

APEO: OVERVIEW OF THEIR APPLICATIONS AND ALTERNATIVES

Ethoxylated alkylphenols (APEOs) are nonionic surfactants, among which the two most commonly used subgroups are ethoxylated nonylphenols (NPEOs) and, to a lesser extent, ethoxylated octylphenols (OPEOs).

NPEOs can be used as emulsifiers¹ for the emulsion production of polymers², paints, adhesives, additives or as dispersing agents³, especially for ink formulation. However, the legal framework governing the use of NPEOs is becoming increasingly stringent.

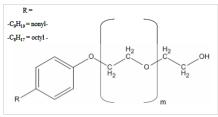


Figure 1/ Structure of APEOs

OPEOs are mainly used as emulsifiers for the production of emulsion polymers such as SBR (styrenebutadiene polymer used in tyres), vinyl-acrylic and styrene-acrylic polymers. They are also emulsifiers and dispersants for the formulation of water-based paints and pesticides. The surfactant properties of OPEOs allow them to integrate the formulation of detergent/cleaning and anti-foam products. OPEOs are part of the synthetic reagents of octylphenol ether sulfates used in water-based paints for their emulsifying properties.

To date, there are many alternatives to NPEO and OPEO when the latter are used to form and stabilize an emulsion (emulsifier) or to limit the flocculation phenomenon (dispersing agent). This article is not intended to provide an exhaustive list of all alternatives available on the market, but to list the main alternatives to APEOs for uses that are not yet restricted by regulation.

To date, alcohol ethoxylates

are the most commonly used products to replace nonylphenol ethoxylates. Alcohol ethoxylates are non-ionic surfactants composed of hydrophobic fatty alcohols⁴ combined with a varied number of ethoxylate groups.

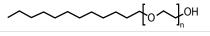


Figure 2/ Structure of alcohol ethoxylates

There are several hundred alcohol ethoxylates with different physical and chemical properties depending on the length of the alcohol and ethoxylate chains. Alcohol ethoxylates can replace APEOs when the latter are used as emulsifiers for the production of paints and adhesives and as dispersing agents for the formulation of paints and inks. A priori, alcohol ethoxylates would generally be more expensive than NPEO (20 to 30%), however, it is possible that some surfactants (or mixtures of surfactants) may require lower concentrations at equal performance. For example, BASF and HUNTSMAN produce the LUTENSOL® and SURFONIC® respectively based on alcohol ethoxylates.

> ¹ Additive for forming and stabilizing an emulsion
> ² ABS, ESBR (styrene-butadiene rubber), ENBR, PVC, PTFE (Polytetrafluoroethylene), PVA (PolyVinyl Acetate), PMMA, polyacrylates for paints
> ³ Additive to limit the flocculation phenomenon
> ⁴ long carbon chain





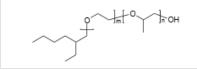


Figure 3/ Structure of Alcohol ethoxylate/ propoxylate

Alcohol ethoxylate/propoxylate

copolymers correspond to a class of chemical substances similar to alcohol ethoxylates, with the difference that one or more propoxylate group(s) is (are) used instead of a corresponding number of ethoxylated group(s).

These substances replace APEOs as dispersants and emulsifiers and have applications such as paints and coatings or inks. For example, DOW markets the ECOSURF[™] range of surfactants based on 2-((1-((2-ethylhexyl)polyoxy) poly-propan-2-yl)oxy)ethanol (n°CAS 64366-70-7).

Another alternative to APEOs is the use of sulphur-based anionic emulsifiers and dispersants such as **alkyl or aryl ethoxy sulfates, sulfonates and alkyl sulfates.** For example, CLARIANT has developed various alkyl and aryl ethoxy sulfates which, depending on the product used, promote the emulsion of various polymers (acrylic, styrene-acrylic, vinyl acetate, styrene-butadiene, PVC), these products are grouped together in the EMULSOGEN® ranges (EMULSOGEN APS, EPA 073, LA 083, LCA 213, FP...).

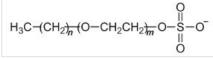
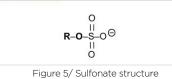


Figure 4/ Structure of alkyl ethoxy sulfates



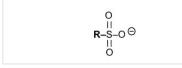


Figure 6/ Alkyl sulfate structure

Marketed, among others by ADDAPT CHEMICALS BV via its PEX[™] range, alkyl phosphates, anionic surfactants, can replace APEOs both for the emulsion production of polymers and for the formulation of pesticides (OPEOs can be used as dispersing agents).

