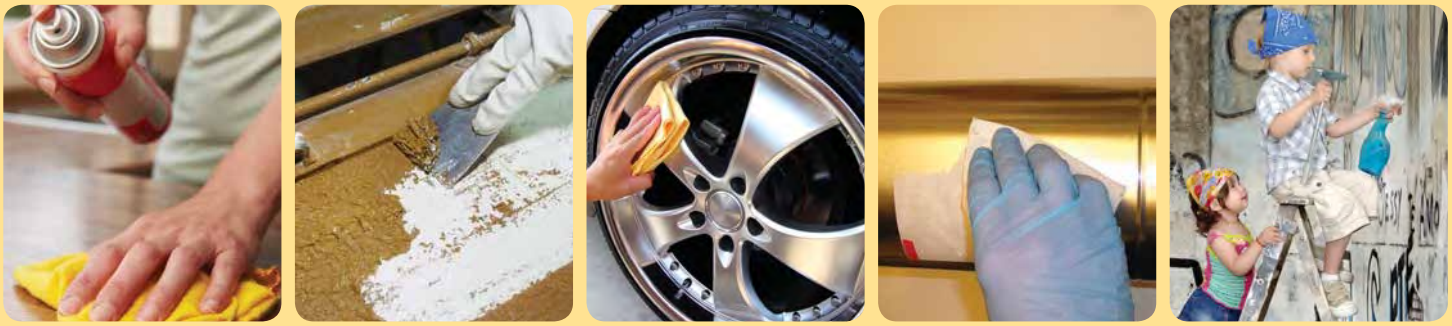
LAMBIOTTE & CIE S.A.



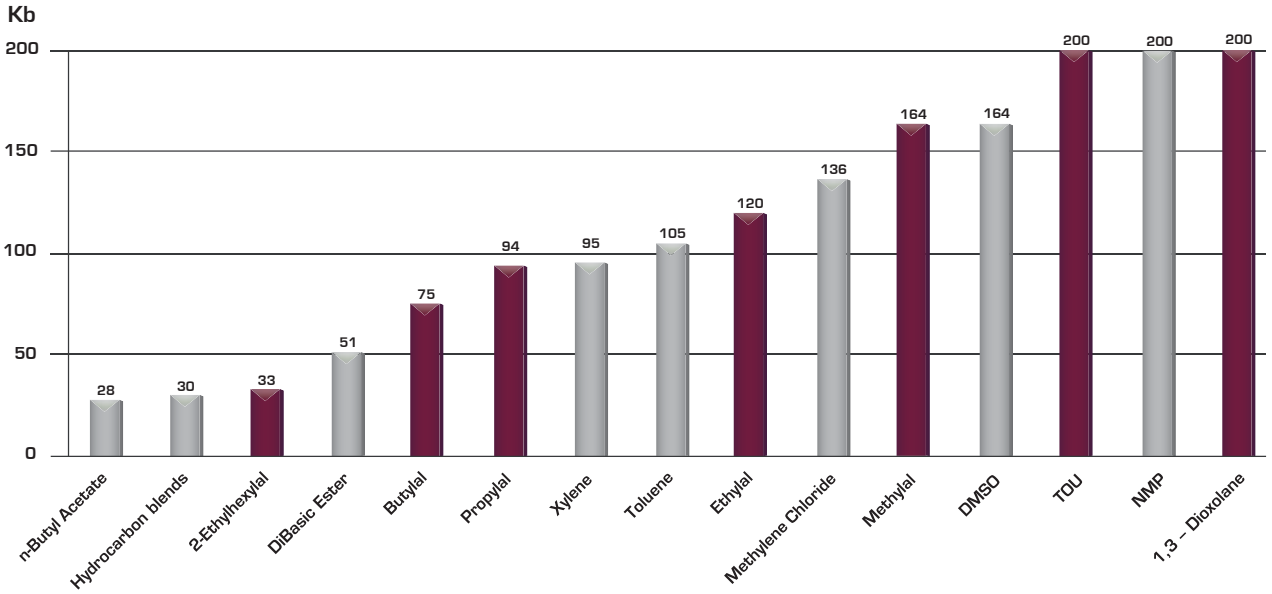
Acetals

Acetals in Cleaning

Lambiotte &Cie

I. SOLVENT POWER

The Kauri-Butanol is an international, standardized measure of solvent power, and is governed by an ASTM standardized test, ASTM D1133. The result of this test is a scaleless index, usually referred to as the "Kb value". A higher Kb value means the solvent is more aggressive or active in the ability to dissolve certain materials.



The solubilization even in high amounts of different types of resins and polymers, including polyurethanes and epoxies, can be achieved with acetals. In the formulation of paints, graffiti and adhesive removers, dichloromethane or N-Methyl Pyrrolidone can be substituted by Methylal, Dioxolane or TOU.

II. ORGANIC SOLVENTS MISCIBILITY

Acetals are miscible with most of organic solvents. This feature allows working on tailored solvent/co-solvent systems to reach specific properties (solvency, evaporation rate, etc…).

