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# facts

## Novel water-free face scrub tablet with Trisodium Citrate Anhydrous

## Introduction

As an effective, inexpensive and safe solvent, water is ubiquitous in cosmetic and personal care formulations. But although water might seem to be plentiful, less than 0.4% of the Earth's fresh water is actually readily accessible for use and many areas of the world could come under significant water stress in the near future.[1] It is thus clear why water conservation has become an important aspect of sustainability efforts. This makes the development of more concentrated products and even completely water-free formulations extremely desirable. Removing the water from the formulation also significantly reduces the product's volume and weight, potentially meaning less packaging waste and a reduction in the emissions associated with shipping.

But solid, water-free dosage forms offer other benefits apart from sustainability. For instance, the reduction in water activity may limit the need for preservatives – a clear advantage from a clean label standpoint. In addition, novel dosage forms such as tablets create an easier-to-handle product for consumers. Nevertheless, converting a product to a solid dosage form is not without its challenges.

Jungbunzlauer, one of the world's leading producers of biodegradable and naturally occurring ingredients, has made significant investments in technology to cater to the rise in water-free formulations. For instance, it is in the process of modifying common ingredients such as citric acid to improve stability in anhydrous formulations.

Many of the ingredients used in cosmetics and personal care products are liquid, oily or waxy in nature. Surfactants are a notable example of this. Incorporating these into water-free formulations usually requires a carrier agent.
An ideal carrier will adsorb large quantities of liquid ingredients while delivering optimum density and remaining free-flowing. Some examples include silica, microcrystalline cellulose, and talc. This study will focus on one such ingredient: trisodium citrate anhydrous. A commonly used chelator and buffering agent, trisodium citrate anhydrous has also proved to be a very effective carrier agent.

Jungbunzlauer offers two forms of trisodium citrate: trisodium citrate dihydrate (TSC) and trisodium citrate anhydrous (TSA). Both are covered under the listing of trisodium citrate as a generally permitted food additive in the EU and they have GRAS status in the US. TSA is derived from TSC by removing the water from the crystal lattice.[2] This creates a solid, porous material ideal for the adsorption of liquids. Once loaded, TSA remains free-flowing and retains its initial powder characteristics. This is ideal for the production of water-free formulations. In addition, TSA is compressible and can thus be used in tablet applications.[3]

## Water-free application: face scrub

Face scrubs are skincare products that are applied to facial skin in order to remove dead skin cells – a process called exfoliation – and thereby give the skin a younger, fresher appearance. Face scrubs are popular products worldwide and account for 33% of all facial skincare products.[4] TSA can perform multiple functions in face scrub products in powder or tablet format. First, it brings liquid surfactants into the formulation without impairing the powdery condition of the product and allows the conversion of the powder into tablets. Second, it acts as an abrasive agent by mechanically removing dead skin cells.

Consumers apply these products topically to the face by massaging gently. The product is then rinsed off. Face scrubs are available as creams, lotions, pastes and powders. Despite the different consistencies, face scrub products are usually composed of the following ingredient types: water, abrasives, surfactants, moisturisers, thickeners, preservatives and perfume.

Abrasives are small solid particles that are able to loosen and remove dead skin cells mechanically from the outermost layer of skin (*stratum corneum*). They are hence used to achieve the desired physical exfoliation effect. Surfactants are essential ingredients that are able to clean and degrease the skin. Thickeners give the product a creamy texture and moisturisers leave the skin feeling hydrated and refreshed.

The aim of this study was to develop a face scrub formulation in tablet format with surfactant-loaded trisodium citrate anhydrous as the main ingredient. The challenge was to achieve satisfactory stability of the tablets during transport and storage while ensuring excellent performance of the product during application.

Only natural,[5] biodegradable and non-allergenic skin care ingredients were used in the formulation.

## Trisodium Citrate Anhydrous as an abrasive

The most frequently used abrasives in face scrub products are of either plant or mineral origin. Commonly used abrasives of mineral origin are silica, kaolin, perlite, talc and pumice. Some examples of plant-based abrasives are charcoal powder, cornflour, apricot seed powder and microcrystalline cellulose. As yet, there are no face scrub products on the market featuring TSA as the abrasive.[4] Using TSA as the abrasive in such formulations is therefore a completely new and innovative approach.

