Jungbunzlauer

From nature to ingredients®

facts

Functional acids with added value in effervescent systems

Introduction

Citric acid is bio-based and biodegradable and is the most widely used organic acid in pharmaceutical, food and non-food applications. It has excellent properties as an acidulant and pH control agent and is commonly used in effervescent systems. In the food sector, effervescent powders and tablets are used for a wide range of products: Vitamin and mineral supplements, sports or electrolyte drinks. In addition to these established product types, the trend towards innovative beverage tablets is increasing. Rising demand for sustainable products, dry products and plastic-free packaging are fuelling the growth of effervescent systems – not only in food applications but also in solid formulations for cleaning purposes. Various products in dry formats use active ingredients in a highly concentrated form, which allows the packaging of such products to be made smaller, and enables more environmentally friendly packaging options to be used than conventional liquid-product packaging. This results in significantly less bulk of product needing to be transported, thus reducing the product's overall carbon footprint.

However, the widespread use of citric acid in dry formulations – in particular, effervescent formulations – poses major challenges for manufacturers around the production and subsequent storage of the final products.

Combining the core product of citric acid with unique surface modification techniques and high-quality additives provides an exceptional range of functional acids to meet manufacturers' needs for customising key product properties, such as tablet hardness, dissolution time and storage stability of solid formulations.

Challenges in effervescent systems

Effervescent systems typically comprise citric acid ($C_6H_8O_7$) and sodium bicarbonate ($NaHCO_3$). Upon contact with water, the effervescent reaction starts and results in the release of carbon dioxide (CO_2) and fizz-like bubbles rising to the surface.[1,2]

$$C_6H_8O_7\ _{(aq)} + 3\ NaHCO_3\ _{(aq)} \rightarrow Na_3C_6H_5O_7\ _{(aq)} + 3\ H_2O\ _{(l)} + 3\ CO_2\ _{(g)}$$

Usually, effervescent components are hygroscopic and moisture sensitive. Absorption of water during processing and storage can trigger an undesired premature effervescent reaction.[3] Other ingredients in formulations can aggravate this effect if they contain water or if they are also hygroscopic, as it is the case with natural extracts or flavourings for beverage tablets or powders. A premature effervescent reaction results in the recrystallisation of trisodium citrate ($Na_3C_6H_5O_7$), which leads to caking of the solid product and the release of CO_2, causing foaming and bursting the packaging. In effervescent tablets, premature reaction can result in mottling of tablets, changes in tablet hardness and dissolution time.[4]

However, these formulation challenges can be overcome by modifying the particle surface of citric acid using a coating or agglomeration process. This technical paper focusses on the characteristics of Jungbunzlauer's functional acids portfolio when formulated in effervescent systems. Analyses of powder flow, tableting characteristics, dissolution time, storage stability and reactivity were carried out, highlighting the greatest advantages of each functional acid for its applications.

Jungbunzlauer's functional acids

Each product in the functional acids range addresses different challenges with a view to improving processability during production and the properties of the final product.

Citric Acid DC

Citric acid DC is a directly compressible citric acid with a thin layer of maltodextrin on the surface of the particles. Use of citric acid DC eliminates the need for agglomeration prior to the tableting process, which saves time and energy. It also provides greater tablet hardness at a lower compression force than it is the case with regular citric acid, thus allowing the friability of pressed tablets during packaging and transport to be reduced.

CITROCOAT® N

CITROCOAT® N is the Jungbunzlauer trade name for citric acid with a monosodium citrate coating. Compared to regular citric acid, CITROCOAT® N is less hygroscopic and less reactive with other ingredients. Various powder and tablet applications which are sensitive to humidity – in particular, effervescent formulations – can benefit from these properties.

CITROCOAT® EP

CITROCOAT® EP is an agglomerated effervescent compound, bringing citric acid and sodium bicarbonate together in the right composition to create a highly reactive but storage-stable effervescent powder with a target pH of 5.5. Due to the excess acidity, a rapid effervescent reaction is to be expected and the slightly acidic pH value ensures a fresh flavour. In order to prevent premature reactions, the citric acid used in CITROCOAT® EP is coated with a thin layer of monosodium citrate. The two effervescent components are agglomerated using a binder, reducing the potential for segregation and improving compressibility. This leads to significantly harder tablets than with a formula based on regular citric acid and sodium bicarbonate.

Performance of functional acids in effervescent systems

In the experiments regular citric acid and Jungbunzlauer's functional acids in effervescent formulations were compared. To investigate the performance of effervescent systems during the tableting process and the performance of the resulting effervescent tablets, dissolution and stability tests were conducted and the reactivity of powder formulations was analysed.

