

our preservatives are the safety belt for your cosmetics



Personal care products must remain safe with regard to microbial count and not only when purchased but also during the use-up period. In addition, their ingredients are required to be safe for human health as used. The pressure generated from NGOs on traditional preservative systems and the changing regulatory restrictions all around the world make it more challenging for the formulator of personal care products to find a solution that fits all, but quality and safety are of topmost importance to personal care products. The reduced pallet of preservatives is negatively impacting the microbial quality, thus compromising consumer safety. Recently, there have been several product recalls due to the growth of undesirable microorganism in personal care products.

At Ashland, we understand the importance of antimicrobial protection and our technologies offer a safety belt for your cosmetic products. Have a look into the following application data to learn more about our progressive preservative solutions that have a long history of safe use.



Ashland progressive preservative solutions - a perfect fit for a wide variety of cosmetic applications

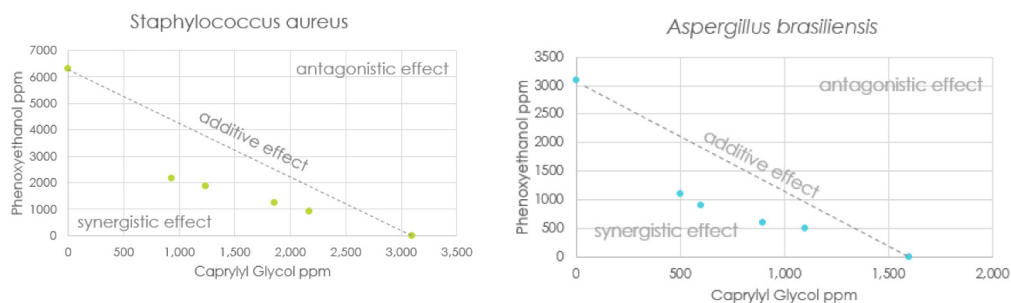
The microbial quality and safety of personal care products are of paramount importance for producers to succeed in delivering innovative personal care products with outstanding performance and integrity to consumers. With the limited pallet of available preservatives for use, finding the most efficient preservative is the critical path for success.

Ashland progressive preservative systems, based on phenoxyethanol, are globally approved and compatible with many different personal care products. Phenoxyethanol is well known for its antimicrobial efficacy against gram-negative microorganism. However, it is weak against fungi and certain gram-positive bacteria. Ashland progressive preservative solutions leverage the synergy between phenoxyethanol and caprylyl glycol. The synergistic effect between phenoxyethanol and caprylyl glycol vs. *Aspergillus brasiliensis* and *Staphylococcus aureus* is shown in **figure 1**. >>



Compared to an additive effect where the efficacy expected is roughly equal to the combined efficacy of each substance on their own, the synergistic effect shows that less phenoxyethanol is needed to achieve antimicrobial efficacy. Reducing the concentration of ingredients can also reduce the likelihood of skin irritation for the end user.

figure 1: synergistic effect between phenoxyethanol and caprylyl glycol vs. A. niger and S. aureus



The advantages of Ashland progressive preservative systems based on phenoxyethanol and caprylyl glycol are shown through preservative efficacy challenge tests in different representative products, a non-ionic emulsion, a sunscreen and in baby wipes. The efficacy was compared to that of phenoxyethanol: ethylhexylglycerin (90:10). The various preservative solutions tested are shown in **table 1**.

table 1: preservative solutions tested

trade names	INCI name	benefits	typical use levels	pH range	max temp	form
Optiphen™	phenoxyethanol caprylyl glycol	<ul style="list-style-type: none"> o global benchmark formulation o broad spectrum activity including wipes o focus on emulsions and leave-on 	0.75 – 1.5%	4 - 8	below 80 °C	liquid
Optiphen™ 200	phenoxyethanol caprylyl glycol	<ul style="list-style-type: none"> o leave-on and rinse-off focus o broad spectrum activity including wipes 	0.75 – 1.3%	4 - 8	below 80 °C	liquid
Optiphen™ Plus	phenoxyethanol caprylyl glycol sorbic acid	<ul style="list-style-type: none"> o enhanced efficacy in slightly acidic products o benchmark product 	0.75 – 1.5%	up to 6	below 80 °C	liquid
Phenoxyethanol / Ethylhexylglycerin 90:10	phenoxyethanol ethylhexylglycerin	<ul style="list-style-type: none"> o broad spectrum activity including wipes o rinse-off and leave-on applications 	0.75-1.1%	4 - 8	below 80 °C	liquid

