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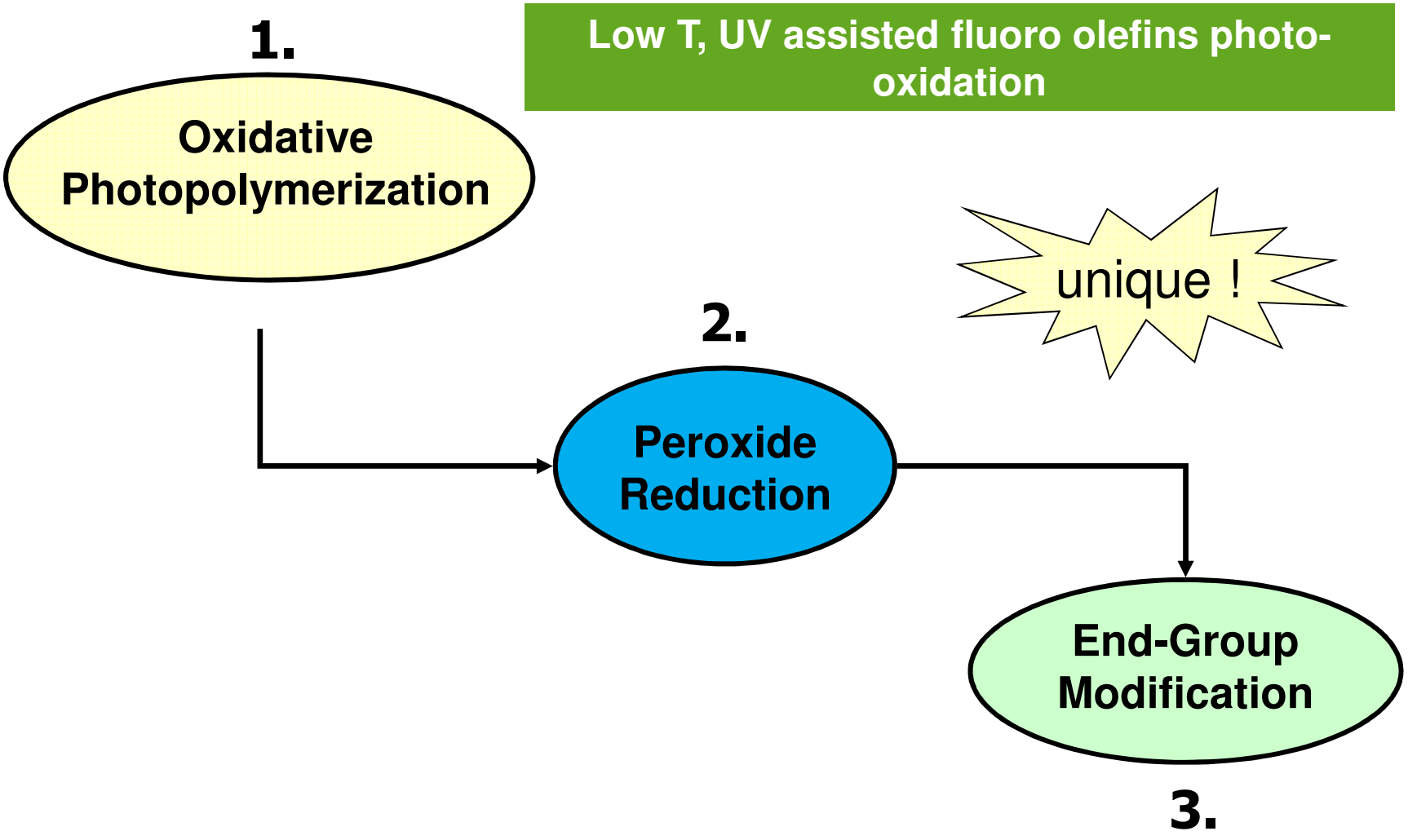
FLUOROLINK® for Low Surface Energy Coatings

SPECIALTY POLYMERS

Agenda

- PFPE Technology
- PFPE Polymer Modifiers
  - ✓ Fluorolink® E10H
  - ✓ Fluorolink E-series
- Solvent-based Surface Treatments
  - ✓ Fluorolink® S10
- UV-curable PerFluoroPolyEthers
  - ✓ Fluorolink® AD1700
- Waterborne Surface Treatments
  - ✓ Fluorolink® P54 / TLS 5018
  - ✓ Fluorolink® P56

The Technological Platform



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Fluorolink® Product Line

$$R_H\text{-}CF_2O\text{-}(CF_2CF_2O)_m\text{-}(CF_2O)_n\text{-}CF_2\text{-}R_H$$

- Amide (A10P & PA100E) - $CONHR_H$
- Amido Silane (S10) - $CONH(CH_2)_3\text{-}Si(OEt)_3$
- Ethoxylated alcohol (E10-H, 5147X) - $CH_2(OCH_2CH_2)_nOH$
- Polyurethane dispersion (P56) - Anionic PUD
- Urethane (Meth)Acrylates (AD1700, MD700) - $COOCR_H{=}CH_2$
- Phosphate (P54, TLS 5018, F10) - $R_HOPO(OH)_2$

