

The Future of Metal Cleaning in North America

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Introduction

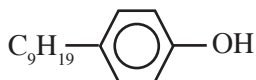
By now, everyone is aware of legislation limiting the use of certain hazardous ingredients in automotive and electronic consumer goods. Acronyms such as ROHS, WEEE, ELV and PEL have all become part of our daily language in the metal finishing industry. Not nearly as many people, however, are as familiar with the equally important directive 76/769/EC passed by the European Union in 2003.

Nonylphenol (NP) and nonylphenol ethoxylates (NPE) are organic chemicals produced in large quantities in the United States. They are used as detergents and emulsifiers in many common products such as laundry detergent, dish soap as well as many proprietary blends used in metal finishing. Because of nonylphenol's chemical environmental persistence and widespread use as a chemical intermediate, concerns have been raised over the potential risks posed to aquatic life.

Following a risk assessment of organic surfactants, the European Union, passed amendment 76/769/EC that states that NP and NPE type surfactants "may not be placed on the market or used as a substance or constituent of preparations in concentrations equal or higher than 0.1% by mass." This legislation essentially outlawed the use of some of the most common surfactants used in metal cleaning today. Similar legislation is currently in place in Canada, and will likely affect the United States in the near future.

This paper discusses the common uses of NP and NPE, particularly as they relate to the metal finishing industry. It will review what dangers they present to the environment as well as how this legislation came about. Lastly, I will discuss what alternatives are available for metal finishers to meet these new regulations while still offering the same performance and cost savings.

NP and NPE type surfactants and the environment



4-nonylphenol (NP)



R = C₂H₅, nonylphenol ethoxylates (NPE)

Surfactants constitute an important group of products in the global chemical industry with their wide variety of applications within industry and household consumer goods. Often considered a relatively innocuous component of cleaners, many of the surfactant products commonly used are facing issues related to new legislation and environmental pressures. One common surfactant family

that has come under close scrutiny is nonylphenols (NPs) and nonylphenol ethoxylates (NPEs).

A nonylphenol is an organic chemical used as an intermediate in the production of nonionic surfactants. Nonionic surfactants are chemically stable, and highly versatile, surfactants used in a large number of industrial products such as acid and alkaline metal cleaning formulations, wetting agents, and as emulsifiers or co-emulsifiers. They are also used as dispersants, solubilizers, coupling agents and rewetting agents in a variety of applications.

In the early and the mid-1990s, scientists began to raise concerns regarding the environmental persistence of NP-related compounds,¹⁻³ as well as their toxicity. Studies show that while the ethoxylate portion of the surfactant breaks down quickly, the parent NP is left behind. As a consequence, nonylphenol has been found in sediments,^{4,5} and there has been concern that NP could accumulate to levels which harm the environment.

The main concern with these ingredients is not for human health but rather for aquatic life. Male fish have been shown to become feminized when exposed to NP, as well as when exposed to sewage effluent, which also contains other more potent endocrine disrupting substances. NP acts like the hormone estrogen, causing male fish to produce a protein needed for egg production normally only found in female fish. If exposure is high enough, it can interfere with reproduction.

Regulatory actions

As a result of these issues, regulatory agencies in Europe, the US, Canada, and Japan have been closely reviewing the environmental safety of both NP and NPE's.

In Europe, under Council Regulation (EEC) 793/93 of 23 March 1993, a risk assessment of NP and NPE to the health and environment was performed. This study identified a need for reducing the risks from NP and NPE to the environment. In its opinion of 6/7 March 2001, the European Commission Scientific Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) confirmed the conclusions of the assessment and the need to reduce risks to the environment.

Legislative action began shortly after with the European Union passing an amendment to directive 76/769/EC to include restrictions on the marketing and use of NP and NPEs.⁶ The directive states that NP and NPE "may not be placed on the market or used as a substance or constituent of preparations in concentrations equal or higher than 0.1% by mass."

This directive, which was implemented into national law in January 2005, effected most industrial applications including proprietary formulations commonly used in the metal finishing industry. Platers throughout Europe were forced to discontinue immediately use of any NP or NPE-containing materials and replace them with environmentally acceptable alternatives.

Norway imposed even more comprehensive restrictions that included all nonylphenols, octylphenols and their ethoxylate derivatives. Effective January 1, 2002, Norway banned the import, export, sale and use of these substances and preparations contain-

ing them, except in paints, varnishes and lubricating oils, or for research purposes. The regulations, however, do not apply to solid articles made with these substances.

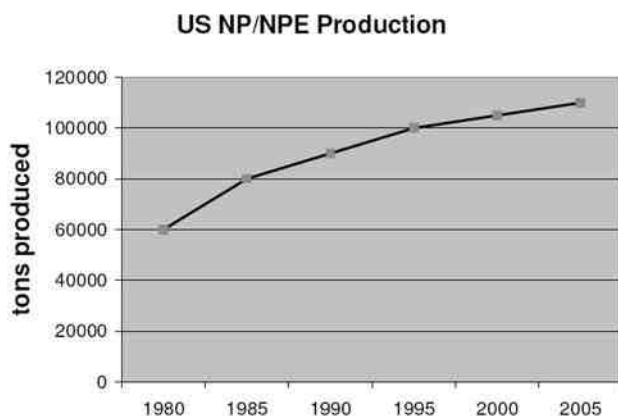
In Canada, a technical and socio-economic report found the cleaning products sector was responsible for 60% of the total Canadian NP/NPE market, and that end-users of these products were responsible for 75% of total NP/NPE releases to the Canadian environment. Areas of concern include all industrial and institutional cleaning applications except systems with special treatment where the washing liquid is recycled or incinerated.

