

preservatives newsletter

march 2018

preservative trends in hair gels

Styling hair gels remain an important product class for cosmetics. As illustrated in figure 1 on the right, according to Mintel's trend scouting, 1339 launches took place globally from 2014 to 2016. Nearly 52% are true new product launches, which underlines the positive innovation dynamics. EMEA, followed by Latin America and Asia Pacific, are the leading innovation regions for hair gels. Product claims often cover:

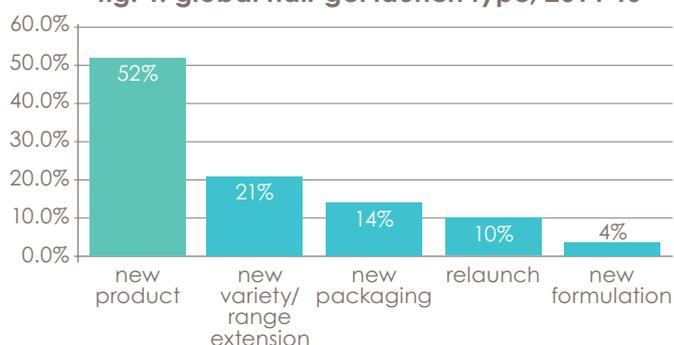
- o **no stickiness and no residue while providing strength from root to tip**
- o **natural ingredient (e.g. botanical herbal ingredients) and natural shine**
- o **alcohol-free formula**
- o **pH neutral**

These claims influence as well the choice of preservatives. Alcohol free formulations can cause difficulties in dispersing certain types of antimicrobials in the gel, which could cause turbidity issues. Formulating in a pH neutral environment limits the use of the antimicrobials further.

When reviewing the preservatives used, phenoxyethanol remains the number one active ingredient in all regions, followed by cost efficient isothiazolones and formaldehyde donors. Benzyl alcohol and short chain parabens show increased use in most regions. To broaden the antimicrobial profile of the product, some hair gels contain glycols or diols like caprylyl glycol.

Tables I-II: (next page) Mintel GNPD data showing detailed regional preservative trends.

fig. 1: global hair gel launch type, 2014-16



Ashland's application and antimicrobial specialists initiated a study to determine modern and classic preservative technology recommendations for clear hair gels. We compared aspects such as microbial stability, performance and applicability to select the best fit preservative following the below criteria:

- o **protection from production until product is used up**
- o **no negative influence on clarity, color and smell**
- o **retain styling performance**
- o **no change of viscosity and rheology behavior**
- o **in line with cosmetic regulations and market trends**



tables I-II: Mintel GNPD data showing detailed regional preservative trends

Ingredient	2014 EMEA	2015 EMEA	2016 EMEA	% change: 2014 - 2016 EMEA	Total Sample EMEA	2014 NA	2015 NA	2016 NA	% change: 2014 - 2016 NA	Total Sample NA	2014 LATAM	2015 LATAM	2016 LATAM	% change: 2014 - 2016 LATAM	Total Sample LATAM
Diazolidinyl Urea	3	5	11	267%	19	6	3	0	0%	9	5	12	11	120%	28
Ethylparaben	3	13	8	167%	24	0	1	3	3%	4	2	2	2	0%	6
Phenoxyethanol	58	83	123	112%	264	13	8	25	25%	46	8	21	33	313%	62
DMDM Hydantoin	34	34	68	100%	136	8	7	6	6%	21	18	29	57	217%	104
Methylparaben	27	35	40	48%	102	5	7	4	4%	16	16	19	33	106%	68
Propylparaben	10	8	13	30%	31	2	3	1	1%	6	6	5	4	-33%	15
Benzyl Alcohol	42	44	48	14%	134	5	5	9	9%	19	3	8	16	433%	27
Iodopropynyl Butylcarbamate	23	4	26	13%	53	6	4	3	3%	13	3	14	15	400%	32
Methylchloroisothiazolinone	25	26	27	8%	78	4	3	2	2%	9	32	47	70	119%	149
Methylisothiazolinone	45	49	44	-2%	138	6	3	8	8%	17	36	56	82	128%	174
Imidazolidinyl Urea	5	4	4	-20%	13	0	0	0	0%	0	1	5	3	200%	9