Fluorolink® Key Benefits & Applications

$$R_H\text{-}CF_2O\text{-}(CF_2CF_2O)_m\text{-}(CF_2O)_n\text{-}CF_2\text{-}R_H$$

- **Surface Tension Reduction**
  - ✓ **Water/Oil Repellency**
  - ✓ **Stain/Soil Release**
- **Easy Cleanability**
- **Chemical Resistance**
- **Optical Properties**
- **Friction Reduction**
- **Wear Reduction**

Surface Treatment

Building Block Additives for Polymers & Paints

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PFPE- Polymer Modifiers

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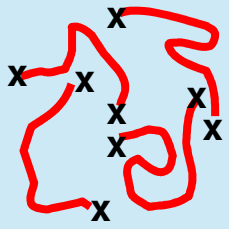
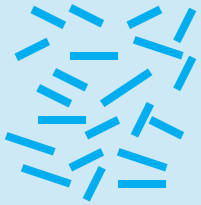
Polymer Modification - Concept

FLUOROLINK®
- bifunctional derivatives
- different reactive groups
- different molecular weight



+

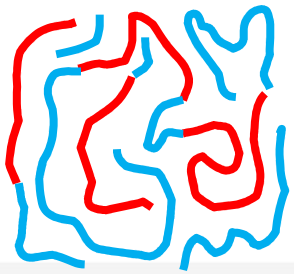
Hydrocarbon-based monomers



Insertion of Fluorolink® as a reactive building block during the polymerization

Partially Fluorinated block copolymers

Low PFPE content (1-20% w/w)
- Improved Surface Properties
  - ✓Water/Oil repellency
  - ✓Stain/soil release
  - ✓Low CoF
- No change in the bulk properties



High PFPE content (> 20% w/w)
- Improved Surface Properties
  and
- Enhancement of chemical resistance
- Change in the mechanical properties

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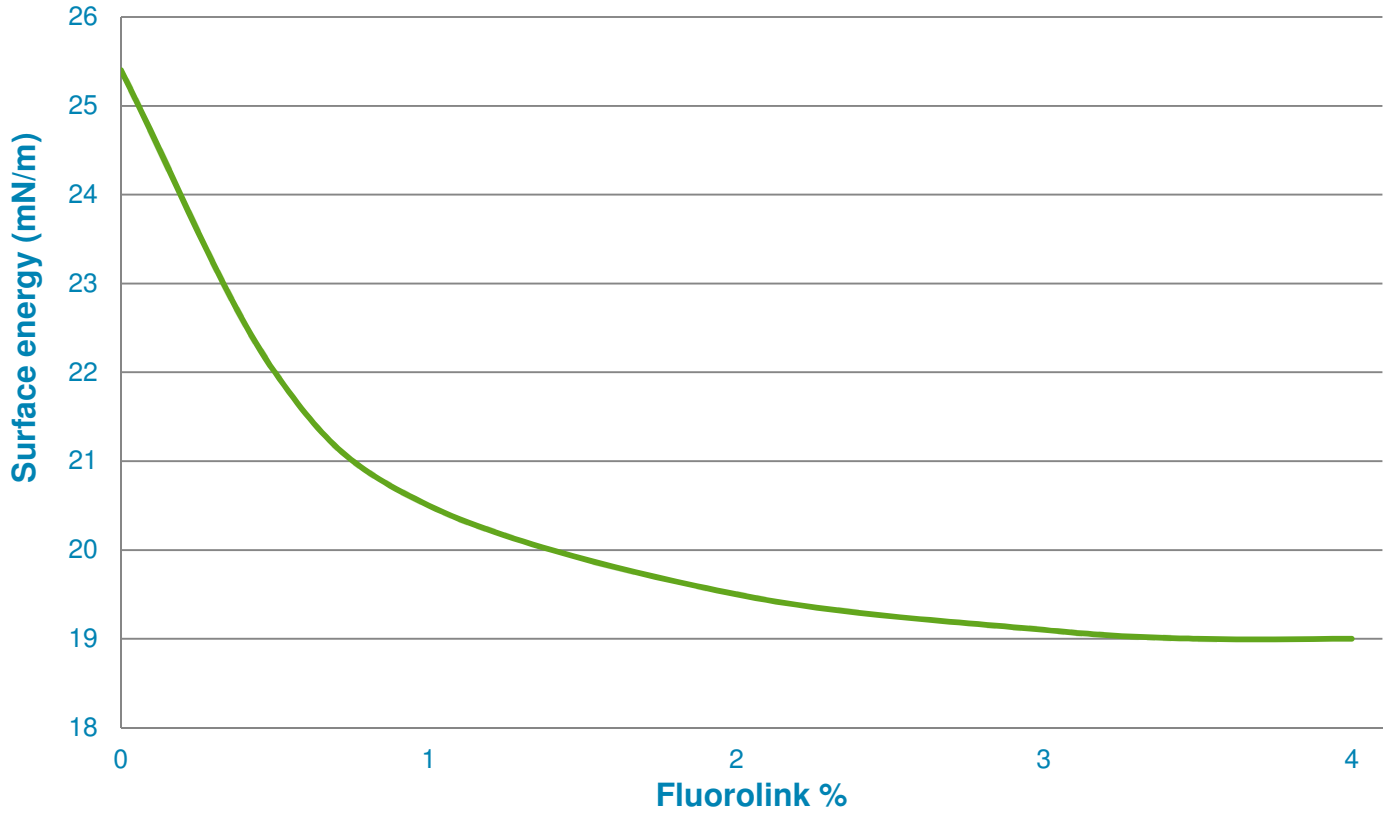
Polymer Modifier – Fluorolink® E10-H

$$HO\text{-}_n(CH_2CH_2O)\text{-}CH_2\text{-}CF_2O\text{-}(CF_2CF_2O)_m\text{-}(CF_2O)_n\text{-}CF_2\text{-}CH_2\text{-}(OCH_2CH_2)_n\text{-}OH$$

