Alcohol-free Solutions for Personal Care Product Preservation

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abstract

Preservatives are key ingredients in personal care products to protect consumers from infections and to prevent microbial spoilage of the product. The pallet of preservatives for formulators to choose from is rapidly decreasing. Taking advantage of innovative antimicrobial delivery systems, we have developed preservative solutions based on nature identical active ingredients that provide excellent antimicrobial protection while keeping the level of the actives as low as possible.

Introduction

The microbial quality and safety of personal care products is of paramount importance for a producer to succeed in delivering innovative solutions with outstanding performance an integrity to consumers. Yet, formulators are faced with reduced pallet of preservative ingredients due to regulatory restrictions and pressure from NGO on traditional preservative systems.

The list of available preservative ingredients must contend with constantly-changing global regulatory guidelines and consumer's demands which are, in general, based on perceptions with little or no scientific basis. Phenoxyethanol is one such ingredients. While the Scientific Committee on Consumer Safety (SCCS) has concluded that phenoxyethanol is safe at use levels of 1% in cosmetics and the calculated Margin of Safety (MoS) also covers children and babies [1], some companies are trying to find alternative preservation strategies to those based on phenoxyethanol preservatives.

Ashland's solution to the shrinking list of preservative alternatives is to develop new technologies based on innovative ingredients that can solve current needs for preservation solutions.

One such approach is the use of Optiphen™ DLP or Optiphen™ DP preservatives that are based on nature identical actives, embedded into optimized delivery systems that maximize the efficacy of the actives at the oil/water interface, thus enhancing their bioavailability and in turn allowing the actives to work at lower levels while reducing the exposure to high level of preservatives. These are new to the world combination without alcoholic antimicrobials based on skin friendly ingredients.

Performance Data

The performance of various preservatives solutions was evaluated in different personal care products. The description of Ashland's preservative alternatives tested is shown in **Tab. 1**.

Preservative challenge tests with 2 inoculations were conducted in different products.

The microbial inoculum consisted of a bacterial composite containing: *Pseudomonas aeruginosa, Staphylococcus aureus, Escherichia coli* and *Burkholderia cepacia* and yeast or a mold composite containing *Aspergillus brasiliensis* and *Candida albicans*.

The products were inoculated at the onset of testing (0 hours) and sampled at 2, 7, 14 and 21 days. At 21 days, the formulations were re-inoculated, and sampled at 28 and 35 days. The final inoculum concentration in each sample was 10^5–10^6 cfu/ml.

Trade name	INCI	Features and Benefits
Opitphen DP preservative	Propylene Carbonate, Benzoic Acid, Dehydroacetic acid (DHA), Propanediol	Optimized delivery system. Effective up to pH 6.0; Global use; Cost effective;
Optiphen DLP preservative	Propylene Carbonate, Dehydroacetic acid (DHA)	Antifungal activity at low levels; full antimicrobial spectra at high levels. Cost effective; Optimized delivery system. Effective up to pH 6.4; Global use

Tab. 1 Ashland alcohol free preservation technologies, based on nature identical active ingredients.

Conarom™ b aromatic is an effective solution that meets the growing consumer demand for multifunctional and sustainable ingredients. The aromatic adds a gentle flowery-to-spicy fragrance and delivers broad antimicrobial protection to differentiate and impart additional allure to the end use formulation. It is based on naturally derived hops extract and the nature identical Phenylpropanol.

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In the first set of experiments the efficacy of Optiphen™ DLP preservative (DHA in a delivery system) was compared to the efficacy of DHA powder or to Sorbic acid alone in a Creme emulsion, pH 5.4 (**Tab. 2**).

As shown in **Fig. 1**, in a product that supported microbial growth (control) the addition of 1,500 ppm of DHA in a delivery system (2.14% Optiphen™ DLP) controlled the growth of bacteria, yeast and mold. This is, some levels of bacteria, yeast and mold were detected after the inoculation, but they died off. The addition of 1,500 ppm of sorbic acid or 1,500 ppm of DHA alone had no impact on bacterial growth. Furthermore, the sorbic acid was not as effective in controlling yeast and mold growth. The use of an optimized delivery system for DHA (as in Optiphen™ DLP) allows the active to reach the water/oil interface were microorganism are growing thus enhancing the bioavailability of the active which is evident from the difference in performance.

