

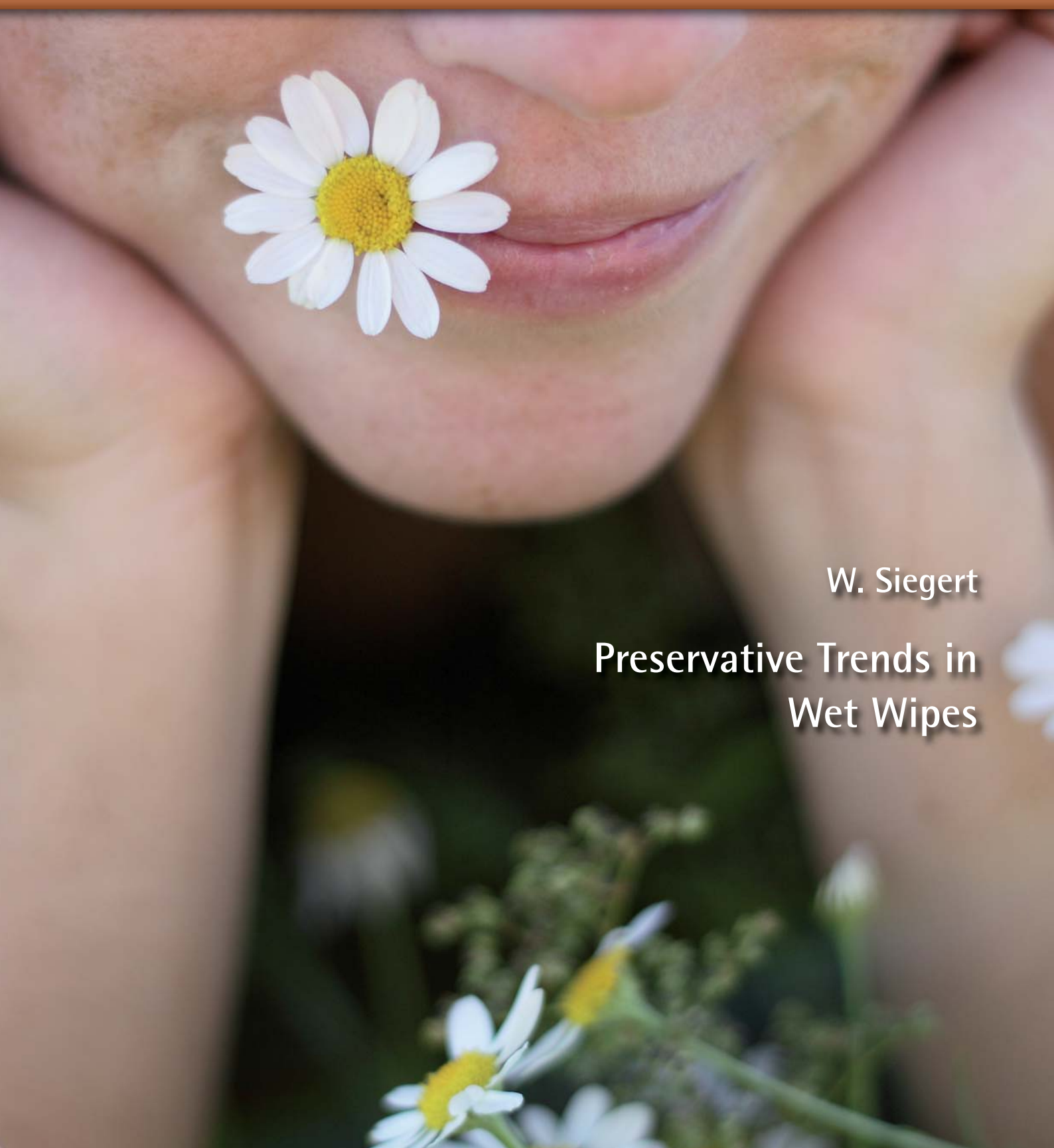
**SOFW**

**JOURNAL**

**5-2011**

**English Edition**

International Journal for Applied Science  
• Personal Care • Detergents • Specialties



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Preservative Trends in  
Wet Wipes

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# Preservative Trends in Wet Wipes

## Introduction

The wet tissues market is a growing business. Besides cleansing tissues like wet toilet paper, baby wipes or hard surface wipes other products such as sun protection lotion or deodorants are offered as wipes.

