

Alkylphenol Ethoxylates and Replacement Surfactants

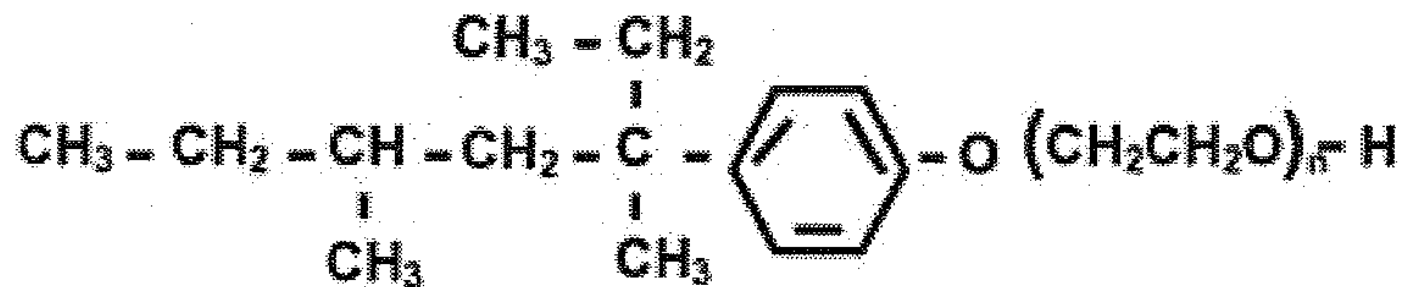
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Alkylphenol Ethoxylates

- 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, compatibilizing

Applications

- Agricultural chemicals
- Emulsion polymerization
- Fragrance emulsification
- I & I cleaners/degreasers
- Metals processing
- Paints & coatings
- Paper
- Textiles

