Cosmetic Preservation
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If there is any water present in a cosmetic product it will be prone to microbial spoilage unless it is self-preserving or contains one or more ingredients that will inhibit microbial growth. If the product is to be sold within Europe any preservative added to the product should be listed in Annex V of Regulation (EC) No 1223/2009. This lists nearly 60 permitted preservatives however less than half are in current use and if formaldehyde donors, halides and isothiazolinones are avoided only organic acids, parabens and phenoxyethanol and benzyl and dichlorobenzyl alcohol remain. To comply with COSMOS this number is further reduced as parabens and phenoxyethanol are removed.

This is creating a major challenge for the cosmetics industry, which is faced with three conflicting requirements; to offer products that are safe for human health, that are preserved with materials listed in Annex V and that meet consumer approval. If a product can support microbial growth it cannot be considered safe for human health. The listed organic acids are only effective at low pH and benzyl alcohol is a known potential allergen. Consumer approval is affected by what is read or heard in the media, regardless of its provenance.

Periodically David Steinberg analyses use of preservatives in cosmetics in North America and recently compared figures from 36,881 products in 2010 with those from 48,423 in 2014. Looking at the most popular preservatives we can see that despite a drop of almost 8% in frequency of use parabens are still the first choice in the USA. After parabens phenoxyethanol is second favourite and in 2014 organic acids and their salts take third place.

Ingredient	2010	2014	Change
Methylparaben	36.43%	28.54%	-7.88%
Propylparaben	28.26%	21.92%	-6.33%
Phenoxyethanol	24.07%	26.86%	+2.78%
Formaldehyde Donors	16.90%	13.85%	-3.04%

Isothiazolinones	12.59%	16.15%	+3.56%
Organic acids/salts	12.01%	16.68%	+4.67%
Caprylyl glycol	4.64%	7.59%	+2.95%

Figures from Euromonitor about usage in European skin care make for an interesting comparison.

Ingredient	2010	2014	Change
Parabens	63.37%	61.35%	-2.02%
Phenoxyethanol	30.85%	24.78%	-6.07%
Isothiazolinones	0.01%	0.29%	+0.28%
Organic acids/salts	5.77%	13.59%	+7.82%

The major difference in isothiazolinones is probably because Steinberg's figures include hair and other wash-off products whereas the European figures are solely for skin care. Despite the decline in market share of parabens, in discussions with preservative manufacturers and suppliers it would appear that the consumer is less paranoid about them than in recent years. This is good news for the cosmetic industry, however there is still a significant market for "paraben free" products.

Over the next year the growth in use of isothiazolinones is likely to be reversed and it will be interesting to see if their place is taken by parabens, organic acids or unlisted materials like caprylyl glycol. There are approved preservatives that are seldom used and these are worth exploring. Chlorobutanol is an example; it is permitted at up to 0.5% except it is not to be used in sprays.

More commonly used in pharmacy than in cosmetics, chlorobutanol has been widely employed as a very effective preservative in eye drops without producing clinically recognised ocular disturbance [Ref. 1]. It is soluble in hot

water, glycols and volatile oils and is stable in solution at pH5 or lower.

According to one supplier, **Athenstaedt**, chlorobutanol is a well-accepted and widely used effective preservative in many pharmaceuticals and cosmetic products. It has antibacterial and antifungal properties and has been used for more than 125 years.

The frequency of use of chlorphenesin more than doubled from 2010 to 2014 in the USA. It is permitted to a maximum of 0.3% in Europe and the CIR Expert Panel concluded that chlorphenesin is safe in the present practices of use and concentration. It is water-soluble to 0.6% and soluble in glycerin and glycols and, although weak against bacteria, it is effective against fungi. Because of this it may be found in antifungal foot and nail products or combined with other preservatives such as phenoxyethanol. An example of this is Sharon CP10 from **Sharon Laboratories**, which also supplies chlorphenesin in combination with 1,2 hexanediol and phenylpropanol as Sharomix CHP20 and with phenylpropanol and caprylyl glycol as Sharomix CPC 30. All three mixtures are described as pH independent broad-spectrum preservative systems.