In addition, the delivery systems can reduce yellowing when added to certain products, as shown in **Fig. 2**. A significant yellowing effect is observed when the product is stored at 4 weeks at 50 °C in the dark in the presence of 1,500 ppm of sorbic acid. Some yellowing was

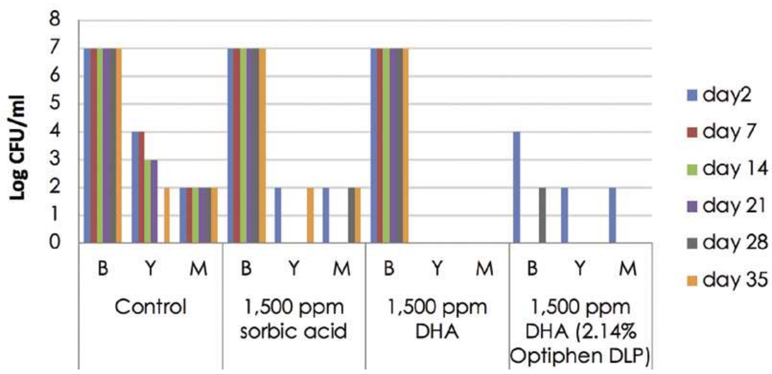

Fig. 1 Challenge test creme emulsion, pH 5.4.

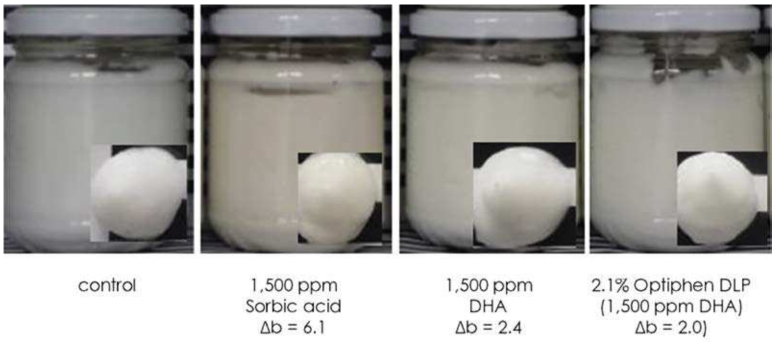

Fig. 2 Color development 4 weeks at 50 °C.

Phase	Ingredients (Trade Name)	INCI Name	% w/w	Supplier
A	Water	Aqua	Q.S. 100	Local
	Ultrathix 20	Carbomer	0.20	Ashland
B	Ceraphyl 368	Octyl palmitate	5.00	Ashland
	Emulgade 1000 NI	Cetearyl alcohol and ceteareth 20	2.00	BASF
	Cerasynt 945	Glyceryl stearate and laureth-23	2.50	Ashland
	Carnation white	Mineral oil	5.00	Local
C	TEA 99 %	Triethanolamine	0.20	Local
	Water	Aqua	0.20	Local
D	Solugel 5000	Hydrolyzed gelatin	0.50	PB Leiner
	Water	Aqua	5.00	Local

Procedure:
1. Add Ultrathix 20 in water under stirring mix it well and heat up to 75 °C. Hold for 45 min.
2. Heat phase B and at 75 °C in main vessel, mix it till it becomes homogeneous for 10 to 15 min. Add to Phase A.
3. Allow the mixture to cool at 45 to 50 °C and then add Phase C.
4. Allow mixture to cool to 35 °C and mix and add Phase D.

Typical Properties:
pH – 5.4; Apparence: white ; viscosity – 39,000 cps

Tab. 2 Crème emulsion (formula# NE1C-S) .

