Gaylord Chemical Company L.L.C.

World Class producer of dimethyl sulfoxide (DMSO) and dimethyl sulfide (DMS)

Coatings / polymer applications
Coating Applications

The dominant trend for DMSO in coatings application has been in remover / cleaning products.

This is driven by regulatory pressure on more hazardous solvents (methylene chloride, NMP).

Examples

- Paint Stripping products that are more safe and environmentally responsible than methylene chloride and NMP- based products
- Formulations to clean equipment which process polyurethane and polyester resins (fiberglass)
- Rework of coated parts (powder coating)
DMSO Benefits: Paint stripping / polymer cleaning

- A safer alternative to existing products
- Lower volatility than methylene chloride-based products
- Regulatory compliance
- Odor / cosmetic advantages relative to methylene chloride-based products
EU Regulatory pressure on competitive solvents

N-methylpyrrolidone (NMP)

- EU: 31\textsuperscript{st} ATP NMP labeling requirement in place

<table>
<thead>
<tr>
<th>NMP as raw material:</th>
<th>T: R 36/37/38-61</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMP in a formulated product:</td>
<td>≥ 5%</td>
</tr>
<tr>
<td>NMP in a formulated product:</td>
<td>≥ 10%</td>
</tr>
</tbody>
</table>

Products, which contain ≥ 5% NMP, will be prohibited for the use in DIY-applications – and agrichemical use in some EU countries.

- Similar in spirit to some US regulatory efforts (California Prop 65)

- Are EU formulators taking this more seriously? Perhaps too early to tell, but anecdotal information (microelectronics) suggests yes.
EU Regulatory pressure on competitive solvents: methylene chloride

European Parliament Press Release (1/14/2009)

“The dangerous chemical compound Dichloromethane (DCM) in paint-strippers will soon be banned for consumers and many professionals, after the adoption of a legislative report by the European Parliament”

• “paint-strippers containing dichloromethane in a concentration equal to or greater than 0.1% by mass shall not be placed on the market for the first time after 18 months for supply to the general public or to professionals..

• they shall not be supplied to them after 30 months after the entry into force and shall not be used by professionals 36 months after entry into force [ASM reading – entry date 3 Jan 2009]”

Industry is pushing back with unclear results

Methylene Chloride drop-dead date: January 2012?

Full press release at:
Formulation

Paintstripping formulat(ors) are constrained with respect to solvent replacement choices:

- Of the few VOC exempt solvents available on EPA list, most have other baggage (HFCs, acetone, methyl acetate, water, CO2..)
- DMSO and NMP are the only polar solvent alternatives, but are 100% VOC
- Only a few useful VOC exempt solvents, and formulators are converging on polar solvent mixtures of these
- The only choices as cosolvents: DBE >>> Jeffsol PC\(^1\), dimethyl carbonate\(^1\) >> PCBTF, BTF)
Safety and Handling

Hand Protection: Butyl rubber or nitrile gloves
Storage: HDPE / HDPE, mild & 304, 316 Stainless Steel, Al 6061-T6
Gaskets/ Polymers: PFTE, Kalrez®

For detailed information regarding materials of construction, storage conditions, piping, and unloading conditions, refer to Gaylord Bulletin 107 (available from www.gaylordchemical.com)
**Formulation!**  
*Cosolvents for DMSO stripping products*

Dibasic Esters (DBE, DME): ↑safe, miscible ↓solvent strength

Propylene carbonate: (Jeffsol) ↑safe, miscible ↓solvent strength

P-series glycol ethers: (DPM, TPM) ↑solvent power, miscible ↓cost

Ethyl lactate: ↑safety ↓solvent strength

Benzyl alcohol?

AR-100,150,200: ↑cost ↓’moth ball’ smell

D-limonene / citrus terpenes: ↑smell ↓DMSO solubility

$t$-butyl acetate: ↑VOC content ↓flashpoint

Water: ↓negative affect on stripping performance

Oxsol? ↑VOC content, solvent strength ↓safety, availability
Additives for DMSO Stripping Products

- **Viscosity modification**: Methocel OS, Klucel H, Carbopol 934
- **Activators**: Monoethanolamine (MEA), triethanolamine (acids, peroxides not recommended)
- **Inhibitors**: Cobratec 928 (copper, zinc at lower pH), Alox products (mild steel, low pH) – plastic packaging is preferred
- **Fragrance**: pine oil, limonene, citrus oil
- **Surfactants nonionics**: Igepal OD-410 (Rhodia), Triton (Dow), Ethomeens (Akzo Nobel), Ninol (Stepan)
## Sample Formulation

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMSO</td>
<td>38-44%</td>
</tr>
<tr>
<td>AR-I50ND®</td>
<td>15-23%</td>
</tr>
<tr>
<td>DBE®</td>
<td>19-30%</td>
</tr>
<tr>
<td>EEP</td>
<td>8-17%</td>
</tr>
<tr>
<td>Methocel® 311</td>
<td>1%</td>
</tr>
<tr>
<td>Ethanolamine</td>
<td>0.5%</td>
</tr>
<tr>
<td>Rhodasurf® DA-630</td>
<td>0.5%</td>
</tr>
</tbody>
</table>

**Preparation:** Ethanolamine and DMSO are combined at room temperature, and Methocel® 311 is added with stirring. As the mixture thickens, DBE, EEP and AR150 are added sequentially. Rhodasurf® DA-630 is added last; Final product has a viscosity of ~7000 cps. Package in HDPE.

