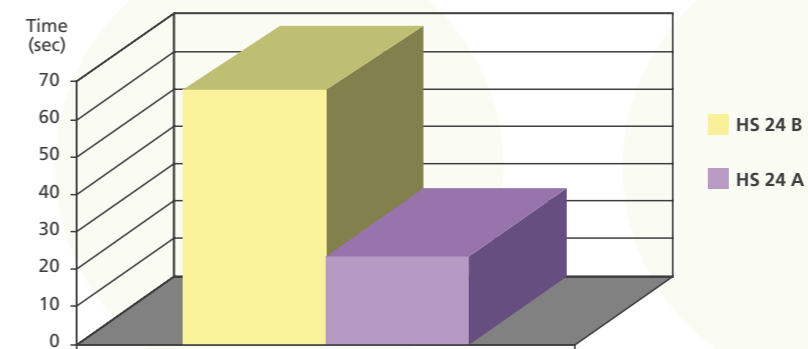
- Reduction of the average particle size: 18 microns
- Improvement of the particle size homogeneity: smaller particle size difference between the biggest particles (vol. med. 90%) and the smallest particles (vol. med. 10%).



Methylal shortens the drying time

A practical test* with hair spray HS 24 B and A (ethanol- and methylal-based) shows the following:
 (*Half head study by Hazel Pool UK (panel))

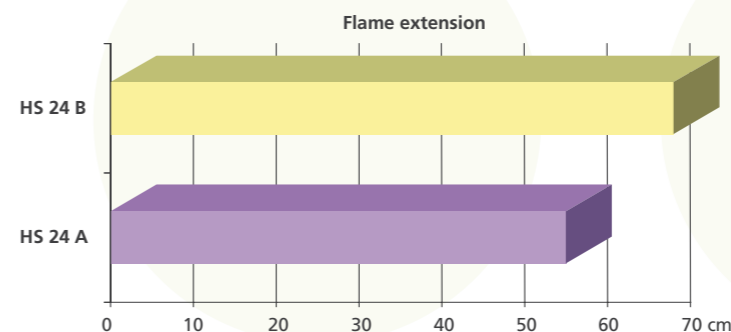
Average drying time on various hair types



Methylal reduces the drying time from 67 seconds to 23.5 seconds in salon conditions (average time, dry state appreciated by the panel)

Methylal reduces the flammability characteristics

The aerosol is sprayed at 15cm from a candle. This test is measuring the flame length. The longer the flame is, the more flammable and dangerous the aerosol is.



APPLICATIONS

TOILETRIES

DEODORANT

Aerosol

⇒ Non flammable aerosol deodorants (CO₂)

Methylal allows the filling with CO₂ and improves the spray quality.

It makes it easier to fill with CO₂. Moreover, with 40% of Methylal into the formula, you get the same spray quality as with propane/butane

⇒ Alcohol free deodorant

PARAPHARMACEUTICALS

- Freezing spray
- Haemostatic spray
- Plaster spray
- Insect repellent

Freezing Spray (Muscular decontracting spray)

Through its high evaporation rate, Methylal emphasises the cooling effect.

Ingredients	%	Function
Methylal	60	Solvent - cooling feeling
Ethanol	36.5	Solvent
Camphor	1.5	Denaturing agent
Menthol	1.5	Denaturing agent
Methyl salicylate	0.5	Analgesic agent CAS: 119-36-8
Total	100	

This formula can be packaged in a pump or an aerosol.

Aerosols can be filled with propane butane and other propellants.

HOUSEHOLD

Thanks to their physical and chemical properties, acetals have a wide range of applications.

In household aerosols, they can be formulated in:

- Insecticides
- Spot removers
- Oven cleaners
- Air fresheners

INSECTICIDES

Methylal shows big advantages on the efficiency of insecticides:

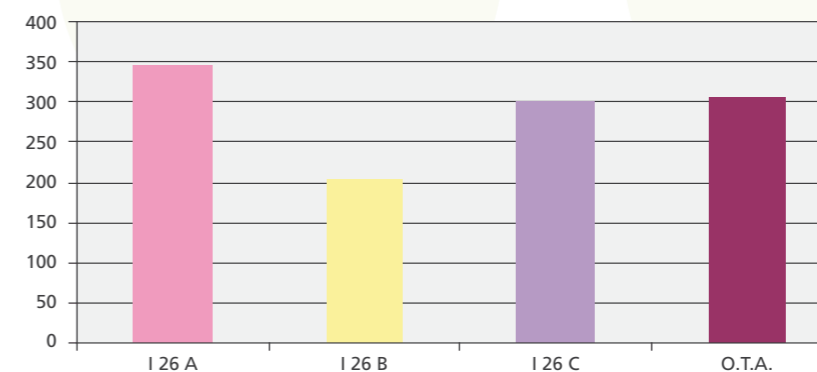
- Improvement of the knock down count in solvent-based aerosol insecticides
- Single phase water-based aerosol formula (no shaking required before use)
- Efficiency boosted in water based formulations
- Improvement of the penetration of actives into the insect hydrophobic secretions

Study on the efficiency of different types of formulations

INGREDIENTS	I 26 A	I 26 B	I 26 C
Bioallethrine	0.075	0.075	0.075
Tetramethrine	0.250	0.250	0.250
Permethrine	0.075	0.075	0.075
Piperonyl Butoxide	0.750	0.750	0.750
Methylal	38.850	0.000	19.420
Isopar C	0.000	38.850	19.420
Propane-butane	60.000	60.000	60.000