Phase	Ingredients (Trade Name)	INCI Name	% w/w	Supplier
A	Deionized Water	Aqua	a.d. 100 %	Local
	Dissolvine® Na	Disodium EDTA	0.15	AkzoNobel
	N-Hance™ 4572 conditioning polymer	Guar Hydroxypropyltrimonium Chloride (and) Acrylamidopropyltrimonium Chloride/ Acrylamide Copolymer	0.15	Ashland
B	Glycerin GG	Glycerin	3.00	Local
	Benecel™ E10M Rheology modifier	Hydroxypropyl Methylcellulose	0.30	Ashland
	Trimiron® MP 10001	Mica (and) Titanium Dioxide	0.10	Merk
C	Iselux® LQ-CLR-SB	Sodium Lauroyl Methyl Isethionate (30 %)	19.00	Innospec
	Lumoral® K5019	Disodium Laureth Sulfosuccinate (and) Sodium Lauryl Sulfoacetate (30 %)	8.30	Zschimmer & Schwarz
	Betadet® HR	Cocamidopropyl Betaine (30 %)	6.70	Kao
	Perfume	Parfum	0.30	
	preservative		a.n.	Ashland
D	Deionized water	Aqua	3.00	
	SurfaThix™ N	Acrylates Copolymer	3.00	Ashland
E	Sodium Hydroxide (33 %)	Sodium Hydroxide	0.30	Local
	Sodium Chloride	Sodium Chloride	0.50	Local
Total			**100.00**	

Procedure:
1. Phase A: dissolve the N-Hance 4572 in the water with good stirring.
2. Phase B: Disperse the Benecel E10M and the Timiron MP1001 in the Glycerin and add to Phase A. Stir well till fully hydrated (30 min).
3. Phase C; Add the surfactants and ingredients in order with good agitation.
4. Phase D: Premix the acrylates Copolymer in the water and add to the batch.
5. Phase E: Add ingredients to reach desire pH and viscosity.

Typical Properties :
pH – 6.1; Apparence: pearly liquid ; viscosity – 6,000 – 8,000 mPas ;

Tab. 3 Super pearly sulfate free low surfactant shampoo (#Z-327-23).

also evident in the presence of 1,500 ppm DHA. No significant yellowing was observed in the presence of Optiphen™ DLP (1,500 ppm DHA).

In another set of experiments, the efficacy Optiphen™ DLP preservative was compared to the efficacy of DHA powder or sorbic acid alone in a pearly shampoo formulation, pH 6.1 (**Tab. 3**).

Fig. 3 shows the results of the challenge tests comparing the various preservatives in a pearly shampoo formulation. Optiphen™ DLP offers better protection than the other 2 preservative treatments at same ppm of the acids. This is 1,500 ppm of sorbic acid did not control bacteria and fungal growth, while some recoveries of the various microbes were observed when adding 1,500 of DHA powder. The Optiphen™ DLP exhibited a faster kill rate than to DHA powder for all microbes tested.

Fig. 4 shows color development at 40 °C after 4 weeks (samples kept in the dark). While all of the preservative treated products developed some yellowing, the yellowing of the pearly shampoo containing the Optiphen™ DLP yellowed

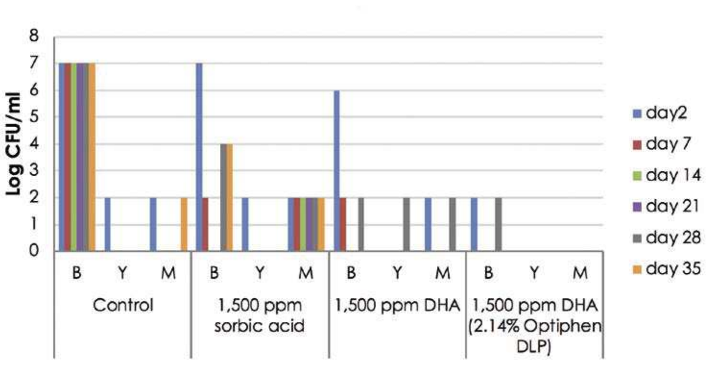

Fig. 3 Challange test pearly shampoo pH 6.1.