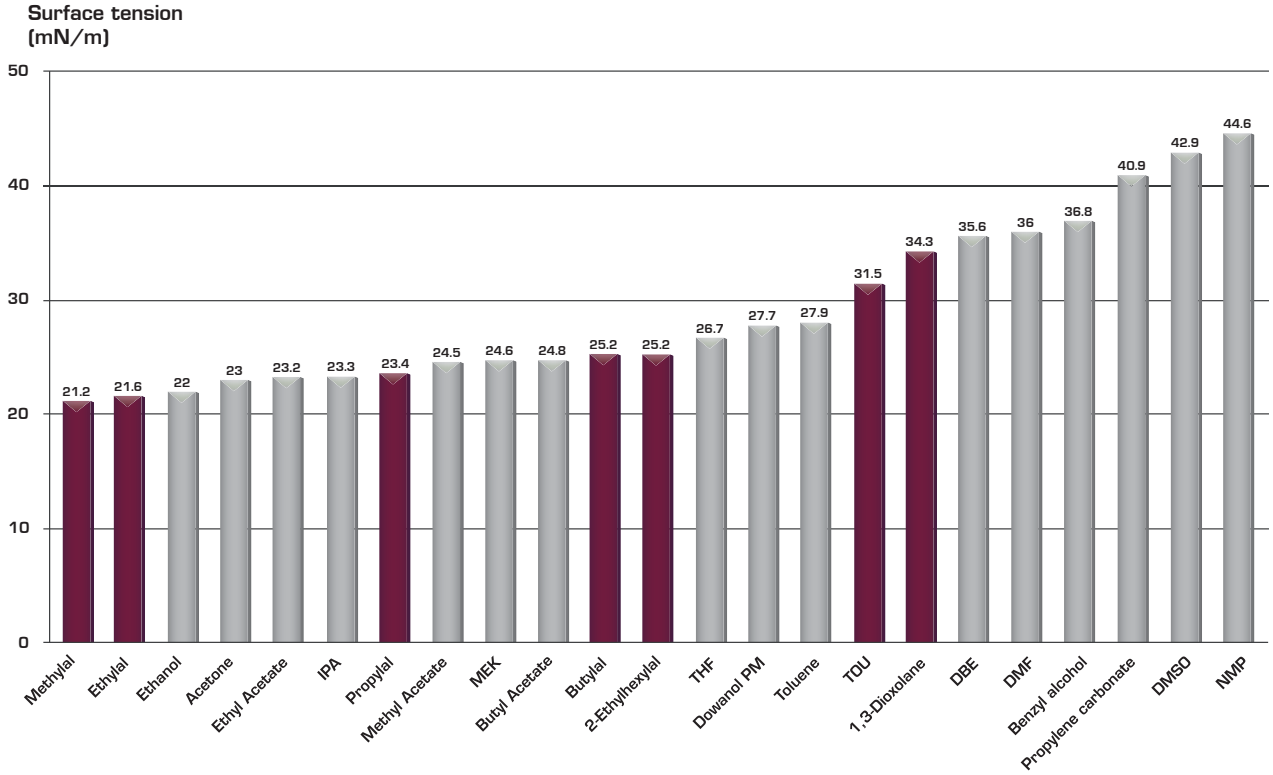
III. WATER MISCIBILITY

Acetals are miscible with water to various extents and therefore act as co-solvents in waterborne systems. Acetals that are partly miscible with water can become fully miscible in presence of an alcohol/ketone or any third solvent… In cleaning processes acetals that are fully water miscible may be easily rinsed through water flushing.

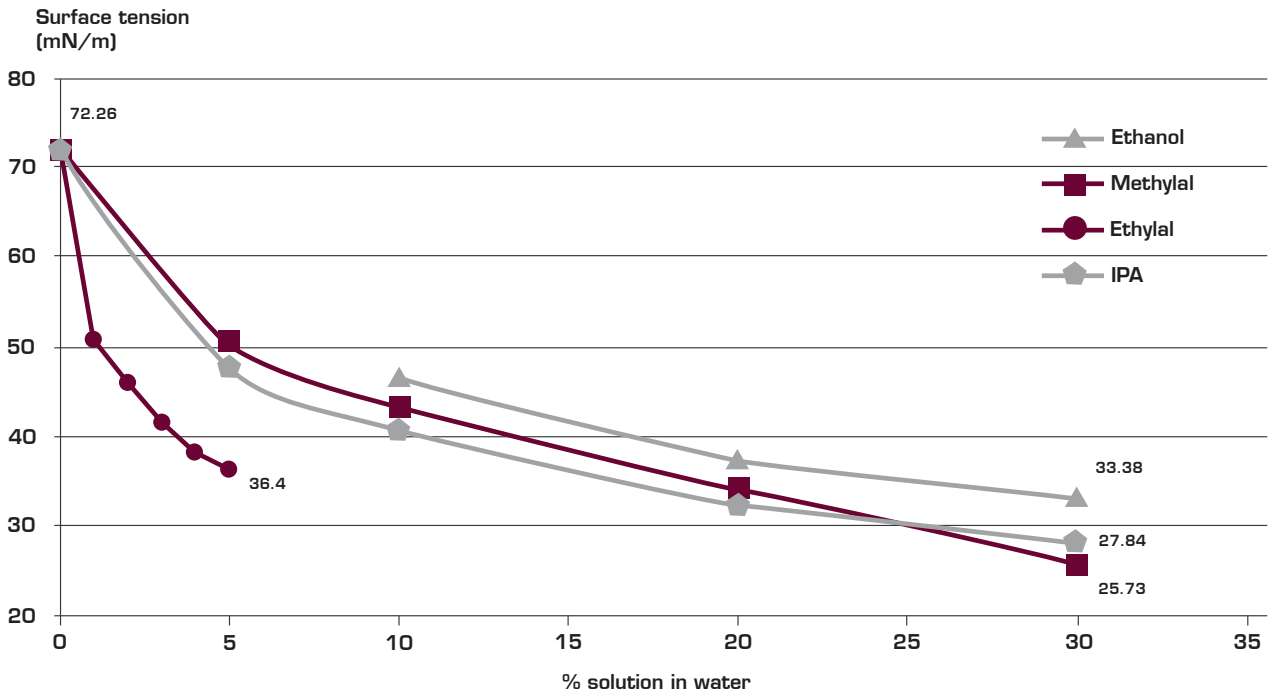
Acetal	Acetal solubility in water (%)	Water solubility in acetal (%)
Methylal	33	4
Ethylal	7	1.21
Propylal	0.365	0.45
Butylal	0.022	0.24
TOU	Fully miscible	Fully miscible
2-Ethylhexylal	Not miscible	Not miscible
1,3-Dioxolane	Fully miscible	Fully miscible

IV. WETTING ENHANCEMENT

Thanks to their low surface tension, acetals can enhance the wetting ability of solvent and waterborne formulations; this can be highly beneficial in the case of application on substrates of low energy surface such as plastics, where additives typically are required.



