facts

Surfactant-Loaded-Citrate

A winning combination for automatic dishwashing detergents

Jungbunzlauer

From nature to ingredients®

Introduction

Since the EU regulation on phosphorus limitation in automatic dishwashing detergents (ADWDs) entered into force in January 2017, sodium citrates have become a well-established alternative to phosphates as environmentally friendly builders for ADWDs. An innovative alternative to the commonly used sodium citrate dihydrate (TSC) is the anhydrous form of sodium citrate (TSA) which has an active content of 100%. TSA has excellent tableting properties and can be used as a carrier for liquid active substances due to its porous structure. In that regard, surfactants are of special interest because they are often liquid or waxy and therefore represent a particular challenge in dry formulations (e.g. tablets). An advantageous combination of the two active substances can be achieved by loading TSA with surfactants. Loading TSA with surfactants shows that free-flowing TSA-surfactant powder can be produced. This loading step allows for easy handling of raw materials and, in the final application, excellent tablet properties.

The challenge of producing modern automatic dishwashing detergents

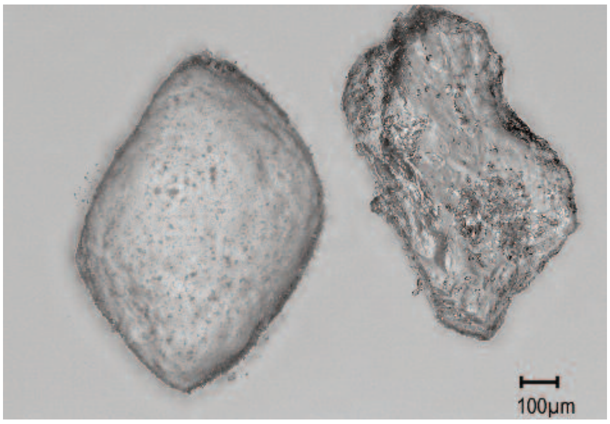
One of the key trends in the automatic dishwashing detergent (ADWD) market is the increased popularity of multifunctional all-in-one products with the main format in Europe being tabs and powder. When changing from the traditional combination of classical detergent, water softener, and rinse aid to a singular multi-benefit product, consumers are not willing to make any concessions in the cleaning performance. Since January 1st 2017, the EU-regulation for the limitation of phosphorus in automatic dishwashing detergents has been in effect.[1] Before the new regulation, sodium tripolyphosphate was commonly used as the main builder ingredient in ADWD formulations. In this context, sodium citrate, usually in its dihydrate form (TSC), has proven to be an ecologically friendly alternative, and has established itself as a “green builder” in phosphate-free ADWDs. It is able to chelate hard water ions, buffers the pH of the washing liquid and is compatible with all other dishwashing detergent ingredients. Furthermore, it is free from phosphorous and thus not eutrophic. Sodium citrate is not only readily biodegraded by many organisms under aerobic conditions, but also under anaerobic waste water treatment conditions and in the natural environment. An innovative water-free alternative to sodium citrate dihydrate is its anhydrous form (TSA), which can be loaded with liquid actives due to its porous structure.

Nowadays all-in-one dishwashing tablets contain different systems, each with a distinct purpose. Examples include builder systems (i.e. builder, co-builder, polymers), bleach systems, enzymatic systems, alkalinity systems, and surfactant systems (i.e. rinse-aid, drying). Formulations typically consist of several different ingredients, the majority being powders. Surfactants are a typical exception with their liquid or waxy appearance. This leads to limitations in production and also increases the complexity of storage, dosage, and manufacture of ADWD formulations. One way to manage these drawbacks is the usage of a carrier system for the surfactants. In this study, the performance of TSA as a carrier for rinse surfactants will be evaluated by analysing the powder and tableting properties of TSA loaded with two market pertinent rinse surfactants.

