

3M Advanced Materials Division

3M™ Fluorochemical Surfactants for Paints, Coatings and Adhesives





3M Fluorosurfactants

- Specialty Chemicals Paints and Coatings Business
- Technical Overview
 - Surfactant basic principles
 - EHS&R (& degradation products)
- 3M Product portfolio
 - Products
 - Applications Fluorosurfactants
 - Formulation tips for 3M™ Fluorosurfactants





Surfactant Basics

Surfactant are “Surface Active Agent”

- Surfactants are ***amphiphilic***
 - Typically have a hydrophobe (lyophobic) and a hydrophile (lyophilic) segment
- => Normally associated with being able to reduce the surface tension of a solution to improve wetting and leveling, and to reduce the coating defects

Surface Tension Reduction Potential of Surfactants

- *Surfactant chemistry:* Fluorocarbons > Silicones > Hydrocarbons

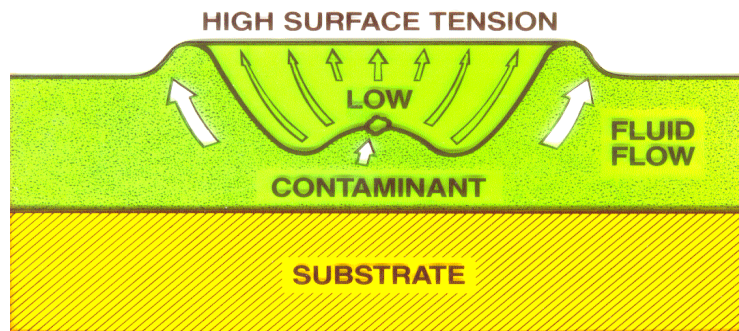
Ionicity

- *Surfactant types:* Nonionic, anionic, cationic, amphoteric, Polymeric, small molecules





Common Coating Defects: Poor Wetting can result in pinholes and cratering (fish eyes)



Pinholes



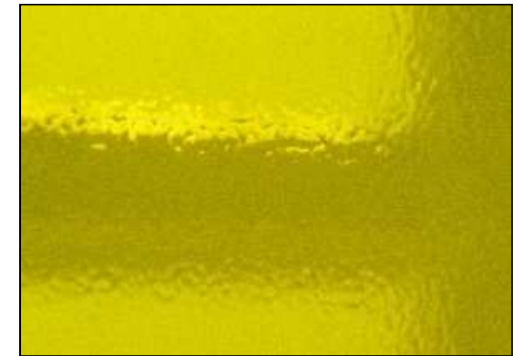
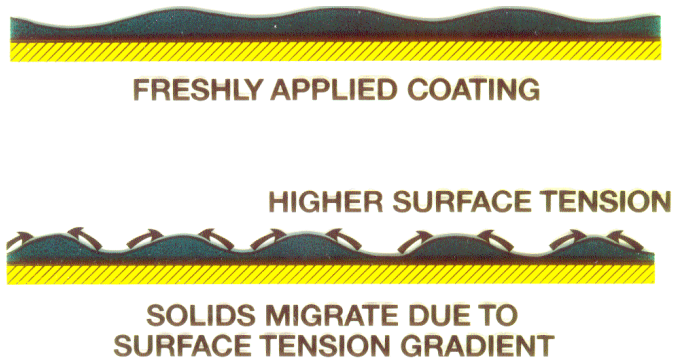
Cratering





Common Coating Defects: Poor Leveling can result in orange peel and picture framing

Poor Leveling



Orange peel due to uneven evaporation of solvent (left picture)

Picture Framing (right picture)





Typical Surfactant Characteristics and Performance

- Surface Tension Reduction
- Flow and Leveling agent
- Wetting agent
- Dirt Pick up & Stain Resistant
- Help in low VOC formulation
- Gloss Enhancer
- Pigment Dispersant
- Emulsifier
- Slip Aid
- Adhesion Promoter
- Rheology Modifier
- Foam or Anti Foam



3M products perform this function well



3M products don't perform this function



3M products may perform this function but needs more data





Fluorochemical Surfactants Basics

All liquids and solids have a surface energy value. Surface energy is the molecular force of attraction that holds a material together.

