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Mixtures of trisodium citrate anhydrous and dihydrate as builders in dishwashing detergents – effects on tablet stability and disintegration

Abstract

Trisodium citrate is an ecologically friendly, non-toxic alternative to phosphorus-based builders in automatic dishwashing detergent (ADWD) tablets. It exists in two forms: trisodium citrate dihydrate (TSC), which contains two water molecules in the crystal; and trisodium citrate anhydrous (TSA). The latter is produced by removing the water of crystallisation from the crystalline matrix, thus creating a porous structure. TSA can be loaded with liquid substances and will remain a free-flowing powder because of these pores. In the present analysis, the effects of TSC, TSA and mixtures thereof on critical tablet parameters, such as disintegration and stability, were examined. The study shows that replacing part of the TSC in the formulation with TSA decreases disintegration time and increases breaking strength after tablet pressing. This finding is supported by an existing patent (EP 3 431 575), which additionally shows that mixtures of TSA and TSC improve tablet cleaning performance. Furthermore, the present study demonstrates that the storage stability in polypropylene of tablets containing TSA/TSC mixtures is comparable to that of tablets which only use TSC as the builder. Thus, TSA and TSC are not only eco-friendly builders, but can be used to modulate tablet disintegration time and stability as needed.

Introduction

Automatic dishwashing detergent (ADWD) tablets consist of various different ingredients, such as surfactants and bleach for dissolving grease and removing stains, and enzymes to remove protein and starch found in food residues. In addition, builders form an essential part of ADWD tablets due to their ability to bind cations, which softens the water and reduces limescale deposits.[1] Trisodium citrate is an excellent builder and has experienced a tremendous increase in popularity as an ingredient of ADWD tablets over the past five years. Whereas trisodium citrate was essentially not present in any new product launches in 2015, about 20% of all new ADWD tablet product launches in 2019 contained trisodium citrate (Innova Market Insights). This is certainly a consequence of changes in legislation, which have led to strict limitations of the use of phosphates as builders in ADWD tablets due to their detrimental effects on the environment.[2] Trisodium citrate presents a viable, eco-friendly alternative builder.

Jungbunzlauer offers two forms of trisodium citrate: trisodium citrate dihydrate (TSC) and trisodium citrate anhydrous (TSA). Both forms occur as white, granular crystals and are chemically stable when stored at ambient temperatures. TSC and TSA are non-toxic, fully biodegradable and can be disposed of with regular waste. 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. TSC is produced by complete neutralisation of citric acid with a highly pure sodium source and subsequent crystallisation. TSA is manufactured from TSC by removing the water molecules from the dihydrate crystals without destroying the original crystal matrix.[3]

The resulting TSA crystals have a porous structure that can be used as a carrier for inorganic and organic substances such as perfumes, peroxides and surfactants. Due to the water having been removed, TSA has an active content of 100% and does not add water to the formulation – unlike TSC, which has a water of crystallisation content of 12% (dihydrate). TSC and TSA can be used as builders in ADWD tablets either on their own or together as mixtures.
The aim of this study was to elucidate the impact of TSA/TSC mixtures on critical tablet performance parameters, such as disintegration time, tablet breaking strength and storage stability.

Experimental procedure

A hydraulic tablet press was used to produce the ADWD tablets. The tablets had a weight of 16 g and were pressed according to formulation I in table 1 for all experiments, apart from the analysis of storage stability. For the latter experiment, the formulation was slightly adjusted: 2.25 wt% of sodium sulfate was replaced with a non-ionic surfactant (formulation II). The trisodium citrate used was either in the form of TSA alone, TSC alone or different mixtures of TSA and TSC.

Table 1: ADWD tablet formulation.

Ingredients	Formulation I [wt%]	Formulation II [wt%]
Sodium Carbonate	40	40
Trisodium Citrate	**30**	**30**
Sodium Percarbonate	10	10
Sodium Disilicate	5	5
Sodium Sulfate	13	10.75
PEG	2	2
Surfactant	0	2.25

In order to analyse the disintegration time, the tablets were placed in a basket with a mesh size of 5 mm in a water bath at 30°C. The basket was agitated in the water in an up-and-down motion (60 times/min). The time taken for the tablets to fully disintegrate with no remains left in the basket was then measured. To examine crack formation, tablets were put into an agitated water bath (150 times/min at 22°C). After 2 minutes or 6 minutes, the tablets were removed and shock frozen in liquid nitrogen to preserve their surface structure. The tablet surfaces were then examined for signs of cracks using an electron microscope (40x magnification).

Breaking strength was determined by measuring the force which had to be applied to a tablet to break it into two distinct parts. This analysis was performed immediately after the tablets had been pressed.

