Cosmetic Preservation
1st Published in SPC - 2013
John Woodruff

The Legal Bit

Preservatives are added to all manner of products in the personal care and cosmetic industry. Preservatives inhibit the growth of bacteria and fungi, thereby increasing the products shelf life and consumer safety. Current EC Regulation No 1223/2009 [1] defines preservatives as substances which are exclusively or mainly intended to inhibit the development of micro-organisms in the cosmetic product.

EC 1223/2009 came into effect in July 2013 and Article 14 states that cosmetic products shall not contain preservatives other than those listed in Annex V and preservatives which are listed there but not used in accordance with the conditions laid down in that Annex. In the introduction to EC 1223/2009 it also states substances which are intended to be used as preservatives should be listed in Annexe V in order to be allowed for this usage.

There are 57 substances listed as preservatives in Annex V of EC No 1223/2009 and in addition the salts and esters of many of these are also permitted thereby increasing the number available. However many are very restricted in their usefulness by their ionic character, by pH requirements or other considerations. This is the same number as listed in 2003.but at that time the EC Directive included the following provision in the preamble to the list of permitted preservatives “Other substances used in the formulation of cosmetic products may also have anti-microbial properties and thus help in the preservation of the products, as, for instance, many essential oils and some alcohols. These substances are not included in this Annex” This provision has been interpreted very widely to allow numerous other materials to claim antimicrobial action equivalent to that of permitted preservatives but it does not appear in EC 1223/2009.

The historical bit

The author has a collection of early cosmetic textbooks and they make interesting reading, thus in 1929 Poucher [2] made no reference to preservatives but did cite a patent for an absorbent tissue treated with cold cream – the first wet wipe? In 1934 Chilson [3] listed a table of 18 common preservatives, the majority of which are still in use. The table included p-hydroxy benzoic acid esters i.e. parabens, benzoic acid, salicylic acid, p-chloro-m-cresol and formaldehyde. In 1941 de Navarre included a whole chapter on preservatives in his text book on cosmetic chemistry [4]. In it he listed 21 preservatives including the parabens with recommended dosage, solubilities and type of media in which effective. Most of those listed are still in use and in the 2nd edition published in 1961 the chapter was much expanded with particular reference to using parabens. There are also tables of aromatic compounds and essential oils and their effect on mould growth, which make interesting reading.

Cosmetic preservatives today

For decades parabens have been the preservatives of choice with formaldehyde donors and phenoxyethanol as runners up. Unfortunately adverse publicity has created consumer resistance to using cosmetic products containing the most commonly used preservatives and many of the materials that had long fallen out of favour have been making a comeback, despite their relative ineffectiveness, especially at neutral and alkaline pH.

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Because the introduction of new preserving materials is such a slow and expensive process there are few new ones on the market and the majority are no longer protected by patents. This reduces the materials to being commodity items and price becomes the main criteria when selecting a supplier. This has resulted in some suppliers introducing mixtures that improve the efficacy of individual ingredients and mixtures of approved preservatives that avoid those perceived as being unwanted.

Examples are provided by **Brasca** in its BiosControl Synergy Line that includes BiosControl Synergy BAS as a mixture of benzyl alcohol and dehydroacetic acid and BiosControl Synergy BDP, which is a mixture of phenoxyethanol, benzoic acid and dehydroacetic acid. Altogether there are 17 different mixtures in the range, each targeted at different products. **Brasca** has published a very comprehensive brochure [5] that illustrates the toxicity, irritation potential and solubility, effect of pH and temperature of incorporation for each mixture and also for the individual substances.

For many years the Nipa brand name was synonymous with preservatives, particularly Nipagin M for methylparaben, Nipasol M for propylparaben and Phenonip, which was the industry standard for a multi-paraben mixture in phenoxyethanol.. The brand is now owned by **Clariant** and the names continue plus some additional blends including Phenonip ME, methylparaben and propyl paraben with phenoxyethanol; Nipaguard PO-5, which is piroctone olamine with phenoxyethanol and Nipaguard POB, which is piroctone olamine and benzoic acid with phenoxyethanol.