Since most of the abrasives used are of either mineral or plant origin, they are considered to be natural cosmetic ingredients and are therefore usually COSMOS approved. Jungbunzlauer's TSA is also considered a non-toxic and non-allergenic skincare ingredient and is COSMOS approved. It can therefore be used in the formulation of natural skincare products that are certified according to the COSMOS standard.[5]

TSA in dry face scrub formulations offers several benefits at once. It is readily biodegradable and it is water-soluble. In addition, TSA provides optimal conditions for gentle but effective exfoliation. The round shape of its particles allows the gentle removal of dead skin cells without injuring the skin. Despite their water solubility, the TSA particles do not entirely dissolve during application (2–3 min). This is due to the relatively large particle size compared to the amount of water added. However, as soon as the formulation is rinsed off the face, the TSA particles dissolve completely, leaving no residues in the sink or the waste water.

Finally, TSA has an excellent loading capacity for liquid ingredients such as surfactants. This aspect will be discussed in the following section.

## Trisodium Citrate Anhydrous as a carrier for liquids

One of the most pressing challenges presented by the market trend towards dry powder formats is the incorporation of liquids, such as surfactants or perfumes, into such formats. Few solid surfactants are available and liquid surfactants often perform better. As a result, viscous or liquid surfactants have to be applied on a carrier in order to be converted into a dry substance.[6] However, although the carrier plays a vital role in adding liquid ingredients to the formulation while simultaneously maintaining the product's dry consistency, it does not normally have any active function during the application itself. A multifunctional carrier would have obvious advantages, given the limited dimensions of a tablet.[7]

The use of trisodium citrate anhydrous as an active carrier for liquids offers a solution to this challenge. Figure 1 shows its porous crystal matrix.

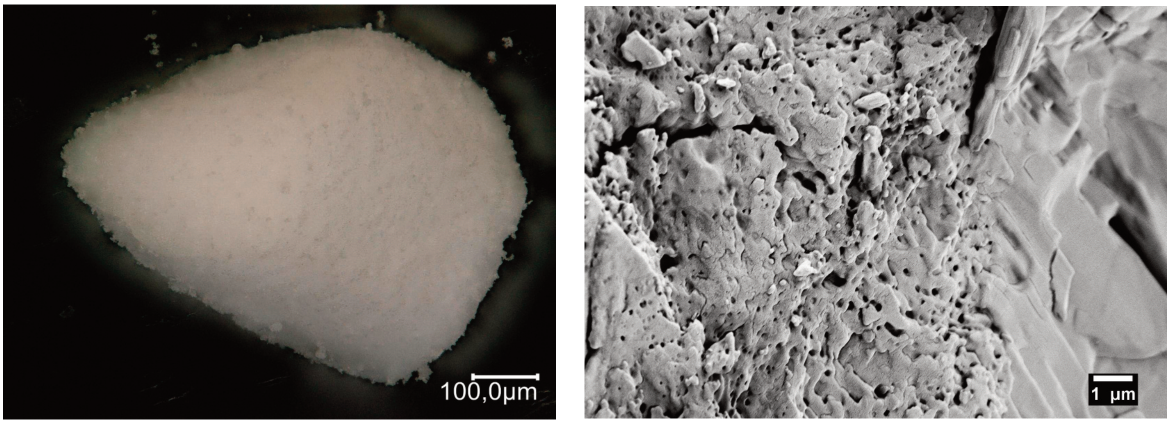



**Figure 1: Porous structure of TSA (left: optical microscope image, right: scanning electron microscope (SEM) image)**

These pores can be loaded with liquids such as surfactants or perfumes. Whilst other abrasives are able to act as carriers, TSA also demonstrates other activities. It can act as a buffering agent and builder, and also improves tabletting behaviour as shown in a previous study.[3]

## The loading process

The loading process requires a nozzle for atomising the liquids into small droplets and a mixer to ensure homogenous application. While a fluid bed ensures homogenous spraying as well as very good heat and mass transfer,[8] most typical mixing devices are perfectly adequate for this purpose.[9]

During the loading process, the small liquid droplets hit the surface of the TSA particles and fill the available pores. The maximum loading capacity of TSA is 12%, based on the amount of water removed from the dihydrate in the drying process. The loading capacity to obtain a free-flowing loaded powder is highly dependent on the properties of the liquid, such as viscosity and surface tension.[10] In this project the surfactants listed in Table 1 were sprayed onto TSA. The different surfactants were chosen based on market trends such as surfactant mildness and certification as well as the trends towards natural solutions.[11] The chosen surfactants differ in their chemical composition, their surfactant charge and most importantly in their viscosity profile.