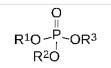


Figure 7/ Structure of phosphate ester

There are also biosourced solutions available to replace APEOs for applications to emulsify polymers: these are mainly **emulsifiers synthesized from glucose.** For example, SEPPIC has developed the MONTANE[™] range, which includes non-ionic emulsifiers obtained by esterifying sorbitol with a fatty acid.

SMA (Styrene Maleic Anhydride n°CAS 9011-13-6) is a copolymer able to substitute dispersing agents based on NPEO or OPEO for pigments, inks, coatings, adhesives...

There are two major producers of SMAs on the market, namely: SOLENIS (SCRIPSET™) and POLYSCOPE POLYMERS (XIRAN®).

Sources :

Technical and economic data on octylphenols and ethoxylates (in French)

Technical and economic data on nonylphenols and ethoxylates (in French)

KEMI (2013) ANNEX XV RESTRICTION REPORT - NONYLPHENOL AND NONYLPHENOLETOXYLATES IN TEXTILES

SUBSPORT (2013) Specific Substances Alternatives Assessment – Nonylphenols and Nonylphenol ethoxylates

BYK PUT ON THE MARKET A RELEASE OF BYKETOL-WS WITHOUT APEO

BYKETOL-WS is a leveling agent with anti-foaming properties designed for water-borne coatings (undercoats and top coats for the automotive sector and varnishes for the wood and furniture sector). The BYKETOL-WS is designed to prevent surface defects in the coating («pinholes», bubbles, orange peel, craters) and to improve its levelling. Its composition combines high-boiling solvents, substances with anti-foaming properties and 4-nonylphenol, branched and linear, ethoxylated (n°CAS 127087-87-0).

Soon, European regulations on the use of chemicals will require authorization for 4-nonylphenol, branched and linear, ethoxylated (CAS No. 127087-87-0). In this context, BYK (ALTANA group) reformulated the additive BYKETOL-WS by removing this APEO from its composition, leading to the creation of BYKETOL WA.

According to BYK, BYKETOL-WA would have almost identical performance to its APEO-containing counterpart (BYKETOL WS).

Sources : https://www.byk.com/fr/additifs/additifs-parnom/byketol-wa.php

AN ON-LINE TOOL FOR RESEARCHING ALTERNATIVES TO PHTHALATES

In order to simplify your search for phthalates alternatives, a table in Microsoft® Excel format compiling all the information on this subject and posted on the phthalates substitution website has just been published. Via this table, you can search for alternative solutions: for PVC or other materials; for an application sector (for example: medical, construction, textiles...) or for a particular application (floor coverings, PVC foams...). This table also includes information on the alternative material or substance: examples of the trade name of the alternative and identification of developers and/or producers and/or suppliers. For more information about an alternative solution, the hypertext link associated with it allows you to directly access the document that generated the information. In the future, this tool will be updated with each major modification of the phthalates substitution website.

https://substitution-phtalates.ineris.fr/sites/ substitution-phtalates/files/documents/drc-165804-00941a_outil_de_recherche_phtalates_vf_0.xls

COMING SOON

Workshop "The substitution of chemicals in the textile sector", in La Défense (France) on January 9.

This workshop, organized by INERIS in collaboration with the Ministry of Ecological and Solidarity Transition, aims to bring together actors from the textile sector, as well as civil society stakeholders, in order to promote exchanges on the challenges, obstacles and drivers of chemical substitution in this sector.

It will also be an opportunity to communicate on the needs and availability of alternatives, and to report on the industrial implementation of alternative solutions.

The programme will be communicated soon.

For more information, contact: pierre.boucard@ineris.fr

FACHPACK 2019 in Nuremberg (Germany) from September 24th to 26th, 2019

This show is an appointment for professionals in packaging, marking and handling, all industrial sectors combined (food, beverage...). Innovative bisphenol-free solutions are likely to be presented.

https://www.fachpack.de/en

K 2019 in Düsseldorf (Germany) from October 16th to 23th, 2019

The triennial K trade fair for the plastics and rubber industry will be organized around four themes including raw materials and auxiliaries. On this occasion, plasticizer producers able to replace phthalates will be present.

https://www.k-tradefair.fr/

INPRINT 2019 in Munich (Germany) from November 12th to 14th, 2019

The INPRINT exhibition is for professionals in many printing sectors (ceramics, textiles, packaging, aerospace, automotive ...). It offers the opportunity to discuss the latest innovations that could replace alkylphenol ethoxylates.

https://www.inprintmunich.com/

If you have any questions. please contact us: https://substitution.ineris.fr/en/contact

https://substitution.ineris.fr