

Preservatives – germs et al. under control

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Microbiological stability is a must for cosmetic products. Consequently preservatives are among the essential additives in cosmetics. They protect the products against microorganisms during the manufacturing process as well as during storage and application and they also are the deciding factor for the duration of their shelf life.

Preservatives are indispensable whenever a cosmetic product contains water. Without water microorganisms can neither reproduce nor live. Pure oils and lipids perhaps require antioxidants to prevent rancidity but no preservatives though.

The preservatives approved for the use in cosmetic products are listed in the appendix of the German Cosmetic Decree (KVO). Preservatives have a microbiocidal or microbiostatic effect on bacteria, yeasts and mould. Microorganisms do not only threaten the shelf life of a product: when they reproduce they may be a serious risk for the consumer's health. A further problem is the transmission of germs from one person to another via cosmetic products especially when using the still very popular jar products which are particularly sensitive due to the frequent opening and reaching into them. Therefore the idea of adding preservatives to the products already was developed some time ago.

Formaldehyde et al. ...

One of the very first preservatives used to be formaldehyde which already is highly effective in small quantities. Due to its pungent odor and its allergenic potential already some years ago it was reduced to a content of 0.2 percent and was mostly replaced by so-called formaldehyde donors where imidazolidinyl urea, benzyl hemiacetal, and 4.4-dimethyl-1.3-oxazolidine belong to. Also bronidox (5-brom-5-nitro-1.3-dioxan) and bronopol (2-brom-2-nitro-1.3-propandiol) may release formaldehyde under certain conditions. This has to be taken into consideration in case of formaldehyde sensitivity.

Benzoic acid and para-hydroxy benzoic acid (paraben) as well as their esters methyl paraben, ethyl paraben, propyl paraben and butyl paraben have been used for a long time. Due to the sensitization problems as mentioned above efforts have constantly been made to increase the research for new substances with the objective of a better tolerance for the consumer. Unfortunately it has turned out that the newly developed

substances even showed a higher allergenic potential than the substances used before.

A good example here is the introduction of a mixture of methyl and chlormethylisothiazolinone which initially appeared to involve fewer side effects than parabens while a far lower concentration was needed. Originally, when the circulation of the substance still was limited the allergy rate seemed to be comparatively low. However, later on exactly the opposite effect had to be stated. A similar experience can currently be observed with dibromdicyanobutane (methyl dibromo glutaronitrile) which unlike in past, today is far ahead of the parabens in the top list of sensitization rates. On a long-term perspective preservatives cannot be seen as unproblematic substances, a fact which does not only apply for cosmetic products which are subject to the regulations in the food law but also in the area of dermatics which are subject to the German Drug Law (AMG).

Apart from the problems regarding the tolerance and the allergy rates the preservation of emulsions and aqueous solutions is a science in itself as every single product is subject to new frame conditions.

Preservatives need to have to appropriate water solubility but they also have to include lipophilic properties as this is their only way to effectively fight microorganisms. Even though, depending on the composition of the cosmetic product they are differently partitioned in the aqueous and oily phase. The technical term here is partition coefficient and it is specific for every single composition.

Parabens e.g. frequently show a stronger tendency to the lipid phase which leads to the fact that the dosage of the preservative should be increased in order to achieve the so-called minimal inhibition concentration (MIC) in water. The MIC practically means that in preservative concentrations below the MIC microbes may continue to reproduce whereas they are killed in concentrations above the MIC. Hence, a threshold concentration is required here to achieve the desired effect.

In a safe product by no means the preservative content is allowed to fall below the MIC starting

from the manufacturing of the product until the best-before date. This requirement is not too easy to meet as even preservatives are not to a 100 percent chemically stable. For instance parabens may slowly be hydrolysed into hydroxybenzoic acid and the appropriate alcohols. Benzyl alcohols may slowly be oxidized whereas higher temperatures may accelerate these reactions. Furthermore hydrolyses depend on the respective pH value. Plastic materials (packaging) or seals absorbing considerable amounts of preservatives might be another source of error. As a matter of fact, these effects have to be considered when developing a new product in order to guarantee the appropriate safety. Therefore rather higher concentrations of preservatives are used. Particularly for parabens frequently phenoxyethanol is additionally applied as a solvolytic assistant so that quite often in combination with phenoxyethanol several parabens can be found on the INCI list.