The wet tissue liquids are mostly aqueous, the cellulose is a good nutrient, the non-woven is always moderately contaminated with microorganisms and the

storage temperature is nearly optimal for microbial growth. All factors for microbial attack (Fig. 1) are fulfilled. To produce microbiological faultless wet tissues, an integrated microbiological quality management is necessary, consisting of good raw material quality, good production hygiene and a validated preservative system (1). The influence of the non-woven, the production process, the choice of preservatives, preservative efficacy testing, responsible care and hygiene measures have to be taken into consideration.

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## The Need of Preservation

Microorganisms can grow on almost every substance existing in nature and are often able to attack or even decom-

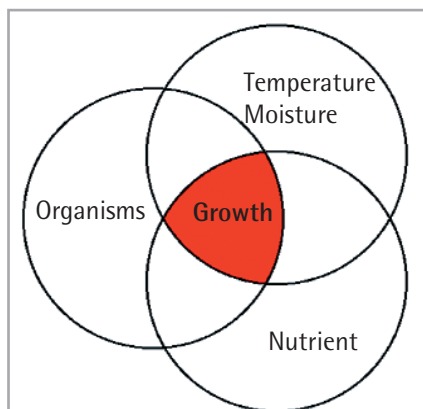


Fig. 1 Factors for microbial attack

## Abstract

The topic of preservation is always of importance to formulators and finished goods marketers. Formulators are aware of the necessity to adequately preserve their products in order to ensure product safety and be in compliance with legislation. This task is made much more difficult when marketing requirements are added to the factors influencing the preservative choice. Demands such as global approval, soft preservation, »free of...«, etc. have limited the number of acceptable actives.

### Microbicide and degradable: no conflict !

Dependence on the concentration and usability of bacteria toxicity shown for alcohols (ethanol) as an example

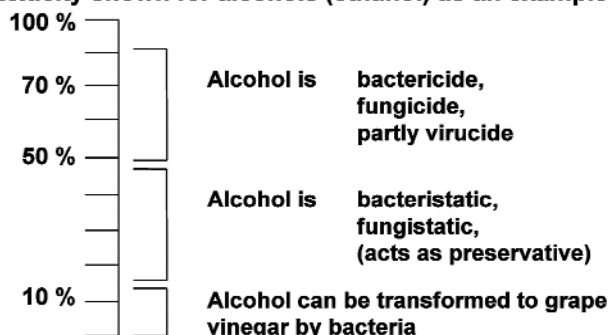


Fig. 2 Microbial degradation of ethanol

pose them. The biological degradation has to be stopped for a certain period. A preservative must be added, but for environmental reasons the preservative should be biodegradable, too. This is no conflict; for example a concentration of ethanol between 50 and 90 % it is a good disinfectant, between 13 and 50 % it acts as preservative, but below 13 % ethanol will be biologically degraded to acetic acid (Fig. 2).

For wet wipes the need for preservation can be summarised as follows:

- Wet tissues are an excellent environment for the growth of bacteria, yeasts and moulds.
- The demand for flushable wipes and the increased use of natural fibres make mould growth with its easily visible staining more likely.
- Environmental requirements (e.g. from the EU Detergent Directive) to use only biodegradable detergents increase the susceptibility of the wet tissues to microbial growth.
- The demands for flushable wipes and the increased use of natural fibres make mould growth with its easily visible staining more likely.
- To ensure product and consumer safety, the addition of preservatives is necessary.

■ Parameters which Influence the Performance of the Preservation

The performances of the preservatives are mainly influenced by:

- Formulation of the wet tissue liquid
- Type of nonwoven
- Quality of raw materials
- Quality of nonwoven
- Type of preservative
- Amount of liquid per tissue
- Production process
- Distribution of the wet wipe liquid onto the wipe

■ Trends within Preservatives in Wipes

In a study from Biocide Information Limited about biocides in wipes the most sought after properties of preservatives in wipes are:

- Broad spectrum of activity (bacteria & fungi)
- Effective over a wide pH range
- Easy to use and handle
- Compatible in raw material and formulation

- Cost effective at low concentrations
- Practically free from odour and colour
- Extremely low toxicity to humans
- Environmentally acceptable
- Approved for use by many regulatory bodies world-wide

■ Selection of Preservation

When selecting preservatives for wet tissues a number of factors have to be considered.

Legislation is an essential issue (Fig. 3).

