Acids and bases from A to Z

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Acids somehow have a spectacular image in skin care. They either have caustic effects in the true sense of the word or they are the magic cure for a beautiful skin per se. Bases, as their counterparts, only live a wallflower existence as neutralizers. Details and backgrounds are covered in the following article.

■he term acidic denominates a generally acknowledged flavour variant perceived by the tongue. Although it is a particularly sensitive organ, the human tongue is not able to identify all the different types of acids. Stearic acid (candle wax) for instance is not perceived as acidic but as fatty, a fact which serves as a good example for the different characteristics of acids. In the cosmetic field. acids in the narrower sense are substances with one or more hydrogen atoms (H). In combination with water (H2O) these atoms can be released as positively charged protons (H⁺). This process involves a charge separation leading to a negatively charged acid radical and finally to a balance:

Acid (HA) + water (H_2O) <=> acid radical (A^-) + H_3O^+

The more or less acidic sensation perceived by the human tongue, depending on the concentration, is labelled as H_3O^+ . In case of the water-insoluble stearic acid, the concentration is rather low only and the fatty note dominates in sensorial respect. There is also a charge separation in pure water:

Water (H_2O) + water (H_2O) <=> $HO^- + H_3O^+$

Acids and pH-value

The concentration of a water molecule attached proton H⁺ is extremely low and amounts in this specific case to 0,0000001 g/l of water. Since this number is difficult to handle, the pH-value has been defined. 7 digits after the decimal point means pH 7. The negatively charged HO particle that generates is characteristic for bases (alkaline solutions). Since acids and bases equalize, water is neutral. PH-values below 7 indicate an acid. The stronger the acid the lower is the pH-value. Minor deviations of the neutral point as for instance pH 6 are irrelevant in skin physiological terms due to the low quantities. The acid mantle of the skin has an average pH value of 5.5. Media with pH-values of about 3 or even lower will cause irritations and even chemical burns in case of very low pH values. That is

why cosmetic active agents with acidic function are generally neutralized or at least partly neutralized with a base unless an irritating effect is explicitly intended as for instance the effects caused by fruit acid peelings.

From base to salt

The number of bases available is rather small compared to the number of acids. For the most part they are metal hydroxides as well as organic amines. During the neutralizing process salts are formed as e.g. sodium stearate from stearic acid and sodium hydroxide. Occasionally also the name of the base used for the neutralizing process is mentioned in the INCI as e.g. sodium hydroxide. As a matter of fact, this base is no longer present. Another way of neutralizing the acid function is the transformation of the acid with the help of alcohol. In this process, esters form which can again be hydrolyzed into their basic components by the enzymes in the skin. They occur very widely in natural environment. The triglycerides of vegetable oils for instance are esters of the trivalent alcohol glycerin and three fatty acids. Occasionally, alcohols may serve as precursors for physiologically interesting acids. After the passage through the skin barrier pantothenic acid forms from Dpanthenol and vitamin A acid from vitamin A. If acids are used as preservatives, their activity decreases with their progressing neutralization and increasing pH-value. The same applies for the keratolytic effects of fruit acids: the neutralizing process leads to a loss of efficacy altogether.

Acids in cosmetic products

Aconitic acid (1,2,3-propene tricarboxylic acid) is a component of Christmas rose or yarrow extracts and a constituent of the human citric acid cycle.

Adipic acid, a dicarboxylic acid (double acid) in form of its esters as e.g. diisopropyl adipate or dibutyl adipate is used as a spreading

agent. They are fluid oils which facilitate the spreading of creams.

Alginic acid has a polysaccharide structure whose basic elements consist of mannuronic acid and guluronic acid (sugar acids). Alginic acid and its calcium salt (calcium alginate) are insoluble in water but may soak; alginic acid is used as a consistency agent. It forms a moisturizing film on the skin. It is also able to bind heavy metal ions. The sodium and potassium salts of the alginic acid (sodium alginate, potassium alginate) are water-soluble.