**Table 1: Liquid surfactants sprayed onto TSA as a carrier**

| INCI | Surfactant charge | Active concentration |
|---|---|---|
| Coco-Glucoside | Non-ionic | 52 wt% |
| Cocamidopropyl Betaine, concentrated | Amphoteric | 48 wt% |
| Sodium Cocoyl Glutamate | Anionic | 27.5 wt% |
| Glycolipids | Non-ionic | 50 wt% |

For viscosity profiling, temperature ramps between 20°C and 70°C were implemented using a rheometer with cone/plate geometry. The surfactant was sheared at 250 $s^{-1}$, while the temperature was increased linearly by 0.1°C/s. The resulting viscosity profiles are shown in figure 2.

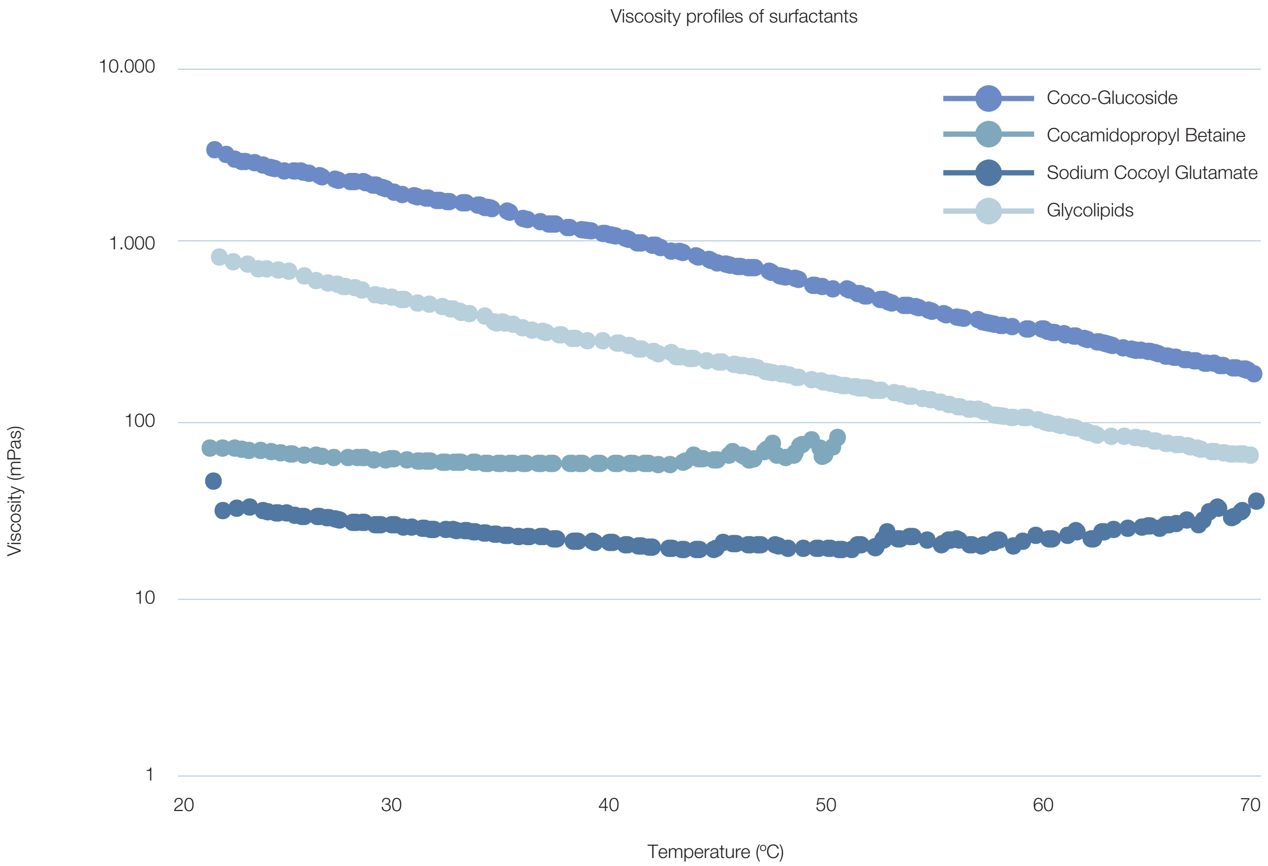



**Figure 2: Viscosity profiles of the chosen surfactants**

The chosen surfactant dilutions differ in terms of their viscosity profiles. Over the entire temperature range investigated, from 20°C to 70°C, coco-glucoside has the highest viscosity, starting at 3570 mPas at 20°C and falling to 204 mPas at 70°C. The glycolipid surfactant shows a similar slope, but overall viscosity is lower (881 mPas at 20°C and 66 mPas at 70°C). In contrast to the non-ionic surfactants, both cocamidopropyl betaine and sodium cocoyl glutamate demonstrate viscosity profiles that are almost temperature-independent, at about 80 mPas for cocamidopropyl betaine and 35 mPas for sodium cocoyl glutamate. The measurements for cocamidopropyl betaine had to be stopped at 50°C due to the formation of artefacts on the surface. Based on the different rheology profiles, it is expected that the loading process will also differ because the physical properties of the liquids influence the size of their atomised droplets, the spreading of the liquids on the surface of the TSA and the diffusion of the liquids into the porous structure.[10] These impacts are discussed in the following section.

## Characteristics of loaded Trisodium Citrate Anhydrous

The surfactant-loaded TSA samples were analysed for the following properties:

- Maximum loading capacity of each surfactant based on the active concentration
- Particle size distribution, analysed by sieving
- Flowability, analysed using the funnel method in accordance with EN ISO 6186:1998[12]
- Bulk density according to DIN ISO 697[13]
- Storage stability following storage in closed tubes at 40°C (evaluation of caking)

An overview of the results is given in table 2. The most important characteristic is the maximum active substance loading capacity while maintaining a free-flowing powder. The surfactants tested in this project differ in their maximum active component loading capacity, ranging between 3.48 wt% and 9.46 wt%. The highest loading capacity was achieved using sodium cocoyl glutamate as a surfactant. Considering the active concentration and the viscosity profile, sodium cocoyl glutamate has the lowest values of 27.5 wt% active concentration and a viscosity of about 35 mPas between 20°C and 70°C. This means that the surfactant can easily be atomised into fine droplets and these penetrate quickly into the porous surface of the TSA. The maximum possible loading of 12 wt% was not achieved because all the surfactants were more viscous than water, which has a viscosity of 1 mPas.