Trisodium Citrate Anhydrous – a readily biodegradable builder with carrier functionality

Trisodium citrate anhydrous is produced from the dihydrate crystals of trisodium citrate by removing the water molecules in a patented process which does not destroy the original crystal matrix.[2] Due to the absence of crystal water in TSA its molar mass is around 12% lower than its hydrated form. As a consequence, less undesired water is introduced into the detergent formulation and a lower dosage is needed in the final detergent. Unlike TSC, TSA has a porous, sponge-like structure (figure 1). This leads to improved compressibility and allows the loading of TSA with liquid actives such as surfactants.

Figure 1: Microscope image of a trisodium citrate anhydrous particle (left) and a trisodium citrate dihydrate particle (right)

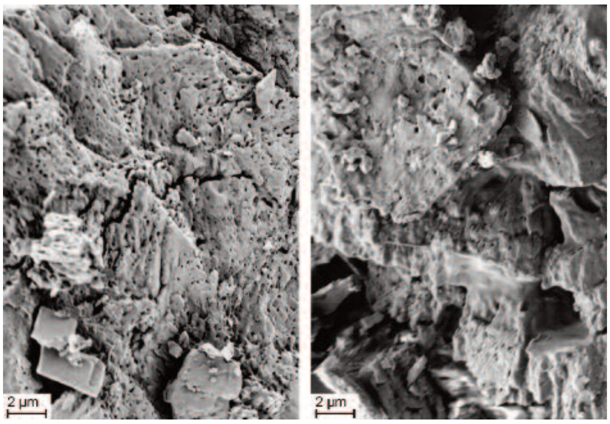


Surfactant-Loaded-Citrate – a smart 2-in-1 solution for automatic dishwashing detergents

According to the German Stiftung Warentest (German consumer organisation) the drying and rinse performance occupies a large percentage (15% each) in the evaluation of cleaning performance of multi tabs.[3] Responsible for this property are surfactants.[4] Because of their importance in the washing process and due to the fact that the handling and incorporation of the more liquid or waxy surfactants is often difficult in the manufacturing process of dishwashing tabs, another approach would simplify the process. Since TSA has a porous structure, the idea was to use the particles as active carriers for the surfactants. This avoids the use of otherwise inactive carriers for the surfactants, which have no other task in the washing process and could ultimately lead to deposits on the dishes.

To evaluate the handling properties of TSA-surfactant-citrate powder and their applicability in ADWDs, the citrate was loaded with a liquid and a wax-like surfactant, respectively. The small drops of the sprayed liquid collide with the fluidized powder particles and can thus be adsorbed by the pores of the TSA. It was determined that a loading of 7 wt.% is the optimal surfactant level. The pores of the unloaded particles caused by the removal of the water are clearly visible in the SEM pictures shown in figure 2 (left). In the loaded TSA (figure 2, right), the pores are mostly filled with the surfactant.

Figure 2: SEM pictures of TSA particles, unloaded (left) and loaded with surfactant 1 (right)



Test methods: Evaluation of powder and tablet properties

Powder characteristics

To be suitable for the processing and tableting of ADWDs, the loaded citrate must display powder and tableting properties comparable or superior to unloaded citrates. In parallel, homogeneous mixing with other ingredients must be guaranteed. The main characteristics used to describe the powder are its **flowability, bulk density and particle size distribution.** The flowability of a powder is usually tested via the funnel flow test. In this test, 200 g of powder are funnelled through an orifice with 10 mm diameter, whereby a short flow time indicates good flowability. The particle size distribution is a crucial powder parameter for detergent producers and is measured with the sieving test.

Tablet characteristics

The properties of a powder are not only important for storage, handling and processing, but also heavily influence the properties of a detergent tablet. The **breaking strength, friability and disintegration time** are important tablet characteristics to describe the quality of a dishwashing tablet. To characterise dishwashing tablets containing the described surfactant-loaded-citrate, monolayer tablets composed of the main ingredients of typical ADWD were pressed with forces of 20 and 40 kN according to the formulations listed in table 1.