Mechanical stability analysis revealed that the surface modifications present in citric acid DC and CITROCOAT® N remain unaffected by processing and use. CITROCOAT® EP maintains its agglomerate structure after moderate vibrational or rotational stress, with minimal friability. The effects observed in the experiments can therefore be attributed to the added properties of the functional acids.

Powder flow and segregation

A homogeneous mixture is essential to ensure the desired reproducible effervescent reaction. Non-uniform mixtures can arise through segregation, influencing the product quality (e.g. composition in bulk, a sachet or a tablet). As the acid and bicarbonate used in effervescent systems typically have different particle sizes, the powder flow during pre-processing and tableting may cause the formulation components to segregate.[5,6]

Segregation was investigated using a Sifting Segregation Tester in accordance with ASTM Standard D6940-12 (n = 3), where the bulk solid is discharged from a silo to form a pile, allowing segregation to take place. The deviation in mass between different powder fractions from the first cup is analysed and the corresponding pH values measured (figure 1). CITROCOAT® EP was compared to a 1:1 mixture of CITROCOAT® N und sodium bicarbonate.

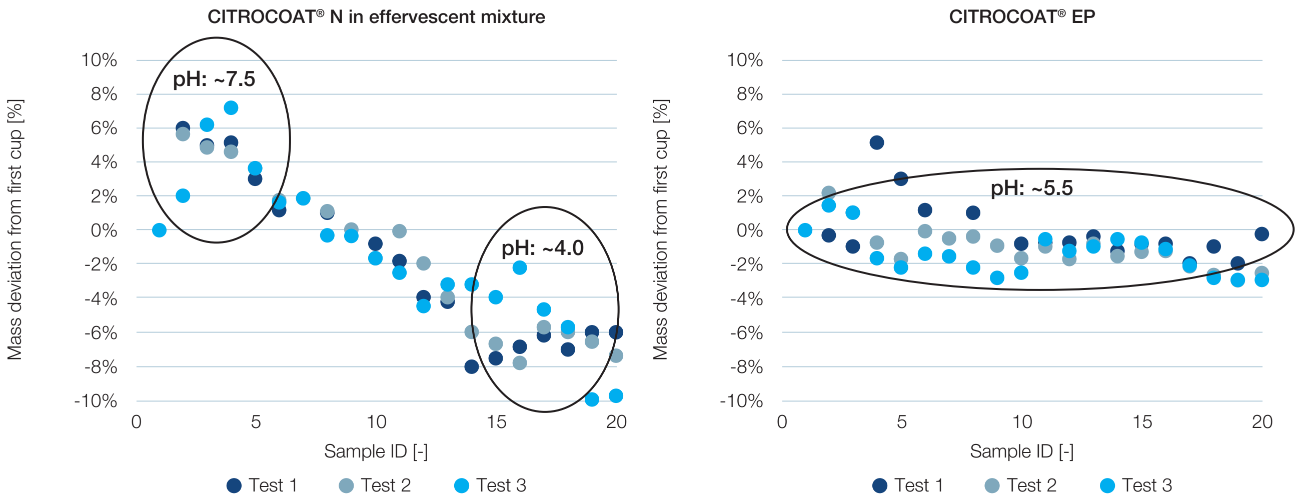

Figure 1: Results of a segregation test in accordance with ASTM Standard D6940-12 for a mixture of CITROCOAT® N and sodium bicarbonate (left) and agglomerated CITROCOAT® EP (right), performed in triplicate

For CITROCOAT® EP constant masses per fraction were determined and the corresponding pH values equalled the target pH of 5.5. For effervescent mixtures containing CITROCOAT® N and sodium bicarbonate, segregation occurs. Smaller particles flowed out of the funnel first, resulting in a higher mass per fraction and pH values of 7.5 indicate sodium bicarbonate as main component. During flow, larger particles remained longer in the silo, resulting in a composition change towards CITROCOAT® N with lower pH values of 4.0.

This gives CITROCOAT® EP the great advantage that a constant composition is available during pre-processing or tableting, while for CITROCOAT® N the adaption of the bulk particle sizes via additional processing steps is recommended to avoid segregation and thereby ensure the quality and performance of the resulting effervescent product.

