Natural, safe and highly effective?

YES WE CAN!

Presented by:

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Introduction

Awareness of the environment is vital for human well-being and for the health of our planet. Consumer expectations are in flux and the preference for natural and renewable products is creating a new market with strong growth. For the development of personal care products in this segment, Jungbunzlauer offers a wide range of naturally-sourced ingredients which are based on corn or sugar-beets. These raw materials are transformed via fermentation as well as in clean and authorised processes into valuable ingredients which can be applied in natural personal care products.

This article highlights two Jungbunzlauer ingredients which are outstanding natural solutions to replace synthetic ingredients presently used in Personal Care: a highly effective chelating agent and a reliable and efficient active ingredient for deodorants.

The global deodorant sector generated total revenues of approx. $10 billion in 2009 an showed a constant growth of approx. 3.1% over the last 5 years. The largest category in the global market is aerosol antiperspirants, closely followed by body spray, sticks roll-on deodorants. Deodorant gels and creams play only a minor role in the market.

As in other areas, also in the cosmetics industry some ingredients are discussed controversially. Scientific studies have highlighted a potential health risk from certain components of deodorants. For example, aluminium used as an antiperspirant in some deodorants has been suggested to be linked to the development of breast cancer and Alzheimer's.

In light of such implications, many consumers look for alternative products without the offending chemicals. It is up to retailers to reflect consumer demand, and many have begun to stock such natural alternatives.

Personal Care products also often contain metal ions which can come from raw materials like fatty acids or tallow, from the water used in production or from the manufacturing equipment. These metal ions cause problems like rancidity, discoloration, precipitation and degradation of ingredients. To avoid those unwanted reactions chelating agents like EDTA or HEDP (etidronate) are used in almost all kinds of Personal Care and Decorative Cosmetic products.

Almost 25% of all beauty and Personal Care products launched between 2007 and 2009 contained a chelating agent according to a Jungbunzlauer analysis of Mintel Global New Products Database. However there are strong variations in the use of chelating agents between the different Personal Care categories. While at one end of the scale less than 1% of the lip colour and lip care products and less than 10% of the fragrances contain a chelating agent, at the other end more than 50% of the bar soaps and hair colours contain one, sometimes even two.
So far the dominant chelating agent in Personal Care is EDTA. But with the trend of going natural, EDTA and also HEDP – a phosphonate –, which are both made by chemical synthesis from petrochemical raw materials, come under scrutiny.

Produced by a microbial fermentation of renewable carbohydrates, gluconates are their natural alternative. Gluconic acid exists since millennia in the nature, as an acid component in a lot of natural food (e.g. honey).

**What are Sodium Gluconate and Triethyl Citrate?**

Sodium gluconate is the sodium salt of gluconic acid. Gluconic acid can be described formally as an oxidised glucose (Fig. 1). Out of Gluconic acid glucono-delta-lactone and sodium gluconate can be derived. This group of substances is generally summarised as gluconates.

Fig. 1: Formal oxidation of glucose and formal derivatisation of gluconic acid
In nature gluconic acid is the main acid component of honey and royal jelly, occurring in those products in concentrations up to 1%. It can also be found in fermented drinks like wine, Kombucha etc. As a consequence gluconates are widely used in the food industry, e.g. in bakery, dairy, meat products, sauces and beverages. The US Food and Drug Administration (FDA) assigned sodium gluconate the “generally recognised as safe” (GRAS) status and permitted its use in food without limitation other than current good manufacturing practices. Sodium gluconate is listed in Europe as a generally permitted food additive.

Jungbunzlauer produces gluconic acid via fermentation out of renewable carbohydrates (Fig. 2). Strict quality control guarantees that raw materials and organisms used for the fermentation, a process considered as natural, are GMO-free.

Fig. 2: Production flow for sodium gluconate and triethyl citrate

Sodium gluconate is already well known as ingredient for Personal Care products, e.g. in rinse off products or depilatory creams. The excellent chelating properties, in particular for heavy metals like iron and copper, in the typical ph-range of personal care products make the sustainable gluconates to valuable alternatives for synthetic products.
Triethylcitrate is the ethyl ester of citric acid and ethanol. In a modern and solely for this ester-type dedicated plant the product is derived in an acidic esterification process (Fig. 3) in highest pharmaceutical quality and purity. The main raw material, citric acid, is produced by Jungbunzlauer via fermentation out of corn starch or glucose syrup (Fig. 2). The employed ethanol is of plant origin and Triethyl citrate from Jungbunzlauer (trade CITROFOL® Al) can be considered as a natural product.