• Europe: EU Cosmetics Directive New Cosmetic Products Regulation	
• USA: Cosmetic Ingredient Review (CIR)	
• South East Asia: ASEAN Cosmetics Directive	
• Japan: Standards for Cosmetics	

Fig. 3 Different regulations for cosmetic wipes











	<b>Cosmetic Ingredient Review</b>	<a href="http://www.cir-safety.org/findings.shtml">http://www.cir-safety.org/findings.shtml</a>
<b>Cosmetic Ingredient findings: 1976 - current</b>		
<a href="#">Reference Table includes a complete list of all findings</a>		last updated 07/20/10.
<a href="#">Ingredients found Safe as used</a>		last updated 02/02/11.
<a href="#">Ingredients found Safe with qualifications</a>		last updated 02/02/11.
<a href="#">Ingredients for which there are Insufficient data</a>		last updated 02/02/11.
<a href="#">CIR Zero Use Ingredients</a>		last updated 02/02/11.
<a href="#">Ingredients found Unsafe</a>		last updated 02/02/11.
<a href="#">Hairdye Epidemiology</a>		last updated 01/06/10.
<a href="#">Re-review ingredients</a>		last updated 02/02/11.
<a href="#">Ingredients Prohibited / Restricted</a>		last updated 02/02/11.

Fig. 4 CIR Database

Cosmetic wipes marketed in the European Union have to be in compliance with the Cosmetics Directive 76/768/EEC <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:1976L0768:20090225:EN:PDF> and the New Cosmetic Products Regulation 1223/2009 <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:342:0059:0209:EN:PDF>, which applies latest from 11 July 2013. The EU regulation is similar adopted from many countries as e.g. the ASEAN Cosmetics Directive. Beside this, the most important regulation is related to the USA. Most producers of a cosmetic product follow the CIR recommendations (Fig. 4).

Wet tissues that are claimed for cleansing of hard surfaces have to be preserved according to the Biocidal Product Directive (BPD) <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2003R2032:20070104:EN:PDF>. The scope of the BPD is very wide and covers disinfectants for home and industrial use as well as preservatives for manufactured and natural products.

■ **Difference in Regulations on the Example of IPBC**

Fig. 5 shows the different evaluations in the EU compared to the CIR recommendation.

The lowest use concentrations in the different regulations are the recommended ones for international formulations. Fig. 6 shows an example of an acid based preservative.

■ **Preservative Actives in Focus**


Most preservative actives are in a certain public discussion. In most cases scientific assessment of the suspected risks is not completed yet. Typical examples are:

**Formaldehyde/Formaldehyde-donors**  
 DMDMH, imidazolidinyl urea, diazolidinyl urea

- suspected of carcinogenic potential

**Organic Halogen Compounds**  
 Isothiazolinones, methyl dibromoglutaronitrile, IPBC

- sensitisation potential

<b>Substance</b>	Iodopropynyl butylcarbamate; (IPBC); 3-Iodo-2-propynylbutylcarbamate CAS No: 55406-53-6		
<b>CAS #</b>	55406-53-6		
<b>EINECS/ELINCS #</b>	259-627-5		
<b>INN/ISO/AN</b>			
<b>Cosmetic Directive</b>	2007/22/EC 		
<b>Other Directives/Regulations</b>	<b>EU Database</b>		
<b>Annex/Part,Ref #</b>	VI/1,56		
<b>Maximum authorized concentration</b>	(a) Rinse-off products: 0.02% (b) Leave-on products: 0.01%, except in deodorants/antiperspirants: 0.0075%		
<b>Limitations and requirements</b>	Not to be used in oral hygiene and lip care products. (a) Not to be used in preparations for children under three years of age except in bath products/shower gels and shampoos (b) - Not to be used in body lotion and body cream (*) - Not to be used in preparations for children under three years of age		
<b>Conditions of use and warnings which must be printed on the label</b>	(a) Not to be used for children under three years of age (**) (b) Not to be used for children under three years of age (***)		
<b>SCCS opinions</b>	<a href="#">0193/99 - Opinion on 3-Iodo-2-propynylbutylcarbamate (IBPC)</a> <a href="#">0826/04 - Opinion on Iodopropynyl Butylcarbamate</a>		

prohibited for baby wipes



**Quick Reference Table**  
 Cosmetic Ingredient Review reports through June 2010

S - safe as used; SQ - safe with qualifications; I - insufficient data to support safety;  
 Z - insufficient data, but no uses; U - unsafe

Ingredient Name	Review Conclusion				Maximum "as used" concentration for safe as used conclusion *	Explanation Concentration or other limitation on use for safe with qualifications conclusion	Safety concern leading to unsafe conclusion	Journal Citation
	S	SQ	I	U				
Iodopropynyl Butylcarbamate (IPBC)		X				safe for use at ≤0.1%; should not be used in products intended to be aerosolized		IJT 17(55):1-37, 1998

safe for use at ≤0.1%; should not be used in products intended to be aerosolized

Fig. 5 Different evaluations in the EU compared to the CIR recommendation

**Product based on: \*)**

Phenoxyethanol	74 %
Benzoic acid	12 %
Dehydroacetic acid	7 %
Aqua	4 %
Ethylhexylglycerin	2 %
Polyaminopropyl biguanide	1 %