Tableting characteristics

Good compressibility of the powder mixture is crucial for tablet applications, as agglomeration to improve compressibility is difficult because water-based processes would lead to premature reaction of the effervescent components. The tableting properties of the materials used in an effervescent tablet influence its hardness and thus its dissolution properties. Any water absorbed by effervescent powder mixtures before and during tableting can also result in the tablets sticking to the punches of the tablet press, which further complicates the process.[7,8] In summary, compacting effervescent tablets is generally considered a technical challenge.[3]

Round flat tablet punches with PE inlays were used in a hydraulic single-punch press (FlexiTab® by Röltgen, Solingen, Germany), and the mixtures of acids and sodium bicarbonate were lubricated internally with 2 wt% polyethylene glycol (PEG 4000). PEG 4000 was also used for additional external lubrication. The compression force and filling depth were adjusted to achieve tablets with comparable mass of 5.0 ± 0.2 g and hardness (75 ± 10 N, corresponding to approximately 260 ± 20 kPa for 25 mm tablets; figure 2).

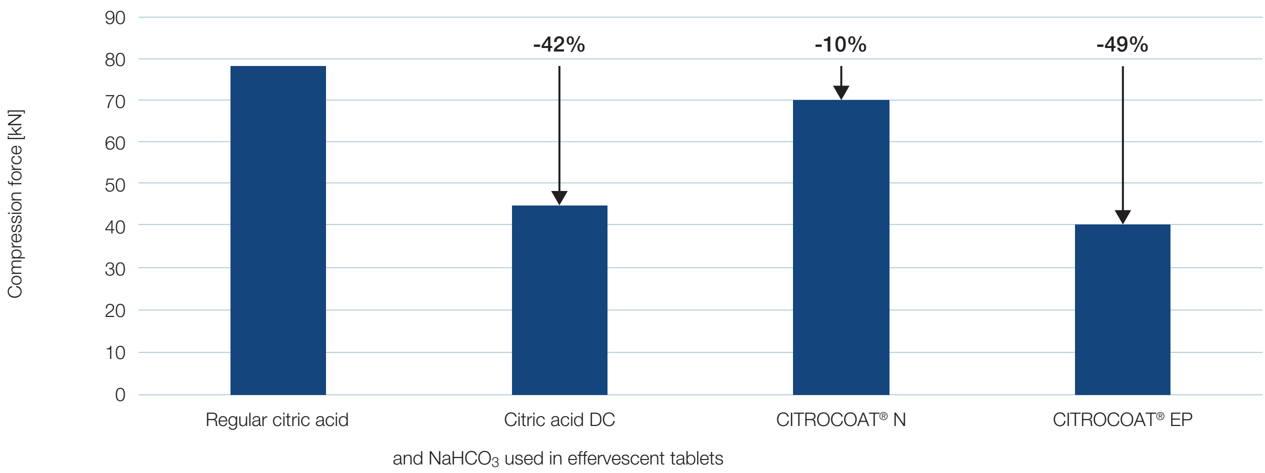

Figure 2: Compression forces required for different effervescent mixtures (with additional lubrication using 2 wt% PEG 4000) to achieve comparable tablet hardness of 75±10 N. Percentage reductions in compression force are given relative to the regular citric acid mixture

The results show that functional acids enable tablets of comparable hardness to be produced at lower compression forces. Citric acid DC and CITROCOAT® EP resulted in particularly large reductions in compression force, reducing wear on the tablet-pressing machinery and thus allowing longer maintenance intervals. It should be noted that CITROCOAT® EP, which is an agglomeration of CITROCOAT® N, sodium bicarbonate and a binder, enabled tablets of comparable hardness to be produced with 43% less compression force than was necessary for the mixture of CITROCOAT® N and sodium bicarbonate.

Dissolution time of effervescent tablets

The dissolution time can be a critical property of an effervescent tablet. Dissolution time was investigated by dissolving one tablet in 200 mL of water and measuring the time required to completely dissolve the tablets. The test was performed in quadruplicate for tablets with comparable hardness.

All tested tablets dissolved readily, although use of functional acids resulted in faster dissolution (figure 3). The faster dissolution times for citric acid DC and CITROCOAT® N compared to regular citric acid can be attributed to the lower compression forces needed during tableting to achieve comparable tablet hardness and the properties of the coating material. Dissolution times for CITROCOAT® EP were only half as long as for regular citric acid. CITROCOAT® EP tablets also had the least variable dissolution times as a result of their homogeneous composition.