1. non-ionic emulsion, pH 6.0 described in **table 2**.

table 2: non-ionic emulsion

ingredients	INCI name	% W/W	supplier
phase A			
deionised water	water	79.40	
Carbopol™ Ultrez 10	carbomer	0.20	Lubrizol
phase B			
Ceraphyl™ 368	ethylhexyl palmitate	5.00	Ashland
Emulgade™ 1000 NI	cetearyl alcohol (and) ceteareth-20	2.00	Cognis
Cerasynt™ 945	glyceryl stearate (and) laureth-23	2.50	Ashland
carnation white	mineral oil	5.00	Sonneborn
phase C			
triethanolamine 50%aq	triethanolamine	0.40	Hedinger
phase D			
Polypro 15000	hydrolyzed collagen	0.50	PB-Leiner
deionised water	water	5.00	

procedure:

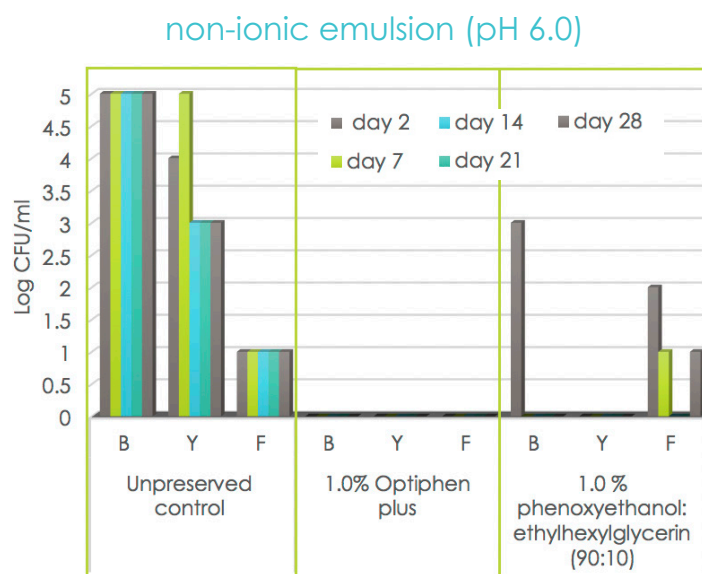
1. Heat phase A to 75°C for 45 Min.
2. Heat phase B to 75°C.
3. Add phase B to phase A, homogenize with Turrax.
4. Add phase C, homogenize with Turrax, cooling down to 35°C.
5. Add phase D at 35°C to the mixture, homogenize with Turrax.

white shiny cream

Briefly, the preservative efficacy data was generated following a double repetitive inoculation test. The samples were inoculated with a bacterial pool containing *S. aureus*, *E. coli*, *P. aeruginosa* and *B. cepacia*, and a fungal pool consisting of *A. brasiliensis* and *C. albicans*. The inoculums were added at the beginning of the experiment (time=0) and after 21 days. Growth of the microorganism at different time intervals was recorded.