*AR-150ND®* is a product of the ExxonMobil Corporation.  
*DBE®* (dibasic ester blends) are products of DuPont. Monsanto markets a similar product line (DME® blends)  
*EEP* (3-ethoxyethylpropionate) is produced by Eastman Chemical Company  
*Methocel®* thickeners are produced by Dow Chemical.  
*RhodaSurf®* DA-630 is a product of Rhodia.
Frequently asked questions:

**DMSO use in paint stripping products**

- Specific concerns related to skin penetration enhancement of lead paint: Data for DMSO is favorable

<table>
<thead>
<tr>
<th>Product name</th>
<th>% applied dose</th>
<th>Ratio</th>
<th>ng/cm²</th>
<th>Ratio</th>
<th>ng/cm²/h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strimix 433E</td>
<td>1.8</td>
<td>1.9</td>
<td>204.3</td>
<td>1.4</td>
<td>4.3</td>
</tr>
<tr>
<td>Dimethyl sulphoxide</td>
<td>0.4</td>
<td>0.4</td>
<td>36.1</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Classical paint stripper</td>
<td>1.0</td>
<td>1.0</td>
<td>149.6</td>
<td>1.0</td>
<td>3.1</td>
</tr>
<tr>
<td>Citristrip</td>
<td>3.2</td>
<td>3.3</td>
<td>475.1</td>
<td>3.2</td>
<td>9.9</td>
</tr>
<tr>
<td>N-Methyl pyrrolidone</td>
<td>0.7</td>
<td>0.7</td>
<td>102.0</td>
<td>0.7</td>
<td>2.1</td>
</tr>
</tbody>
</table>

- Cost / performance expectations relative to MC

- Practical use limitations based on VOC content (40 wt% in US. Similar in Europe?)
Relative Performance

- DMSO and NMP-based products perform similarly on paints.
- Both require 2-3 times as long to work than MC-based products.
- DMSO-based products are especially effective at stain/varnish removal.
- Formulation considerations nearly identical for DMSO & NMP.
DMSO FAQs

Does DMSO penetrate human skin?
Does it enhance the penetration of other chemicals?

DMSO can penetrate human skin, but it is not unique in this ability. As an example, NMP penetrates the skin at nearly the same rate as DMSO but is itself more toxic.

Not all materials can be transported through skin by solvents. This effect depends on the chemical, and we can provide guidance to help answer specific customer questions.

Supporting resources: a) Gaylord bulletin 106
b) paper: “Permeability of Commercial Solvents” on Gaylord webpage
The 1995 study “Permeability of Commercial Solvents Through Living Human Skin” measured solvent permeation potentials and offers some perspective based on evidence:

- All the dipolar aprotic solvents (DMAc, DMF, NMP, DMSO) have the ability to penetrate skin.
- NMP and DMSO have nearly identical permeability constants.

Doesn't DMSO smell bad?

No, pure DMSO is nearly odorless, with a mild oyster-like odor. Poor quality DMSO has the odor of its impurities, which can be materials like methyl mercaptan and carbon disulfide.

Gaylord’s purification technology produces only DMSO which is essentially odorless.
Is DMSO toxic?

No. DMSO is not toxic by dermal, oral, or inhalation exposure. It isn’t a suspect carcinogen, a reproductive toxin and it does not bioaccumulate in the body.

<table>
<thead>
<tr>
<th>Toxicological Indicator</th>
<th>DMSO</th>
<th>DMAc</th>
<th>NMP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oral LD-50</td>
<td>14,500-28,300 mg/ kg rat</td>
<td>4,300 mg / kg rat</td>
<td>3,914 mg/ kg rat</td>
</tr>
<tr>
<td>dermal LD-50</td>
<td>40,000 mg / kg rat</td>
<td>2,240 mg / kg rat</td>
<td>8,000 mg/ kg rabbit</td>
</tr>
<tr>
<td>Inhalation (rat)</td>
<td>none @ 2,900 mg/ m³</td>
<td>2,475 mg / kg @1 hr</td>
<td>NA</td>
</tr>
<tr>
<td>Reproductive toxin</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Proposition 65</td>
<td>no</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>

Supporting resources: Gaylord bulletin 106
Handling frozen DMSO / Material compatibility

Freeze / Thaw Stability of DMSO is excellent, based on long-term stability testing

When frozen, **DMSO is commonly thawed** with warm water, in a ‘hot box’ or warm storage area, or by using heating bands

Often useful to thaw drum material while on pallets

**Personel Protective Equipment:** butyl rubber or nitrile (NBR) rubber gloves (such as TNT Nitrile Glove produced by Ansell Healthcare VWR cat # 32889-888)

**Compatible polymers:** PFTE, HDPE, HDPP, Chempac 92 or Kalrez gaskets

**Compatible metals:** 304, 316 Stainless steel (mildly corrosive to aluminum, copper, Zinc, mild steel)

Supporting resources: Gaylord bulletin 106
For more information, please contact:

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