Ingredient	2014 RoA	2015 RoA	2016 RoA	% change: 2014 - 2016 RoA	Total Sample RoA	2014 China	2015 China	2016 China	% change: 2014 - 2016 China	Total Sample China
Diazolidinyl Urea	6	5	2	-67%	13	0	1	0	n/a	1
Ethylparaben	1	3	1	n/a	5	0	0	0	n/a	0
Phenoxyethanol	8	11	16	100%	35	2	2	5	150%	9
DMDM Hydantoin	15	14	14	-7%	43	3	10	1	-67%	14
Methylparaben	11	9	13	18%	33	0	9	3	0%	12
Propylparaben	3	4	3	0%	10	0	2	0	n/a	2
Benzyl Alcohol	4	4	5	25%	13	1	2	2	100%	5
Iodopropynyl Butylcarbamate	5	5	2	-60%	12	0	2	1	0%	3
Methylchloroisothiazolinone	3	6	3	0%	12	1	1	0	n/a	2
Methylisothiazolinone	3	9	7	133%	19	2	3	1	-50%	6
Imidazolidinyl Urea	1	2	4	300%	7	0	0	0	n/a	0

Ashland solutions to preserve clear gels

Hair styling gels are designed to hold hair in a fixed shape. Choosing the right preservative for a clear gel can be challenging as the preservative may impact the clarity of the gel or affect its rheological properties. For example, a change in rheological properties of the gel can change the application feel as it is smoothed through the hair as well as the final hold of the gel. A good formulated gel should be flexible while applying and stiffen as it dries.

We conducted a study to identify the best Ashland preservative solutions for clear gels. We chose gels based on PVP (Polyvinyl pyrrolidone) as the styling polymer and Carbomer (acrylic polymer) as the thickening system. The two prototypes used are described in Table III.

table III – clear gel prototypes

	ingredients	INCI name	% w/w	supplier
pH 6.5-7.5 viscosity: 15,000–20,000 mPa.s/25C	phase A			
	DI water	Aqua	Ad 100%	
	Ashland 980 carbomer	Carbomer	0.6	Ashland
	Glycerin	Glycerin	2.0	
	Triethanol amine 99%	Triethanolamine	0.9	
	phase B			
	DI water	Aqua	30.0	
	PVP K90 powder	PVP	1.5	Ashland
	phase C			
	Preservative		a.n	Ashland
pH 6.5-7.5 viscosity: 10,000–15,000 mPa.s/25C	phase A			
	DI water	Aqua	Ad 100%	
	Ashland 980 carbomer	Carbomer	0.4	Ashland
	Aquastyle SH-100	Acrylates Copolymer	3.34	Ashland
	Glycerin	Glycerin	2.0	
	Triethanolamine 99%	Triethanolamine	0.9	
	phase B			
	DI water	Aqua	30	
	PVP K30 powder	PVP	1.0	Ashland
	phase C			
Preservative		a.n	Ashland	

The Ashland carbomer was dispersed in water and mixed well until totally hydrated. The other ingredients of Phase A were added and mixed until a clear gel was formed. The ingredients of Phase B were combined.

Phase B was added to Phase A and mixed slowly. Phase C ingredient was then added to Phase A+B and mixed until fully homogenized.