Fig. 3: Formal esterification of citric acid with ethanol

In the food and pharmaceutical industry Triethyl citrate is applied since years due to its toxicological and ecological safety. The US Food and Drug Administration (FDA) assigned also triethyl citrate the "generally recognised as safe" (GRAS) status and permitted its use in food without limitation other than current good manufacturing practices. Triethyl Citrate (E 1505) is listed in Europe as generally permitted food additive,

But also in the cosmetics industry Triethyl citrate is well known as a versatile ingredient for Personal Care products, e.g. in Sun Care products, in lipsticks and as active ingredient in deodorisers. In addition Triethyl citrate is widely used as solvent and fixative in fragrances.

**Sodium Gluconate as natural chelating agent in Personal Care Applications**

Appeal, properties and performance of cosmetics products can be affected by development of rancidity, discoulouration, precipitation or degradation of key ingredients like fragrances, vitamins or essential oils. Frequently the presence of metal ions is the source of the trouble, as those interact with ingredients in the formulation. Therefore chelating agents are used to stabilise the products.

EDTA (INCI: TETRASODIUM EDTA) was and is still used very much in the Personal Care industry because it is well known as chelating agent. However EDTA is fully synthetic, irritating to eyes and showed some positive responses in sensitisation tests. Further its biodegradability is poor.

Sodium gluconate is a strong chelating agent for iron and copper and shows a high chelating capacity for those ions in the pH range of Personal Care products (Fig. 4). Made by fermentation of renewable raw materials, it is non-toxic, non-irritating non-sensitising. Thus sodium gluconate is a natural and safe alternative to EDTA and other comparable agents. Readily biodegradable, it is not only good for the human being, but also for his environment.
A standard organic UVA filter in Sun Care products, BMDBM (butyl methoxydibenzoylmethane) is well known for its incompatibility with iron. Indeed, BMDBM forms an intensive red coloured complex in presence of only traces of iron. Thus a strong chelant is needed to prevent this phenomenon. Today EDTA is used (concentration 0.1 – 0.5%).

To demonstrate the capability of sodium gluconate as effective alternative to EDTA Jungbunzlauer compared the stability of a sun care lotion with:
A) EDTA as chelating agent
B) sodium gluconate as chelating agent
C) no chelating agent

Fig.5: UV filter and chelating agent contents in the sun care lotions

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ingredients</th>
<th>Formula A</th>
<th>Formula B</th>
<th>Formula C</th>
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<tr>
<td>UV Filter</td>
<td>OCTOCRYLENE</td>
<td>10%</td>
<td>10%</td>
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<tr>
<td></td>
<td>BUTYL METHOXYDIBENZOYL METHANE</td>
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<tr>
<td></td>
<td>TITANIUM DIOXIDE, SILICA</td>
<td>1%</td>
<td>1%</td>
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<td>Chelating Agent</td>
<td>TETRASODIUM EDTA</td>
<td>0,2%</td>
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<td>---</td>
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<tr>
<td></td>
<td>SODIUM GLUCONATE</td>
<td>---</td>
<td>0,2%</td>
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</table>

All formulations were stored for 3 months at 4°C, 20°C and 40°C, and for 1 month at 45°C. Evaluation of the stability occurred visually.
Fig.6: Visual evaluation after 3 months of storage at 40°C

As you can see from the picture, after 3 months at 40°C orange-red coloured spots developed in Formula C which contains no chelating agent. The formulations which contained either EDTA or sodium gluconate did not develop such spots. This elementary test could demonstrate that Junbgunzlauer sodium gluconate works as well as EDTA when strong iron chelation is demanded in Personal Care products.