Results: Flowability, bulk density and particle size distribution

The TSA powders loaded with surfactants had a flowability comparable to TSC (12.7 sec.) and improved flowability compared to pure TSA (13.8 sec.). The bulk densities of the combined products, with values from 950-980 kg/m³, are comparable to regular TSC, which has a density of about 970 kg/m³. Compared to pure TSA (approx. 890 kg/m³), the TSA-surfactant powder has a higher bulk density because the pores of the TSA are filled with the surfactant. The sieving results indicate that the TSA-surfactant powder has a significantly lower fine content but a similar coarse fraction compared to TSC and pure TSA. The low fine particle fraction reduces the risk of dust formation during the handling and processing of the powder.

Table 1: ADWD formulations for tablet characterisations

Formulation	A	B	C	D
Citrate Type	TSC	TSA	Surfactant 1-loaded-TSA	Surfactant 2-loaded-TSA
Sodium Carbonate [%]	40			
Trisodium Citrate Dihydrate [%]	30	–	–	–
Trisodium Citrate Anhydrous [%]	–	30	–	–
TSA loaded with 7 wt.% Surfactant [%]	–	–	32.25	32.25
Sodium Percarbonate [%]	10			
Sodium Disilicate [%]	5			
Sodium Sulphate [%]	10.75			
Polyethylene Glycol 6000 [%]	2			
Filler [%]	2.25	2.25	–	–

Results: Breaking strength

The breaking strength of a pressed tablet characterises its stability under the influence of an external force, e.g. during storage. A stable tablet is hereby characterised by a high breaking strength. In the test procedure, the tablets are exposed to an increasing force until the tablets break.

Figure 3: Breaking strength of tablets prepared according to the formulations listed in table 1

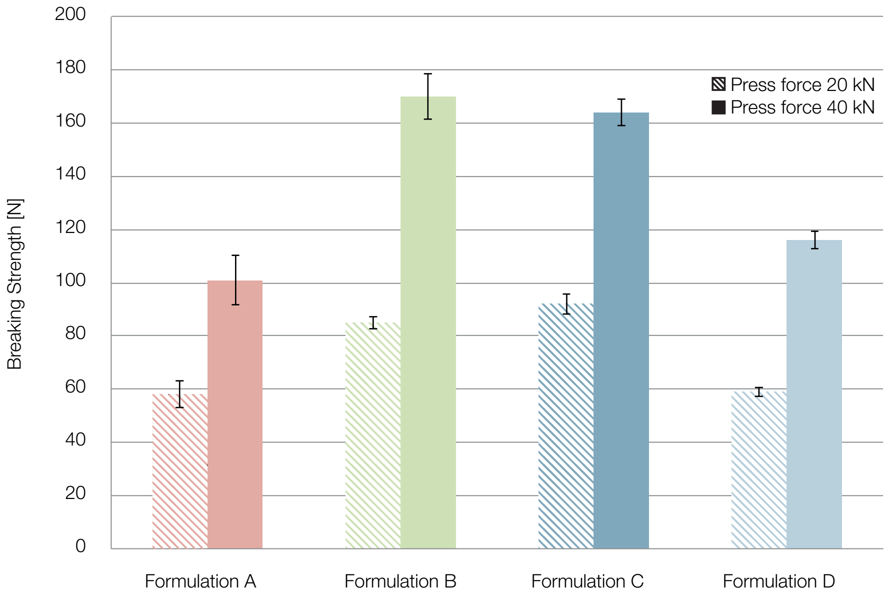
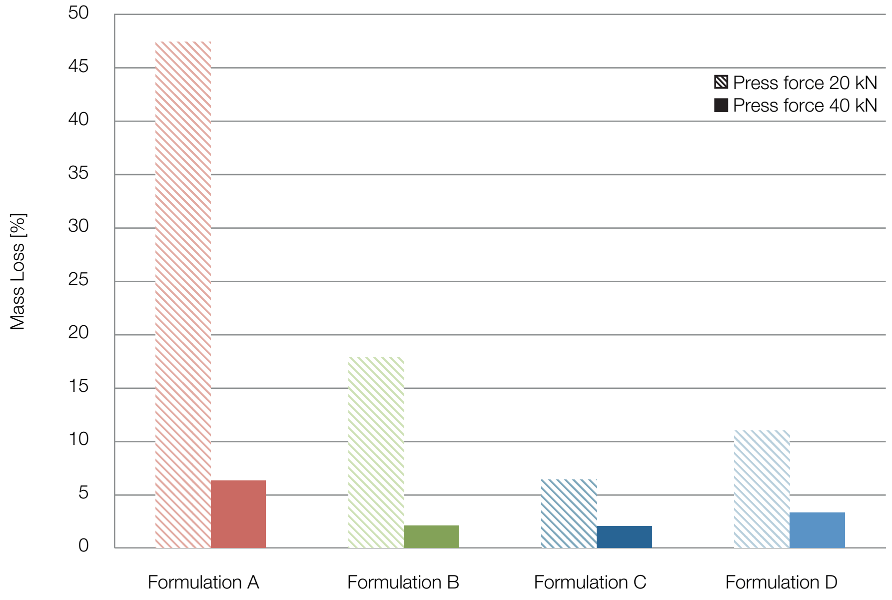