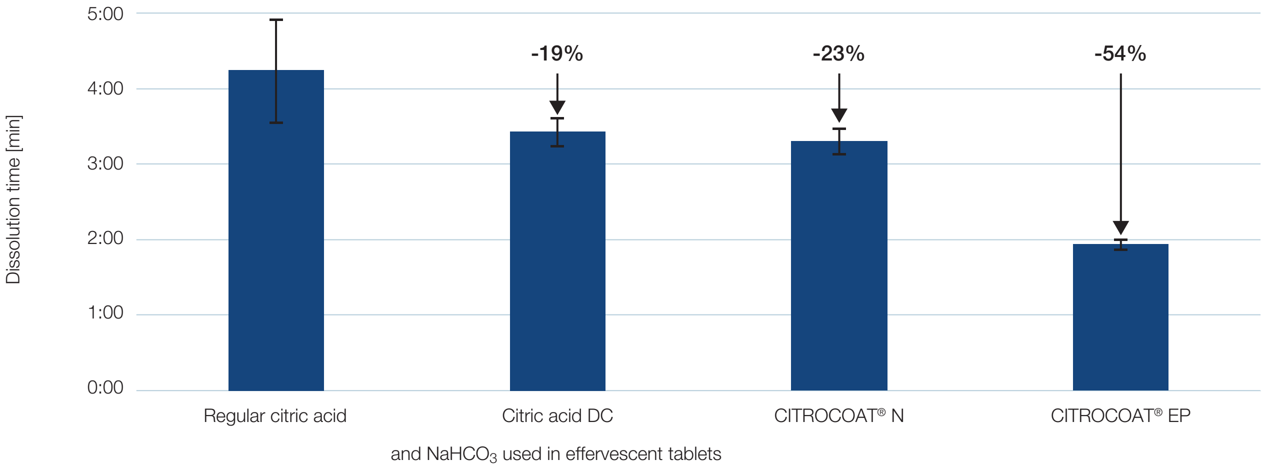

Figure 3: Comparison of dissolution times for effervescent tablets of equal hardness (n = 4). Percentage time savings are given relative to the regular citric acid mixture

Storage stability of effervescent systems

While high reactivity is a desirable attribute when an effervescent system is in use, this is not the case during storage, where the aim is to prevent the materials from reacting prematurely. This would result in a loss of reactivity, significantly impacting performance in the system's final application.

Different methods were used to investigate the storage stability of effervescent tablets or powder mixtures in an open storage test under harsh conditions (30°C, 60% relative humidity).

A visual assessment of the powder mixtures and tablets was undertaken to provide an initial indication of the stability of the effervescent systems. Tablets using regular citric acid and citric acid DC exhibited surface roughening and surface foaming (formation of carbon dioxide), while the surface of CITROCOAT® N and CITROCOAT® EP tablets did not undergo any macroscopic changes (figure 4).

Regular citric acid **CITROCOAT® EP**

Figure 4: Visual assessment of effervescent tablets after being stored open for 88 days under harsh conditions (30°C, 60% relative humidity), with foaming and caking visible for regular citric acid tablets and no change visible for tablets with CITROCOAT® EP

In powder mixtures with regular citric acid and citric acid DC, significant foaming and caking was observed, which led to the samples solidifying such that they could not be broken up. Powder mixtures with CITROCOAT® N and CITROCOAT® EP exhibited only slight caking of the upper layer of particles, which could easily be broken up.

The change in mass due to formation of CO_2 during the storage period was also determined. CITROCOAT® EP tablets had the smallest changes in mass, followed by CITROCOAT® N (figure 5). The coating layer of monosodium citrate used in these two products acts as a physical barrier, preventing moisture from migrating and triggering a premature effervescent reaction. In the case of CITROCOAT® EP, the binder used in the agglomeration process also improves storage stability. For regular citric acid, the greatest change in mass occurred within the first day, indicating immediate reaction when stored open and thus placing higher demands on packaging materials to prevent such a premature reaction from occurring. Loss of mass was less pronounced with powder formulations because the distance between the reactants – the acid and bicarbonate particles – was greater.