Methylal and Ethylal can significantly enhance the wetting ability of water-based systems. While Methylal slightly outperforms IPA at same ratio, a 5% Ethylal solution into water is found to have a surface tension value equivalent to a 20% Ethanol solution.

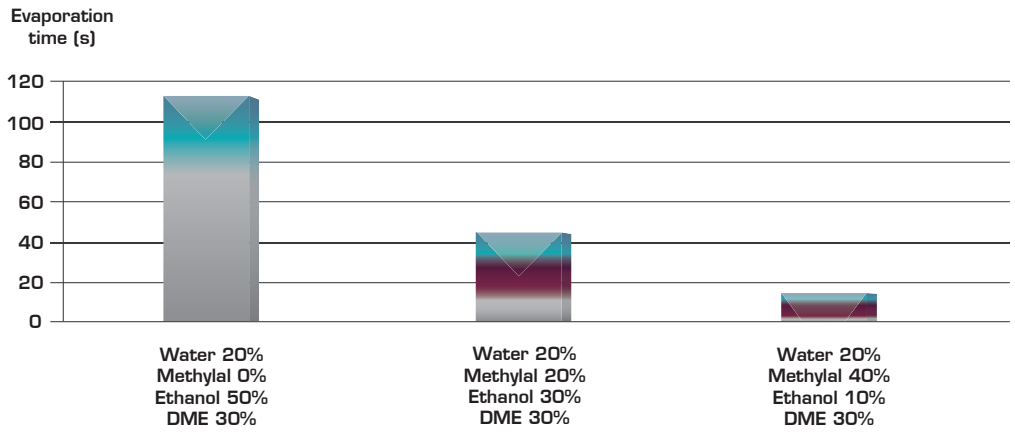


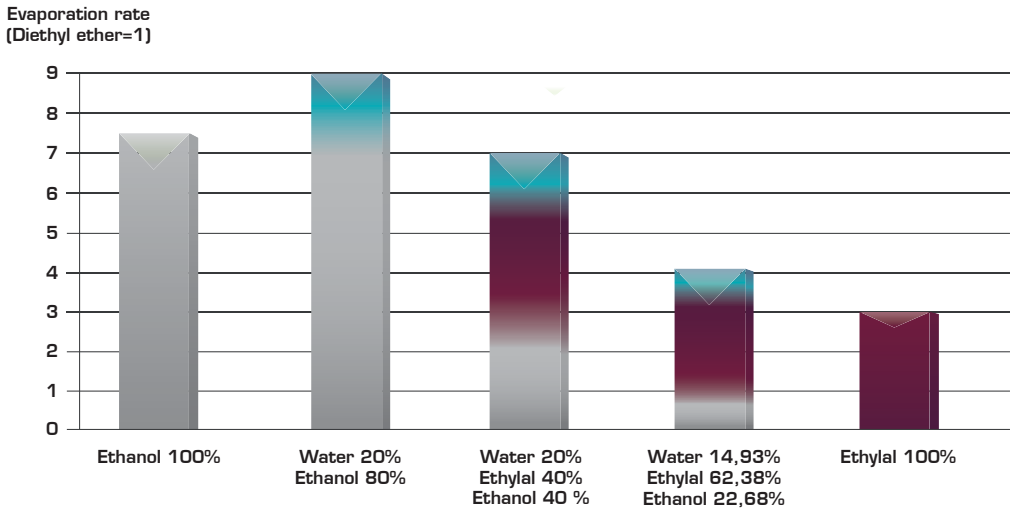
V. EVAPORATION RATE

Another key feature of acetals is their evaporation rate, as they can considerably positively impact the drying time of the cleaning formulation; this can be highly beneficial in applications where no cleaning solvent residues are expected.

Acetal	Evaporation rate (Diethyl ether = 1)	Evaporation rate (Butyl acetate = 1)
Methylal	1.36	0.11
Ethylal	3.0	0.25
Propylal	14.0	1.25
Butylal	Not available	5.54
TOU	Not available	17.38
2-Ethylhexylal	No evaporation	No evaporation
1,3-Dioxolane	3.6	0.29

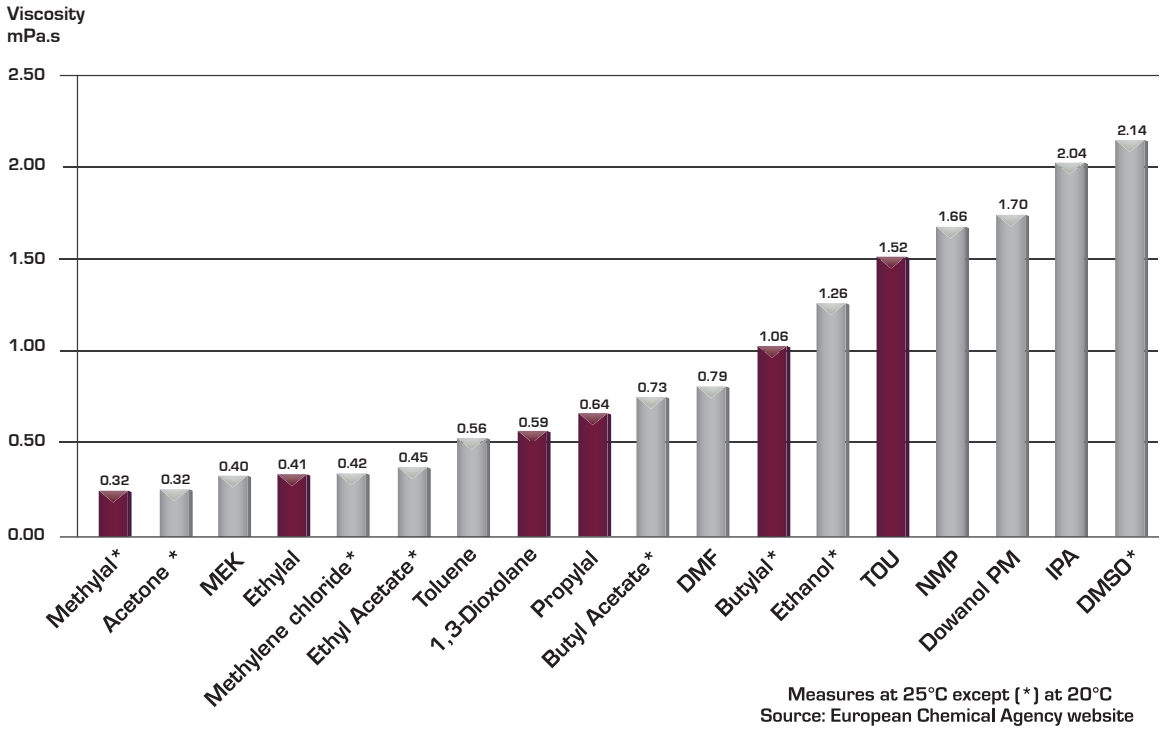
The drying time of waterborne systems can also be dramatically decreased in presence of acetals like Methylal, Ethylal or Dioxolane, compared to Ethanol, Ethyl Acetate, etc...