the various Ashland solutions tested are shown in table IV

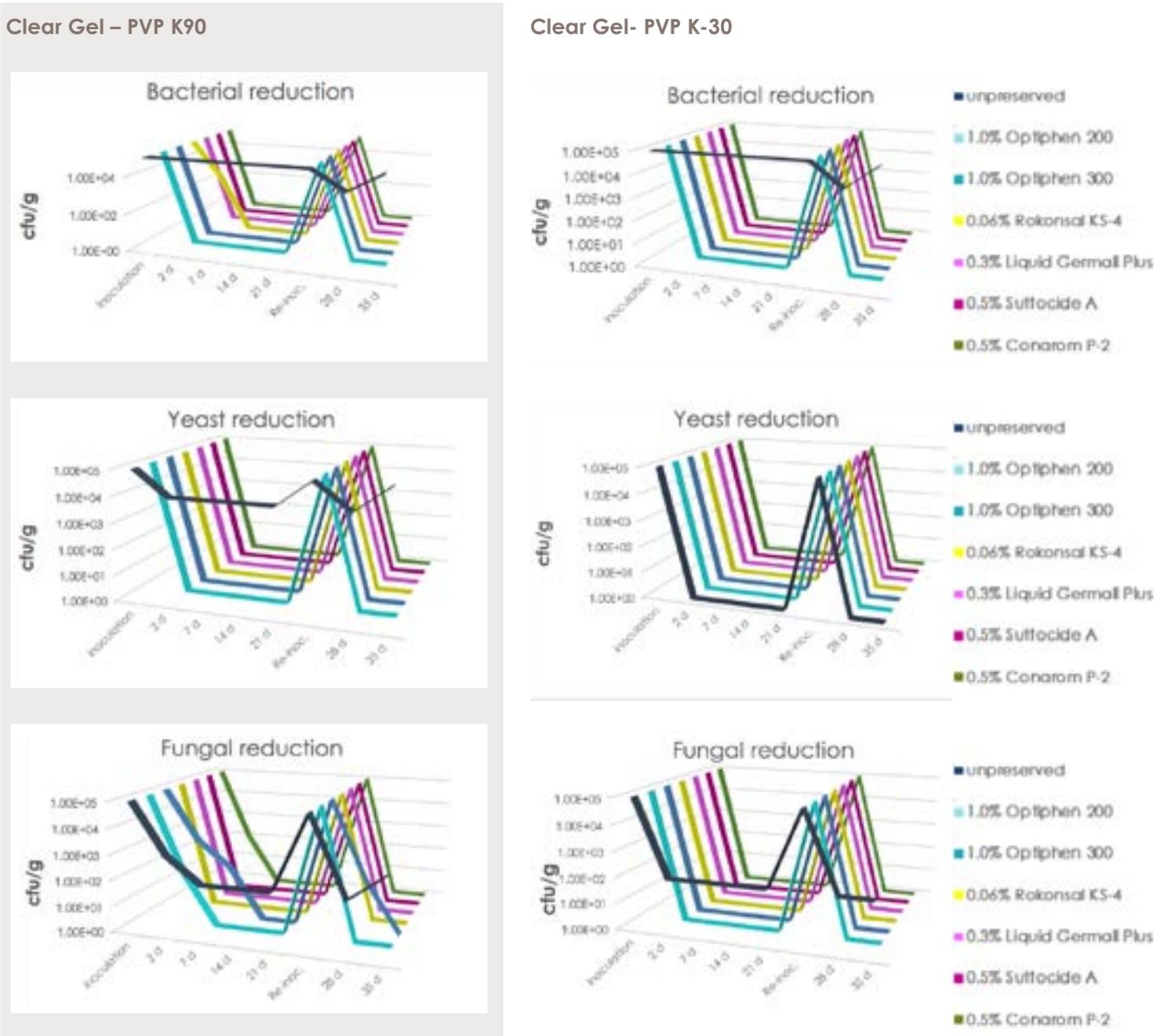
table IV

trade name and dosage	properties	INCI
Optiphen™ 200 @ 1%	<ul style="list-style-type: none"> Robust technology Effective pH range 4 - 8 	Phenoxyethanol and Caprylyl Glycol
Optiphen™ 300 @ 1%	<ul style="list-style-type: none"> Robust technology Effective pH range 4 – 8 Cost effective 	Phenoxyethanol and Caprylyl Glycol
Rokonsal™ KS-4 @ 0.06%	<ul style="list-style-type: none"> Fast acting and very cost efficient Effective pH up to 8 Prohibited in some regions, including EU for leave-on application (e.g. hair gels) 	Propylene Glycol and Benzyl Alcohol and Methylchloroisothiazolinone and Methylisothiazolinone
Liquid Germall™ plus @ 0.3%	<ul style="list-style-type: none"> Classic preservative with long history of use Broad pH range 3 - 8 Easy to incorporate 	Propylene Glycol and Diazolidinyl Urea and Iodopropynyl Butylcarbamate
Suttocide™ A @ 0.5%	<ul style="list-style-type: none"> Long history of use for efficacy Very wide pH applicability 3.5 – 12.0 	Sodium Hydroxymethylglycinate
Conarom™ P-2 aromatic @ 0.5%	<ul style="list-style-type: none"> Nature identical fragrance additive with naturally derived emulsifier system Complements aroma of final formulation Effective pH range 4 - 8 	Phenethyl Alcohol and Caprylyl Glycol and Propanediol and Polyglyceryl-4 Laurate/Sebacate and Polyglyceryl-6 Caprylate/Caprates

results:

- Preservative efficacy tests:** 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 tested preservative systems controlled microbial growth in both hair gel formulations after 2 repetitive challenges. The control was susceptible to microbial growth (except for the *C. albicans* which did not grow in the clear Gel PVP K-30 control).

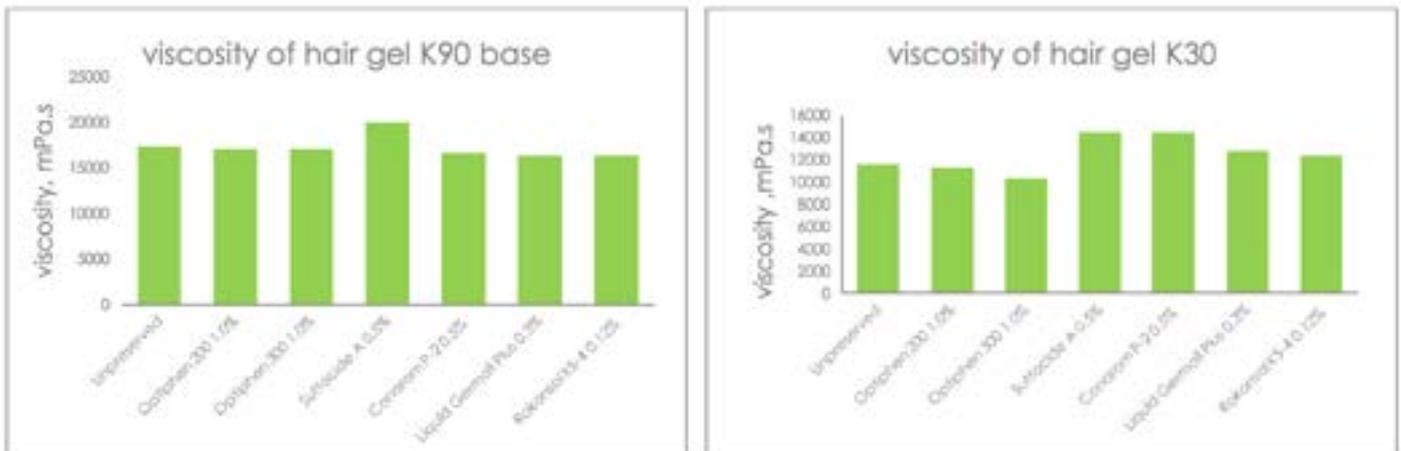
figure 2 – preservative efficacy data



results:

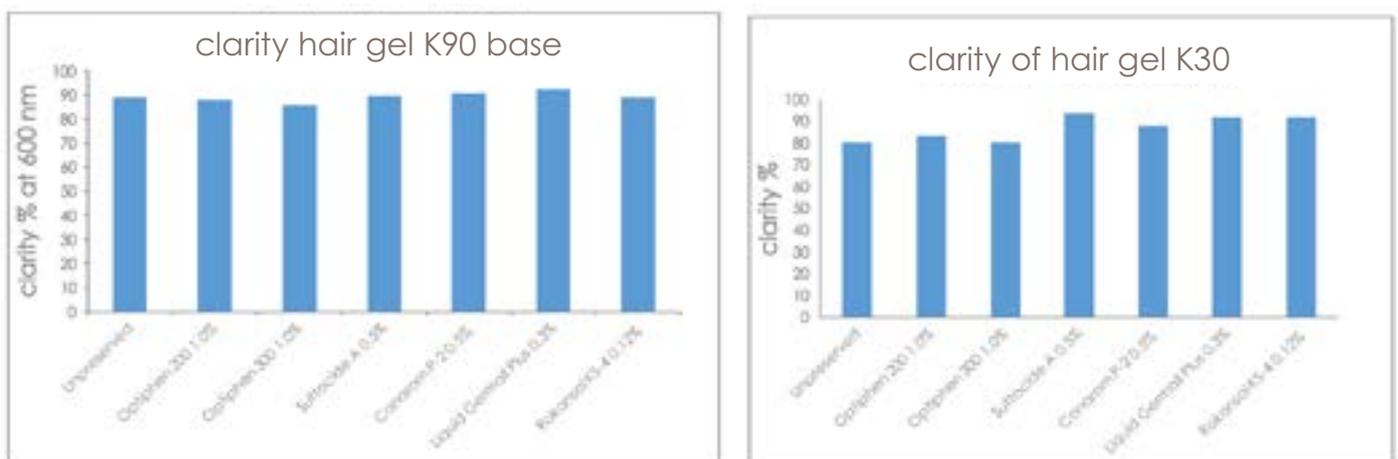
- 2. Viscosity measurements:** The samples were tested at a fixed shear rate of 20 1/s (25C) using an Anton Paar Rheopulus 32 instrument. As shown in Figure 3 the preservative systems tested did not have a negative impact on the viscosity of the hair gels. Suttocide A in the PVP K90 base gel and Suttocide A and Conarom P-2 in the PVP K30 base gel helped to boost the viscosity of the gels.

figure 3: viscosity measurements



- 3. Clarity measurements:** The samples were tested at 600 nanometers using an Agilent Cary 60 UV-vis spectrophotometer. As shown in Figure 4, the clarity was not affected by any of the preservative systems tested (all measurements above 80% are considered clear).