Amino acids (AS) are neutral as they have an acidic function in addition to their alkaline amino group; we are dealing here with an intramolecular neutralization. AS with various acid or amino groups, however, show acidic respectively alkaline reactions. α -Amino acids are components of the NMF and have radical scavenging functions. Nicotinic acid (niacin, vitamin B₃) also belongs to the amino acids.

Ascorbic acid is a potent antioxidant. Higher concentrations have keratolytic effects similar to fruit acids. Integrated in liposome or nanodispersions, the sodium salts of the phosphoric acid ester (sodium ascorbyl phosphate) or of the palmitic acid esters (ascorbyl palmitate) can penetrate through the skin barrier and stimulate the collagen formation.

Azelaic acid in concentrations of up to 1 % is allowed as a consistency agent in cosmetic products. With its two acid functions and nine C-atoms it belongs to the group of saturated dicarboxylic acids and is an excellent active agent in acne and rosacea products.

Benzoic acid has a benzene ring and that is why it is identified as an aromatic acid. It is used as a preservative. Even more effective are the esters of the p-hydroxybenzoic acid which is widely used in form of parabens. The o-hydroxybenzoic acid (salicylic acid) is a ß-hydroxy acid and has antimicrobial effects as well. In higher concentrations it also has keratolytic effects. Concentrations of up to max. 2 % are allowed in skin care creams and 3 % in shampoos. Ethylhexyl salicylate (octyl salicylate) is used as UV filter. Gallic acid is a benzoic acid with 3 hydroxy groups. It has astringent and antioxidant effects and occurs in various plants.

Betulinic acid occurs in plane tree (sycamores) and birch bark extracts and is a natural antigen against monads and fungi. In lower concentrations it supports the apoptosis (programmed cell death) of melanoma cells.

Bile acids are components of the bile. The predominant acids here are cholic acid and desoxycholic acid. If cholic acid is linked via amide bonds with the amino acids taurine and glycine, taurocholic acid and glycocholic acid will form. In cosmetic products they are used as anionic emulsifiers for lipid substances and they support lamellar structures.

Boric acid can be formulated in skin care products but is subject to certain restrictions - as a preservative in powders for instance. Borax is a sodium salt of the boric acid. Formerly it was a widely used component of cold creams.

Boswellia acids (frankincense extract) inhibit the collagen degradation process in the skin after UV stress as well as the inflammation triggering enzyme 5-lipoxygenase.

Carbonic acid: In the presence of water effervescent tablets consisting of sodium bicarbonate (sodium hydrogen carbonate) and citric acid release carbonic acid in form of carbon dioxide.

Cinnamic acids are unsaturated aromatic carboxylic acids. Their esters as e.g. 2-ethylhexyl methoxy cinnamate or isoamyl methoxycinnamate are UV filters.

Dehydroacetic acid is used as a preservative.

Fatty acids are the generic term for monocarboxylic acids which have an acidic -COOH group attached to a hydrocarbon chain. In addition to the above mentioned formic acid the group comprises for instance acetic, propionic, butyric, caprylic, caprinic, palmitic, stearic and behenic acid. They are partly used in their free form, as salts or esters and particularly as triglycerides. The sodium and potassium salts of longer fatty acids are typical soaps and can emulsify lipids as e.g. sodium palmitate and sodium stearate. Caprylic/capric triglyceride is the mixed ester of caprylic acid (8 C-atoms) and capric acid (10 C-atoms) and widely used as emollient neutral oil. Esters of short chained acids like butyric acid frequently have a fruity

Formic acid is the simplest and also strongest monocarboxylic acid. Its use in cosmetic applications is restricted. The acid and its sodium salt (sodium formate) have preserving characteristics.

Fruit acids are the generic term for the organic hydroxycarboxylic acids and dicarboxylic acids occurring in fruits. Glycolic, lactic, malic,

tartaric and citric acid belong to the group of AHA acids (α -hydroxycarboxylic acids) in the narrower sense. The free acids are used for peeling purposes, the salts partly as moisturizing agents and citric acid is applied as a chelating agent against heavy metal traces and as buffer agent to stabilize the pH-value. Glycolic acid is often used in combination with pyruvic acid (α -ketocarboxylic acid) for fruit acid peelings. Fruit acids can have caustic effects and in this respect they can be compared with dilute mineral acids.