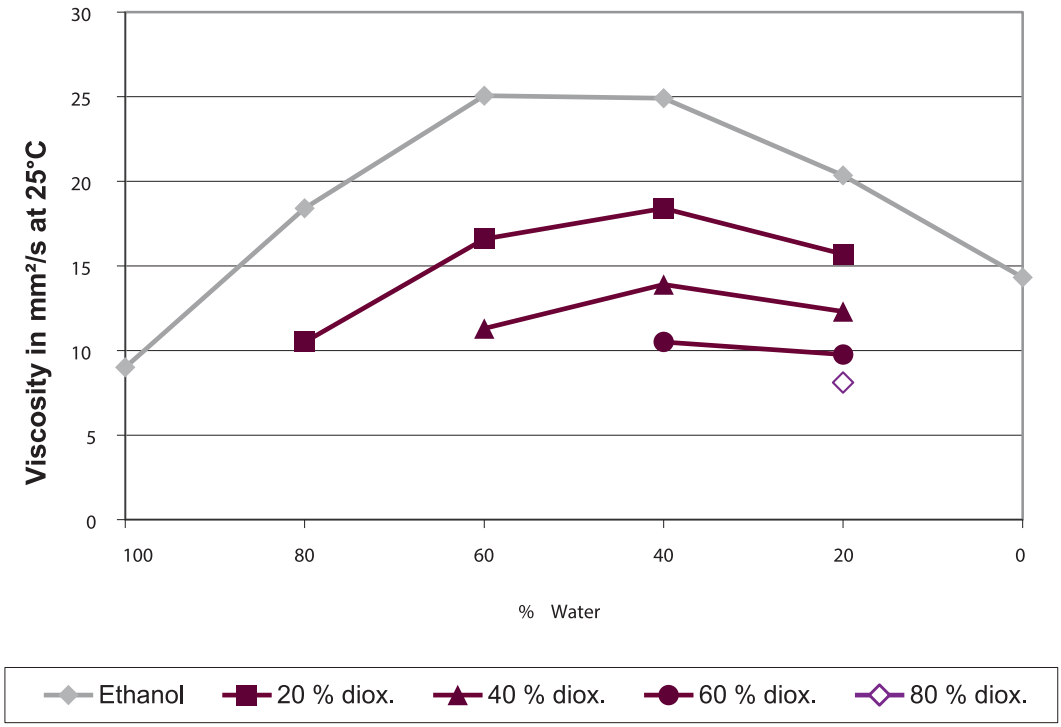


VI. VISCOSITY

Acetals exhibit a range of low to very low viscosity values. The lowest viscosities are ideal for deep penetration into porous substrates; they also enable low shear during application by spray. If used as co-solvent they may help tailoring the rheology of the system.



Once in water, acetals such as Methylal and Ethylal are known to increase the viscosity of the solution; this effect might lead to a lower need of rheological additive. Dioxolane on its side, contributes to lower and flatter viscosity profile when it progressively substitutes Ethanol in ternary solutions.



VII. SAFETY, LABELING AND REGULATORY COMPLIANCE

Further to the adoption of the "Globally Harmonized System of Classification and Labelling of Chemicals (GHS)" by many countries around the world these last years, substances traditionally used, in cleaning and degreasing processes are progressively heavily re-classified and consequently subject to limitation or restriction.

Many mixtures containing these substances now see their labeling negatively impacted and are in need of reformulation in order to comply with local regulations and/or consumer products standard criteria (Ecolabel,…). Although alternatives to these substances of concern are identified, some are not appreciated because of the drowsiness and dizziness effects they can cause to operators and/or end users, while the use of others is limited by indoor VOC emissions standards.

Under the terms of CLP in Europe or GHS in the rest of the world, acetals are granted exceptionally low toxicological and eco-toxicological labeling, and therefore are ideal candidates for substituting a wide range of hazardous components, such as:

Carcinogenic, Mutagenic and Reprotoxic hazards	Effects on Central Nervous System/ Narcotic hazard	Other hazards
Trichlorethylene	Ethyl acetate	d-Limonene
Perchlorethylene	Butyl acetate	Xylene
Methylene chloride	Isohexane	…
N-Methyl Pyrrolidone (NMP)	White spirit	
N-Ethyl Pyrrolidone (NEP)	Methyl Ethyl Ketone (MEK)	
Tetrahydrofurane (THF)	Isopropyl Alcohol (IPA)	
Dimethylformamide (DMF)	Acetone	
Toluene	Heptane	
…	…	

Source: European Chemical Agency website

⇨ Volatile Organic Compound emissions

2-Ethylhexylal is non-VOC under the terms of the following regulations:

- European Directive 1999/13/EC (Vapor pressure < 0.01kPa at 293.15K)
- European Directive 2004/42/CE (Boiling Point > 250°C at 101.3kPa)

VIII. SUSTAINABILITY

⇨ Bio sourcing

- Ethylal is produced from bio-ethanol
- Other acetals can potentially be produced from bio-alcohols

⇨ Low eco-toxicity

- Most acetals have no eco-toxicological labeling.
- In Germany, acetals are assigned WGK value 1 - low water hazard (Ordinance on facilities for the handling of substances hazardous to water AwSV)

IX. APPLICATIONS

⇨ Paint strippers

Methylal and 1,3-Dioxolane show an exceptional efficiency in paint stripping applications, their combination can be as powerful as Methylene Chloride.