Dehydroacetic acid is another listed preservative that has doubled its frequency in use and now rivals DMDM hydantoin, imidazolidinyl urea and diazolidinyl urea in popularity. The CIR Expert Panel concluded that it is safe to use in cosmetic products and the EU permits this ingredient to be used at a maximum concentration of 0.6% but it must not be used in spray products. It is effective against fungi although poor against bacteria. Because of its poor solubility in water it is usually added as the sodium salt, which releases the free acid below pH6. Alternatively it may be supplied in a solvent such as benzyl alcohol; an example being Neofect BBH from **IMCD-Jan Dekkar**, which is dehydroacetic acid with benzoic acid in benzyl alcohol to provide a COSMOS approved broad-spectrum preservative.

o-cymen-5-ol is closely related to thymol, which occurs naturally in many plants including thyme, where it may represent 60% of its essential oil. It is permitted in Annex V at up to 0.1% in leave-on and wash-off products. The CIR Review shows it as safe at concentrations up to 0.5% and there is no upper limit in Japan provided the product is not intended for use on mucous membranes, when it is limited to 0.1%. It is available from **Symrise** as SymOcide C and from **IMCD-Jan Dekkar** as Dekasol, with reports that it is effective against bacteria and fungi but its use with additional preservatives is recommended. It is poorly water-soluble but can be solubilised using propylene or butylene glycol, benzyl alcohol or phenoxyethanol.

Thymol is a constituent of a number of alternative preservative systems under the SharoSENSE trade name from **Sharon Laboratories**. Introduced at In-Cosmetics 2016 SharoSENSE is based on 'Synthetic Expressions of Natural Materials' and is claimed to help build a bridge between chemical and natural ingredients. This line combines the best features of a natural ingredient with the safety, quality and consistency of laboratory synthesis. They are globally approved and heat stable and offer broad spectrum protection across a wide pH range with recommended use levels of less than 1%. SharoSENSE is a synergistic mixture of thymol with linalool and this mixture is also available in phenoxyethanol, in benzyl alcohol and in phenethyl alcohol.

Phenethyl alcohol is an aromatic alcohol with floral odour and rose character that is found naturally in many fruits and flowers. It has antimicrobial activity against bacteria, especially Gram-negative, and fungi, which makes it of interest when searching for an alternative preservative system. **Novorate Biotech** supplies pure phenethyl alcohol obtained through a fermentation process. **Shulke** combines phenethyl alcohol with ethylhexylglycerin as Sensiva PA20 and **Synerga** combines it with caprylyl glycol as Feniol, which is said to provide cosmetics with a synergistic antimicrobial action offering broad

spectrum protection against all classes of micro-organisms. A similar mix is available from **ISCA** as Iscaguard PFA.

Conarom P2 Aromatic from **Ashland** is an emulsifier and moisturiser that delivers broad antimicrobial protection as a secondary effect within the pH range 4 – 8. It is a mixture of phenethyl alcohol, propanediol, polyglyceryl-4 laurate/sebacate, polyglyceryl-6 caprylate/caprate and caprylyl glycol and is described as a fortifying system containing naturally derived and nature-identical ingredients that add mild flowery fragrance to cosmetic compositions.

Caprylyl glycol is the most commonly used multi-functional ingredient with preservative activity and was found in more than 7% of all cosmetics registered in the USA in 2014. It is widely available as a commodity item or in synergistic mixtures to widen its antimicrobial activity. An example is SymTriol [INCI: Caprylyl glycol, 1,2-hexanediol, methylbenzyl alcohol] from **Symrise**, commonly used at 1% in a wide variety of cosmetics and effective in the pH range of 3 – 8.

IMCD-Jan Dekkar combines caprylyl glycol with benzyl alcohol in Neofect 304, with phenoxyethanol to give Neofect PO and with sorbic acid as Neofect OS. Capryl glycol is combined with phenoxyethanol by **Ashland** to give Optiphen 2000 and in numerous combinations with traditional and non-traditional preservatives by **Jeen**. **Dr Straetmans** combines it with glyceryl caprylate, glycerin and phenylpropanol in Dermosoft LP and with glyceryl laurate, phenylpropanol and dipropylene glycol in Dermosoft MCA or, in a more simple mixture, with pentylene glycol in Dermosoft MCA 2.

With special appeal to formulators of natural cosmetics MicroCurb from **Kemin** is an extract of oregano leaf with caprylic acid that shows broad spectrum activity at acid pH. Caprylyl and hexylene glycolic extracts of oregano, thyme and rosemary feature in **FSS SynerCide Herbal Fusion** from **Active Micro**

Technologies. The glycols act as more than just a solvent as they provide emollient, humectant and broad spectrum antimicrobial properties. Verstatil BOB from **Dr Straetmans** comprises benzyl alcohol and caprylyl glycol with benzoic acid.