Figure 3 shows the breaking strengths for the tablets containing the different citrate powders. The formulation containing pure TSA has a higher breaking strength than TSC, which demonstrates the generally good tableting properties of the porous TSA. The results also show that tablets with the loaded powders (formulations C and D in figure 3) have higher breaking strengths compared to tablets using regular sodium citrate (formulation A in figure 3). Lower press force is required to reach the same tablet hardness as TSC containing tablets when using the surfactant-loaded citrate. This is advantageous because the wear on the presses is reduced. By using a higher press force, tablets become more stable. This means that a reduced tablet fragility can be achieved, which minimises the risk of product damage during transport and storage.

Results: Friability

Low abrasion of tablets is also an important factor for tablet stability and is measured by friability. It describes the mass loss during exposure to mechanical stress in a rotating drum. For stable tablets during production, packaging and transport, a low mass loss is key.

Figure 4: Friability of tablets prepared according to the formulations listed in table 1 (test according to EuAB 8.0[5]) (tablets of formulation A with press force 20 kN were broken)**

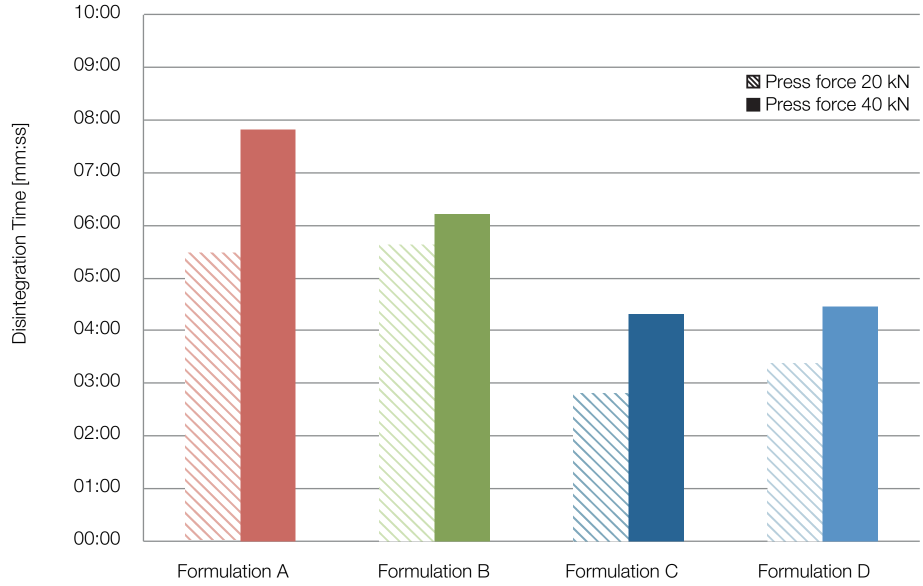


According to the results shown in figure 4, tablets containing the TSA loaded with surfactant show a high stability with low mass loss, especially compared to commonly used citrate (TSC).