PROPERTIES	TYPICAL VALUE
Appearance	Clear Liquid
Average Equivalent Weight (NMR)	900 g/mole
Specific Gravity (20°C)	1.73 g/ml
Kinematic viscosity (20°C)	115 cSt
Fluorine Content	57% w/w
Applicative Field	Reactive Additive for Polycondensation Polymer

Fluorolink® E10-H as a modifier for PUs
Surface Energy



FLK E10-H significantly decreases the surface energy at a low concentration

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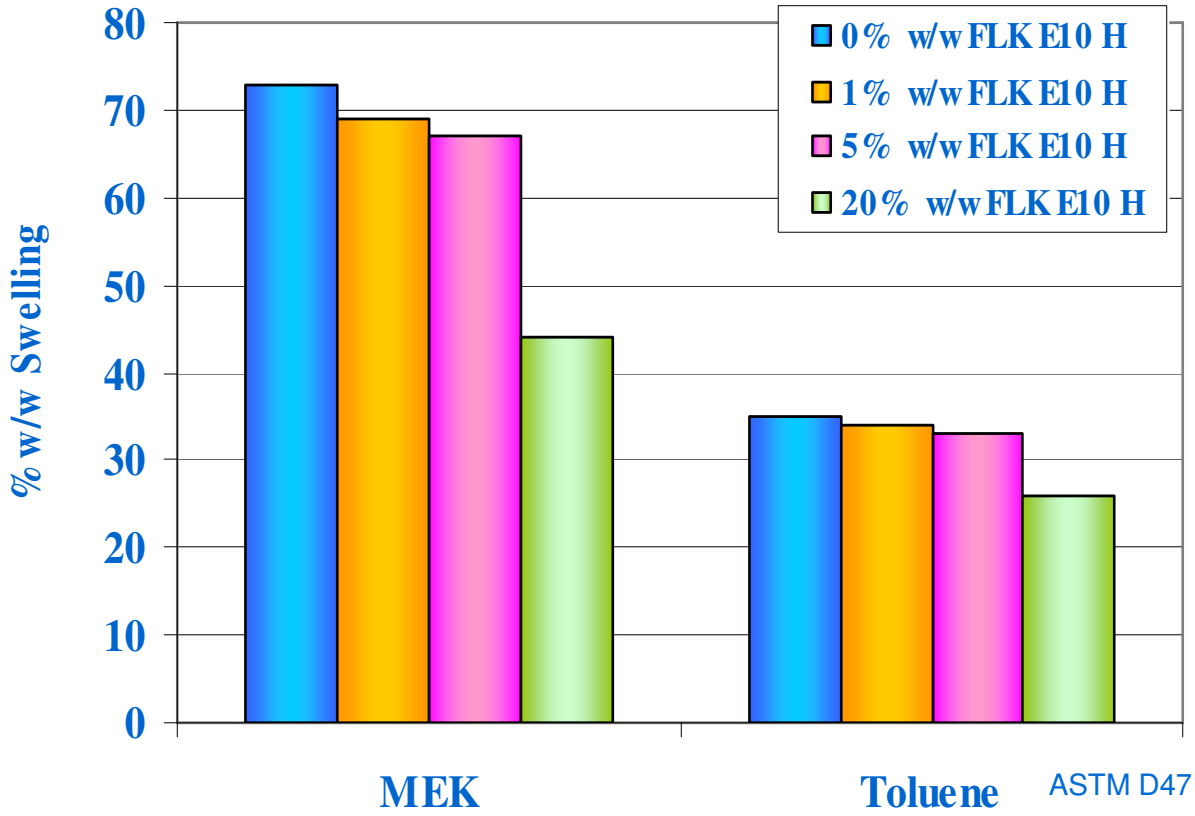
Fluorolink® E10H as a modifier for PUs
Chemical Resistance