To achieve ambient concentrations in Canadian waters that do not exceed Canadian Environmental Quality Guidelines the Ministers of the Environment and Health recommended that NP and NPE surfactants be added to the list of Toxic Substances. Under the Canadian Environmental Protection Act, nonylphenols and ethoxylates were declared "CEPA Toxic" primarily because they were found in wastewater treatment effluent and outfalls at levels of concern.⁷

In the U.S., the EPA has established new water quality criteria that limit the volumes or amounts of NP discharged into the environment,⁸ and is encouraging reduced use through the Safer Detergents Stewardship Initiative (SDSI).⁹

Commercial outlook

According to some of the surfactant manufacturers in the U.S., the EU's assessment of nonylphenol in Europe is based on more conservative assumptions than the assessments conducted by the U.S. Environmental Protection Agency and Environment Canada. This is because many studies in the North American region claim that levels of the key breakdown product, nonylphenol, do not exceed 1 µg/L in North American rivers. On the other hand, studies in the European region have measured levels up to 45 µg/L in Swiss rivers. Examples include some of the studies which document that APE levels in the river Aire were reported to reach up to 330 µg/L.



Over the past year, the environmental impact of consumer products has gone from being a fringe issue raised mainly by activist groups to a mainstream concern confronted by corporate America. Companies such as Procter & Gamble, Wal-Mart and General Electric. They have all begun initiatives towards the elimination of environmentally hazardous ingredients. Wal-Mart has been particularly aggressive in its program to substitute "preferred" ingredients for "chemicals of concern" including nonylphenol and nonylphenol ethoxylates.

Experience tells us that the environmental pressure to replace NP and NPE surfactants will continue to grow. Available data also indicates that the substitution of NP/NPE is feasible from both a

technical and cost perspective in most consumer and industrial use products, including the metal finishing industry. It is important, however, to ensure these substitutions result in a net benefit to the environment, as well as compliance with current legislation. In addition, product effectiveness, availability and operating cost must be assessed to ensure substitution is a practical option.

References

1. M. Ahel, W. Giger & M. Koch, "Behaviour of Alkylphenol Polyethoxylate Surfactants in the Aquatic Environment - I. Occurrence and Transformation in Sewage Treatment," *Water Research*, **28** (5), 1131 (1994).
2. M. Ahel, W. Giger & M. Koch, "Behaviour of Alkylphenol Polyethoxylate Surfactants in the Aquatic Environment - II. Occurrence and Transformation in Rivers," *Water Research*, **28** (5), 1143 (1994).
3. CAS-No.: 84852-284-325-5 and 246-672-0 EINECS-No.: 284-325-5 and 246-672-0, *European Union Risk Assessment Report. 4-Nonylphenol (branched) and Nonylphenol*, European Chemicals Bureau, Institute for Health and Consumer Protection, European Union, 2002; http://ecb.jrc.it/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/REPORT/4-nonylphenol_nonylphenolreport017.pdf.
4. E.R. Bennett & C.D. Metcalfe, "Distribution of Alkylphenol Compounds in Great Lakes Sediments, United States and Canada," *Environmental Toxicology & Chemistry*, **17** (7), 1230 (1998).
5. E.R. Bennett & C.D. Metcalfe, "Distribution of Degradation Products of Alkylphenol Ethoxylates Near Sewage Treatment Plants in the Lower Great Lakes, North America," *Environmental Toxicology & Chemistry*, **19** (4), 784 (2000).
6. "Directive 2003/53/EC of the European Parliament and of the Council of 18 June 2003 amending for the 26th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (nonylphenol, nonylphenol ethoxylate and cement)," *Official Journal of the European Union*, 2003; http://europa.eu.int/eur-lex/pri/en/oj/dat/2003/l_178/l_17820030717en00240027.pdf.
7. *Canadian Environmental Protection Act 1999, Priority Substances List Assessment Report: Nonylphenol and its Ethoxylates*, Environment Canada and Health Canada, Ottawa, 2000; http://www.hc-sc.gc.ca/ewh-semt/alt_formats/hecs-sesc/pdf/pubs/contaminants/psl2-lsp2/nonylphenol/nonylphenol_e.pdf.
8. EPA-822-R-05-005, *Aquatic Life Ambient Water Quality Criteria - Nonylphenol Final*, U.S. EPA Office of Water, Washington, DC, December 2005; <http://www.epa.gov/waterscience/criteria/nonylphenol/final-doc.pdf>.
9. U.S. EPA, 2006. *Safer Detergents Stewardship Initiative*, U.S. EPA Office of Pollution Prevention and Toxics, Washington, DC, 2006; <http://www.epa.gov/dfe/pubs/projects/formulat/sdsi.htm>.

About the Author



Mike Wyrostek is a graduate from the University of Massachusetts with a Bachelors degree in Chemistry. He has worked in the metal finishing industry for over twenty years, the last eleven at MacDermid, Inc. where he currently holds the position of Global Product Manager, Surface Conditioning. Mike works out of the Waterbury, CT office.