Despite their limitations and pH dependence organic acids are the preferred alternative for many products and suppliers are busy offering more effective mixtures**. Shulke** claims that Euxyl K 903 [INCI: Benzyl alcohol, benzoic acid, dehydroacetic acid, tocopherol] provides broad band protection up to pH6 and can be used in non-ionic systems, leave-on and rinse-off products and is suitable for wet wipes. A similar mixture is available from **IMCD** as Neofect BBH and from **Ashland** as Optiphen BD.

Ashland combines benzoic acid with dehydroacetic acid, propylene carbonate, propanediol and PVP to produce Optiphen DP. It is miscible with water and soluble in propylene glycol and is said to provide microbiostatic activity with an optimised delivery system to maximize the efficacy of its actives up to pH6. It is claimed to be free from alcohol, parabens, isothiazolinones, formaldehyde donors and halogenated ingredients and may be described as comprising nature-identical active ingredients and a naturally derived booster system, which can be further enhanced by the addition of caprylyl glycol.

Phenoxyethanol is added to many cosmetic products as part of the preservative system as it is a listed in Annex V and is also an excellent solvent for other preservatives. However it is an ethoxylated compound so does not meet with universal approval. From **Shulke**, Euxyl K 940 [INCI: Phenoxyethanol, benzyl alcohol, ethylhexylglycerin] was developed in order to reduce the amount of phenoxyethanol in cosmetic formulations. The ethylhexylglycerin in Euxyl K 940 affects the interfacial tension at the cell membrane of microorganisms, improving the preservative activity of phenoxyethanol and benzyl alcohol. It

provides broad-spectrum protection up to pH12 and is clearly soluble at 0.75% in water, which is a typical use concentration.

Pentylene glycol is another solvent with preservative activity and is widely available. **Minasolve** obtains it from sugar cane and corn cob by a green process and combines it with sodium benzoate and benzoic acid to create MinaSolv Green B, a multifunctional ingredient with broad spectrum antimicrobial activity. According to Minasolve, each component has been optimised for maximum availability within the aqueous phase of cosmetic products. The same company also markets MinaSolv Hexam+, described as a synergistic blend of pentylene glycol and hexamidine diisethionate that shows broad-spectrum anti-microbial activity. The blend is well suited for aqueous solutions, emulsions and surfactant-based systems and also provides a long lasting skin moisturising effect, comparable to that of glycerin.

Under its Hebeatol trade name **Chemyunion** supplies a number of natural-based moisturising materials with antibacterial activity based on xylitol. The range comprises Hebeatol Plus Chi [INCI: Xylitol, caprylic acid]; Hebeatol BA [INCI: Benzyl alcohol, xylitol, caprylic acid] and Hebeatol PSVG [INCI: Xylitol, caprylic acid, potassium sorbate, glycerin, aqua/water].

Another moisturising ingredient with antimicrobial activity is Prodew P-DS-12 [INCI: Sodium N-caproyl-L-prolinate, aqua/water] from **Ajinomoto.** It is an amino acid-based humectant derived from L-proline and a fatty acid with good moisturising properties and can work as a booster for antimicrobials. It is also effective in wet wipes, where antibacterial agents are often inactivated due to adsorption to wet wipe substrates. It can be combined with Dermosoft 1388ECO [INCI: Water, glycerin, sodium levulinate, sodium anisate] from **Dr Straetmans** to be effective against mould at pH 4.6 – 6.4. Levulinic acid and anisic acid and their salts have recognised antimicrobial activity and a new

product called Verstatil Synacid based on these ingredients was launched by **Dr Straetmans** at In-Cosmetics 2016.

Verstatil Synacid [INCI: Aqua; glycerin; sodium levulinate; sodium salicylate; sodium anisate] is described as a synergistic blend of multifunctional organic acids and salicylic acid. It shows broad antimicrobial activity, is easy to handle and is ideal for application in surfactant-based and aqueous product concepts. In emulsions, the combination with surface active antimicrobial boosting agents is recommended. At In-Cosmetics, Jan Jänichen from **Dr Straetmans** described how his company run approximately 1500 challenge tests per year for clients and it is often found that formulations that pass the standard challenge test fail against in-house organisms. Verstatil Synacid has been extensively tested against in-house organisms and found to be very effective within the pH range 4 - 6.

Many of the materials mentioned have Ecocert and/or COSMOS approval and those interested are advised to contact the suppliers for further information, including a full INCI breakdown.

Ref. 1 Grant, W. M. Toxicology of the Eye. 2nd ed. Springfield, Illinois: Charles C. Thomas, 1974, p. 264

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