**Use-concentrations**

	acc. schülke-recommendation	acc. EU and ASEAN Cosmetics Directive	acc. CIR (USA)
<b>Leave-on</b> (e.g. creams, lotions etc.)	0.20 – 1.00 %	max. 1.35 %	max. 6.76 %
<b>Rinse-off</b> (e.g. shampoos, Bath preparations etc.)	0.20 – 1.00 %	max. 1.35 %	max. 6.76 %

\*) euxyl® K 702

Fig. 6 Observance of different regulations

### Bronopol

- avoid nitrosamine formation

### Parabens

Methyl-, propyl-, ethyl-, butyl-, isobutylparabens suspected of

- pseudo-oestrogenic and androgenic potential
- association with breast-cancer
- association with skin aging (methylparaben)

### Benzyl Alcohol

- listed on Annex III CPD as perfume »allergen«

### Phenoxyethanol

- glycol ether discussion in France

### ■ Possibilities for Future Developments

Most new developments are based on following actives and preservative enhancer:

#### Organic acids

- sorbic acid
- benzoic acid
- dehydroacetic acid

#### Alcohols

- benzyl alcohol
- phenoxyethanol

#### Cationics

- polyaminopropyl biguanide

#### Multifunctional additives

- ethylhexylglycerin
- glycol (butylene glycol, pentylene glycol, etc.)

#### Chelating agents

- EDTA
- tetrasodium glutamate diacetate

### ■ Synergistic Mixtures

To minimise the amount of preservative actives, synergistic mixtures have been developed (2-6):

- Combinations of preservative actives
- Addition of multifunctional actives to boost the antimicrobial effect
- Addition of chelating agents
- Combination of multifunctional actives to achieve self-preserving systems

### ■ Synergistic Combinations of Preservative Actives

The efficacy of a simple acid / alcohol mixture (Product A) was compared with euxyl® K 702 (Product B) using the synergistic effect described in the patents DE4026756 and US5670160 with following compositions:

	Product A	Product B
Phenoxyethanol	74%	74%
Benzoic acid	12%	12%
Dehydroacetic acid	7%	7%
Aqua	7%	4%
Ethylhexylglycerin		2%
Polyaminopropyl biguanide		1%

Dilutions of product A and Product B are prepared with sterile tap water and adjusted with sodium hydroxide to pH 5.5. 50 ml portions of the end solutions are inoculated with 0.5 ml microorganism suspension (initial microorganism count approx. 10<sup>8</sup> cfu/ml) and stirred.

The testing was performed using a serial dilution test to compare the minimal inhibition concentrations (MIC values), a germ count reduction test to compare the biocidal effect and also a repeated challenge test to evaluate the efficacy as preservative under practical conditions.

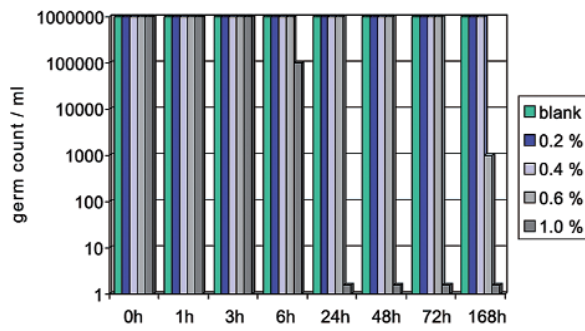
Determination of the minimum inhibitory concentration in serial dilution tests produced the following values at pH 5.5:

Test organisms	ATCC N°
<i>Pseudomonas aeruginosa</i>	15442
<i>Escherichia coli</i>	11229
<i>Candida albicans</i>	10231
<i>Aspergillus niger</i>	6275

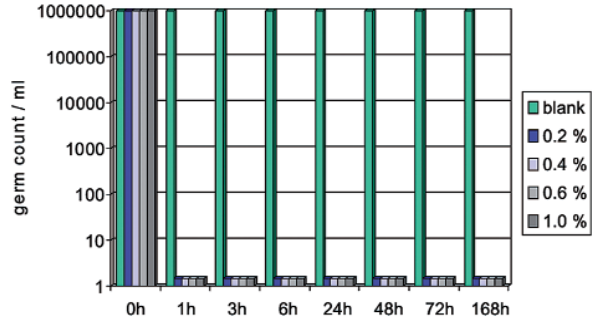
The solutions are streaked out onto tryptone soya agar or sabouraud-dextrose 4% agar after 3, 6, 24, 48, 72 and 168 hours, depending on the test organism.