Akema has created a number of mixtures with broad spectrum efficacy based on organic acids and their salts. They include Kem NK, a mixture of phenoxyethanol, sodium benzoate and potassium sorbate in aqueous solution; Kem PBD, a mixture of phenoxyethanol, benzoic acid and dehydroacetic acid and Kem DHA, which is benzyl alcohol and dehydroacetic acid in water. Like the majority of suppliers **Akema** also provides individual preservatives and synergistic mixtures of the more commonly used. Examples are Kemaben, a solution of imidazolidinyl urea, methyl paraben and propyl paraben in propylene glycol and Kem Plus, which is iodopropynyl butylcarbamate in phenoxyethanol. These preservatives and many others appear in a brochure and preservative selection guide jointly published by **Akema** and **Univar**.

Other suppliers with informative brochures on the problems and solutions to cosmetic preservation include **IMCD, Ashland, Inolex, Nutrinova, Chemyunion, ISCA UK** and **Dr Straetmans**. In addition **Lonza** has an on-line tool named Formula Protect, which allows users to input a wide range of selection criteria to obtain suggested suitable preservatives plus full descriptions about their properties. Further details are available through **Adina Cosmetic Ingredients.**

Azelis markets a wide range of preservatives including materials from **Sharon Laboratories, Merck KGaA and Inolex**. Sharonox 2000 is a mixture of butylparaben, isobutylparaben and polyaminopropyl biguanide in phenoxyethanol. Under its own Paratexin brand name are most preservatives in common use plus some synergistic mixtures. Amongst the latter is Paratexin CPE, a blend of chlorphenesin and phenoxyethanol that appears to be particularly effective against both fungi and bacteria in wet wipes.

ISCA UK is a company that specialises in cosmetic preservatives and as well as offering the more popular materials as individual ingredients it also provides

optimised mixtures. It produces an informative brochure detailing the properties of its materials and describes the various mixtures available. Featured are Iscaguard FPX, a blend of parabens in phenoxyethanol; Iscaguard IPT, which is iodopropynyl butylcarbamate with phenoxyethanol and Iscaguard DPE that is methyldibromo glutaronitrile, also with phenoxyethanol.

Phenoxyethanol is ubiquitous in traditional preservative systems, in those involving organic acids and in alternative mixtures that have an antimicrobial action. Although it does not have Ecocert approval it appears to have escaped the negative publicity aimed by the uninformed against so many traditional preservatives It is not a strong biocide but does have preservative activity against gram negative bacteria however it is an excellent solvent for the majority of other substances used in preservative systems and is itself soluble in both oil and water at in-use concentrations. It is stable over a wide pH range and at temperatures up to 85°C and it also has world-wide approval for use up to 1%. Steinberg reports [6] that it is inactivated by highly ethoxylated compounds and must be used with caution in anionic systems.

Preserving Alternatives

The wording of EC 1223/2009 would appear to preclude the addition of preservatives to cosmetics that are not listed in Annex V. There was a provision made in the preceding regulations that enabled other materials to be added providing there were no safety issues and many materials were used under this provision. How they will now be perceived is an interesting point but in the meantime alternative materials still excite a lot of interest.

Dr. Straetmans was one of the first suppliers to offer alternative ideas based very much on he antimicrobial properties of caprylyl glycol and certain fatty acids and glyceryl esters. Dermosoft OMP is methylpropanediol, caprylyl glycol and phenylpropanol, which has a recommended use level of 2.5% to 4% for o/w emulsions, aqueous products and wet wipes. It is not affected by pH but the higher levels may be necessary if formulations contain polar oils such as UV absorbers. An alternative is Dermosoft MCA Variante [Caprylyl glycol, dipropylene glycol, glyceryl caprylate] that is said to be odour-free, effective at 1% or less and to be sufficiently mild to be used in baby products and products for very sensitive skin.

Caprylyl glycol is an aliphatic diol with a chain length that appears to destabilise and disrupt microbial cell membrane. It addition to its antimicrobial properties it is also used as a skin conditioner, emollient and humectant and is one of the most popular multifunctional ingredients for the replacement of traditional preservatives. In mixtures the wetting properties of caprylyl glycol enhances the penetration of associated substances into the intercellular walls of the organism.

