

Preservatives

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Preservatives are added to cosmetics in order to prevent product deterioration and combined with it to avoid any possible health risks involved for the consumer. In the following you will be informed about products which particularly require these additives, about the basics of preservatives and about possible alternatives.

Besides the physical and chemical stability the microbiological stability of cosmetic products is an essential factor for their shelf life. Germs preferably develop in moist conditions. This is the reason why water-containing products need some protection. Pure oils and lipids, however, do not require protective measures. Depending on the composition they may become rancid, however not the presence of microorganisms but the influence of atmospheric oxygen is the reason for the instability. The slogan "free of preservatives" sometimes used in ads for oils and lipids actually is illegal as it goes without saying that there are no preservatives needed.

Stability - facts and figures...

Specifically at risk are products with fine dispersions of oils and lipids in water (O/W emulsions). On the other hand, water in oil emulsions (W/O) generally are less sensitive as their outside phase is almost 100 per cent water-free. Compared with dispenser products with double bottom mechanism, preparations filled in jars definitely show disadvantages as with every removal of cream the product gets in touch with the germ-contaminated skin and subsequently becomes re-contaminated. This, by the way, is the reason why for products with a shelf life of more than 30 months which are not subject to a respective imprint on the package, legislation demands for stating a maximum best-before-date after the opening of the product; the symbol in this case is a jar with open lid and the date counted in months. The new regulation applies for all preparations although e.g. water-free oleogels in jars may be applied out of the jars without any risk of contamination. The same applies for water-free massage oils.

A specific feature of water-containing products is that their susceptibility to germ contamination depends on their respective concentration, a characteristic which has been known from time immemorial. Thus, fruit juices (low sugar content) for example deteriorate very fast while concentrates and jams with a

high sugar content generally are less perishable. The same applies to concentrated saline solutions (conservation of fresh fish) or alcohol-containing solutions. Bacteria in wine may still turn the alcohol into vinegar whereas brandy is a completely hostile environment for them. Hence, alcohol, alcohol-like and sugar-related substances are an alternative to the preservatives listed in the German Cosmetic Decree (KVO).

The substances in particular

An appendix in the German Cosmetic Decree (KVO) deals with the maximum concentration of preservatives and above all which substances may be used under which conditions. Legislation intended here to minimize the risks as well as the sensitizations occurring with the use of cosmetic products. These conditions however apply for the healthy skin. The barrier-damaged skin may still be a lot more sensitive. For the individuals affected, products which are free of preservatives are more appropriate.

Preservatives kill germs, yeasts and mould or at least impede their growth which means that they interfere in the metabolism or other vital mechanisms of the microorganisms. This only is possible when they show a partial solubility in water, an excellent penetrability as well as a high chemical reactivity. Therefore, in preservatives tiny amphiphilic i.e. hydrophilic as well as lipophilic molecules are predominant which preferably migrate between the interfaces of aqueous and lipid phases and that is exactly where the germs are found.

Natural or synthetic?

Seen from the chemical point of view, preservatives with aldehyde groups, sulfur-nitrogen compounds, halogen groups (chlorine, bromine and iodine) or phenolic groups as well as aromatic alcohols and acids respectively their esters prevail. It is insignificant for their effect and their sensitizing potential whether they are synthetic, natural or

nature-identical substances. Benzyl alcohol and benzoic acid for example can ubiquitously be found in the flora, parabens in the fauna and aldehydes in both areas. Hence, according to the German law against unfair competition the slogan "containing natural preservatives" is illegal as it insinuates an advantage to the consumer which actually does not exist. Also many aromatic principles as e.g. attar of roses or rosewater have germicidal effects due to their aldehyde, ketone and aromatic alcohol contents; however, they are not really beneficial. On the contrary, allergy sufferers may be confronted with problems as the relevant components are only partly declared in the INCI and the manufacturer is allowed to offer his product "free of preservatives" unless it contains the preservatives listed in the German Cosmetic Decree (KVO).

Mind the indications!

Many of the preservatives allowed in the German Cosmetic Decree have to be specifically referred to as e.g. "contains iodine" for iodine propinyl carbamate (dosage of more than 0.02 per cent); the same applies for mercury compounds, chlorbutanol, chloracetamide and glutaraldehyde. In combination with amines, 5-bromo-5-nitro-1,3-dioxane (bronidox) and 2-bromo-2-nitro-1,3-propanediol (bronopol) may form carcinogenic nitrosamines; thus the manufacturer is obliged "to avoid the formation of nitrosamines". A number of preservatives may only be used in products which are not intended to remain on the skin after the application.