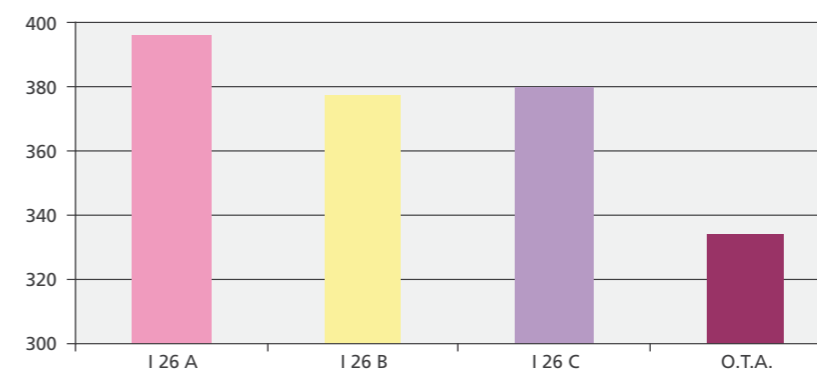
Fallen flies

Knock down on 800 flies (after 5 minutes)



Fallen mosquitoes

Knock down on 400 mosquitoes (after 15 min)



The higher is the Methylal content of the formulation, the higher is the knock down.



APPLICATIONS

SPOT REMOVER

Methylal and Dioxolane are the ideal solvents to substitute 1,1,1-trichloroethane and pentane.

AUTOMOTIVE

Methylal and Dioxolane are also widely used in automotive applications.

- Lubricant / oil / silicone
- Engine cleaner
- Carburettor cleaner
- Brake cleaner
- Rims cleaner
- Wax cleaner
- Resin from trees (sap)

Methylal is a really good solubiliser for oil, grease, silicone. Thanks to its high Bunsen coefficient, Methylal helps to formulate lubricants filled with compressed gases like CO₂.

For heavy duty cleaning, such as engine cleaning, Methylal can be combined with Dioxolane. Thanks to its high solvent power, Dioxolane can easily remove residues like burnt particles, rubber, silicones...

Butylal is also an acetal that gives higher efficiency in cleaning and degreasing in the automotive industry. Butylal is the ideal substitute to terpene.

TECHNICAL

PAINT

Methylal shows also great advantages in aerosol paints.

The reduction of the particle size thanks to the lower viscosity allows:

- ⇒ An improvement of the pulverisation
- ⇒ A better gloss and surface quality: thinner film
- ⇒ A sag-free film
- ⇒ A smooth film
- ⇒ A reduction of the drying time
- ⇒ A higher efficiency of additives
- ⇒ A possibility to use aqueous formulae

PAINT STRIPPER

Methylal and Dioxolane show an exceptional efficiency in stripping.

The combination of both products is similar to Methylene Chloride, but without the toxicity.

Used alone or together, they will enable you to formulate very efficient paint strippers for different kind of paints such as:

- Alkydes
- Polyurethanes: 1 component (hygroscopic drying)
- Polyurethanes and epoxy: 2 components
- Vinylic and acrylic dispersions

The two standard paint stripper types (to scratch or rinseable) are easy to formulate with those solvents that are both miscible with water and presenting a low toxicity.

The solvent powers of Methylal and Dioxolane are exceptional, in terms of their action on polyurethane, epoxy and acrylic (including crosslinked) resins, and on the plasticisers used in paints.

Since they are small molecules, Methylal and Dioxolane diffuse rapidly and penetrate quickly the paint film.

The high vapor pressure of Methylal accelerates film removal, even at low temperatures.

The water miscibility of Methylal and Dioxolane allows the formulation of targeted strippers for paints such as latex, PVA (PolyVinyl Acetate) and interior paints.



APPLICATIONS

GRAFFITI REMOVER

Methylal and Dioxolane are also good solvents to produce efficient and suitable formulations for a wide range of graffiti and surfaces.

The miscibility of Methylal (up to 33%) and Dioxolane (fully miscible) with water and other solvents allows moderating the aggressivity of the products toward the painted surfaces.

Lambiotte has developed several formulations which are Methylal, Dioxolane and water based, and adapted to the surface to clean.

ADHESIVES

Methylal and Dioxolane present also interesting properties in sprayable adhesives.

Indeed, thanks to their high solvent power, they have a good compatibility with a wide range of plastics and rubbers. They can replace numerous toxic solvents formerly used in this kind of application.

Adhesive type	Acetals	MeCl	DMF	THF	Dioxane	Aromatics	Chlorinated	Ketones
PVAC Polyvinyl acetate Ex. for wooden floor	→ Methylal	✓	✓	✓	✓	✓	✓	✓
PMMA PolyMethylMethAcrylate	→ Methylal → Dioxolane	✓	✓	✓	✓	✓		✓
PSF Polysulfone	→ Dioxolane	✓	✓	✓	✓			
SBR & SBS StyreneButadieneRubber StyreneButadieneStyrene	→ Methylal → Butylal → Dioxolane					✓		
ABS AcrylonitrilButadieneStyrene	→ Methylal → Dioxolane		✓	✓				
Natural latex	→ Butylal							



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