As shown in **figure 2**, the addition of 1% of Optiphen™ Plus shows a significant advantage vs. a 1% of blend containing phenoxyethanol and ethylhexylglycerin. No growth was detected in the product preserved with Optiphen™, while the product containing the phenoxyethanol: ethylhexylglycerin blend was not effective against mold and had a slower kill rate vs. bacterial. The unpreserved control was susceptible to microbial growth.

figure 2: preservative efficacy testing in a non-ionic emulsion



2. sunscreen formulation, pH 6.2 described in table 3.

table 3: water in silicone sunscreen, SPF 10

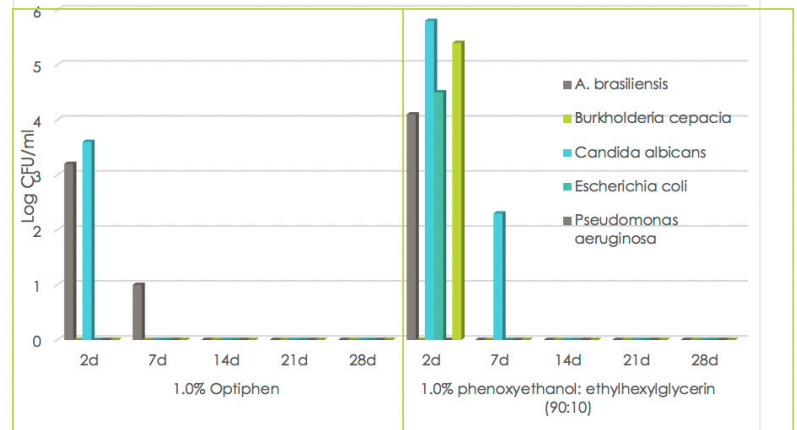
ingredients	INCI name	% W/W	supplier
phase A			
Si-TEC DMC 3071	cetyl PEG/PPG-15/15 butyl ether dimethicone	2.0	Ashland
Carnation light #70	mineral oil	3.0	Witco
Ceraphil™ 368	ethylhexyl palmitate	1.0	Ashland
Escalol™ 587	ethylhexyl salicylate	5.0	Ashland
Castor wax	hydrogenated castor oil	0.5	Frank B. Ross
Refined Yellow Beeswax prills	beeswax	0.5	Frank B. Ross
Escalol™ 557	ethylhexyl methoxycinnamate	7.5	Ashland
Permalene 400 polyethylene	polyethylene	1.0	New Phase
Arlacel P135	PEG-30 dipolyhydroxystearate	2.0	Uniqema
phase B			
SI-TEC CM 040	cyclopentasiloxane	5.0	Ashland
SI-TEC DM 350	dimethicone	5.0	Ashland
phase C			
	preservative	1.0	
phase D			
	sodium chloride	0.6	
	deionized water	Q.S. 100	

1. Combine ingredients in phase A. mix and heat to 90 °C until uniform. cool back to 70°C.
 2. At 70 °C add phase B to phase A. mix and cool to 50 °C.
 3. Combine ingredients in phase D. mix and heat to 55°C.
 4. With fast agitation, combine phase D to phases A&B. the incorporation should take at least 10 min.
 5. Mix and cool to 35-40 °C, homogenize phase C into batch when uniform.
- viscosity 21.200 cps

The preservative efficacy data was generated as described for the non-ionic emulsion except that each microorganism was inoculated individually. As shown in **figure 3**, the addition of 1% Optiphen™ had faster kill rate than the addition of the phenoxyethanol: ethylhexylglycerin blend.