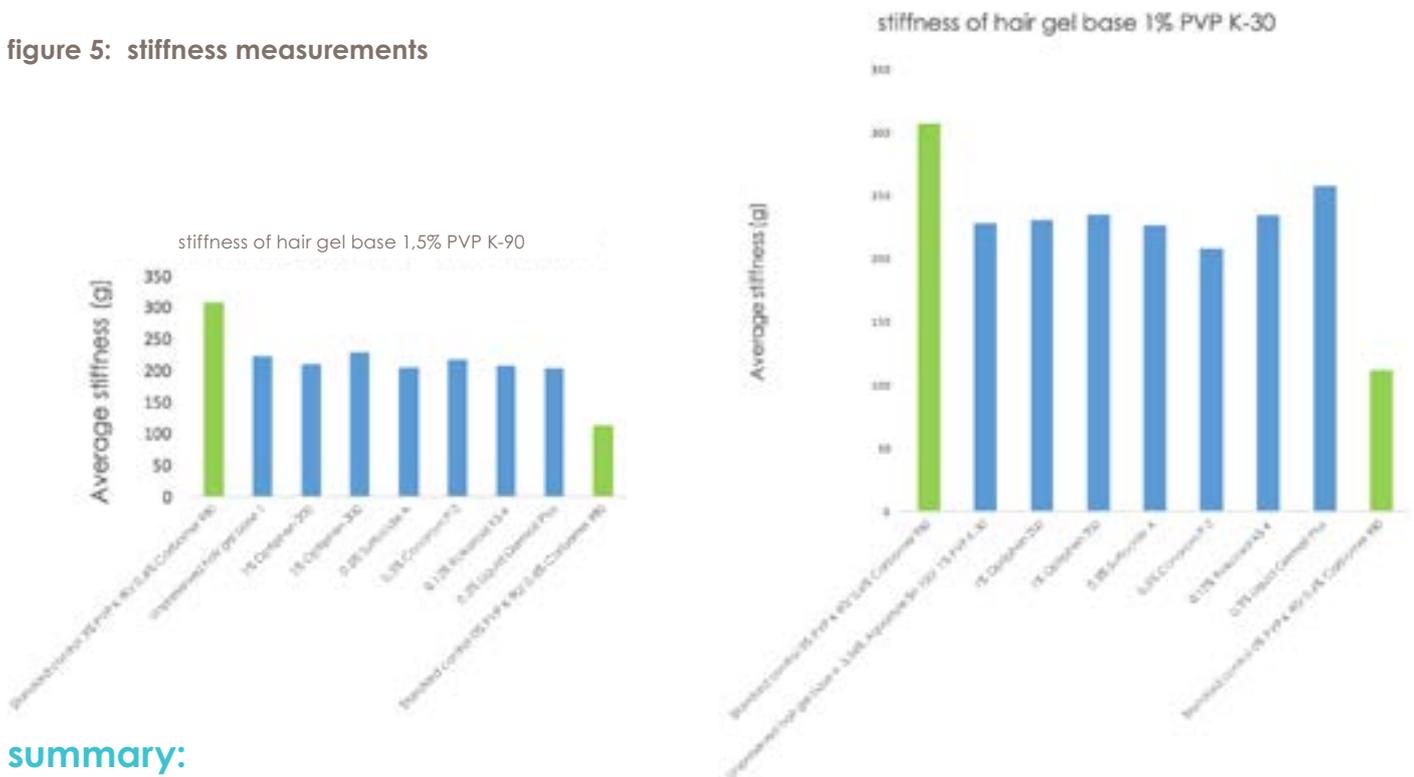
figure 4: clarity measurements



results:

4. **Stiffness measurements:** Tested by the three-point bending method, the preservative systems that were added did not compromise the stiffness of the gel or demonstrate a negative influence on the hold properties of the gels (see Figure 5).

figure 5: stiffness measurements



summary:

These test results demonstrate that various Ashland preservative solutions, comprised of classic and modern technologies, are suitable for use in hair gels. These preservative solutions could offer long-term protection against microbial spoilage without negatively impacting the viscosity, the clarity or stiffness of the hair gels. Some of the properties and advantages of specific Ashland preservatives are shown in Table V.

table V

trade name	comments
Optiphen 200 and Optiphen 300	Modern preservative system. No negative influence of viscosity, clarity and stiffness. Effective at pH range 4 - 8.
Rokonsal KS-4	Classic preservative system. Very cost effective. Fast acting at low use levels. No impact on viscosity, clarity and stiffness. Broad pH range 3 - 8.
Liquid Germall plus	Classic preservative system. No negative influence on viscosity, clarity of stiffness. Broad pH range 3 - 8.
Suttocide A	Classic preservative system. Helps to boost viscosity. Broad pH range 3.5 - 12.
Conarom P-2 aromatic	Aromatic with antimicrobial properties. No negative influence on viscosity, clarity and stiffness. Complements aroma of final formulation. Effective at pH range 4 - 8.

misleading “free from” claims addressed at european level

A new tool to assist companies on the subject of “free from” claims for cosmetics has been issued in the European Union and endorsed by the Working Group on Cosmetic Products¹.

The tool comes in the form of guidance contained in Annex III of the Technical Document on Cosmetic Claims, which is published within the European Commission’s website under Claims and Guidance section in the Cosmetics Legislation page:

https://ec.europa.eu/growth/sectors/cosmetics/legislation_en

<https://ec.europa.eu/docsroom/documents/24847>

According to Commission Regulation (EU) No. 655/2013, claims on cosmetic products should conform to the following common criteria:

- 1. Legal compliance**
- 2. Truthfulness**
- 3. Evidential support**
- 4. Honesty**
- 5. Fairness**
- 6. Informed decision-making**

Annex III of the Technical Document provides guidance for the application of the common criteria to “free from” claims and to help protect against misleading claims. The guidance is structured as a table listing each criterion and how it relates to “free from” claims, along with illustrative examples of such claims.

To the right and below are some of the examples which are relevant to preservatives with descriptions. Please follow the link above to read the full Annex.

It has been agreed by the members of the Working Group on Cosmetic Products that the guidance that was added to Annex III of the Technical Document on Cosmetic Claims should be effective as of the 1st of July 2019.

¹The Working Group on Cosmetic Products is chaired by the European Commission and is composed of representatives from all EU Member States and other non-governmental stakeholders such as EffCI and Cosmetics Europe.

honesty

“Free from” claims or claims with similar meaning should not be allowed when they refer to an ingredient which is typically not used in the particular kind of cosmetic product.

Example: Fine fragrances usually contain such a high amount of alcohol that the additional use of preservatives is not necessary. In this case, it would be dishonest to highlight in advertising the fact that a certain fine fragrance does not contain any preservative.