Fumaric acid is an unsaturated fruit acid with 2 carboxyl groups (dicarboxylic acid). It serves as an acidifier and the sodium salt (sodium fumarate) is used to prevent bad and hyperactive skin (psoriasis).

Hyaluronic acid is a natural polysaccharide of the body gained in a biotechnological manufacturing process and consists of alternating Dglucuronic acid and N-acetyl-D-glucosamine units. It has moisturizing, plumping and smoothing effects.

Lipoic acid is a radical scavenger and a strong antioxidant.

Mineral acids: The following strong inorganic acids belong to the mineral acids: hydrochloric acid, sulfuric acid, nitric acid. In the cosmetic field they only play a role in form of their salts. The sodium salt of the hydrochloric acid (sodium chloride) - synonymous with table salt condenses PEG-containing shampoos. The calcium salt of the sulfuric acid (calcium sulfate) has a hardening effect in modelages. Sodium salts of sulfuric acid esters are used as detergents and emulsifiers. Examples are sodium lauryl sulfate and sodium cetyl sulfate. Aluminum chlorohydrate which forms from hydrochloric acid and aluminum hydroxide has astringent and antiseptic effects. The salt of the sulfuric acid (aluminum sulfate) and mixed salts like alum have similar effects.

Nitrous acid is a weak inorganic acid. Its sodium salt (sodium nitrite) is allowed as a corrosion inhibitor for cosmetic applications.

Pantothenic acid (vitamin B_5) forms in the skin from D-panthenol.

Phosphoric acid is used in esterified form as an emulsifier (as e.g. sodium cetyl phosphate). Phosphoric acid salts are characteristic buffer substances to formulate a stable pH value.

Phthalic acid in its form of diethyl phthalate is the most important denaturing agent for alcohol (alcohol denat). Phthalic acid esters are also well-known plasticizer.

Polyacrylic acids (polyacrylates, carbomers) have consistency improving properties particularly after they have been neutralized (sodium carbomer). They are contained in ultrasound gels.

Silicic acid (silica) is a light inorganic powder with extensive surface. Horse tail extracts contain silicic acid and are used as an additive in facial tonics and hair care products. Dispersed (colloidal) silicic acid serves as a consistency agent for nonpolar oils like paraffin oil.

Sorbic acid (hexa-2,4-dienoic acid) and its potassium salt (potassium sorbate) have preserving effects.

Sugar acids form with the oxidation of monosaccharides. As other polyhydroxy compounds they can retain the skin moisture.

Sulphurous acid is used in form of its salts (sulfites, bisulfites) for preserving purposes and for the hair care.

Sulfonic acids are components of azo dyes and UV filters as e.g. 2-hydroxy-4-methoxy-benzophenone-5-sulfonic acid.

Thioglycolic acid: Its ammonium salt (ammonium thioglycolate) is used for depilation purposes and for permanent waves.

Tranexamic acid is used in Asia (Japan, Taiwan, China) to whiten the skin.

Trichloroacetic acid is licensed for chemical peelings in dermatological practices.

Undecylenic acid is an unsaturated monocarboxylic acid with preserving characteristics.

Unsaturated fatty acids are e.g. oleic acid and linoleic acid, α - and γ -linolenic acid. The last named three acids are essential fatty acids for the human metabolism and occur in form of triglycerides in vegetable oils.

Vitamin A acid forms in the skin from vitamin A. It is used to treat atrophic skin, acne and cornification disorders.

Bases in cosmetic products

Amines: They neutralize acids and thus activate anionic emulsifiers. Primary and tertiary amines are preferred, as secondary amines tend to form carcinogenic nitrosamines. Widely

used are triethanolamine and trometamol [Tris(hydroxymethyl)-aminomethane].

Ammonium hydroxide: neutralizing agent (cf. thioglycolic acid)

Potassium hydroxide: neutralizing agent

Sodium hydroxide: neutralizing agent

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Note: This paper is nearly identical with the article "Acids and bases in cosmetic products from A to Z: A systematic approach" in Kosmetik International 2010 (8), 26-30