UV-Curable PFPE-(Meth)acrylates: a new class of UV-Curable Resins
# PFPE-(Meth)acrylates - Portfolio

<table>
<thead>
<tr>
<th>Product</th>
<th>Functionality</th>
<th>Fluorine content (% by wt.)</th>
<th>Chemical-physical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorolink MD700</td>
<td>Bifunctional Urethane Methacrylate</td>
<td>52</td>
<td>Appearance = clear R.I. = 1.342 Viscosity (25°C) = 430 cP</td>
</tr>
<tr>
<td>Fluorolink AD1700</td>
<td>Tetrafunctional Urethane Acrylate</td>
<td>24</td>
<td>70% w/w dry content in Butyl Acetate / Ethyl Acetate [Acrylics] = 2.67 Eq/kg</td>
</tr>
<tr>
<td>Fomblin MD40</td>
<td>Bifunctional Urethane Methacrylate</td>
<td>58</td>
<td>Appearance = clear R.I. = 1.313 Viscosity (25°C) = 695 cP</td>
</tr>
</tbody>
</table>
PFPE-(meth)acrylates: structure – property relationship

- PFPE Molecular Weight:
  - 1000
  - 1500
  - 2000
  - 4000
  - RELEASE
  - SHRINKAGE
  - OPTICAL TRANSPARENCY
  - COMPATIBILITY

- Type of End-group:
  - METHACRYLATE
  - ACRYLATE
  - REACTIVITY
  - RADIANT ENERGY FOR FULL CURE
UV- curable Perfluoropolyethers

Bifunctional

PFPE-urethane (meth)acrylates
**Fluorolink MD700: chemical-physical properties**

- R.I. (25°C) = 1.342, [F] = 52% (w/w), η (25°C) = 430 cP
- Miscible with conventional acrylic monomers, but only in a well defined window
- Blooms very effectively to the surface of the coating, imparting low surface energy, water/oil repellence, antisticking properties
**Fomblin MD40: chemical-physical properties**

- R.I. (25°C) = 1.313, [F] = 58% (w/w), η (25°C) = 695 cPoise
- Soluble only in fluorinated solvents (Galden from Solvay Specialty Polymers)
- Compatible with: Darocur 1173 (≤ 1% w/w), Irgacure 184 (≤ 0.5% w/w)
- The homopolymer is an elastomer with outstanding chemical resistance, low surface energy and exceptional antisticking properties, low elastic modulus

![Chemical structure of Fomblin MD40](chart)
UV-curable Perfluoropolyethers

Tetrafunctional

PFPE-urethane (meth)acrylates
Fluorolink AD1700: chemical-physical properties

- Tetrafunctional derivative
- \([F] = 24 \% \text{ (w/w)}\)
- Soluble in AcOEt, MEK, BuOAc
- Good compatibility with commercial UV-curable paints
- Suggested use: low surface energy additive for UV-curable paints, effective in providing easy removal of fingerprints
UV-curing conditions: remarks

• PFPE-(meth)acrylates are strongly affected by oxygen inhibition.

• Curing under nitrogen is recommended for all the formulations with a high PFPE content; PFPE-acrylates (Fluorolink AD1700) can be cured in the air by choosing the proper package of reactive diluents and photoinitiators.

• Standard curing in the air can be applied when using PFPE-(meth)acrylates at additive levels.

• Among the many possible combinations of photoinitiators, Darocur® 1173 (optionally in combination with Irgacure® 127) gives the best performance.
UV- curable Perfluoropolypropylythers

Materials Characterization
**Shrinkage upon curing**

<table>
<thead>
<tr>
<th>Material</th>
<th>Molecular Weight (AMU)</th>
<th>Shrinkage upon curing</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLK MD700</td>
<td>1800</td>
<td>6.0%</td>
</tr>
<tr>
<td>Fomblin MD40</td>
<td>4000</td>
<td>1.7%</td>
</tr>
</tbody>
</table>

The shrinkage is inversely proportional to the Molecular Weight of the oligomer (distance between two crosslinking sites)
## Surface Properties Characterization

<table>
<thead>
<tr>
<th>Cured Material</th>
<th>SYLГARD 184</th>
<th>FLK MD700</th>
<th>Fomblin MD40</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.C.A. vs. H₂O</td>
<td>101°</td>
<td>113° ± 2°</td>
<td>113° ± 2°</td>
</tr>
<tr>
<td>S.C.A. vs. n-C₁₆</td>
<td>___</td>
<td>58° ± 2°</td>
<td>52° ± 2°</td>
</tr>
</tbody>
</table>

- PFPE-based elastomeric materials show an outstanding W/O Repellency.
- Silicones display a higher surface energy than PFPEs and are not oil repellant.
### Chemical Resistance (Swelling)