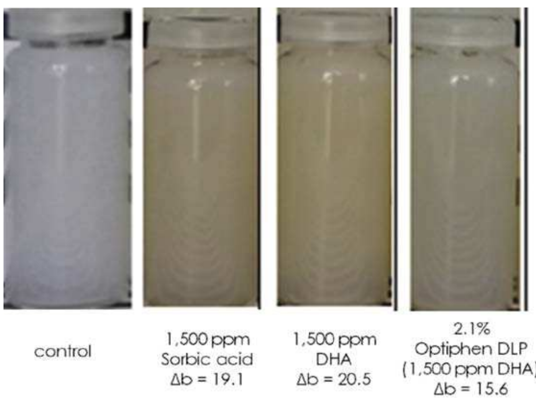

Fig. 4 Color development 4 weeks at 40 °C.

significantly less than the other 2 treated samples.In another set of experiments in a mild clear conditioning shampoo formulation, pH 5.5 (**Tab. 4**) the efficacy of Optiphen™ DP was compared to that of DHA alone at same concentration.

As shown in **Fig. 5**, the addition of 800 ppm of DHA alone did not inhibit bacterial growth in this product and some mold was recovered at different time intervals. The addition of 800 ppm DHA as Optiphen™ DP offered full protection as no microorganisms were recovered thought the challenge test. Optiphen™ DLP performed better than DHA powder, providing full antifungal protection even with 2 inoculation cycles.

Ingredients	INCI name	% w/w	Supplier
De-ionized Water	Water	75.41	
Tego Betain F50	Cocoamidopropyl Betaine	6.50	Evonik
SLES (70 %)	Sodium Laureth Sulphate	13.00	Kao
Ceraphyl 41	C12-15 Alkyl Lactate	1.00	Ashland
Citric acid (25 % aq).	Citric acid	0.50	
Sodium Chloride (25 % aq.)	Sodium Chloride	4.00	

Procedure:
Incorporate all ingredients one by one and stir until completely dissolved.

Typical Properties:
pH – 5.5; Apparence: Clear.

Tab. 4 Mild clear conditioning shampoo (#MM LB 4/52)

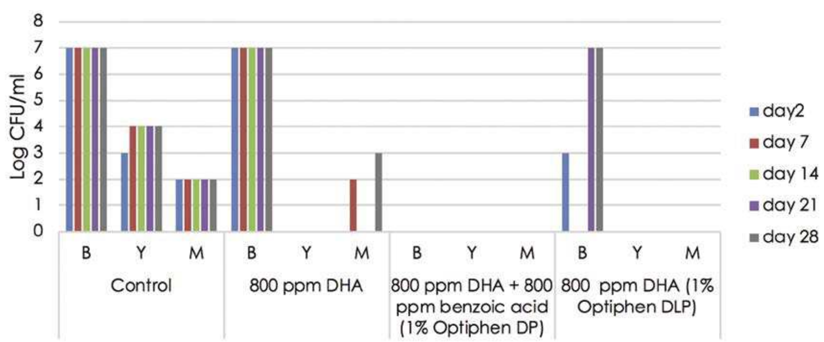

Fig. 5 Challenge test simple shampoo pH 5.5.

Conclusions

Working with preservatives that offer optimized delivery systems provide alternatives to develop innovative products with outstanding microbial quality and safety. Lower levels of the active ingredients are required to protect the products from microbial growth thus providing a more sustainable preservation approach for products. Ashland´s innovative tools Optiphen™ DLP and Optiphen™ DP preservative are suitable to solve alternative preservation challenges.

References

[1] *Lilienblum, W.* (2016): Opinion of the Scientific Committee on Consumer Safety (SCCS) – Final version of the opinion on Phenoxyethanol in cosmetic products. Regulatory Toxicology and Pharmacology. 82:156. https://doi.org/10.1016/j.yrtph.2016.11.007.

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