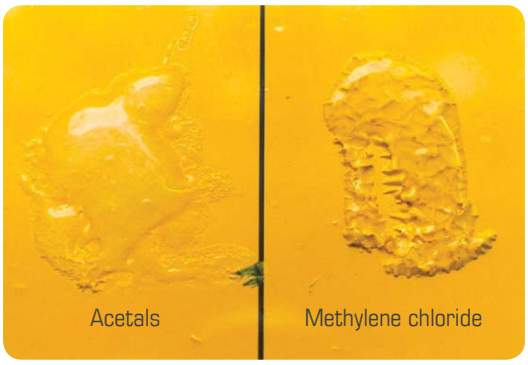
Used as standalones or combined together, they allow formulating very efficient strippers to different paint technologies, including:

- Alkyds;
- Polyurethane – 1 component (hygroscopic drying);
- Polyurethane and epoxy – 2 components;
- Vinyl and acrylic dispersions;
- Powders

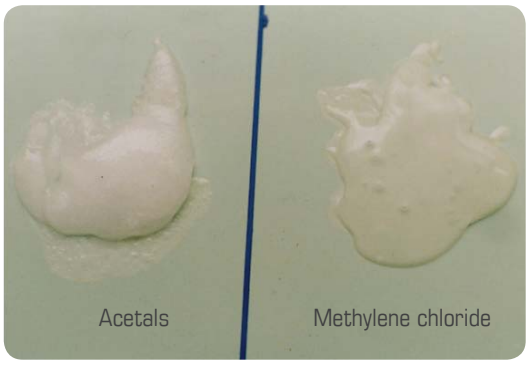
Thanks to its low viscosity and surface tension values, Methylal easily penetrates into the paint film, and acts as a vector to carry 1,3-Dioxolane deeply through paint layers. The high solvent power of 1,3-Dioxolane then easily removes the coatings.

The pictures below illustrate the efficiency of an acetal-based paint stripper formulation in comparison to Methylene Chloride.

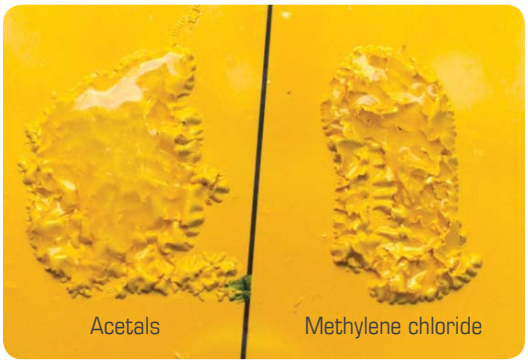
Alkyd enamel
After 30 seconds



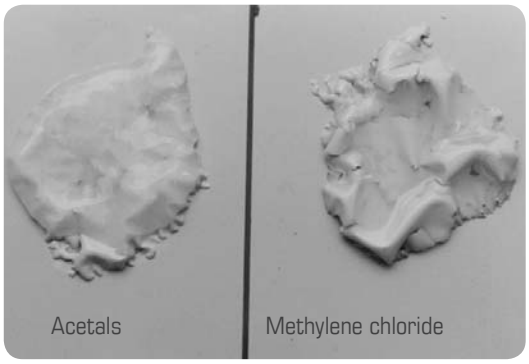
Polyurethane - 1K
After 0 second



After 120 seconds



After 90 seconds



Due to the toxicological labeling of Methylene Chloride, the market progressively substituted it with formulations based on high flash point solvents such as NMP, NEP, DMSO, glycols, etc…

Most of these alternatives being now of concern or in turn labeled for toxicity as well, an acetal such as TOU represents the best solution to produce efficient and safer paint stripping products.

⇨ Graffiti removers

Methylal, 1,3-Dioxolane and TOU also are good active components in the formulation of graffiti removers.

The miscibility of Methylal (up to 33%), 1,3-Dioxolane and TOU (fully miscible) with water, other organic solvents and surfactants allows the development of cleaning formulations whom the aggressiveness can be easily adapted to the specific sensitivity of any covered surface.

⇨ Blanket and roller wash

Acetals offer a range of roller and blanket cleaner products available ranging in drying time, solvent strength and environmental and safety requirements.

TOU offers strong solvent power and safe handling in both conventional and UV-curing printing systems. In the example below, some dried ink was successively removed by means of hydrocarbons then TOU. Pure TOU shows stronger solvent power than the hydrocarbons. Thanks to its compatibility with organics, it can therefore be blended with hydrocarbons as additive or co-solvent and act as a powerful booster to improve the cleaning performance.

TOU was successfully tested by the FOGRA Research Institute for Media Technologies in Germany, on roller material representing UV-only applications.

For people looking for emulsions, Lambiotte proposes Butylal. An emulsifying solvent is very useful for the medium to large sheetfed or web printer since dual action cleaning can be achieved in one step. The solvent cut the ink while the water removes papers, gum and other water soluble materials from the blanket and rollers. The emulsion also helps suspend the ink and carry it away.

⇨ Adhesives and resin residues removers

Thanks to their good compatibility and solvent power on a wide range of polymers and resins, acetals are suitable solvents to formulate adhesive and resin residues removers.