Alkylphenol Ethoxylate Concerns

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

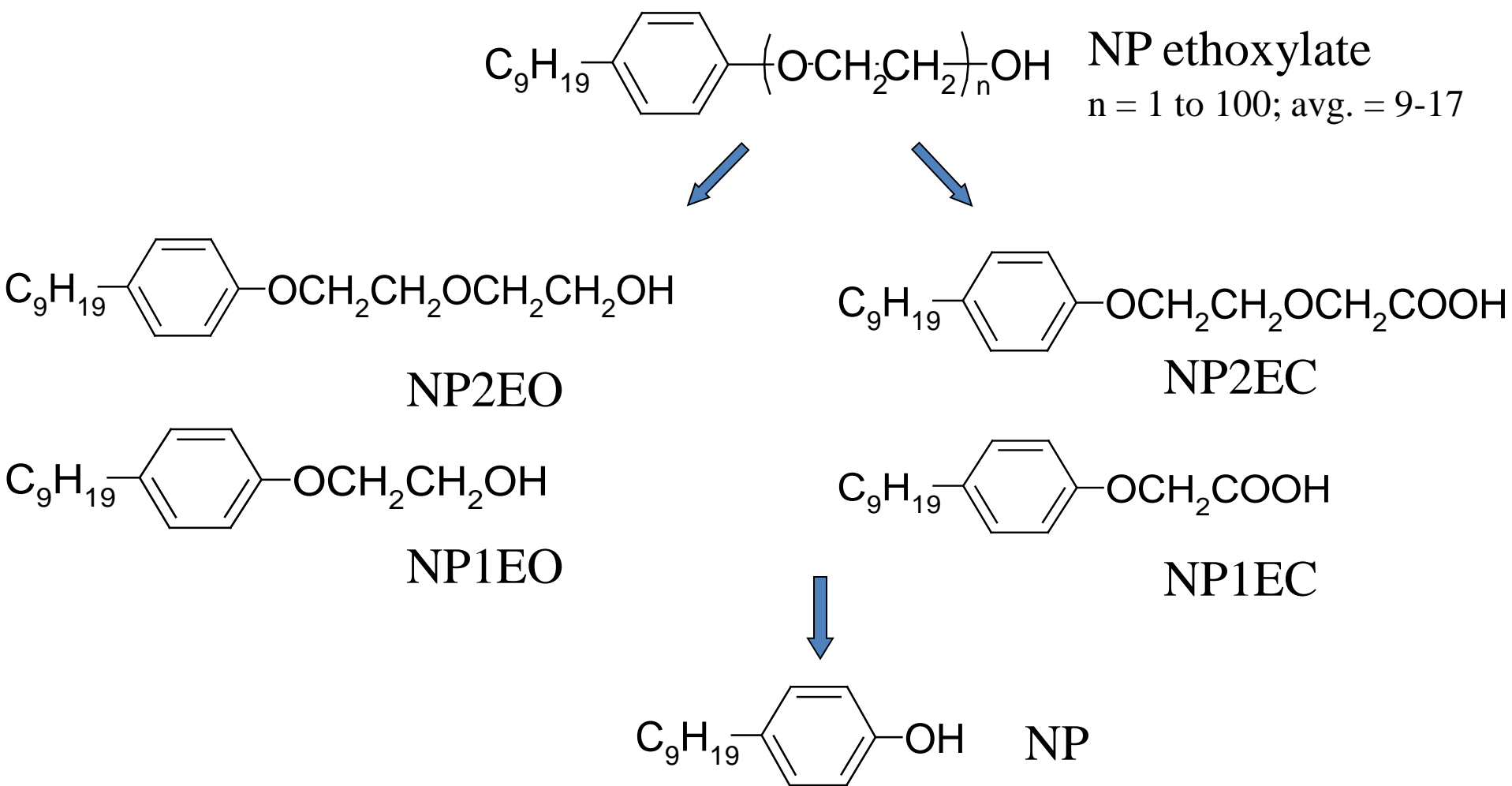
Biodegradability

- “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 TM 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)



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)

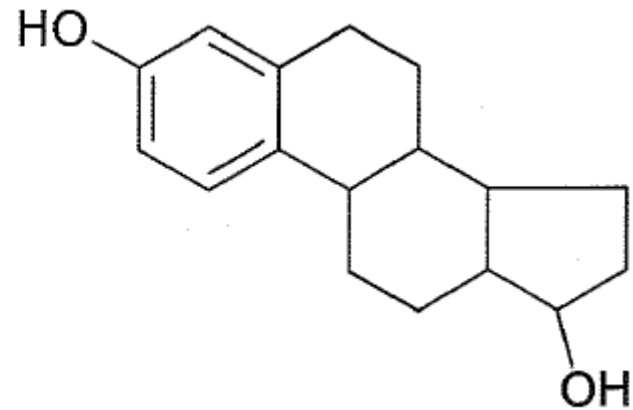
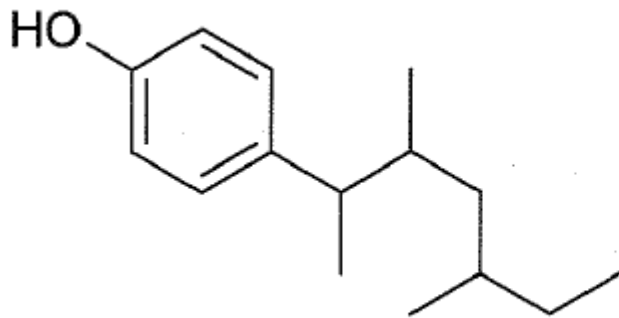
Bioaccumulation

- 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 17 β -Oestradiol



Relative potencies on rainbow trout (Jobling and Sumpter, 1993)

• 17 β -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 $1\mu\text{g/L}$.
- 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 $27.9\mu\text{g/L}$ and a chronic WQC of $5.9\mu\text{g/L}$
- 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 ($>60^{\circ}\text{C}$)
- 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 solublizers
- 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