ASTM D471-98 Test Method

FLK E10-H improves the chemical resistance of PU

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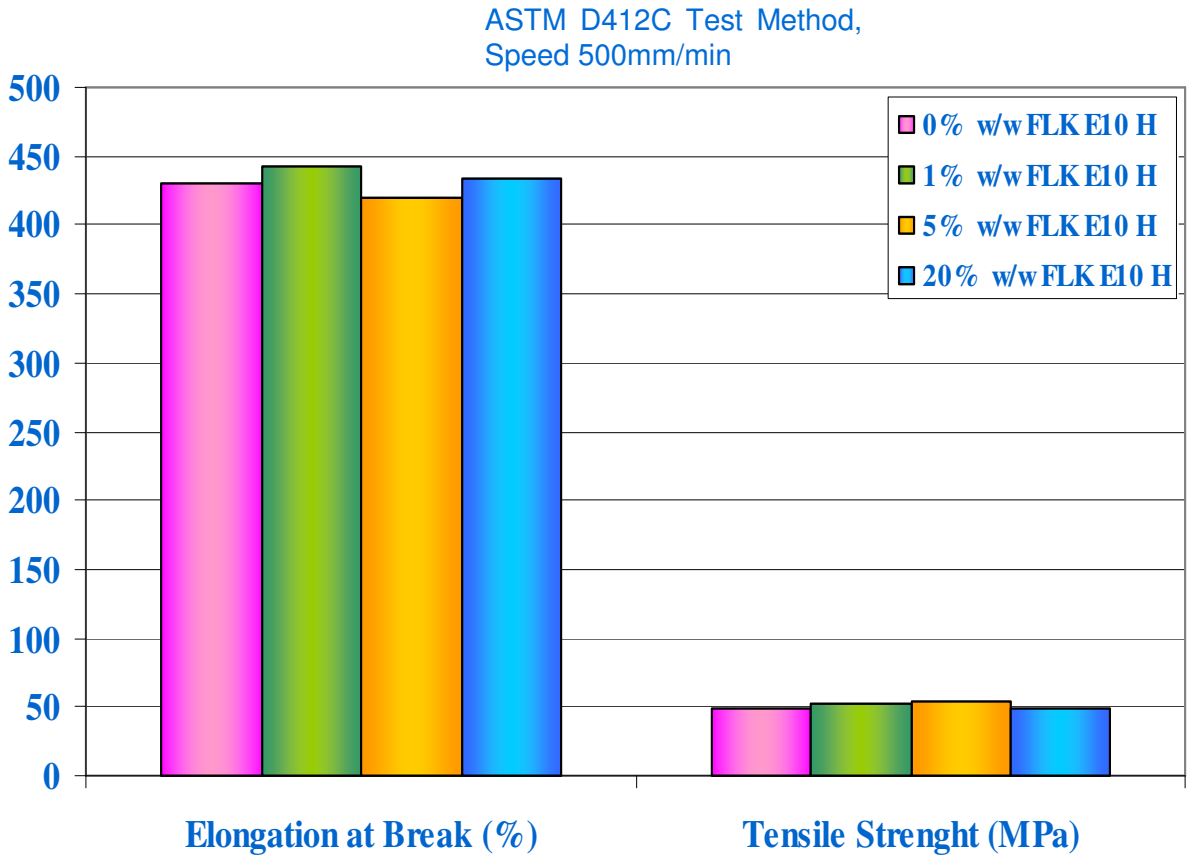
Fluorolink® E10H as a modifier for PUs
Mechanical Properties



A loading content of FLK E10H ≤ 20% w/w doesn't change the typical mechanical properties of Polyurethanes

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New PFPE-ethoxylated diol : Fluorolink E-series

$$H(OCH_2CH_2)_p\text{-}OCH_2CF_2O\text{-}[\text{-}(CF_2CF_2O)_m\text{-}(CF_2O)_n\text{-}]\text{-}CF_2CH_2O\text{-}(CH_2CH_2O)_pH$$

Ethylene oxide spacer

p > 4
(vs 1.5 for FLK E10H)

Ethylene oxide spacer

Characterization of "longer ethoxylated"	
Degree of Ethoxylation	4.6
Av. Molecular Weight (AMU)	1984
Av. Equivalent Weight (AMU)	1074
[H_2O] ppm	3052

n= 4.6 Typical Properties	
Solubility in organic solvents at 30% w/w	Ethyl Acetate: ✓ (soluble from 10% w/w) Toluene: ✗ THF: ✓ MEK: ✓
Solubility in H_2O (ppm)	1000
Viscosity (cSt)	349
Density (g/cm³ at 20°C)	1.60

E-series PFPE: competitive advantages

- Tunable degree of ethoxylation: from 4 to 8 or higher
- Higher compatibility with hydrogenated reactants (for ex. diisocyanates) and formulations
- Improved solubility into organic solvents (depending on the degree of ethoxylation)

Conclusions

- Fluorolink® E10-H and Fluorolink E-series are particularly effective as building blocks for the modification of PolyUrethanes
- Small amounts (0.5-2.0%w/w) improve the surface properties
- Higher amounts impart an exceptional chemical resistance to the modified PolyUrethane
- A three-stage process is recommended in order to minimize the phase segregation during the synthesis of the fluoro-modified PU

Polymer Modifiers: applications

- Modification of acrylic Hard-Coats
  - ✓ Anti-fingerprint
  - ✓ Stain/Soil release
- PU top-coats for Architectural Coatings
  - ✓ anti-graffiti
  - ✓ stain/soil release
- Modification of Epoxy paints
  - ✓ Improved chemical resistance
  - ✓ Reduced permeability to water
  - ✓ Low surface energy

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Solvent-based Surface Treatments: Fluorolink® S10

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Fluorolink® S10: structure and typical properties

$(EtO)_3Si\text{-}(CH_2)_3\text{-}NH\text{-}C(O)\text{-}CF_2O\text{-}[\text{-}(CF_2CF_2O)_m\text{-}(CF_2O)_n\text{-}]\text{-}CF_2\text{-}C(O)\text{-}NH\text{-}(CH_2)_3\text{-}Si(OEt)_3$

