Alkylphenol Ethoxylates and Replacement Surfactants

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Alkylphenol Ethoxylates

• Versatile, cost effective surfactants
• Used in a wide variety of applications
• Historically, >1,000,000,000 used annually worldwide
Nonylphenol ethoxylates structure
Surface Active Properties

- Wetting – For hard and “soft” surfaces
- Detergency – hard surface cleaners, industrial laundry, degreasers
- Emulsification – From oil emulsification to emulsifiers for emulsion polymerization
- Dispersing, solubilizing, stabilizing, compatabibling
Applications

• Agricultural chemicals
• Emulsion polymerization
• Fragrance emulsification
• I & I cleaners/dgreasers
• Metals processing
• Paints & coatings
• Paper
• Textiles
Alkylphenol Ethoxylate Concerns

- Biodegradability
- Toxicity of degradation products
- Bioaccumulation
- Endocrine disruptor
Biodegradability

• “Based on stringent OECD test guidelines, this material cannot be considered as readily biodegradable; however, these results do not necessarily mean that the material is not biodegradable under environmental conditions.” From The Dow Chemical Company MSDS for Tergitol™ NP-9 Surfactant
OECD Readily Biodegradable

- 60% minimum biodegraded within 28 days
- Meets 10 day window – once 10% degraded, must reach 60% within 10 days
- Published results for NP-9 vary from 16 - >50% biodegraded in 28 days. Will not meet 10 day window
Common Environmental Metabolites of Nonylphenol Ethoxylates (Adapted from Ahel et al., 1994; Naylor, 1992)

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\text{NP ethoxylate} \quad n = 1 \text{ to } 100; \text{ avg. } = 9-17
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\begin{align*}
\text{NP1EO} & \quad \text{C}_9\text{H}_{19}-\text{OCH}_2\text{CH}_2\text{OH} \\
\text{NP2EO} & \quad \text{C}_9\text{H}_{19}-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \\
\text{NP1EC} & \quad \text{C}_9\text{H}_{19}-\text{OCH}_2\text{COOH} \\
\text{NP2EC} & \quad \text{C}_9\text{H}_{19}-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{COOH} \\
\text{NP} & \quad \text{C}_9\text{H}_{19}-\text{OH}
\end{align*}
\]
Aquatic toxicity

- Daphnia magna (48 hours) - mg/L
  - NP – 0.035 (EC50)
  - NP-4 – 4.9-5.7 (LC50) 1.6-10 (EC50)
  - NP-9 – 9.3-21.4 (LC50)
  - NP-15 – 23.1-71.8 (LC50)
Bioaccumulation

- Low mole APEO’s are not water soluble
- Readily adsorbed onto surfaces
- Can lead to accumulation in sludge at treatment plants and sediment in waterways
- Can lead to accumulation in aquatic species
Endocrine disruptors

- Chemicals that interfere with endocrine (hormone) systems in animals
- Can cause cancerous tumors, birth defects and developmental disorders
Structure of 4-nonylphenol and 17β-Oestradiol
Relative potencies on rainbow trout (Jobling and Sumpter, 1993)

- 17β-Oestradiol: 1
- 4-nonylphenol: 0.000009
- NP2EO: 0.000006
- NP9EO: 0.0000002
- NP1EC: 0.0000063
Current restrictions of APE use

• European Parliament approved market and use restrictions on 7/17/2003. Cannot be used at 0.1% or greater in a wide variety of applications.

• EC regulation NO. 648/2004 requires the use of biodegradable surfactants unless special allowances are made.
Current restrictions of APE use

• In 2001, Canada issued an environmental quality guideline for nonyl phenol and its ethoxylates. The EQG in fresh water is 1µg/L.
• Proposed regulations to reduce the use of NP/NPEO’s used in cleaning products, textile wet processing, and pulp and paper production by 95% by the end of 2010.
Current restrictions of APE use

• US EPA (2004) recommended an acute ambient Water Quality Criteria for NP of 27.9µg/L and a chronic WQC of 5.9µg/L
• Green product certification programs specifically ban the use of APE’s
• Local municipalities have restricted discharge of APE’s to POTW
• Many industrial sites with treatment facilities have banned APE use in their facility
Proposed California Amendments

- Would prohibit the use of Alkylphenol Ethoxylate Surfactants in –
  - General purpose cleaners (nonaerosol)
  - General purpose degreasers (nonaerosol)
  - Glass Cleaners (nonaerosol)
  - Heavy-duty hand cleaners or soaps (nonaerosol)
  - Oven or grill cleaners
APE Replacement Surfactants

- Based on linear alcohol ethoxylates
- Readily biodegradable
- No persistent aquatic toxicity
- Approved for use in third party certified green products
- No known use restrictions
APE Replacement Surfactants

- Wetting – Typically faster wetting than APE’s. Better dynamic properties give better performance in applications with short contact times
- Detergency – Better low temperature detergency than APE’s. Normally not as good as APE’s at higher temperatures (>60°C)
- Cold water solubility – readily soluble with no gelling
APE Replacement Surfactants

• Emulsification/solubilizing – In most cases, APE’s give better emulsification and are more effective solubilizers

• Cost – APE replacement surfactants are more expensive than APE’s
CONCLUSIONS

• Replacement of APE’s has been driven by restrictions on the use of APE’s
• Suitable replacements are available
• Costs of the replacement surfactants are higher