Jar, dispenser or tube?

Packing in **jars** automatically involves a higher germ contamination during the application of the product than with a tube or dispenser packaging. Thus jar products contain a higher reserve of inhibitors. Furthermore jar products involve another phenomenon which is quite disagreeable and has to be dealt with. Changes in temperature which happen e.g. when stored in the bathroom may involve condensation residues in the lid. These water residues are an ideal precondition for the growth of germs due to the presence of traces of inorganic substances which cannot be avoided.

The packing in **dispensers** avoids this specific problem as they generally have a second bottom part which automatically moves up while emptying the receptacle and thus prevents the air to penetrate. Depending on the material **tubes** pose different conditions. The good old aluminum tube with its creases actually makes a pretty poor optical impression; its use however is very hygienic because it is impossible that germ-contaminated air penetrates while emptying the tube. Plastic tubes have the disadvantage of resuming their former shape when emptying which means that they suck in external air into their interior and together with it germs. Judging from the hygienic and the optical standpoint as well as regarding the lowest possible dosage, dispensers will be the future number one packing material.

It's the mixture that counts...

As not every single microorganism reacts to the same preservative mostly a combination of preservatives is used. This is the reason why very often more preservatives than substances for the skin care are listed on the INCI.

During the product development the manufacturers ensure the effects of preservatives by so-called germ-contamination tests during which the products are inoculated with standard germs and measures regarding their decrease are taken in given intervals. Is the number of germs continually decreasing and finally reaches zero the product is regarded to be microbiologically safe.

Strict dosage required

The effect of preservatives is influenced by other ingredients. Lecithin for instance is a typical component which may lead to a complete inactivation. Cationic preservatives as for example chlorhexidine may be inactivated by anionic emulsifiers. A comparatively high pH value of the cosmetic formulation decreases the activity of acidic preservatives as e.g. sorbic acid, propionic acid, benzoic acid, hydroxybenzoic acid, dehydroacetic acid or salicylic acid.

Higher concentrations to cover the imbalance however are limited as possible negative effects on the tolerance cannot be excluded. Therefore the legislator has stated proportional maximum amounts for all preservatives. Furthermore some preservatives have to be equipped with warnings as e.g. for mercury compounds, chlorbutanol, chloracetamide, and glutaraldehyde. A dosage of more than 0.02 percent of iodine propinyl carbamate officially requires the warning "contains iodine". Frequently also the applicability is limited which means e.g. that specific preservatives are only approved for products which will not remain on the skin like cleansing products (rinse-off products). Other substances like 5-brom-5-nitro-1,3-dioxane and 2-brom-2-nitro-1,3-propandiol are able to generate cancerogenic nitrosamines. Hence the German Cosmetic decree (KVO) states the principle of "avoiding the formation of nitrosamines". This however cannot be excluded to a 100 percent if the consumer also applies other products.

As acidic preservatives are not very effective, require high concentrations and are not compatible with many thickeners their percentage has decreased in the meantime.

...falling by the way side...

The application of chlorophenols and chloro-cresols involves a similar experience as they have lost a lot of ground since the dioxin discussion. They have a relatively high allergenic potential. Also halogen free phenolic compounds can hardly be found today. The most frequently used preservatives are formaldehyde donors, parabens, phenoxy-ethanol and dibromdicyanobutane.

Today most of the cosmetic products on the market contain the preservatives approved by the German Cosmetic decree (KVO). The disadvantage of all the preservatives approved in the KVO is their allergenic potential especially for individuals with chronic skin barrier damages (dehydrated skin). As the percentage of individuals with dehydrated skin constantly is on the rise it is no wonder that the allergy rate also proportionally increases. It is of no significance whether the preservatives are synthetically produced or as e.g. benzoic acid and benzyl alcohol come from natural sources. A general trend from KVO (German Cosmetic Decree) preservatives towards products free of preservatives has been observed for some time now.

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