Typical properties	Value
Av. Molecular Weight (AMU)	1750 - 1950
Appearance	Clear Liquid
Color	Pale Yellow
Specific Gravity (20° C)	1.51 g/ml
Kinematic Viscosity (20° C)	173 cSt
Refractive Index (20° C)	1.349
Solubility (25° C)	
Water	Insoluble
Isopropyl alcohol	1% - 10% w/w

Fluorolink® S10: formulation and WOR

IPA-based formulation:

0.1% - 0.2% wt	Fluorolink® S10	
0.4% - 0.8% wt	Water	(4/1 wt ratio H_2O/Flk S10)
0.1% - 0.2% wt	HCl 10%	(1/1 wt ratio HCl/Flk S10)
99.4% - 98.8% wt	Isopropyl alcohol (IPA)	

Shelf life of this formulation: 2-3 days

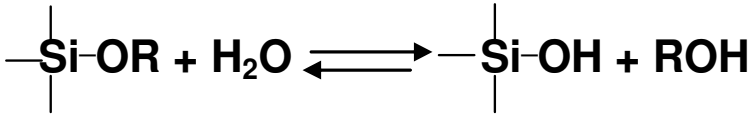
0.1% wt FLK S10 in IPA catalyzed by HCl

	Non treated Glass	Glass treated with FLK S10: 0.1% w/w
S.C.A. vs. Water	38 ± 5°	102 ± 3°
S.C.A. vs. Hexadecane	28 ± 7°	59 ± 3°

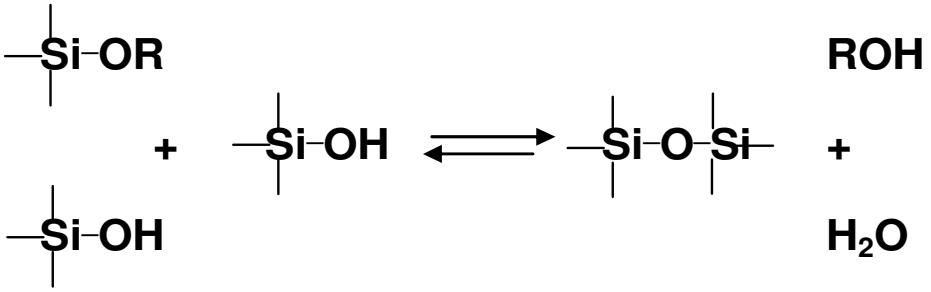
γ= 17 mN/m

Fluorolink® S10: curing mechanism

1) Hydrolysis:



2) Polycondensation:



- Dilute Fluorolink® S10 in IPA at 0.1-0.2% by wt., add H_2O and the acid catalyst. The solution could turn slightly cloudy, but this will not affect the final performance
- Wait for 30 minutes before applying (by roll, dipping or spraying) in order to allow the hydrolysis of the triethoxysilane groups
- The product has to be cured at T=100°C for 15 min + T=150°C for 15 min. Room temperature curing is also possible but this will lead to a much longer curing time

Fluorolink® S10: remarks

- Fluorolink® S10 is an effective superhydrophobic coating for glass, metals and siliceous surfaces in general
- Imparts an excellent W/O Repellency and easy removal of stains/fingerprints
- Displays a good weathering and chemical resistance
- Can be effectively used to modify the surface properties of Sol-Gel coatings

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UV-curable PerFluoroPolyEthers

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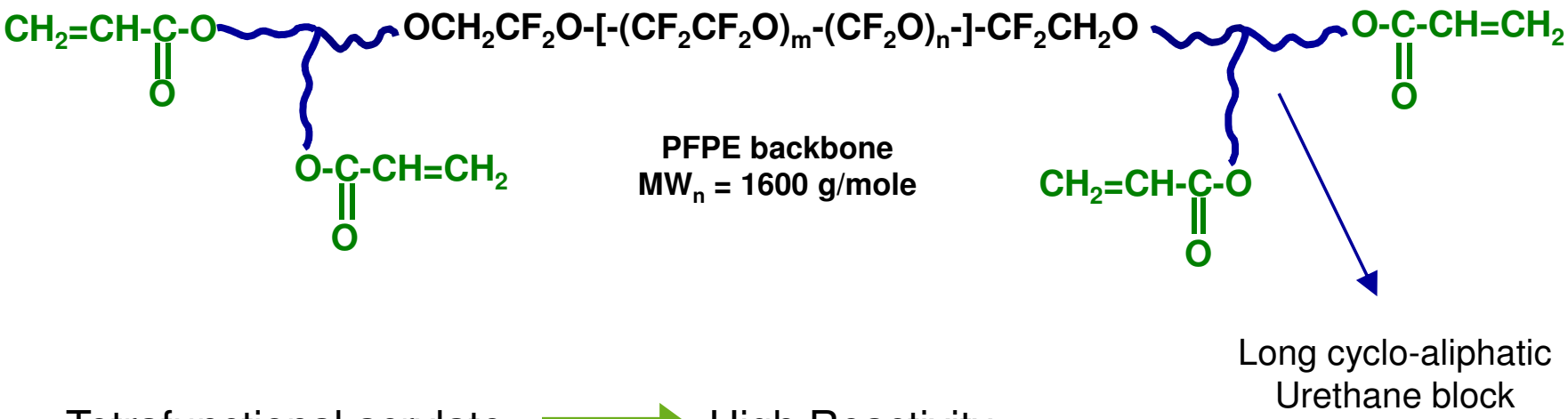
FLK AD1700: chemical-physical properties