“Free from” claims or claims with similar meaning addressing functional groups of ingredients should not be allowed if the product contains ingredients with multiple functions and among these is the function that the product is claimed to be free from. Exceptions might be possible (e.g. based on challenge test results of the formula without the particular ingredient(s)).

Example: 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).

fairness

“Free from” claims or claims with similar meaning should not be allowed when they imply a denigrating message, notably when they are mainly based on a presumed negative perception on the safety of the ingredient (or group of ingredients).

Examples: 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.

It is recognised in Annex III that there are cases when “free from” claims are acceptable because they give specific target groups of end users an informed choice about cosmetic products. These cases fall under the 6th criterion of Informed Decision Making and some examples are given to the right/above:

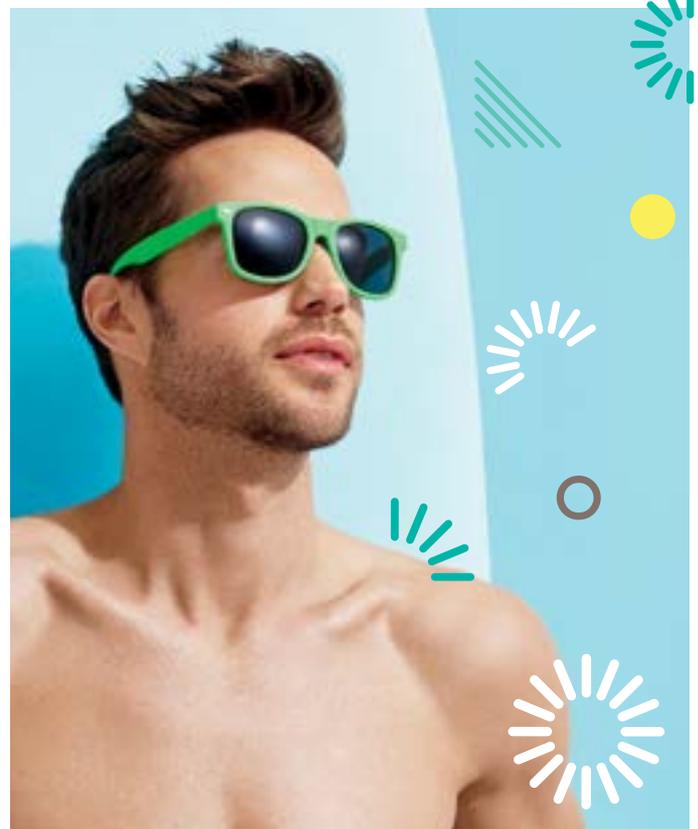
informed decision-making

“Free from” claims or claims with similar meaning should be permitted when they allow an informed choice to a specific target group or groups of end users.

Examples: The following claims should be permitted if they also comply with the other common criteria:

‘free from alcohol’, e.g. in a mouthwash intended as a family product;

‘free from animal-derived ingredients’, e.g. in products intended for vegans.



North America — Dublin, OH USA
Tel: +1 614 790 3361

Europe — Barcelona, Spain
Tel: +34 93 206 5120

India — Navi Mumbai
Tel: +1 800 209 2475

Asia Pacific — Shanghai, P.R. China
Tel: +86 21 2402 4888

Latin America — Araçariquama, Brazil
Tel: +55 11 4136 6477

ashland.com/contact

® Registered trademark, Ashland or its subsidiaries, registered in various countries
™ Trademark, Ashland or its subsidiaries, registered in various countries
© 2018, Ashland

The information contained in this brochure and the various products described are intended for use only by persons having technical skill and at their own discretion and risk after they have performed necessary technical investigations, tests and evaluations of the products and their uses. Certain end uses of these products may be regulated pursuant to rules or regulations governing medical devices, drug uses, or pesticidal or antimicrobial uses. It is the end user's responsibility to determine the applicability of such regulations to its products.

All statements, information, and data presented herein are believed to be accurate and reliable, but are not to be taken as a guarantee of fitness for a particular purpose, or representation, express or implied, for which seller assumes legal responsibility. No freedom to use any patent owned by Ashland, its subsidiaries, or its suppliers is to be inferred.