Formaldehyde donors like imidazolidinyl urea, benzyl hemiacetal which also releases benzyl alcohols, and 4,4-dimethyl-1,3-oxazolidine are widespread substances in this field. Bronidox and bronopol may also release formaldehyde. Today dibromodicyanobutane can be found in many cosmetic products. In recent years there has been observed a sharp rise in the rate of allergic reactions towards this substance. Also for quite some years now, methyl resp. chloromethylisothiazolinone which is used in very low dosages, has been ranging among the top sensitizing substances. It is a very reactive molecule as it may react with the sulfhydryl as well as the amino groups of amino acids and peptides. In cases of dry and atopic skin which shows an increased penetrability, special caution is recommended when using these products.

Parabens & Co

The esters of the parahydroxybenzoic acid (paraben), methylparaben, ethylparaben, propylparaben and butylparaben are the standard substances among the preservatives. They have to be used in comparatively high dosages. Yet, regarding their practical use, there is also the most extensive collection of data available. As they are not readily soluble frequently phenoxyethanol is added as a solubilizer. Less effective are acids like sorbic acid, propionic acid, benzoic acid, dehydroacetic acid or salicylic acid and this is also the reason why they are less frequently used today. Their effect of course depends on the pH and steadily decreases with an increasing pH through formation of the respective salts. Mostly several preservatives are used in combination as every single substance shows specific effects which do not apply to all the germ families. The advantage of preservatives is that they can be used in very small and cost-effective quantities. This might be the main reason why the alternatives described in the following still are not very popular among the manufacturers.

There are indeed alternatives...

Terpenes as well as mono and diglycerides of specific acids may increase the microbiocidal properties of deodorants when the pH factor is low, however they are rarely used in other products. Moreover there is a continued search for substances which are not listed in the German Cosmetic Decree (KVO) but show comparable effects and allow the indication "free of preservatives". It is therefore recommended to closely examine the INCI. Sometimes, extracts which were pre-treated with preservatives are added to products without any indication. Said products then are offered as "natural cosmetic products". The respective authorities however are successfully investigating in these cases.

Besides the use of **water-free oils and lipids** one of the true alternatives though is the **sterile manufacturing** of products which means that the substances applied are mixed and bottled in sterile conditions. This is an **expensive manufacturing procedure** limited to products which are used in a relatively short period after opening as for example ampoule products. A whole range of sensitive natural substances however cannot be used for heat sterilization.

A further alternative may be **alcohol** as already mentioned above. Alcohol is a multi-functional substance which is also used as a

solvent, a penetration assistant or applied because of its cooling effects. Alcohol in medium concentrations has antiseptic effects and in contrast with the preservatives listed in the German Cosmetic Decree (KVO) it belongs to food, easily degrades and is free of any allergenic potential. Yet, alcohol is more appropriate for the oily skin as it may have dehydrating effects especially in higher concentrations. The manufacturing of alcohol-containing cosmetics is comparatively expensive as a relatively high concentration of 10 to 12 per cent has to be observed whereas on the other side some preservatives listed in the German Cosmetic Decree (KVO) are already effective in concentrations of parts per thousand or parts per million. As alcohol is a volatile substance the receptacles of alcohol-containing products have to be tightly closed. Otherwise the concentration falls short of the minimum content required and the products are susceptible to microorganisms.

Glycerin which can also naturally be found in the skin is chemically related to alcohol. Glycerin in animal and vegetable lipids is bound to fatty acids and will be released during the biochemical degradation process of lipids.

In contrast to alcohol (one alcoholic group) it has 3 alcoholic groups and is not volatile. Similarly structured are **butylene glycol**, **pentylene glycol**, **propylene glycol** and **hexylene glycol** (each with 2 alcoholic groups as well as **sorbitol** (6 alcoholic groups and popular as a sugar substitute for diabetic patients) and all natural sugars (5 alcoholic groups as a rule). In contrast to alcohol all the substances mentioned show a water binding effect and accordingly are used as moisturizers. Compared to alcohol, already low concentrations of glycols have antiseptic effects.

... without any allergenic potential

There is practically no allergenic potential as compared with the preservatives listed in the German Cosmetic Decree (KVO). In contrast to previous reports, studies at the Skin Hospital of the University of Karlsruhe have proved that in recent years even for propylene glycol there have not been found any cases of sensitization. This presumably is due to quality improvement and the elimination of contaminations.

Depending on the cosmetic product the substances mentioned are used individually or in combinations. They are mostly used in products with high penetrability of single components as e.g. liposomes, nanoparticles and emulsifier-free systems with membrane

structures. As the products mentioned are predominantly used for sensitive problem skin, preservatives as listed in the German Cosmetic Decree (KVO) are out of question. Also a combination with preserved products is not recommended in these cases.

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