[14] After sodium cocoyl glutamate comes coco-glucoside, 8.94 wt% of which can be loaded onto TSA. While the coco-glucoside is a viscous liquid at room temperature, its viscosity can be dramatically reduced by heating (see figure 1). With the reduced viscosity the coco-glucoside droplets can diffuse more easily into the TSA particles and the resulting loading capacity is increased. Comparing this result to glycolipids, it can be seen that the difference in viscosity affects the loading capacity. Although coco-glucoside has the higher viscosity, the amount (5.80 wt%) of glycolipids that can be loaded onto the TSA particles while ensuring that the crystals remain free-flowing is smaller. Possible reasons are the other physical characteristics of the surfactants, such as surfactant charge and surface tension.[10] Cocamidopropyl betaine has the lowest loading capacity, at 3.48 wt%. The loading capacity of cocamidopropyl betaine is low because of its viscosity profile and the fact that it forms artefacts with increased temperature. As a result, this surfactant is not suitable for application in a heated process chamber.

**Table 2: Overview of the characteristics of surfactant-loaded TSA**

| Surfactant | Coco-Glucoside | Cocamido-propyl Betaine | Sodium Cocoyl Glutamate | Glycolipids |
|---|---|---|---|---|
| Max. loading capacity based on the active concentration (wt%) | 8.94 | 3.48 | 9.46 | 5.80 |
| Mean particle size (x50, µm) | Comparable mean particle size between 380 µm and 415 µm; loading process with very few agglomerates | | | |
| Flowability (s) | Free-flowing powder with flow times of 2.5 s to 4.0 s | | | |
| Bulk density (g/L) | Comparable bulk density of 816 g/L to 898 g/L | | | |
| Storage stability | Free-flowing after seven months of storage at 40°C in sealed tubes, no caking visible | | | |

The flowability of the powder must be investigated in order to determine storage methods and precise dosing. If a liquid is added to an unsuitable powder, cohesion can occur, making conveyance and storage impossible.[10] The porous surface of TSA enables it to absorb the liquid and thereby remain a free-flowing powder. This characteristic was tested using the funnel method, in accordance with EN ISO 6186:1998.[12] The time for 100 g loaded TSA to flow through a 10 mm orifice was between 2.5 s and 4.0 s for all loaded substances, which indicates a free-flowing powder. Storage stability at 40°C in sealed tubes was also investigated. All loaded TSA samples remained free-flowing after seven months of storage and no caking was apparent.