Adhesive tested	% Swelling							
	My	Ey	Py	By	2-EH	TOU	Dx	Elcorem T (My + Dx)
Styrene-acrylate copolymer	696	516	651	557	4	599	**D**	**D**
Polyvinyl acetate dispersion	101	13	3	Not available	Not available	57,5	93	202
Neoprene	**D** After 2h	**D** After 2h	**D** After 2h	**D** After 2h	17	**D** After 2h	**D** After 2h	**D** After 2h
MS Polymer	112	82,5	57	46	12	38	88	144,5
Polyurethane	206	29	12	14	1	**Soluble** After 2h	**Soluble** After 2h	**Soluble** After 2h
Polyacrylate	D	609	582	243	4,5	**D**	**D**	**D**
Epoxy	Not available	Not available	Not available	Not available	Not available	Not available	**D**	**D** After 3h

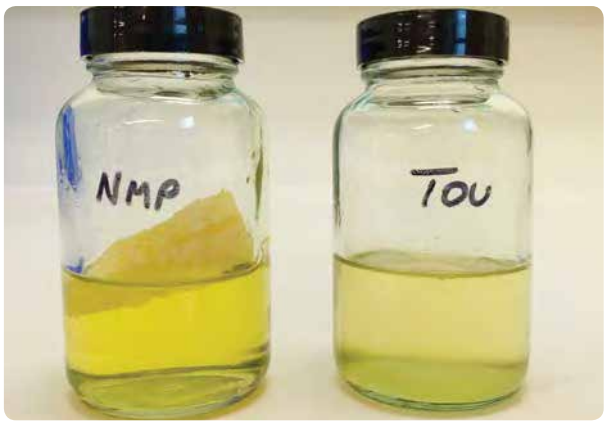
Adhesives cured at room temperature and aged for 14 days at 40°C, sample size: ±12 x 80mm.

Swelling percentage measured after 24h immersion in 50mL acetal at room temperature, static conditions. D = Destructuration

⇨ Polyurethane residues cleaning

In the polyurethane industry, the cleaning of molds and application tools can be made easier thanks to the strong solvent power of Dioxolane and TOU, as alternatives to Methylene Chloride, NMP/NEP, DMSO…

Below the result of a 5 minutes immersion of a sample of rigid polyurethane foam into TOU, in comparison to NMP.



⇨ DEGREASING PROPERTIES

Methylal, Ethylal and Butylal are excellent degreasers with evaporation rates ranging from fast (Methylal) to slow (Butylal).

Household

In household applications, Methylal and Ethylal can substitute alcohol or IPA in many cleaning formulations with the following benefits:

- Better degreasing power
- Quicker drying, no residues

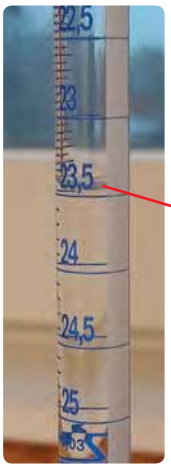
Detergency

In industrial cleaning, the terpene family is well known and commonly used, however it suffers from heavy labeling and fluctuating market availability. Orange terpene or d-Limonene now have found a non-labeled alternative with similar or better performance : Butylal.

0.5g of maintenance grease (Multi lube EP 2) are weighted on metal plates

The metal plates are positioned under 25mL-burrets filled with Butylal (left) and Orange Terpene (right). The liquids are allowed leaking drop by drop directly on the grease sample. A timer is started.

While Orange Terpenes even in excess are barely able to remove half of the grease, it takes lower amounts of Butylal to completely degrease the metal plate.



0,50 g (100%) grease removed

0,25 g (50%) grease removed

Metal degreasing

In the field of metal degreasing, chlorinated solvents have been considered for years as THE reference. This no longer is the case further to their heavy labeling and restricted use by the authorities.

	Trichloroethylene	Perchloroethylene
Toxicity	Carcinogenity Cat. 1B Germ cell mutagenicity Cat. 2 Eye irritation Cat. 2 Skin irritation Cat. 2 Specific target organ toxicity - single explosure Cat. 3 Chronic aquatic toxicity Cat. 3 	Carcinogenicity Cat. 2 Chronic aquatic toxicity Cat. 2 
Flammability	Not	Not
Water miscibility	Not	Not
Kauri Butanol	~ 129	~ 90
Evaporation rate (Ether)	6,4 (compared to BuAc)	8,1

In the safe and environment friendly industry of the 21st century, those solvents must be replaced by alternatives with better toxicological profile.

Thanks to their exceptional degreasing properties, acetals are the best suited solution.

Butylal in particular offers some outstanding metal degreasing feature, no matter the conditions :

Type of grease/lubricant considered ;

Thin or thick layer ;

In static or dynamic conditions ;

High efficiency even at room temperature ;

Fast effect, time efficient.

In order to demonstrate this feature, some grease/lubricant was applied in excess on the surface of the stainless steel plate, then a part of this substrate is dipped into a beaker filled with Butylal.

The plate was removed, the excess of Butylal was gently wiped out by means of a paper cloth, the rest was evaporated by compressed air then the degreasing efficiency was evaluated by means of a droplet of water :

- Where the grease is present, the surface is more hydrophobic, therefore the contact angle of the water bead will be high (rounder shape)
- Where the grease has left, the surface is less hydrophobic, therefore the contact angle of the water bead will be low (flatter shape)

Different types of grease/lubricant have been tested :

- Petroleum jelly (vasoline) ;
- Lithium/calcium grease ;
- Copper paste.