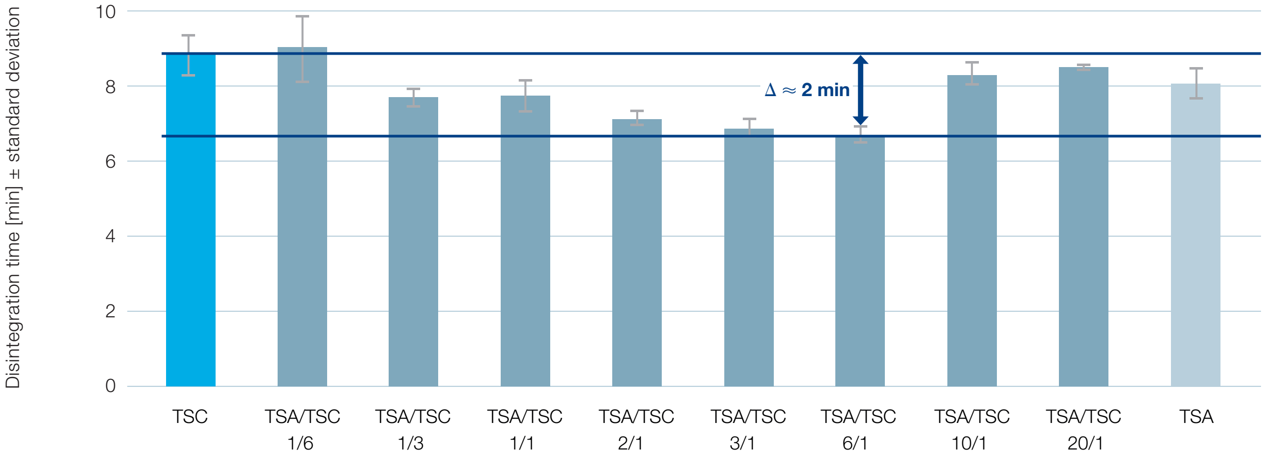
For storage stability tests, the tablets were wrapped and sealed in 28 µm thick polypropylene foil immediately after pressing. After this, the tablets were stored at 25°C and 60% relative humidity for 8 days, then unwrapped and visually evaluated for crack formation and crumbling.

Results

Mixing TSA and TSC accelerates tablet disintegration

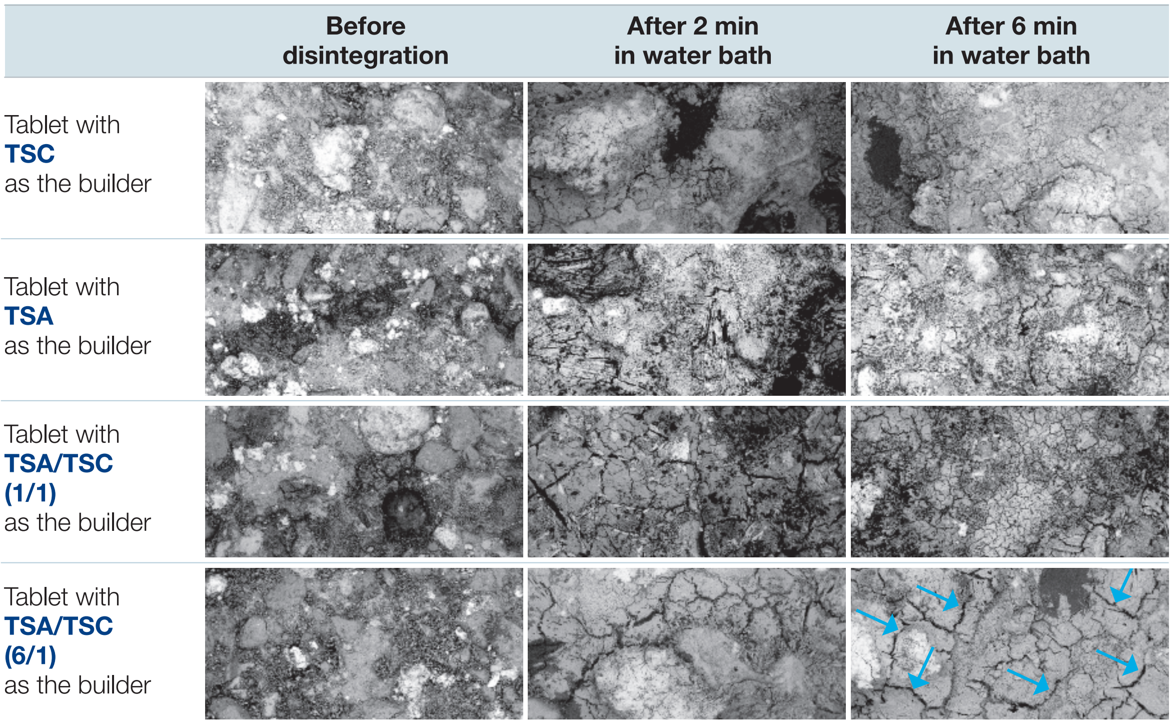
Tablets were pressed according to formulation I, containing TSA, TSC or different mixtures thereof as builders. The disintegration time was then analysed as shown in figure 1. Tablets with either TSA (8 min 6 s) or TSC (8 min 48 s) demonstrated similar disintegration times. Ratios of TSA/TSC between 1/3 and 6/1 decreased the disintegration time in a manner proportional to the amount of TSA in the tablet. Tablets with a 6/1 TSA/TSC mixture had the fastest disintegration time of 6 minutes 42 seconds, which was around 2 minutes faster than with TSC alone as the builder. A further increase of the TSA content to a 10/1 ratio of TSA/TSC did not lead to a further reduction in disintegration time; these tablets had a disintegration time of 8 minutes 18 seconds, similar to tablets containing only TSA as the builder.