- Tetrafunctional acrylate → High Reactivity
- [F] = 24 % (w/w)
- Soluble in AcOEt, MEK, BuOAc
- Good compatibility with commercial UV-curable paints
- Low surface energy additive for UV-curable paints: effective at 3-5% w/w in providing WOR, easy removal of stains and fingerprints

Formulation example

Composition (parts by weight)	Chemical-physical properties	Substrate	Pencil Hardness	MEK d.r.	Cross Cut Test
- Fluorolink® AD1700 50 - HDDA 15 - THFFA 50 - Darocur 1173 4 - Sartomer CN386 1 - Benzophenone 1	Thickness = 60 µm Visc.(25°C) = 65 cP % PFPE = 13.3 γ_c = 19.9 ± 0.2 mN/m	Aluminum Q-panels	H	> 200	100%

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

- Low surface energy and outstanding chemical resistance

- Self-Healing effect: the coating flows back into the scratch, returning the surface to its original smooth state (effect of the low T_g of the PFPE chain)

Fluorolink® AD1700 as a surface modifier

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

Test	Blank	1% w/w FLK AD1700	2% w/w FLK AD1700	5% w/w FLK AD1700
Static Contact Angle vs. H_2O (°)	**82 ± 5**	**103 ± 3**	**109 ± 3**	**113 ± 1**

Fluorolink® AD1700 improves the water repellency at a low dosage and shows good compatibility with commercial UV-curable formulations

Fluorolink® AD1700: applications

Low surface energy modifier for:

- ✓ UV-curable Hard-Coats for plastics
- ✓ UV-curable inks
- ✓ UV-curable clearcoats for car refinishes

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Waterborne Surface Treatments

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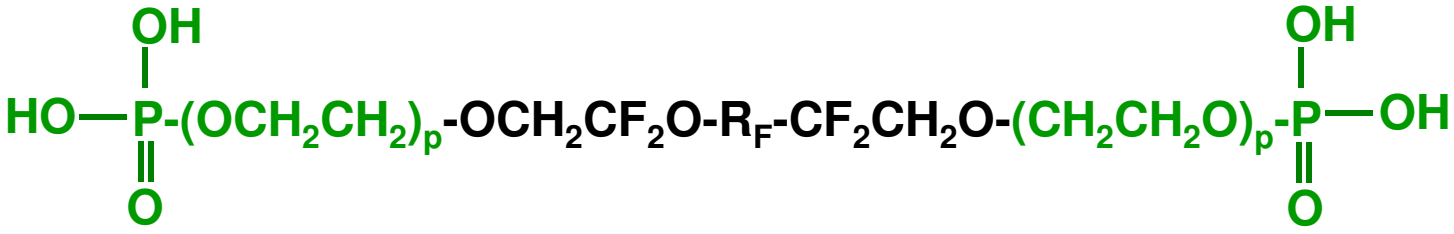
Fluorolink® P54 / TLS 5018

Phosphate Ester structure



Typical Properties	FLK P54	FLK TLS 5018
Functional Groups	Phosphate ester Ammonium salt	Phosphate ester Ammonium salt
Dry content	20% wt.	10% wt.
Solvent content	< 10% w/w (DPM, dipropylene glycol methyl ether)	33% wt. (IPA)
Viscosity (20°C)	< 100 Mpa*s	< 300 mPa*s
pH (20°C)	7-8	7-8
Flash point	none	23°C

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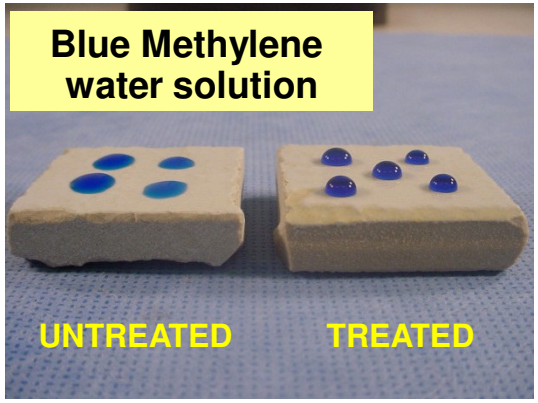
Gres Porcellanato polished
FLK TLS 5018 Treatment

Static Contact Angle (DSA Krüss)
(T=25°C ; θ±4°)