figure 3: preservative efficacy testing in a water in silicone sunscreen

water in silicone sunscreen



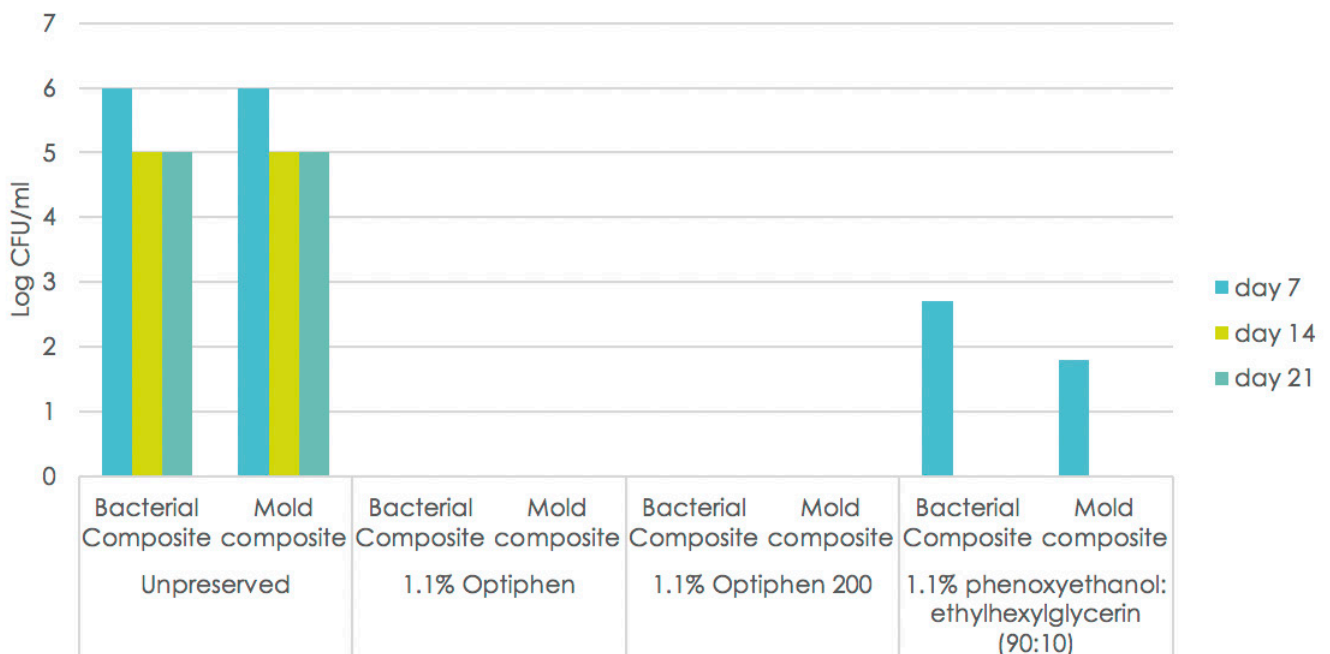
3. baby wipe (cellulosic non-woven), pH 5.5

The samples were inoculated with a mixed microbial suspension (*S. aureus*, *E. coli*, *P. aeruginosa*, *P. expansum*, *T. viride*, *A. brasiliensis* and *C. albicans*), put into plastic bags and then closed tightly by melting the open end of the bags together. After 7, 14 and 21 days the microbial count was determined.

As shown in **figure 4**, the addition of 1.1% Optiphen™ 200 resulted in no microbial recoveries throughout the different time intervals. The same level of a combination of phenxyethanol: ethylhexylglycerin resulted in a lower kill rate. The unpreserved control supported microbial growth.

figure 4: preservative efficacy testing in baby wipes

baby wipes (pH 5.5)



In addition to the efficacy advantages highlighted above, sensory self-evaluation tests conducted on one time use facial masks (pH 6.0) containing either 0.25% Optiphen™ 200 vs. 0.25% of the combination phenoxyethanol: ethylhexylglycerin showed that,

the addition of the Optiphen™ 200 resulted in lower stinging sensation in the panelists. The tests were conducted with Asian panelist and the protocol described below in **figure 5**.

figure 5: sensory tests with water facial masks for one-time 15-minute use (pH 6.0)

sample	stinging	burning
0.25% Optiphen™ 200	1 person	0 person
0.25% phenoxyethanol: ethylhexylglycerin 90:10	4 persons	0 person

testing protocol:

- Balancing:** panelists were relaxed in the clinical lab 30 min. after receiving a face cleaning.
- Application:** the different preservatives were applied using a non-woven fabric water facial mask in half of the face at the same time. A blind test was conducted. One half received one treatment, the other half the second treatment.
- Recording:** stinging/burning was recorded as 0 (none); 1 (feel stinging/burning). Facial mask was worn for 15 minutes and panelists conducted the self-evaluation while wearing the mask.
- Volunteers:** 5 persons, Asian skin.