Figure 1: Effect on tablet disintegration time of using TSA, TSC and mixtures thereof as builders.



The formation of cracks on the surface of the tablets was evaluated by electron microscopy. Tablets with TSA alone, TSC alone, a 1/1 TSA/TSC ratio or a 6/1 TSA/TSC ratio used as the builder (formulation I) were tested. As shown in figure 2, no cracks were found in the surface of any of the test tablets before disintegration in the water bath. After disintegration in a water bath, the increase in crack formation was inversely proportional to the observed decrease in disintegration time for tablets containing mixtures of TSA/TSC. Tablets containing TSA or TSC alone displayed very few cracks after 2 minutes and 6 minutes in the water bath. In contrast, more and bigger cracks were noted in the surface of tablets with a mixture of TSA/TSC after 2 minutes and 6 minutes in the water bath. This effect was most pronounced for the 6/1 TSA/TSC ratio, which corresponds to the fact that this ratio had the fastest observed disintegration time.

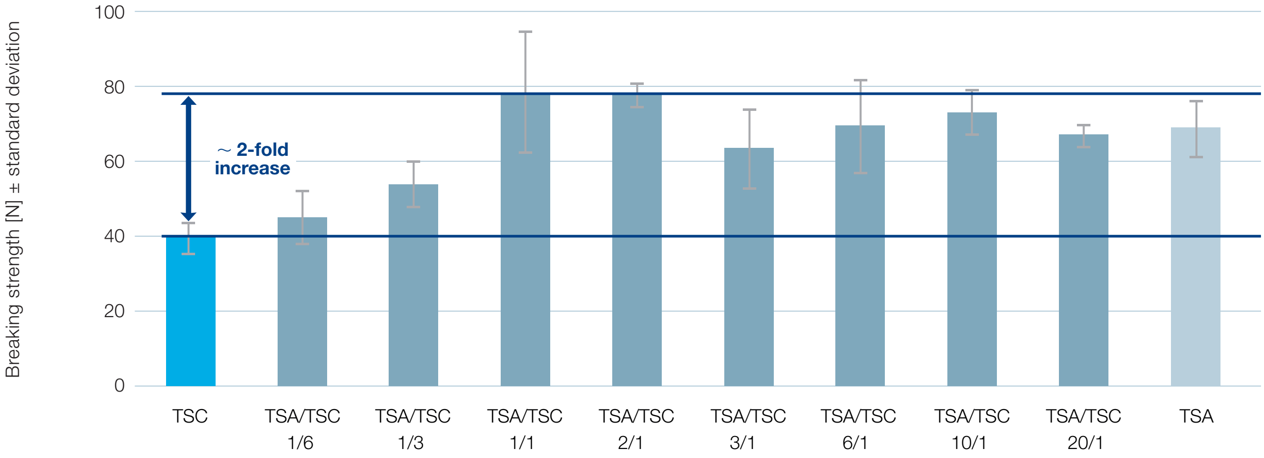
Figure 2: Marked crack formation during disintegration of tablets with TSA/TSC mixtures as builders.