		Product A	Product B
Species	ATCC N°	MIC value [%]	
<b>Gram-negative:</b>			
<i>Burkholderia cepacia</i>	17759	0.50	0.25
<i>Enterobacter gergoviae</i>	33028	0.75	0.06
<i>Escherichia coli</i>	11229	0.25	0.06
<i>Klebsiella pneumoniae</i>	4352	0.50	0.12
<i>Pseudomonas aeruginosa</i>	15442	0.50	0.25
<i>Pseudomonas fluorescens</i>	17397	0.25	0.06
<i>Pseudomonas putida</i>	12633	0.50	0.12
<b>Gram-positive:</b>			
<i>Staphylococcus aureus</i>	6538	0.50	0.12
<i>Staphylococcus epidermidis</i>	12228	0.50	0.06
<b>Mould fungi:</b>			
<i>Aspergillus niger</i>	6275	0.25	0.12
<i>Penicillium funiculosum</i>	36839	0.25	0.12
<b>Yeasts:</b>			
<i>Candida albicans</i>	10231	0.25	0.12

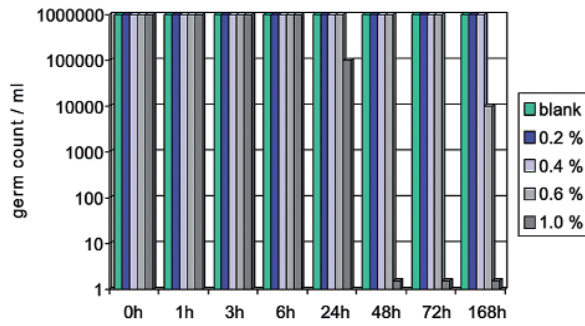
PRESERVATIVES



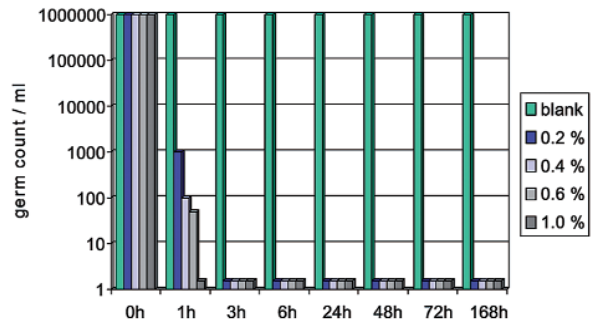
Product A / *E. coli*



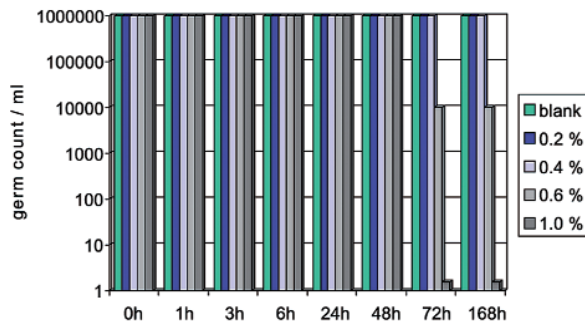
Product B / *E. coli*



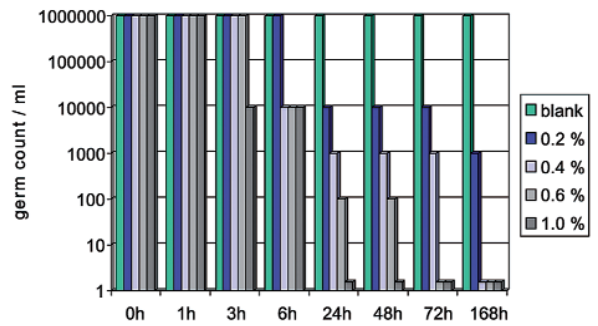
Product A / *A. niger*



Product B / *A. niger*



Product A / *C. albicans*



Product B / *C. albicans*

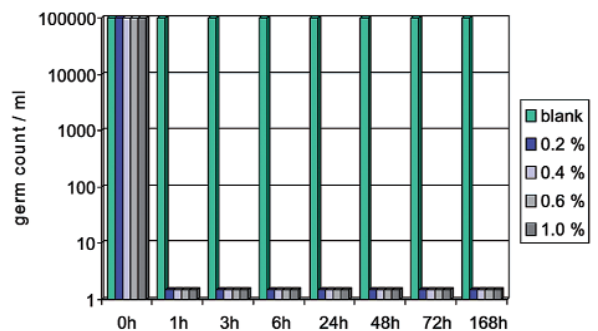
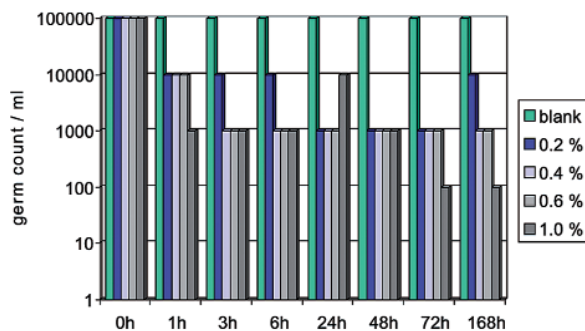


Fig. 7 Reduction of microorganism for product B in comparison to product A

The cultures are incubated for 48 hours at 37 °C, except in the case of *Aspergillus niger*, which is incubated for 72 hours at 25 – 27 °C. The evaluation is made on the basis of a semi-quantitative assessment of the microbial growth of the streaks. In Fig. 7, the microorganism reduction achieved for product B in comparison to product A at pH 5.5 as a function of the contact time and use-concentration is presented for the various test organisms. Product B has a more efficient germ reduction, as evidenced by the greater kill rate at earlier time readings. This is especially useful for pre-contaminated raw materials, such as the production water or the non-woven, as they may be more easily sanitised with product B.