In summary, these test results demonstrate that the various Ashland preservative solutions based on phenoxyethanol with caprylyl glycol offer better efficacy performance when compared to a blend containing phenoxyethanol: ethylhexylglycerin in terms of better overall protection, faster kill rate and potential skin comfort feel.

what is the trend “top 10” in preservatives?

When looking into launch trends provided by Mintel data research, it can be clearly stated that there is a continuing strong trend to use alcohol-based preservation such as benzyl alcohol or phenoxyethanol. Both ingredients show a strong and stable growth in skin care and hair care applications and are within the “Top 10”. Below tables provide the global innovation

trends for the last 5 years and additional views for North America and Europe. The tables show the number of launches per ingredient and year and the total number of launches during the years 2014 to 2018. On the right side, the tables provide the growth rate shown as % range.

figure 6: top 10 preservatives used in new launched global skin care products

ingredient	2014	2015	2016	2017	2018	total sample	% change: P5Y
phenoxyethanol	12,110	13,847	16,659	16,402	18,467	77,485	52%
methylparaben	5,070	5,913	6,577	5,575	5,322	28,457	5%
sodium benzoate (non-food)	3,383	4,022	4,832	5,148	6,527	23,912	93%
potassium sorbate (non-food)	3,194	3,681	4,531	4,756	5,896	22,058	85%
benzyl alcohol (non-food)	3,125	3,625	4,233	4,409	5,019	20,411	61%
propylparaben	3,273	3,526	3,793	3,327	3,018	16,937	-8%
chlorphenesin	1,775	2,001	2,315	2,329	2,530	10,950	43%
methylisothiazolinone	2,273	2,239	2,286	1,563	1,248	9,609	-45%
ethylparaben	1,433	1,555	1,579	1,330	1,148	7,045	-20%
salicylic acid	1,068	1,175	1,418	1,448	1,742	6,851	63%

figure 7: top 10 preservatives used in new launched skin care products – North America

ingredient	2014	2015	2016	2017	2018	total sample	% change: P5Y
phenoxyethanol	1,763	1,647	1,918	1,753	2,179	9,260	24%
potassium sorbate (non-food)	516	487	664	555	786	3,008	52%
sodium benzoate (non-food)	462	461	640	567	812	2,942	76%
benzyl alcohol (non-food)	451	427	469	424	618	2,389	37%
methylparaben	570	473	420	403	400	2,266	-30%
chlorphenesin	293	327	327	328	334	1,609	14%
propylparaben	402	329	256	268	269	1,524	-33%
salicylic acid	186	176	215	189	275	1,041	48%
diazolidinyl urea (non-food)	226	202	142	182	174	926	-23%
sorbic acid (non-food)	148	146	185	138	176	793	19%

figure 8: top 10 preservatives used in new launched skin care products – Europe

ingredient	2014	2015	2016	2017	2018	total sample	% change: P5Y
phenoxyethanol	5,976	6,706	7,161	7,042	7,737	34,622	29%
sodium benzoate (non-food)	2,253	2,609	2,851	3,055	3,775	14,543	68%
potassium sorbate (non-food)	2,103	2,420	2,718	2,884	3,499	13,624	66%
benzyl alcohol (non-food)	1,906	2,280	2,590	2,663	2,900	12,339	52%
methylparaben	1,429	1,644	1,664	1,275	1,096	7,108	-23%
chlorphenesin	994	1,006	976	956	1,049	4,981	6%
dehydroacetic acid	793	846	897	977	1,151	4,664	45%
benzoic acid (non-food)	555	699	821	833	832	3,740	50%
propylparaben	848	845	771	704	513	3,681	-40%
sorbic acid (non-food)	544	693	738	654	698	3,327	28%