TSA increases breaking strength

Tablets were produced according to formulation I, and their breaking strength was measured immediately afterwards as a surrogate for tablet stability. The different test tablets contained TSA only, TSC only, or mixtures of TSA/TSC ranging from 1/6 to 20/1. Tablets containing TSA alone as the builder, as well as tablets with TSA/TSC mixtures containing at least 50% TSA, displayed a breaking strength of between 64 N and 78 N, which is around twice as high as tablets with TSC alone as the builder. TSC-only tablets had a mean breaking strength of 39 N. There was no significant difference in breaking strength of tablets with between 50% and 100% TSA as the builder in the formulation. Thus, replacing at least half of the TSC in the formulation with TSA doubles the breaking strength of the tablet (figure 3). This finding is supported by an existing patent, which covers the use of TSA/TSC mixtures of between 5/1 and 1/5 in the enzyme phase of the tablet.[4] The authors not only found that replacing part of the TSC with TSA increases tablet breaking strength; they also reported that TSA/TSC mixtures enhance tablet cleaning performance.

Figure 3: Replacing part of the TSC with TSA improves tablet breaking strength after pressing.

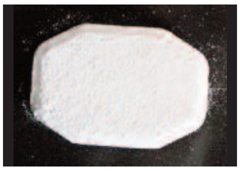
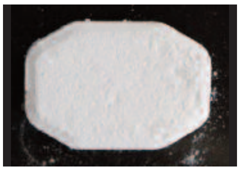


Equally good storage stability in polypropylene

In line with the previous experiments, tablets were pressed according to our experimental formulation, but this time with the addition of 2.25% surfactants (formulation II). Surfactant was added to the tablets for the experiments on storage stability, since the stickiness of the surfactant enhances tablet stability. For trisodium citrate, tablets were tested containing 1/3 TSA/TSC, 6/1 TSA/TSC, TSC only and TSA only. After pressing, the tablets were wrapped and sealed in 28 µm thick polypropylene foil. The tablets were placed in a climate chamber at 25°C and 60% relative humidity for eight days. After this period, the tablets were unwrapped and visually evaluated for signs of crumbling. None of the four builder formulations tested displayed any cracks or signs of falling apart. Thus, the choice of TSA, TSC or a mixture of both in the formulation of ADWD tablets does not seem to affect their storage stability in polypropylene packaging.

In addition to conventional packaging in polypropylene foil, there is also a small market for ADWD tablets in water-soluble packaging and unpackaged tablets, with the aim of reducing packaging waste. Preliminary data indicate that tablets with TSA only and TSC only as builders demonstrate good storage stability in water-soluble polyvinyl alcohol packaging after 16 days of storage under the conditions mentioned above. Using mixtures of TSA and TSC as builders for tablets in polyvinyl alcohol packaging may also be possible if the foil is wrapped very tightly around the tablet. Furthermore, no signs of crumbling in tablets with only TSC as the builder were observed, even when stored completely unwrapped for 16 days.

Figure 4: The choice of TSA, TSC or mixtures thereof as builders has no impact on storage stability in polypropylene.

	Tablet with **TSC** as the builder	Tablet with **TSA** as the builder	Tablet with **TSA/TSC (1/3)** as the builder	Tablet with **TSA/TSC (6/1)** as the builder
Day 0				
After 8 days in polypropylene packaging				

Summary and conclusion

The present study shows that different forms of trisodium citrate have diverse effects on crucial tablet performance parameters, such as disintegration time and tablet breaking strength. Using only TSA as the builder or a combination of TSA and TSC doubles the breaking strength compared to using TSC alone, which indicates higher tablet stability. This is supported by an existing patent, which also shows that mixing TSC with TSA as builder improves tablet cleaning performance.[4] In addition, TSA can be loaded with ingredients such as surfactants and will remain a free-flowing powder due to its porous matrix. Mixtures of TSA and TSC also significantly decrease the disintegration time of ADWD tablets compared to when only TSC is used as the builder. Importantly, all three variants tested – TSA, TSC and TSA/TSC mixtures – demonstrate excellent storage stability in polypropylene packaging. Thus, TSA and TSC represent more than an environmentally friendly alternative to phosphorus-based builders in ADWD tablets. Replacing part of the TSC in the formulation with TSA allows fine-tuning of tablet disintegration time and breaking strength.

References

[1] Gambogi, J.; Kennedy, S.; Ambundo, E. Handbook of Detergents, Part E: Applications, Chapter 3.3: Dishwashing with Detergents, Surfactant Science Series Vol. 141, ed. CRC Press, Boca Raton (2009).

[2] European Commission. Report from the Commission to the European Parliament and the Council (pursuant to Article 16 of Regulation (EC) No 648/2004) (2015).

[3] Kirkovits, A.; Gass, J. Process for the preparation of anhydrous trisodium citrate. Patent US 5,929,276.

[4] Vockenroth, I.; Weber, T.; Bellomi, L.; Schuetz, L. Dishwashing detergent compositions containing citrate dihydrate and anhydrate. Patent EP 3 431 575.

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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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