■ The Importance of pH Control

The pH value is a critical control point for the efficacy of preservatives based on organic acids. The pH value has not only be checked in the wet tissue liquid, but in a liquid squeezed from the tissue. As typical example a wet tissue liquid preserved with 1% phenoxyethanol, benzyl alcohol, potassium sorbate mixture (euxyl® K 700) is demonstrated in Table 1. Particularly Airlaid showed a severe influence of the pH.

Phenoxyethanol is a familiar and well accepted cosmetic preservative. The addition of ethylhexylglycerin enhances the efficacy of phenoxyethanol (euxyl®

Wet wipe liquid itself		Wet wipe liquid squeezed from the tissue	
Immediately after production	After one month storage	Immediately after production	After one month storage
pH 5.1	pH 5.1	pH 5.5	pH 5.5

Table 1 Influence of the nonwoven on the pH value

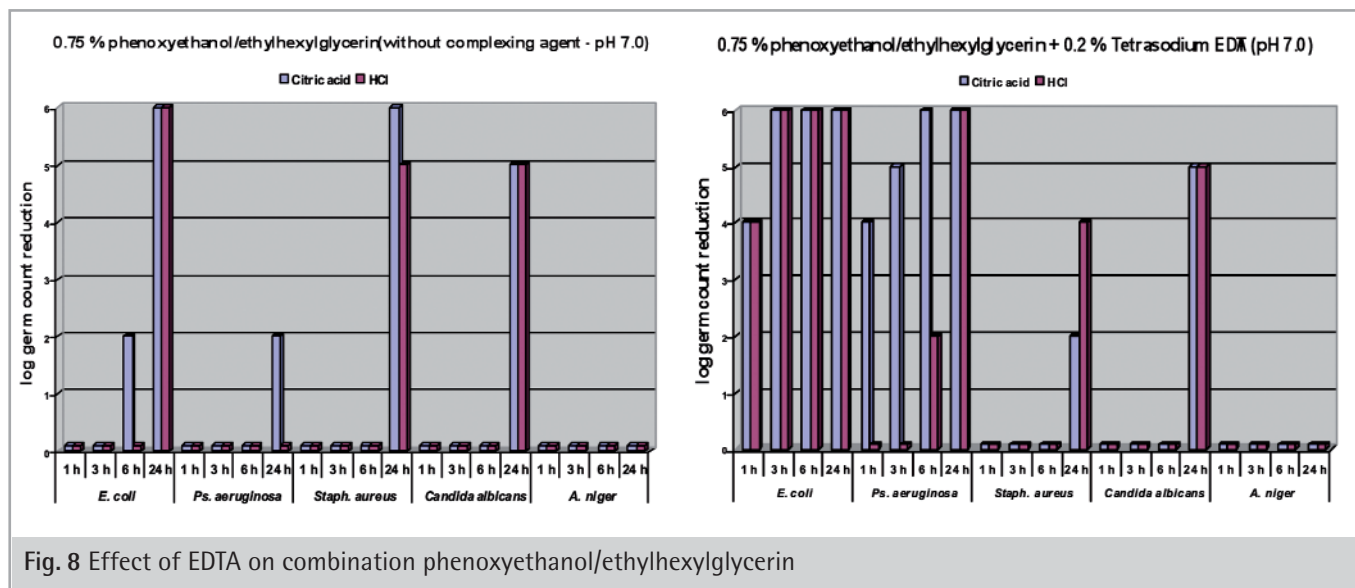
Phase	INCI Name	Function	% w/w
A	Water (Aqua)		43.00
B	Hydroxyethylacrylate (and) sodium acryloyldimethyl taurate copolymer (and) squalane (and) polysorbate 60	Thickener, emulsifier	0.60
	Isopropyl palmitate	Binder, emollient, solvent	5.00
	Mineral oil		5.00
C	Water (Aqua)		q.s.
D	Sodium palmitoyl proline (and) nymphaea alba flower extract	Lipo-amino soothing agent	0.50
	Tocopheryl acetate	Antioxidant	0.10
	Fragrance	Fragrance	0.10
	Phenoxyethanol/ethylhexyl-glycerin (9:1)	Preservative	1.00
			100.00