Results: Disintegration time

Fast dissolution of the tablets in the dishwasher is a key requirement for good performance of ADWDs. The dissolution behaviour of a dishwashing tablet is typically evaluated with a disintegration test, which measures the time until the tablet fully disintegrates into fragments for a uniform and rapid distribution of the active ingredients in the dish washing machine.

Figure 5: Disintegration time of tablets prepared according to the formulations listed in table 1. Test procedure: Measurement of the time until the tablet disintegrates in a rigid frame with a porous bottom and mesh size of 2 mm, which is raised and lowered evenly in 45°C water (test according to EuAB 8.0[6]).



As shown in figure 5, tablets containing the surfactant-TSA combination disintegrate faster than tablets containing TSC or TSA. Thus, fast disintegration is ensured by using the surfactant-loaded citrate and there is low risk of poor cleaning performance due to slow or incomplete dissolution of the tablets.

Conclusion

The loading of trisodium citrate anhydrous with surfactants leads to a suitable and 100% active 2-in-1 combination product for use in ADWD products. The results of the tests reveal that the surfactant-loaded-citrate particles show similar powder and tableting properties compared to unloaded and common citrates. Thus, this combination product of loaded TSA is a new innovative option to the conventional use of liquid components in powders and tabs. Due to the mild loading process, no changes of the surfactants and their performance are expected. The 2-in-1-combination powders show good powder properties, which can lead to an easier handling of raw materials, like the sometimes hard to handle surfactants. Furthermore, by loading the TSA with surfactants additional tableting benefits can be achieved, like a higher breaking strength and a lower friability. This can minimize product damage after the manufacturing process. The surfactant-loaded-citrate-powder thus provides an innovative, convenient way for the improved incorporation of liquid or waxy surfactants into ADWDs, which broadens the range of usable surfactants for ADW detergents.

References

[1] EUROPÄISCHE KOMMISSION, "Bericht der Kommission an das Europäische Parlament und den Rat (Artikel 16 der Verordnung (EG) Nr. 648/2004)," 2015.

[2] A. Ernst and J. Gass, "Process for the preparation of anhydrous trisodium citrate". Patent US 5,929,276, 1999.

[3] Stiftung Warentest, "Von Hui bis Pfui," 56-60, 03 2018.

[4] Stiftung Warentest, "Die Vielversprecher," 52-56, 08 2017.

[5] "Europäisches Arzneibuch 8. Ausgabe," in Friability of uncoated tablets (Ph. Eur. 2.9.7), Deutscher Apotheker Verlag, 2016.

[6] "Europäisches Arzneibuch 8. Ausgabe," in Disintegration of tablets and capsules (Ph. Eur. 2.9.1), Deutscher Apotheker Verlag, 2013.

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The Authors

Sandra Hübner, Application Technology, Jungbunzlauer Ladenburg GmbH
sandra.huebner@jungbunzlauer.com

Dr. Felix Weiher, Application Technology, Jungbunzlauer Ladenburg GmbH
felix.weiher@jungbunzlauer.com

Dominik Buser, Product Manager, Jungbunzlauer International AG
dominik.buser@jungbunzlauer.com

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Headquarters **Jungbunzlauer Suisse AG** · CH-4002 Basel · Switzerland · Phone +41-61-2955 100 · headquarters@jungbunzlauer.com

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