figure 9: top 10 preservatives used in new launched global hair care products

ingredient	2014	2015	2016	2017	2018	total sample	% change: P5Y
methylisothiazolinone	4,668	5,104	6,018	5,866	5,692	27,258	22%
phenoxyethanol	3,395	4,019	5,786	6,239	7,189	26,628	112%
sodium benzoate (non-food)	3,051	3,822	4,840	5,945	6,748	24,406	121%
methylchloroisothiazolinone	4,036	4,330	5,239	5,296	5,234	24,135	30%
cetrimonium chloride	2,630	3,249	4,490	4,570	4,874	19,813	85%
benzyl alcohol (non-food)	2,596	3,056	3,993	4,417	4,501	18,563	73%
behentrimonium chloride	1,955	2,265	3,097	3,428	3,560	14,305	82%
potassium sorbate (non-food)	1,277	1,606	2,151	2,637	3,216	10,887	152%
methylparaben	1,704	1,725	2,042	2,039	1,901	9,411	12%
DMDM hydantoin	1,427	1,719	2,126	1,953	1,898	9,123	33%

figure 10: top 10 preservatives used in new launched hair care products – North America

ingredient	2014	2015	2016	2017	2018	total sample	% change: P5Y
phenoxyethanol	396	316	635	837	769	2,953	94%
methylisothiazolinone	501	334	476	484	448	2,243	-11%
sodium benzoate (non-food)	320	234	390	572	572	2,088	79%
methylchloroisothiazolinone	414	282	409	443	417	1,965	1%
benzyl alcohol (non-food)	287	254	422	447	417	1,827	45%
behentrimonium chloride	260	208	409	479	425	1,781	63%
cetrimonium chloride	230	210	402	470	427	1,739	86%
potassium sorbate (non-food)	165	106	257	359	363	1,250	120%
DMDM hydantoin	167	162	211	212	182	934	9%
iodopropynyl butylcarbamate	112	105	112	159	112	600	0%

figure 11: top 10 preservatives used in new launched hair care products – Europe

ingredient	2014	2015	2016	2017	2018	total sample	% change: P5Y
sodium benzoate (non-food)	1,613	2,062	2,514	3,053	3,524	12,766	118%
phenoxyethanol	1,717	1,914	2,554	2,670	3,210	12,065	87%
benzyl alcohol (non-food)	1,347	1,685	2,130	2,403	2,513	10,078	87%
cetrimonium chloride	1,040	1,318	1,618	1,640	1,832	7,448	76%
methylisothiazolinone	1,329	1,495	1,377	1,284	1,166	6,651	-12%
potassium sorbate (non-food)	831	1,054	1,241	1,501	1,924	6,551	132%
methylchloroisothiazolinone	1,057	1,303	1,176	1,176	1,120	5,832	6%
behentrimonium chloride	798	930	1,161	1,266	1,426	5,581	79%
methylparaben	559	521	567	539	568	2,754	2%
benzoic acid (non-food)	295	401	594	629	670	2,589	127%

Phenoxyethanol – another approved preservative under pressure – what are the facts?

Phenoxyethanol is often described by suppliers and formulators alike as a 'globally approved' workhorse preservative with a good safety profile. Under the European Cosmetics Regulation ((EC) N° 1223/2009), it is allowed as a preservative in all cosmetic product categories up to a maximum concentration level of 1%.

In 2012, the French Authority (ANSM- Agence nationale de sécurité du médicament et des produits de santé) issued a recommendation that phenoxyethanol should not be used in cosmetic products intended for the diaper area and that its use should be lowered to a concentration of 0.4% in other cosmetic product types for children under the age of three years.

Following this ANSM Recommendation, the European Commission mandated its Scientific Committee on Consumer Safety (SCCS) to review and advise on the safety of the ingredient and in 2016, the SCCS re-confirmed in its finalized Opinion that **phenoxyethanol is safe at existing use concentrations up to 1%, including in products for children.** https://ec.europa.eu/health/scientific_committees/consumer_safety/docs/sccs_o_195.pdf

Despite the SCCS Opinion, the French Authorities issued a further 2018 report on this topic and more recently, in March 2019, published a Decision requesting that leave-on cosmetic products containing phenoxyethanol (excluding deodorants, hair styling and make-up products) carry a warning label by December 2019 stating that the products should not be used on the diaper area of children aged three years or under.