Petrolem jelly

Thin layer applied on the surface

Dynamic immersion (stirring)

10-15 minutes

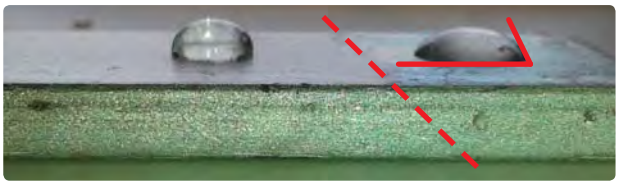
Room temperature

Before dipping

Water droplet contact angle > 90°

Surface **more** hydrophobic

After dipping



Water droplet contact angle < 90°

Surface **less** hydrophobic

Lithium/calcium grease

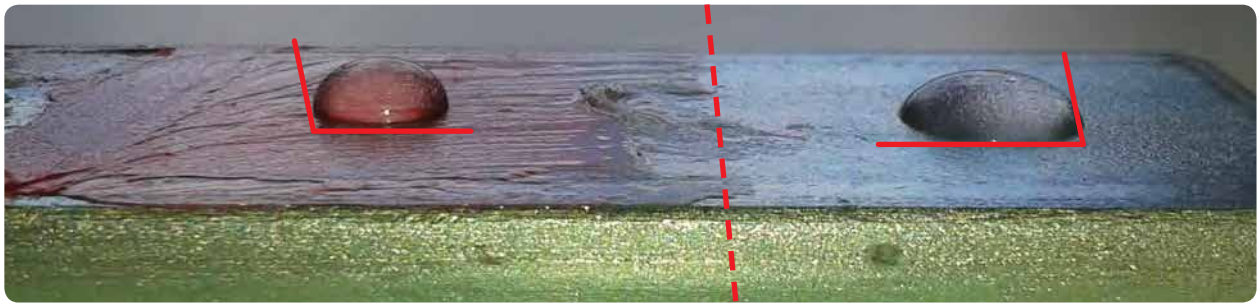
Static immersion

30 minutes

Room temperature

Non-immersed part

Immersed part



Water droplet contact angle > 90°

Surface **more** hydrophobic

Water droplet contact angle < 90°

Surface **less** hydrophobic

Copper paste

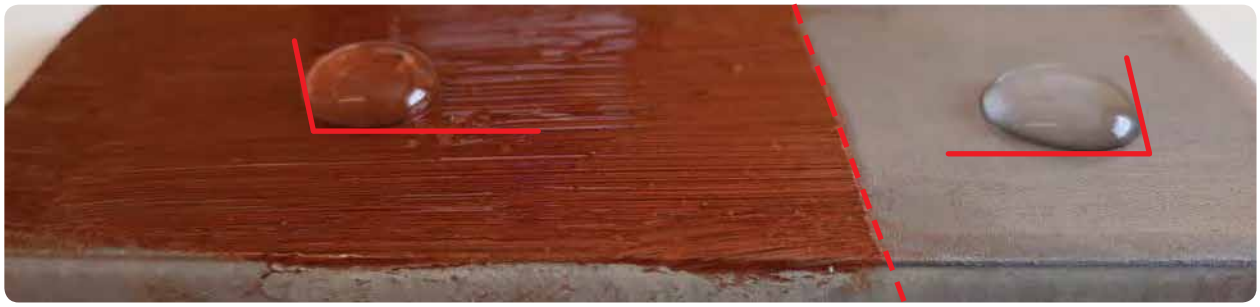
Static immersion

10-15 minutes

Room temperature

Non-immersed part

Immersed part



Water droplet contact angle > 90°

Surface **more** hydrophobic

Water droplet contact angle < 90°

Surface **less** hydrophobic

⇨ CAR CARE

The presence of acetals in products dedicated to the cleaning and maintenance of specific parts of the car, such as engines, carburetors, rims, brakes, cockpit, etc… contribute to improve their performances.

Metal degreasing

Compared to hydrocarbons, Butylal shows strong solvent power on any bitumen-based material.

No matter if used in solvent or water-based formulations (via emulsification), it provides an outstanding cleaning power to remove particles of bitumen or tar sticking to the bottom part of the car body or the rims.

Polishes and waxes

Methylal, Ethylal, Propylal, Butylal and 2-Ethylhexylal are fully compatible with most silicone fluids that are typically promoted in the car care industry. In polishes, their low viscosity and surface tension help improving the spreading, while their low to high evaporation rate allow tailoring the drying time for a perfect application. Combined to silicone fluids, 2-Ethylhexylal also boosts the water beading effect.

The strong solvent power of Butylal and 2-Ethylhexylal allow dissolving selected waxes and paraffins at room temperature.

⇨ HYGIENE

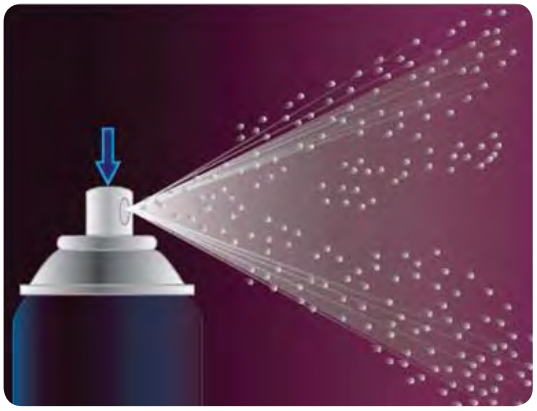
Methylal makes it possible to produce without any heating soft, non-irritating, non-allergenic and transparent single-phase cleaning gels. It also can be useful in hand sanitizers; in addition to ensuring the full compatibility of all the components contained in the formulation, it gives a cooling feeling, boosts the drying time and decreases the tacky effect.

Thanks to its high degreasing power, Butylal allows formulating hand cleansing gel, even for heavy duty cleaning, such as garage soaps.