To ensure that the surfactant droplets diffuse into the porous TSA structure and do not act as a binder to agglomerate the TSA particles, the particle size distribution was analysed by means of sieving. All loaded TSA samples had a comparable mean particle size of between 380 μm and 415 μm. Hence, it can be concluded that the loading process dominates and no agglomeration takes place.

In conclusion, the physical properties of the liquids, such as viscosity, have a major impact on the resulting loading capacity and the characteristics of the loaded TSA crystals. The loading process can be influenced by adjusting a process parameter; for example, the temperature.

## Trisodium Citrate Anhydrous in tablets

Following the trend towards dry powder formats, there have been many new product launches featuring tablet formats.[15] Tablets are easy to handle and enable precise doses. The single-dosage function of a tablet also means that it is a preferred format for travelling.[1]

A face scrub formulation was developed featuring loaded TSA (see table 3). In addition to the loaded TSA described above under “Trisodium Citrate Anhydrous as a carrier for liquids”, this formulation contains an effervescent blend, moisturising and humidity absorption agents, and a thickener for a creamy touch.

**Table 3: Face scrub formulation featuring the loaded TSA**

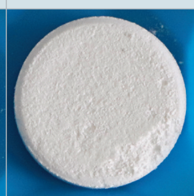
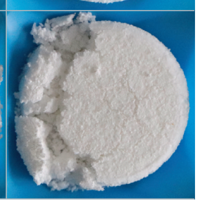
| Ingredients | Function | Quantity (wt%) |
|---|---|---|
| Trisodium Citrate Anhydrous (TSA) | Abrasive and carrier | 55 |
| Surfactant (loaded on TSA) | Cleaning | |
| Sodium Bicarbonate | Effervescent agent | 23.5 |
| CITROCOAT® N10 | Effervescent agent | 10 |
| ERYLITE® Personal Care Grade | Moisturising agent | 10 |
| Trimagnesium Citrate Anhydrous | Humidity absorption | 1 |
| Xanthan Gum FF PC | Thickener, creamy touch | 0.5 |

All ingredients were mixed and tablets were pressed using a single-punch tablet press with the following settings: punch diameter 25 mm, compression force 10 kN, filling depth 7.7 mm and dwell time 100 ms. The resulting tablets have an average height of 6.88 mm and an average tablet weight of 4.22 g.

Figure 3: Pressed tablets and packaging tubes

To evaluate storage stability, the tablets were stored in an open storage test at elevated conditions of 30°C and 50% relative humidity. The tablet appearance was checked daily, and the resulting images for storage times of one week and two weeks are shown in table 4. Tablets with unloaded TSA were also included as a reference.

Table 4: Storage stability of face scrub tablets with different loaded TSA samples at 30°C and 50% relative humidity in an open storage test

| Sample | Unloaded TSA | TSA with Coco-Glucoside | TSA with Cocamido-propyl Betaine | TSA with Sodium Cocoyl Glutamate | TSA with Glycolipids |
|---|---|---|---|---|---|
| Beginning |  |  |  |  |  |
| After one week |  |  |  |  |  |
| After two weeks |  |  |  |  |  |

The tablets vary in terms of their storage stability. After one week of open storage at 30°C and 50% relative humidity, several tablets had already crumbled at the edges. Looking at the tablets with unloaded TSA, major cracks on the surface could be detected after one week of storage. Only the formulations with coco-glucoside and glycolipids as surfactants retained their shape. It can be concluded that the addition of these surfactants can increase the particle binding forces and therefore stabilise tablet shape. After prolonged storage, the cracks increased to the point where the tablet shape of the formulations with unloaded TSA, cocamidopropyl betaine and sodium cocoyl glutamate was no longer visible; all that remained was powder. After two weeks of storage, the formulation with glycolipids showed instability, with major cracks on the tablet surface. The only tablet that was intact after two weeks of open storage contained TSA loaded with coco-glucoside.