Ashland's European trade association, EffCI (European Federation for Cosmetics Ingredients), recently published a Phenoxyethanol Position Paper on its website (<https://effci.com/docs/2019-09%20EffCI%20Position%20Paper%20Phenoxyethanol.pdf>). The Paper further explains this situation as well as a call for the European Commission to take urgent steps to confirm the safety of phenoxyethanol and help bring clarity on the French action with respect to European legislation.

Ashland, along with industry associations, supports the continued use of phenoxyethanol as a vital preservative for all cosmetic product types and users. The SCCS Opinion is recommended reading for further information on the safety and robust dataset of phenoxyethanol.

Will European guidance slow down the 'free from' trend?

It is generally accepted that so called controversial preservative ingredients are under great strain due to regulatory restrictions, NGO & media campaigns and consumer demands. Specifically, the consumer perceptions as well as market trends are, at times, based on little or no scientific basis. This can be frustrating for R&D formulators and safety assessors alike because limited preservative solutions can lead to compromised safety and efficacy as well as a lack of versatility in the marketplace.

It is easy to criticize 'the misinformed consumer' or market trends that take on a life of their own, but should industry consider that part of the blame may lie closer to home? As ingredients or chemistries fall out of favor or fashion, it is natural that companies want to counter or take advantage of these situations and turn them into marketing opportunities. However, the rise of negative claims has helped to damage the reputation of approved and safe ingredients. Over the last ten years, the 'free from' trend has exploded globally and is now so commonplace that consumers often expect to see it on mainstream products.

In June 2017, it was reported that the Deputy General of the European Commission's health directorate, Martin Seychell, addressed Cosmetics Europe's annual conference in Brussels about the public health problem that is created by the reduction of available preservatives. On the topic of 'free from' claims, he was reported as saying that industry needs to avoid "stigmatising the use of preservatives" and that claims of products being preservative-free or paraben-free, when the science committee has concluded that they are not of concern, could "undermine the risk assessment process".³

Not long after, in July 2017, the Commission published the Technical Document on Cosmetic Claims (<https://ec.europa.eu/docsroom/documents/24847>) with a section dedicated to 'free from' claims. This guide although not legally binding came into force in July 2019 so that companies had time to change packaging and claims. There are a number of examples of potentially misleading claims in the document, but some interesting highlights include:

"The claim 'free from preservatives' should not be used when a product contains (an) ingredient(s) showing a protective effect against microorganisms, which are not included in Annex V of Regulation 1223/2009, e. g. alcohol. If the responsible person has evidence that the particular ingredient or the combination of such ingredients does not contribute to the product protection, it might be appropriate to use the claim (e.g. challenge test results of the formula without the particular ingredient)."

"Certain parabens are safe when used in accordance to Regulation (EC) No 1223/2009. Considering the fact that all cosmetic products must be safe, the claim 'free from parabens' should not be accepted, because it is denigrating the entire group of parabens."

"Phenoxyethanol and triclosan are safe when used according to the Cosmetics Regulation. Hence the claim free from these substances should not be accepted because it is denigrating authorised substances."

As we go to print, it is reported that some EU Member State authorities intend to enforce the Technical Document stricter than others. We also continue to see many 'free from' claims on products and in shops. Time will tell if industry uses this as an opportunity to move away from these types of claims and to focus on more positive messages about ingredients.

References: [1] happi journal July 2019, "Preservation Nation" by Christine Esposito. [2] Mintel GNPD trend data. [3] (<https://chemicalwatch.com/57083/industry-must-avoid-stigmatising-preservatives-says-eu-commission>). [4] <https://ec.europa.eu/docsroom/documents/24847>