250% of solution based on the dry weight of the wipe for the substrate SPUNLACE viscose/polyester 65/35 55 g/m<sup>2</sup>

Table 2 Example of a wet wipe formulation passing challenge testing

PE 9010). The innovative, multifunctional additive affects the interfacial tension at the cell membrane of microorganisms, improving the preservative activity of

phenoxyethanol. Due to its water solubility it can be used in clear solutions, which is often a problem with paraben based preservatives. Several hundred ef-



ficacy tests in different leave-on-formulations proved the mixture of phenoxyethanol/ethylhexylglycerin to be far more effective than phenoxyethanol alone and to be comparable with traditional phenoxyethanol/paraben mixtures (5). Table 2 shows an example for a wipe formulation.

■ Addition of Chelating Agents

Chelating agents can enhance the efficacy of »soft preservatives«. Fig. 8 shows the effect of EDTA on the combination phenoxyethanol/ethylhexylglycerin in the before described germ count reduction test.

Glutamic acid, N,N-diacetic acid, tetrasodium salt (GLDA) (Dissolvine® GL) → INCI Tetrasodium Dicarboxymethyl Glutamate, a readily biodegradable chelating agent, that can be used as alternative for EDTA. Especially when used together with citric acid GLDA shows a better effect as EDTA (Fig. 9).

■ Self-preserving Systems

Self-preserving technology is composed of six »hurdles«:

1. Good manufacturing practice (GMP)
  - I. Cold or hot aseptic filling
  - II. Clean-room technology
2. Hygiene-compliant packaging
3. Emulsion form
4. Water activity
5. pH control
6. Multifunctional ingredients with biostatic effect.

Fig. 10 shows antimicrobial ingredients used in »self-preserving« skin care products. Ethylhexylglycerin enhances the antimicrobial efficacy of these ingredients. An optimised combination is 70% Octane-1,2-diol with 30% 3[(2-Ethylhexyl)oxy]1,2-propandiol → INCI Caprylyl Glycol / Ethylhexylglycerin (sensiva® SC 10), it is suitable to formulate wet wipes without classical preservatives.