<table>
<thead>
<tr>
<th>Material</th>
<th>Swelling into MIBK (% w/w)</th>
<th>Swelling into CH(_2)Cl(_2) (% w/w)</th>
<th>Swelling into MEK (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SYLGARD 184</td>
<td>72</td>
<td>133</td>
<td>57</td>
</tr>
<tr>
<td>FLK MD700</td>
<td>11</td>
<td>13</td>
<td>13</td>
</tr>
<tr>
<td>Fomblin MD40</td>
<td>4</td>
<td>7</td>
<td>0</td>
</tr>
</tbody>
</table>

All the measurements were performed at the equilibrium

- PFPE-based elastomers are not swollen by hydrogenated organic solvents
- Cured Fomblin MD40 shows the best chemical resistance
- Only fluorinated solvents are able to swell the cured PFPE elastomers
**UV-curable PFPEs: markets and applications**

PFPE-(METH)ACRYLATES

- > 60% (w/w) PFPE content
- < 5.0% (w/w) PFPE content

**Optics/Photonics**
- Anti Reflective/Antismudge Top Coats
- Polymeric Waveguides, Cladding of Optical Fibers

**Additives for UV-curable paints**
- Surface energy reduction,
  Water/Oil Repellency, Antigraffiti,
  Easy Removal of Fingerprints
# High PFPE content: formulation for aluminum

<table>
<thead>
<tr>
<th>Composition (parts by weight)</th>
<th>Chemical-physical properties</th>
<th>Substrate</th>
<th>Pencil Hardness</th>
<th>MEK d.r.</th>
<th>Cross Cut Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorolink AD1700 50.0</td>
<td>Thickness = 60 μm</td>
<td>Aluminum</td>
<td>H</td>
<td>&gt; 200</td>
<td>100%</td>
</tr>
<tr>
<td>HDDA 15.0</td>
<td>Visc.(25°C) = 65 cP</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>THFFA 50.0</td>
<td>% PFPE = 13.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Darocur 1173 4.0</td>
<td>γc = 19.9 ± 0.2 mN/m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sartomer CN386 1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzophenone 1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Curing conditions (air): 6x10 m/min, H bulb 13 mm, UV power System VPS 1600 (240 W/cm)

- Formulation which combines low surface energy, outstanding chemical resistance and flexibility.

- Self-Healing effect: once the coating is scratched, it flows back into the scratch, returning the surface to its original smooth state (effect of the low T_g of the PFPE chain)
Formulation for aluminum: FLK AD1700 vs. silicone acrylate

<table>
<thead>
<tr>
<th>Composition (parts by weight)</th>
<th>Static Contact Angle vs. H₂O (°)</th>
<th>Static Contact Angle vs. n-hexadecane (°)</th>
<th>Surface Energy (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLK AD1700 - HDDA - THFFA 35(dry content):15:50</td>
<td>109 ± 1</td>
<td>63 ± 1</td>
<td>15.0</td>
</tr>
<tr>
<td>Silicone acrylate-HDDA-THFFA 35:15:50</td>
<td>99 ± 3</td>
<td>28 ± 1</td>
<td>25.0</td>
</tr>
</tbody>
</table>

Curing conditions (air): 6x10 m/min, H bulb 13 mm, UV power System VPS 1600 (240 W/cm)

Fluorolink AD1700 outperforms silicone-acrylates in terms of surface energy reduction
**Fluorolink AD1700 as a coating surface modifier**

Commercial UV-curable formulations loaded with 1%, 2%, and 5% w/w of Fluorolink AD1700 (thickness = 15 μm, Substrate = PMMA):

<table>
<thead>
<tr>
<th>Test</th>
<th>Blank</th>
<th>1% w/w FLK AD1700</th>
<th>2% w/w FLK AD1700</th>
<th>5% w/w FLK AD1700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Static Contact Angle vs. H₂O (°)</td>
<td>82 ± 5</td>
<td>103 ± 3</td>
<td>109 ± 3</td>
<td>113 ± 1</td>
</tr>
</tbody>
</table>

- Fluorolink AD1700 improves the water repellency at a low dosage.
- Excellent compatibility with the hydrogenated formulations.
**PFPE-(meth)acrylates: conclusions**

PFPE-(meth)acrylates are liquid oligomers characterized by unique properties:

- Very low R.I., high thermo-optic coefficient
- Low Surface Energy
- Ability to migrate to the surface of the coating
- Do not contain any PFOS and PFOA

which make them ideal raw materials for manufacturing:

- Coatings having outstanding water/oil repellency, antigraffiti properties, easy cleanability of stains and fingerprints
- Optical coatings for lenses, displays, photonic devices, etc.
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