In addition to the open storage test, the same formulations were packed into tubes that had a desiccant in the lid (see figure 3) and stored at 30°C and 50% relative humidity. They were visually evaluated every month. None of the tablets showed any cracks in their surfaces; therefore, it can be concluded that storage is possible over several months in sealed tubes.

To improve the storage stability of the face scrub tablets, the formulation was adjusted by varying the amount of loaded TSA. Because coco-glucoside was the only surfactant to pass the first open storage test, all further tests were performed with this formulation. To minimise the humidity uptake during storage, the amount of hygroscopic ingredients was reduced. Tablets with 55%, 45% and 35% of loaded TSA were pressed and stored at 30°C and 50% relative humidity. The formulation was adjusted by increasing the amount of effervescent components.

Tablets with all the tested proportions of loaded TSA retained their shape during the two weeks of storage. However, the storage conditions influenced tablet hardness, which decreased slightly over the storage time. In addition, it was observed that tablets with a higher amount of loaded TSA in the formulation could be crushed more easily.

To sum up, the tablet formulation with 35% TSA loaded with coco-glucoside showed the best storage stability and is therefore the recommended formula (composition shown in table 5). The biplanar tablets weigh 4.5 g each and have a pH value of 6.4 (two tablets in 90 mL tap water).

**Table 5: Improved face scrub formulation with coco-glucoside**

| Ingredients | INCI | Supplier | Quantity (wt%) |
|---|---|---|---|
| Trisodium Citrate Anhydrous | Trisodium Citrate | **Jungbunzlauer** | 32.14 |
| Coco-Glucoside | Coco-Glucoside | | 2.86 |
| Sodium Bicarbonate | Sodium Bicarbonate | | 33.5 |
| CITROCOAT® N10 | Citric Acid, Monosodium Citrate | **Jungbunzlauer** | 20 |
| ERYLITE® Personal Care Grade | Erythritol | **Jungbunzlauer** | 10 |
| Trimagnesium Citrate Anhydrous | Trimagnesium Citrate | **Jungbunzlauer** | 1 |
| Xanthan Gum FF-PC | Xanthan Gum | **Jungbunzlauer** | 0.5 |

The face scrub tablet is applied in several steps. First, the tablet is crushed into the wet palms and rubbed between the palms with a little water so that it foams up. More water will soften the scrub effect. Then it is massaged gently over the entire face, followed by a thorough rinse with water. In figure 4 the face scrub is ready to be applied to the face. The abrasive TSA particles as well as the creamy foam are clearly visible.

**Figure 4: Application of face scrub tablet with loaded TSA**

The tablets of the final face scrub formulation were tested by a small consumer panel (15 panellists) and their comments were summarised. The face scrub in tablet format was described as an innovative concept that is good for travelling. The tablets are easy to crush and handle. The scrub effect can be adjusted by varying the amount of water. The abrasive TSA particles are stable throughout the application stage. Foam forms quickly and very well, and the foam has a creamy texture.

In summary, the face scrub formulation in tablet format developed for this study clearly has the potential to meet all consumer expectations and also to satisfy all market trends towards water-free products in a single-dosage format. This concept could be expanded to other exfoliating products, such as body scrubs.

## Summary

It is important to have versatile ingredients when developing water-free formulations. Trisodium citrate anhydrous combines multiple functions in one ingredient, making formulation easier. The porous nature of the compound allows the citrate to act as a good carrier for liquid ingredients. This is crucial to the development of water-free personal care applications, where surfactants are widely used.

This study demonstrates that loading surfactants onto trisodium citrate anhydrous will not impair flowability or processability. The ability to compress the formulation into a tablet format gives formulators more flexibility to develop unique and innovative products for consumers.

The study further demonstrated the usefulness of trisodium citrate anhydrous as an abrasive agent in facial scrub applications. Taking all of these benefits into consideration, it is clear that trisodium citrate anhydrous could be a key ingredient in the formulation of more sustainable and water-free exfoliating products.

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## About Jungbunzlauer

Jungbunzlauer is one of the world's leading producers of biodegradable ingredients of natural origin. We enable our customers to manufacture healthier, safer, tastier and more sustainable products. Thanks to continuous investment, state-of-the-art manufacturing processes and comprehensive quality management, we are able to provide outstanding product quality.

Our mission "From nature to ingredients®" commits us to protecting people and their environment.

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