	θ_{water}	$\theta_{n\text{-}C16}$
Untreated	62	20
Treated	93	65



Surface Energy (mN/m) – Fowkes-

	γ total
Untreated	42.1
Treated	17.9

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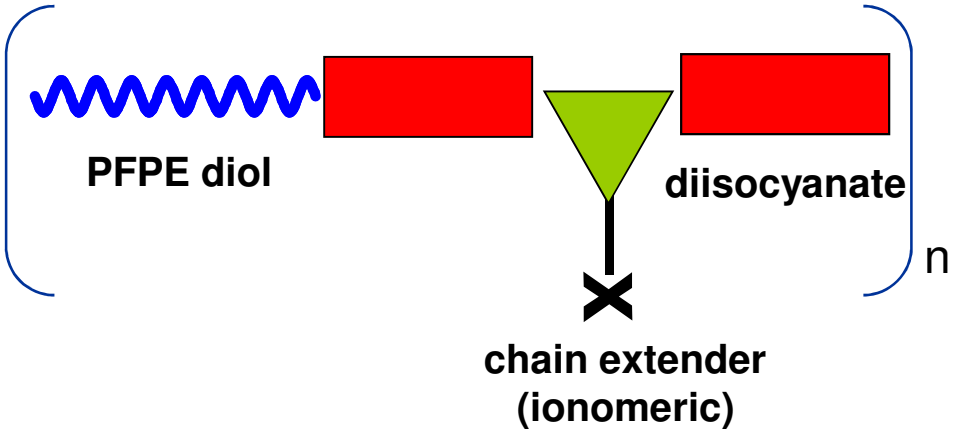
Fluorolink® P56: structure and properties

FLK P56 X = —COO^- NR_3H^+



Typical Properties	Fluorolink® P56
Functional Groups	Carboxylate TEA salt
Appearance	Amber dispersion
Dry content	25% wt.
Solvent content	< 2% wt.
Density (20°C)	1.1 g/cm^3
pH (20°C)	7-9
Viscosity (20°C)	< 300 mPa*s

Low Temperature Curing – Typical formulation

Typical formulation

✓ Fluorolink® P56	(25% solids)	1000,0 g
✓ Dynasylan Glymo*	Epoxysilane	25,5 g
✓ Imicure Emi-24**	(5%wt water solution)	2,5 g

** Degussa: 3-Glycidyloxypropyltrimethoxysilane* — *Crosslinker*

*** Imicure EMI-24 Curing Agent from Air Products and Chemicals* — *Catalyst*

Preparation

Add the crosslinker to FLK P56 and stir for a few minutes. Before applying the coating add the catalyst and stir to obtain an homogeneous solution.

Formulation characteristics

Viscosity:	25 – 100 cPs
Density (20°C)	1,101 g/l
Solids content (total)	26 – 27%
pH	7.5 - 8.5
Appearance	Light hazy

Dry time (24°C, 50% RH)

Film thickness: 25 – 35 µm

Tack free time: 2.0 - 2.5 hours

Curing condition

Room temperature: > 4 days

Oven: 80°C for 30 minutes

Fluorolink® P56

Low Temperature Curing – Film Characteristics

Substrate	Film thickness	MEK double rubs	Pencils Hardness	Adhesion cross cut %	θ water (°)	θ Hexadecane (°)
Glass	35 µm	> 200	3B	100	106	65
Al-QPanels	35 µm	> 200	3B	100	109	66

Fluorolink® P56

Low Temperature Curing – Film Characteristics

Chemical Resistance

(Spot Test)

		Glass		Al - QPanel	
		25 µm	35 µm	25 µm	35 µm
30'	Methanol	+	+	+	-
	Toluene	-	-	-	-
	Ethanol	+ +	+ +	+ +	+ +
	Acetone	+	+	-	-
	MEK	+ +	+ +	+ +	+ +
	Etylacetate	+	+	+ +	+
	Butylacetate	-	-	-	-
24h	HCl 10%	-	-	-	-
	H_2SO_4 5%	-	-	-	-
	NaOH 5%	+ + +	+ + +	+ + +	+ +

Rating :

–	No effect
+	Very light shadow
+ +	Light shadow
+ + +	Film surface lightly damaged
+ + + +	Film surface strongly damaged
+ + + + +	Film destroyed

High Temperature Curing – Typical formulation

Typical formulation

✓ Fluorolink® P56 (25% solids)		1000,0 g
✓ Cymel 303*	Melamines	12,5 g
✓ p-Toluene sulfonic acid triethylammonium salt**	(5%wt water solution)	2,5 g

* *pre-dilute with 1:1 with IPA before adding*

** *reaction catalyst*

Preparation

Adding the crosslinker and the catalyst to FLK P56, then stir for a few minutes to obtain a homogeneous solution.

Formulation characteristics

Viscosity:	50 – 100 cPs
Density (20°C)	1,105 g/l
Solids content (total)	26 – 27%
pH	8.0 - 8.5
Appearance	Light hazy

Dry time (24°C, 50% RH)

Film thickness: 25 – 35 µm

Tack free time : 2.0 - 2.5 hours

Curing condition

Room temperature: > 4 days

Oven: 180°C for 10 minutes

The formulation at room temperature has a good stability if the pH > 8

High Temperature Curing – Film Characteristics

Substrate	Film thickness	MEK double rubs	Pencils Hardness	Adhesion cross cut %	θ water (°)	θ Hexadecane (°)
Glass	20 µm	160	2B	100	107	65
Al-QPanels	20 µm	170	2B	100	106	65

High Temperature Curing – Film Characteristics

Chemical Resistance
(Spot Test)

		Glass	Al - QPanel
		20 µm	20 µm
30’	Methanol	+	+
	Toluene	-	-
	Ethanol	+ +	+ +
	Acetone	-	-
	MEK	+ +	+ +
	Etylacetate	+	+
	Butylacetate	-	-
24h	HCl 10%	-	-
	H_2SO_4 5%	-	-
	NaOH 5%	-	-