**Personal Care Applications for Triethyl Citrate**

CITROFOL® Al, the trademark of Jungbunzlauer (INCI: TRIETHYL CITRATE), has been demonstrated its excellent properties in several cosmetic applications, for example in deodorants. The function of cosmetic deodorants is to remove body odour which develops while the originally odourless sweat is decomposed by micro-organisms. There are different principles underlying the effects of the common cosmetic deodorants.
Triethyl citrate is neither a microbicidal substance nor an astringent or absorber. It inhibits the enzymatic decomposition of the sweat components and consequently prevents the formation of its unpleasant smelling by-products. The main agents in the decomposition of sweat are lipases. CITROFOL® Al inhibits their function without destroying the bacteria involved in the process. From a toxicologically and dermatological point of view it is safe.
The hydrolysis of CITROFOL®AI caused by the esterase on the skin produces free citric acid. The pH – value of the skin goes down, which leads to a reversible reduction of enzyme activity. The decomposition of sweat and other degradable skin products like fat or horn cells is stopped and production of unpleasant smelling compounds reduced. The natural buffer function of the skin slowly neutralises the acid groups of the hydrolysed CITROFOL®AI, the pH – value goes up again and the esterases of the skin are reactivated. They again react with CITROFOL®AI and initiate a long lasting cycle reaction.

To show that CITROFOL®AI has an excellent deodorising efficacy a Sniff-Test was carried out as a half side test vs. untreated axilla. For this test the following Deo Roll-On formulation was prepared:

Fig. 8: CITROFOL®AI - mode of action in deodorants

The diagram shows the following steps:
- Buffer effect of skin
- Deactivation of enzymes
- Raised pH value
- Activation of enzymes
- CITROFOL® AI
- Decomposition of fatty acids
- Odour

Fig. 9: Formulation Deo Roll-On, JBL/PC/60/0005

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ingredient</th>
<th>JBL/PC/60/0005</th>
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<tbody>
<tr>
<td>A</td>
<td>AQUA</td>
<td>83.00 %</td>
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<td></td>
<td>GLYCERIN</td>
<td>3.00 %</td>
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<td></td>
<td>PANTHENOL</td>
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<td></td>
<td>XANTHAN GUM</td>
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<tr>
<td>B</td>
<td>TRIETHYL CITRATE</td>
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</tr>
<tr>
<td></td>
<td>GLYCERYL STEARATE CITRATE</td>
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<tr>
<td></td>
<td>MYRISTIL MYRISTATE</td>
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<tr>
<td></td>
<td>CETEARYL ALCOHOL</td>
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</tr>
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<td>ISOPROPYL MYRISTATE</td>
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<tr>
<td>C</td>
<td>PERFUME</td>
<td>1.00 %</td>
</tr>
<tr>
<td></td>
<td>CAPRYLYL GLYCOL, PHENOXYETHANOL</td>
<td>1.00 %</td>
</tr>
<tr>
<td>D</td>
<td>CITRIC ACID</td>
<td>0.50 %</td>
</tr>
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</table>
The aim of this study was a competitive evaluation of the deodorising efficacy of the Deo Roll-On formulation JBL/PC/60/0005 versus the untreated axilla. 10 volunteers applied randomly selected the Deo Roll-On once on one axilla, whereas the other axilla was left untreated. The Sniff-Test was carried out by 3 experts at time 0, and 12 and 24 hours after application.

The intensity of sweat odour could be reduced to approx. 50% after 12 hours. After 24 hours the intensity of sweat was about 30% lower than the initial value so that a 24 hours efficacy could be demonstrated.

The results are summarized in the figure below. The intensity of the sweat odour is shown according to German school grades (1= no odour, 5 = strong odour).

Fig. 10: Intensity of Sweat Odour

![Intensity of Sweat Odour](image)

**Summary**

It has been shown that sodium gluconate is an effective, safe and natural alternative to EDTA in Personal Care products. The presented results of stabilisation of Sun Care products clearly demonstrate that the performance of sodium gluconate as heavy metal chelating agent is at least equivalent to EDTA. Advantageous for sodium gluconate are its natural production process out of renewable raw materials, its excellent safety profile as well as its environment friendliness. It is thus advisable in all kinds of conventional, but also natural cosmetics where a chelating agent is necessary to sustain the appeal, properties or performance of the product.

Triethyl citrate (CITROFOL® Al) is an ideal active ingredient for modern deodorisers with a very strong and reliable deodorising performance. It does not interfere with the natural biological processes on the skin nor does it concentrate on the skin after

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repeated use. It integrates very well in the formulations without reacting with other components. The beauty of triethyl citrate is the natural derivation from renewable vegetable based resources. The very strong performance allows claims concerning a long lasting deodorising effect of min. 24h.