Combining the activities of caprylyl glycol and phenoxyethanol is Verstatil PC from **Dr. Straetmans** and from the same supplier phenoxyethanol appears with benzoic acid in Versatil BP. **Centerchem** recommends Diocide [Caprylyl glycol, phenoxyethanol, hexylene glycol] as a broad spectrum anti-microbial for cosmetics and personal care products. Said to be equally suitable for rinse-off and leave-on applications. Diocide is stable over a wide pH range, is compatible with most cosmetic ingredients and is globally accepted.

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Euxyl PE 9010 from **Shulke & Mayr GmbH** is a liquid cosmetic preservative based on phenoxyethanol and ethylhexylglycerin. The addition of ethylhexylglycerin affects the interfacial tension at the cell membrane of microorganisms, improving the preservative activity of phenoxyethanol. Euxyl PE 9010 is claimed to provide a broad, balanced spectrum of effect against bacteria, yeasts and mould fungi.

Not including phenoxyethanol is Stabil from **Akema**. This is a mixture of phenethyl alcohol with caprylyl glycol to create a blend of multi-functional ingredients with broad spectrum anti-microbial properties. Phenethyl alcohol has a mild rose-like fragrance. Benzyl alcohol has wide approval for use in cosmetics making organic and natural claims and is combined with glyceryl caprylate and glyceryl undecylenate in Kem Nat from **Akema**. It is described as a synergistic combination of benzyl alcohol with glyceryl monoesters that boosts the preservative action and adds emolliancy. Kem Nat is gentle to the skin and active against bacteria, yeasts and moulds. It is colourless and with very mild odour and is effective in the pH range from 4 to 8.

Iscaguard SAP from **ISCA** is a suggested as a natural preservative containing Ecocert certified ingredients. It is a synergistic blend of propanediol with Salix alba extract and is used at from 0.125% to 1%. Also from **ISCA** are several preservative systems based on optimised blends of organic acids. Aquaguard 9093 [Sodium benzoate, sodium dehydroacetate] is suitable for both leave on and wash off products and exhibits broad spectrum antimicrobial activity up to pH 6.5. Iscaguard BOA [Benzyl alcohol, dehydroacetic acid, benzoic acid] and Iscaguard POA [Phenoxyethanol, dehydroacetic acid, sorbic acid, benzoic acid] also exhibit broad spectrum activity to pH 6.5.

When using organic acids as preservatives it is essential that products are made to the correct pH and that they are suitably stabilised such that the pH does not drift outside the effective pH limits. Organic acids destroy bacteria by the continuous acidification of the cell‘s cytoplasm, increasing the osmotic pressure due to intake of electrolytes (e.g. Na+) and by the loss of energy in the active transport mechanism within the membrane. When the acid is dissolved in water it dissociates and loses its H+ proton and once the protonated acid enters the bacteria’s cell wall it then deprotonates and reduces the pH inside the cell. The cell compensates by expelling protons in exchange for sodium ions, more unprotonated acid then enters the cell, and ultimately this cycle kills the microorganism.

Thus the activity of organic acids and their salts is very pH dependent and the final compositions must be at acid pH; at pH≤2 for salicylic acid and its salts; pH≤3.0 for benzoic acid and benzoates; pH≤4.5 for sorbic acid and sorbates and pH≤6.0 for dehydroacetic acid and its salts. An organic acid that is effective at pH 7 is caprylhydroxamic acid and this appears in Spectrastat from **Inolex,** which also includes caprylyl glycol and glycerin. Caprylhydroxamic acid has chelating properties for ferric and ferrous ions, which are essential for the survival of Aspergillus niger.

Inolex proposes the use of Spectrastat to those formulators seeking enhanced humectant and chelating properties in their formulas. As a secondary benefit Inolex suggests that such formulations may also increase their intrinsic resistance to microbial growth, and may be able to meet required standards for protection without the need for added biocidal preservatives.

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A more complete round-up of alternative preservatives appeared in SPC, October 2012 [7]; it will be interesting to observe whether Regulation (EC) No 1223/2009 has an influence on this aspect of cosmetic formulation over the next twelve months.

1. Regulation (EC) No 1223/2009 of the European Parliament and of the Council
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7. Woodruff, J.B., Preserving Alternatives, SPC, 85(10) 58-65. (2012)

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www.creative-developments.co.uk