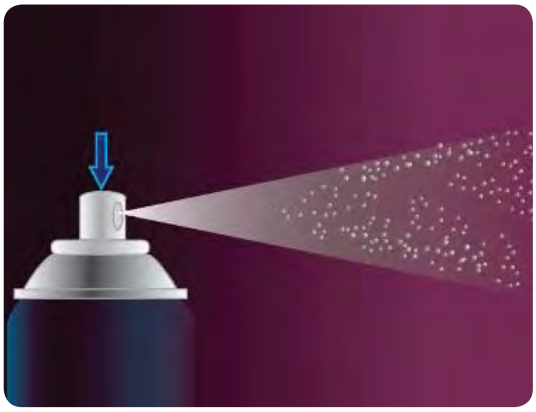
⇨ AEROSOLS AND PUMP SPRAYS

Methylal is the component that each and every cleaning product delivered in aerosol or pump spray must contain:

- Its high solvent power ensures that components will constantly remain solubilized into the liquid phase, even at low temperature, which therefore reduces the risks of precipitation/crystallization and plugging of the tube of the aerosol. Its water miscibility also ensures a better compatibility of apolar substances with waterborne systems;
- In aerosols specifically, the same high solvent power also is responsible of a higher solubility of propellants such as Propane-Butane, Dimethylether, HFCs/HFOs or compressed gases CO_2 and N_2O, into the liquid phase. This property not only results in a pressure decrease in the can, it also helps maintaining enough pressure until the very last drop of liquid will be sprayed, by constantly releasing some of the solubilized propellant into the gaseous phase after each use. In the case of compressed gases, Methylal also makes the can filling process easier;
- With its low surface tension and viscosity Methylal contributes to a reduction of the size of the particles, resulting in a higher spray quality;

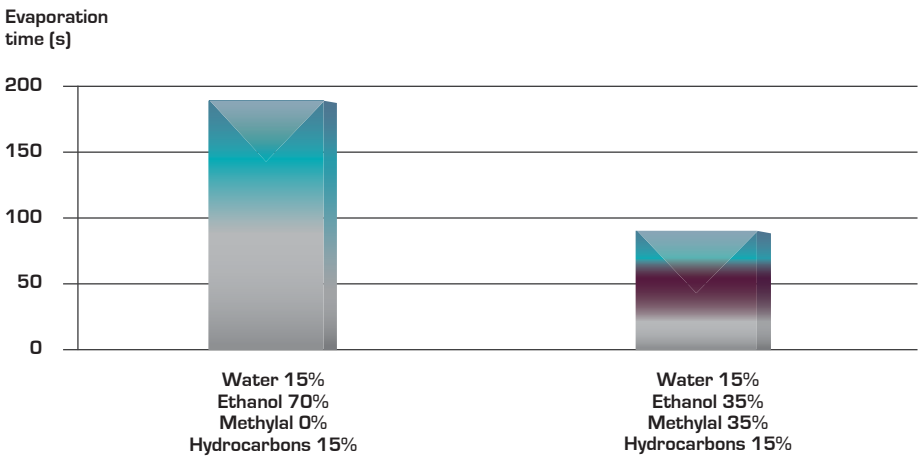


Without Methylal



With Methylal

- No matter the propellant, thanks to its low evaporation rate Methylal makes droplets of solvent or water-based sprayed liquids evaporate much faster than traditional solvents like Ethanol or Acetone, allowing cleaning formulations to leave no residue further to application;

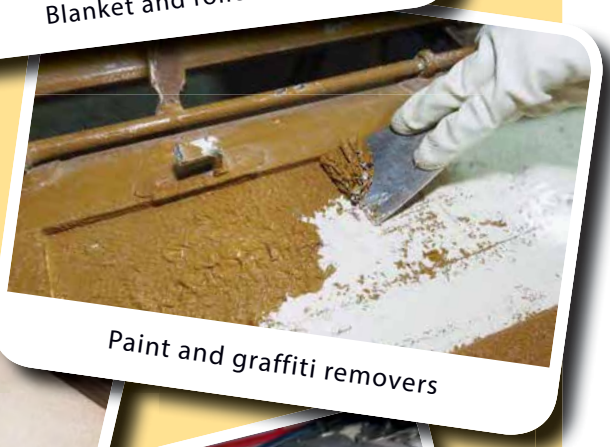


- The water miscibility of Methylal is key for the formulation of low-VOC content aerosols and pump sprays.

Applications

Blanket and roller wash

Barbecue and oven cleaners



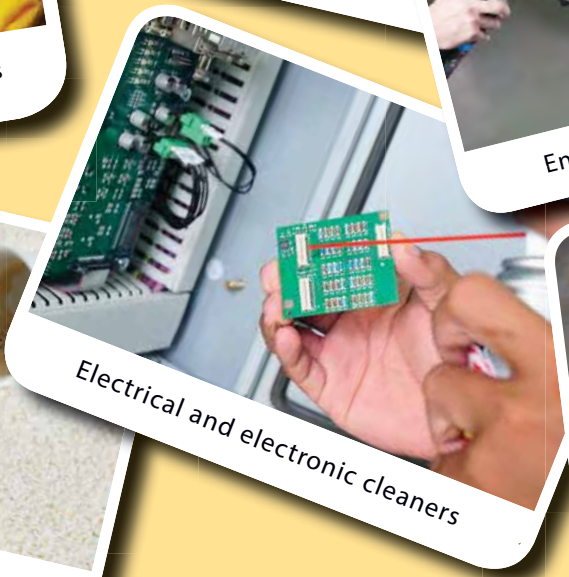
Paint and graffiti removers

Adhesive and resin removers

Carpet cleaning

Engine and carburator cleaners

Stain removers

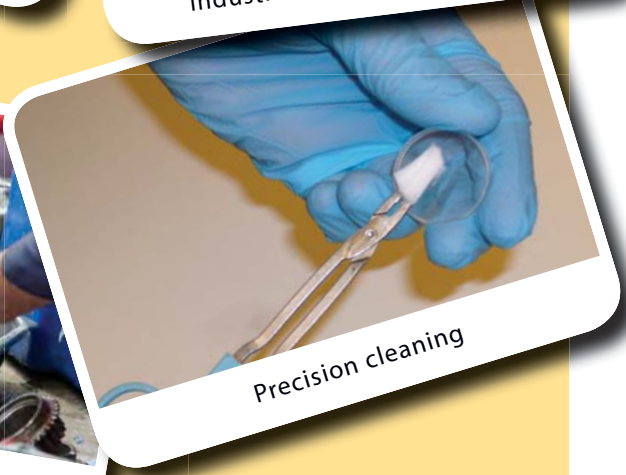


Electrical and electronic cleaners

Industrial/Heavy duty cleaning

Car care

Metal degreasing



Precision cleaning

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