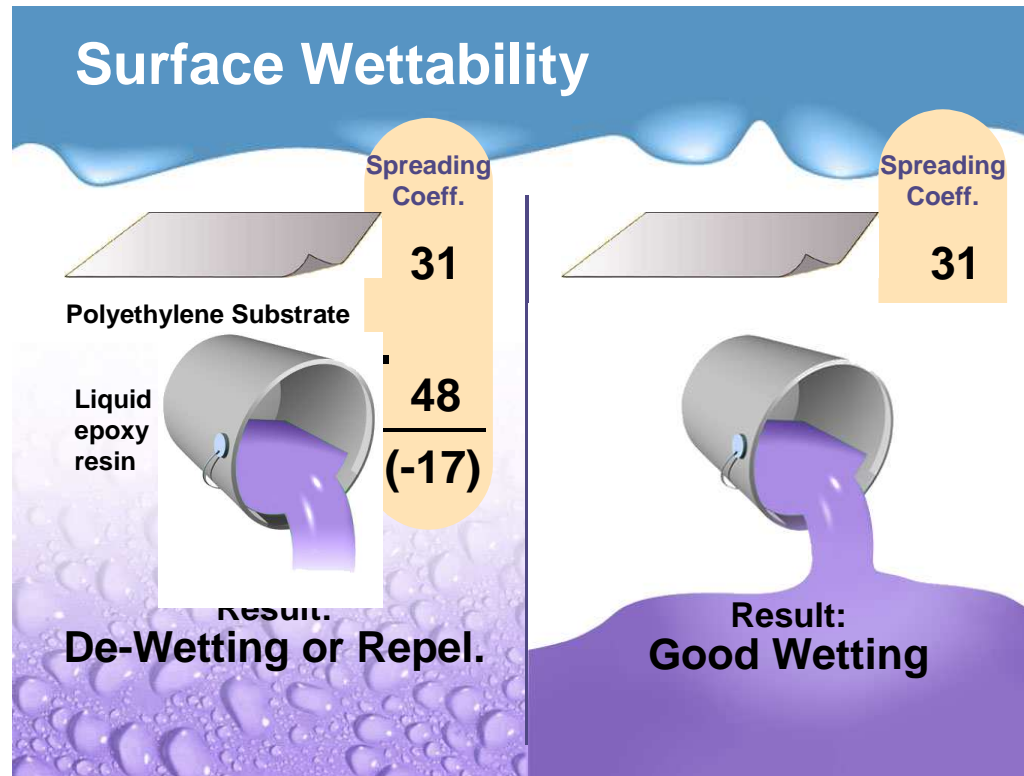
In order to wet out a solid surface, the surface energy of the liquid must be LOWER than the surface energy of the solid.

Spreading Coefficient S.C. = $\gamma_{\text{Solid}} - \gamma_{\text{Liquid}} - \gamma_{\text{L/S}}$	
Surface Energy Values γ_{Solid} for Various substrates	
LIQUIDS	Dyne/cm (mN/m)
Water	73
Lube Oil	29
Silicone	20
RESINS	
Liquid Epoxy	48
Liquid Polyester	35
Alkyd	25
Polydimethyl Siloxane	20
SOLIDS	
Phosphated Steel	43-56
Aluminum	37-45
Polyester	43
Polystyrene	33
Polyethylene	31
Polytetrafluoroethylene	18