Rating :

–	No effect
+	Very light shadow
+ +	Light shadow
+ + +	Film surface lightly damaged
+ + + +	Film surface strongly damaged
+ + + + +	Film destroyed

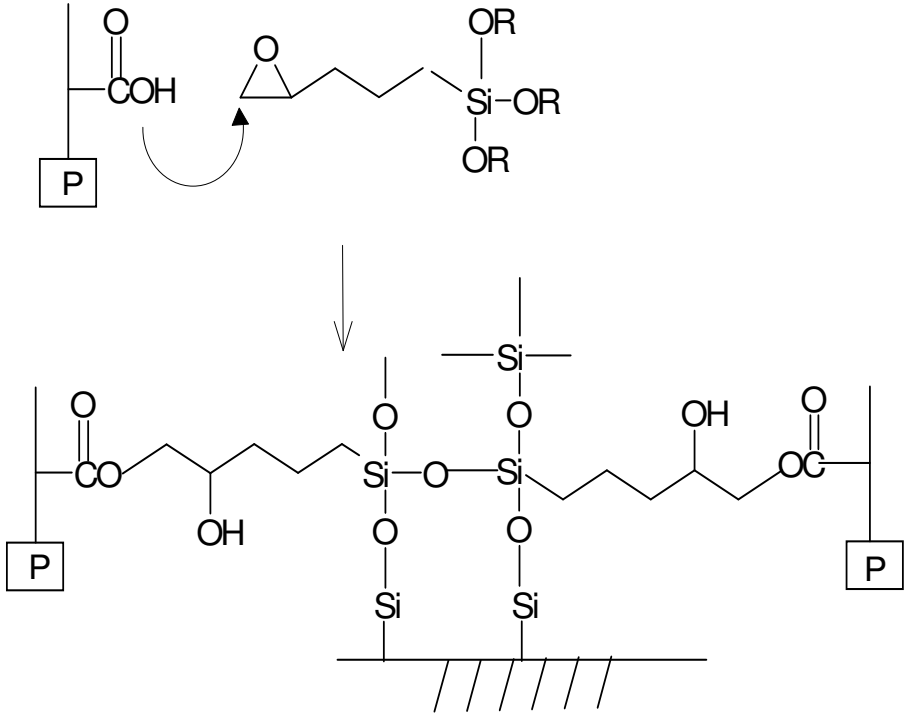
Fluorolink® P56: concluding remarks

- Clear: can be applied on any surface including painted ones
- Gas Permeable Paint: the vapor generated will permeate through
- Low VOC content
- Good Adhesion properties on several substrates
- Excellent WOR
- Non sacrificial anti-stain and anti-graffiti coating: lasts for several cleaning cycles

Low Temp. Curing - Crosslinking mechanism

Low temperature curing

Epoxy silane (es: Dynasylan Glymo®)



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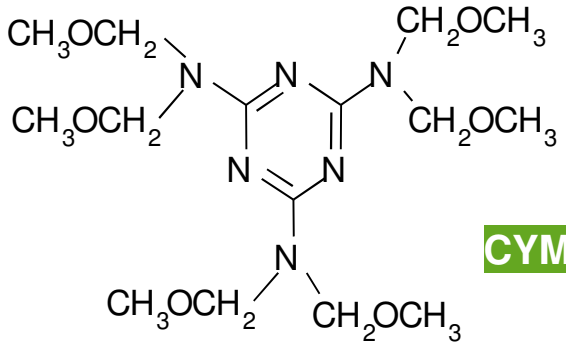
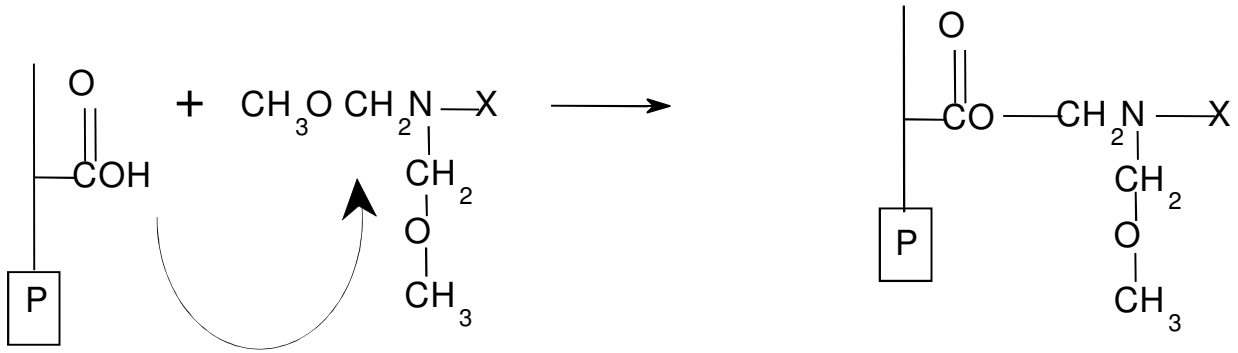
High Temperature Curing - mechanism



CYMEL 303

The crosslinking reaction of Cymel® 303 is catalyzed by a strong acid (pKa < 1)



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