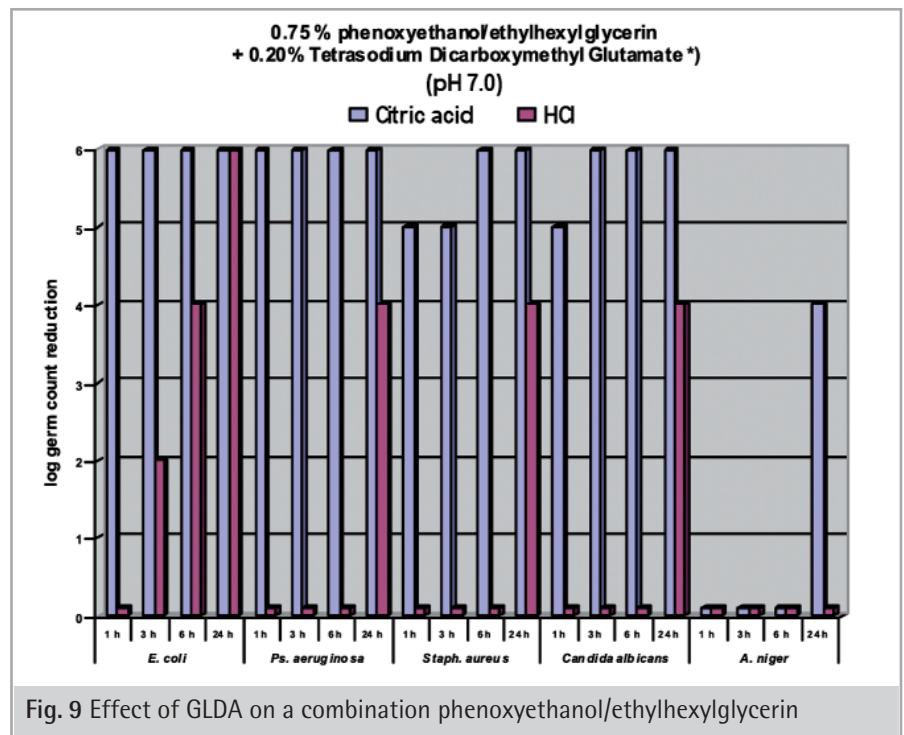


Fig. 9 Effect of GLDA on a combination phenoxyethanol/ethylhexylglycerin

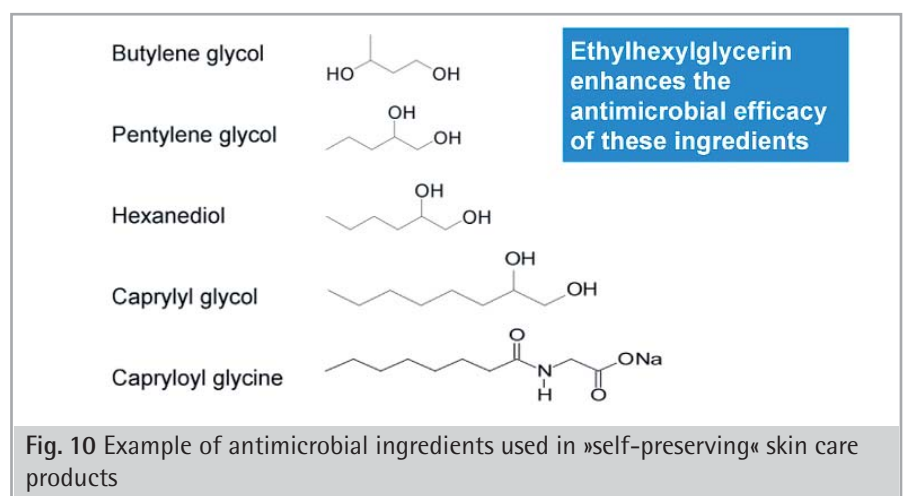


Fig. 10 Example of antimicrobial ingredients used in »self-preserving« skin care products

■ General Technical Aspects

Solution versus Emulsion

The change from solutions to emulsions is changing various aspects:

- Solutions must be preserved with water-soluble actives
- Good physical stability
- Easy to produce
- Only one interface ==> liquid / solid
- Emulsions can be preserved with partly water soluble systems

- Stability must be checked carefully
- One more interface ==> oil / water
- Migration of preservatives into the oil phase might occur
- Special equipment necessary
- Single layer wetting is preferred.

The Influence of the Production Process

The main parameters influencing the microbial stability are listed (7):

- Variation in weight of impregnated

wipes dependent on the method of manufacture.

- An impregnation of the nonwoven prior to conversion into the finished stack of wipes provides a more uniform product.
- Prevent a discharge of actives from an immersion bath – especially cationic compounds are adsorbed on the non-woven.
- Stack impregnation leads to a less uniform distribution of the wet wipe liquid.
- The ingredients of the wet tissue liquid can be separated on the tissue like in a thin layer chromatography.
- Depending on the dosing system you can get a non-uniform impregnation leading to microbiological spoilage.
- Apply the wet wipe liquid uniformly with a shower from the top.

### The influence of using sustainable/ natural sources

Natural raw materials lead to changes in the demand for microbial protection:

- Biodegradable ingredients need better protection  
e.g. sugar-based surfactants
- Flushable wipes need special attention

- Natural fibres, like cotton or celluloses, are changing the typical product-spoiling microorganisms  
e.g. *Trichoderma viride* is a typical cellulose-degrading mould
- challenge testing has to be adapted
- Natural fibres might carry a higher microbial load.

### ■ Summary

Safety and care for consumer and products are legally demanded. A cosmetic product should not damage human health.

The finished product has to be stabilised against microbial growth.

### Market Situation

- Limited number of preservative actives
- Almost every active under public discussion

### New concepts in preservation required

- Formulators are looking for new alternatives to be free of molecules under discussion
- Preservation must be part of new formulation concepts, not an after-thought
- Focus on antimicrobial stabilisers

- substances not listed on any positive list for preservatives (e.g. Europe, Japan)
- claims like »free of harsh preservative«, »paraben-free« are achievable

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