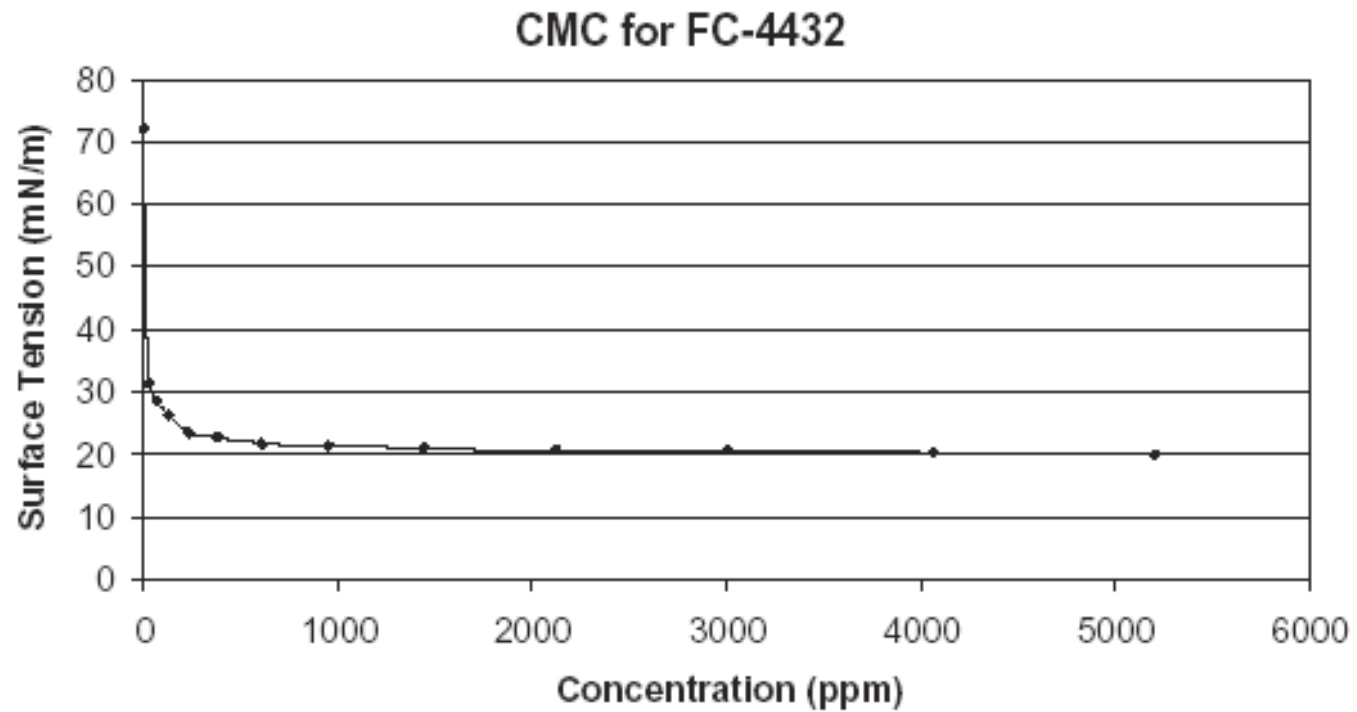


Fluorochemical Surfactants Basics





Efficiency: FC-4430, FC-4432, FC-4434 in water





3M Fluorochemical Surfactants – EHS&R

- Residuals are present at very low levels in product and are expected to degrade to perfluorobutane sulfonate (PFBS)
- The ultimate degradation product, perfluorobutane sulfonate, has low* mammalian toxicity, low* ecotoxicity, low* bioaccumulation potential
- The FC-4430 family is based on polymeric chemistry, which is lower in inhalation toxicity (Capstone® FS-61 and 63 show 4h ALC acute inhalation of 0.047 mg/L rat, thus are restricted in spraying applications)
- The dermal LC50 for FC-4430 is >2000 mg/kg/day, the acute oral LC50 for FC-4430 is >2000 mg/kg/day

*Low as defined by US and European regulations





3M Fluorochemical Surfactants – EHS&R

- All AdMD Fluorochemical Surfactants and Stain Release Additive products are based on perfluorobutane sulfonate, or C4.
 - FC-4430, FC-4432, FC-4434, SRC-220
 - Note: 3M AdMD's "ECC" line of products (e.g. ECC-1000) are made from different fluorine technology not addressed here.
- The ultimate degradation product for 3M C4 based fluorosurfactants is perfluorobutane sulfonate (C4 or PFBS). PFBS has low* mammalian toxicity, low* ecotoxicity, low* bioaccumulation potential, but is persistent in the environment**.

*Low as defined by US and European regulations

**Details available from AdMD EHS&R Group; Paul Loudas 651





Application 3M Fluorosurfactants

- 3M™ non-ionic Polymeric Fluorosurfactants:
FC-4430, FC-4432, FC-4434
- Polymeric Fluorosurfactants (non-ionic)
- General Purpose of these Surfactants
 - Flow/leveling/wetting agent for water borne, solvent borne, high solids, and radiation curable coatings
 - Provides low dynamic surface tensions in aqueous formulations
 - Provides low interfacial surface tensions

Primarily for water and solvent-based paints and coatings, adhesives and soldering flux





Industrial Paints and Coatings

End-Use Market Segments

- *Automotive Paints*
- *Furniture Coatings*
- *General Metal Coatings*
- *Permanent Floor Coatings*
- *(>One year)*
- *Adhesives*
- *Plastic coatings*
- *Inks*





Major Benefits of Fluorosurfactants in Paints & Coatings

- Reduce the surface tension of the paints and coatings
- Providing excellent wetting and leveling, especially on the difficult to wet surfaces
- Reduce coating defects
- [Help reduce dirt pick up and stain resistance](#)
- Allows to formulate into low VOC paints





3M Fluorosurfactants Applications

- Challenging substrates and environments
 - Plastic surfaces have a low surface energy which requires a high performance wetting agent
 - Wood might be difficult to coat due to the presence of rosins (sap) on the surface
 - Metal contaminated with oil/silicones will not coat effectively without a low surface energy coating
- High end coatings where performance and aesthetics are critical
 - Automotive Paints, Furniture Coatings, Electronic Coatings, General Metal Coatings, Permanent Floor Coatings, Adhesives, Plastic coatings , Inks





Interfacial Surface Tensions

Surfactant	Interfacial Tension* Light Phase: Heptane			Interfacial Tension* Light Phase: Cyclohexane		
	200 ppm	0.5%	1.0%	200 ppm	0.5%	1.0%
Control		43.7			51.2	
FC-4430	3.5	2.2		2.5	1.5	
FC-4432	4.2	2.6		4.2	2.1	
SDS ¹	15.4	6.1	5.8	12.9	5.0	4.9
DDBS ²	15.9	4.1	3.7	13.5	2.9	2.6
Silicone Dispersant	14.4	10.9	10.5	11.7	8.8	8.8

¹ Sodium dodecyl sulfate

² Sodium dodecyl benzene sulfonate

* Interfacial surface tensions reported in dynes/cm





Formulation

Surfactant Solids Based on Total Solution / Formulation

- ♦ Aqueous Media
 - Normal Range 100-1000 ppm (0.01-0.1%)
 - Start 200 ppm (0.02%)

- ♦ Water Reducible (emulsion and/or dispersion)
 - Normal Range 500-3000 ppm (0.05-0.3%)
 - Start 1000 ppm (0.1%)

- ♦ Organic Media
 - Normal Range 1000-5000 ppm (0.1-0.5%)
 - Start 2500 ppm (0.25%)





How to Add 3M Fluorochemical Surfactant

- ◆ **Aqueous System**
 - Add FC-4430 or FC-4432 as dilute solution (10-50%) in water/co-solvent for easy handle
 - **Solution Preparation**
 - 1) Weigh 3M surfactant into container
 - 2) Add co-solvent (such as DPM) to make 20 – 50% solution – mix well
 - 3) Dilute with water further or directly added to the formulation to the final required concentration (0.05 – 0.3%)

- ◆ **Organic System**
 - Add 3M surfactant as dilute solution (10-50%) in solvent or monomer
 - **Solution Preparation**
 - 1) Weigh surfactant into container
 - 2) Dilute with appropriate solvent (such as DPM, esters, alcohols etc) or monomer to 10 – 50%
 - 3) Add the dilute solution to the final formulation

MIX WELL





FC-4430/FC-4432 Applications in Adhesive

- **Type of Adhesives**
 - Automotive Adhesives
 - Aerospace / Aircraft adhesives
 - UV adhesives
- **Major Benefits**
 - Wetting agent, especially for difficult to wet surface
- **FC-4430/FC-4432 Additive Level**
 - 0.2 – 0.5% in formulation





FC-4430 in Soldering Flux Application

- Excellent in reducing surface tension
- Fluorochemical bond – Very stable, high thermal stability $> 200^{\circ}\text{C}$, ideal for lead-free solder
- Nonionic surfactant which reduces potential reaction and no ion migration, great surface property in solvent, surface tension ~ 20 dynes/cm in solvent
- Excellent viscosity range
- Does not change the pH of flux



Major customers in China, India and Brazil





Surfactant Efficiencies

	3M Fluorochemical	Silicone	Hydrocarbon
Effectiveness (dynes/cm)	≤ 20	20-25	>25
Efficiency (use level, wt. %)	0.01-0.30	0.10-0.50	0.50-5.0
Effectiveness in: Aqueous	Good	Good	Good
Non-Aqueous	Good	Medium	Poor
Relative Purchase Price	About 50-100	About 10-50	1
Relative Cost per Use	1-2	1-2	1





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