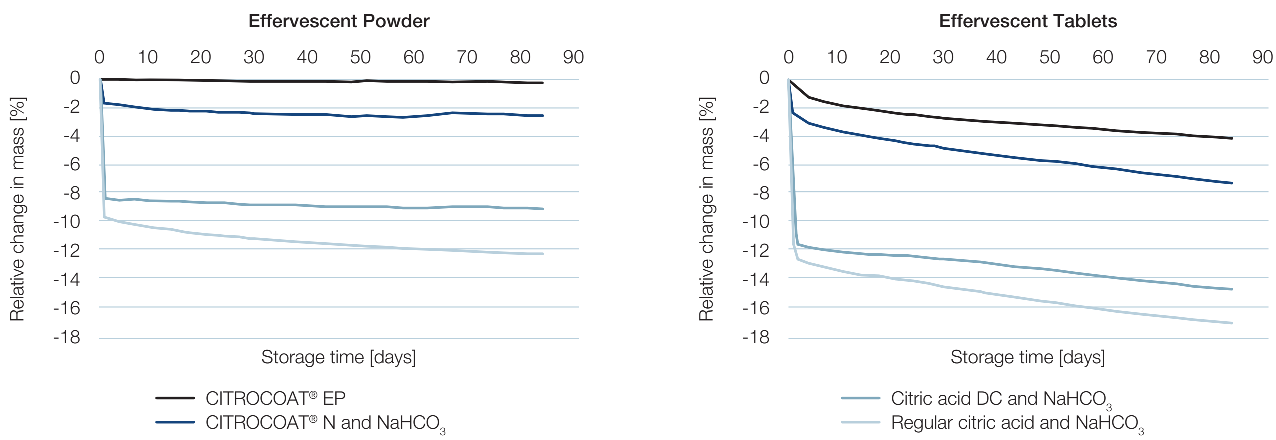

Figure 5: Comparison of relative changes in mass of effervescent powder mixtures and tablets when stored open for 88 days under harsh conditions (30°C, 60% relative humidity); n>3

Reactivity of effervescent powders after storage

The effervescence of the reaction between citric acid and sodium bicarbonate was evaluated by measuring the volume of CO_2 evolved. A comparison of the individual acids in 1:1 mixtures with sodium bicarbonate showed instant reactivity, without any delay caused by the coatings. All of the tested acids have similar kinetics and evolved similar volumes of CO_2.

The reduction in CO_2 formation due to premature reaction during storage was also evaluated (figure 6). The volume of CO_2 produced by the mixture of regular citric acid with sodium bicarbonate fell by almost half (47%) after 88 days of open storage under harsh conditions (30°C, 60% relative humidity). In contrast, the functional acids were more stable in the effervescent mixture – citric acid DC produced 28% less CO_2, CITROCOAT® N produced 22% less CO_2 and CITROCOAT® EP produced only 9% less CO_2 after storage. This means that CITROCOAT® EP remains the most reactive of the functional acids after a long open storage period under harsh conditions, followed by CITROCOAT® N and citric acid DC.

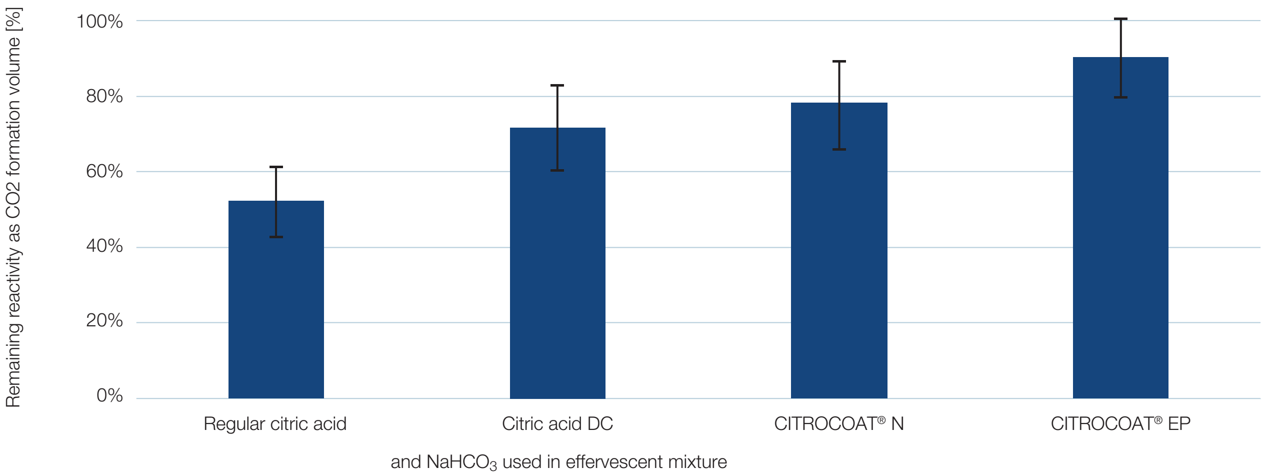

Figure 6: Remaining reactivity of 1:1 powder mixtures of acids and sodium bicarbonate, as assessed by relative quantities of CO_2 formed, after being stored in the open for 88 days under harsh conditions (30°C, 60% relative humidity); n>3

Similar observations were made with all methods used for analysing stability during storage. The results showed that greater losses of mass during open storage under harsh conditions are associated with greater losses of reactivity and, therefore, greater losses in the performance of effervescent systems.

Effervescent systems in beverage tablets

There are several different effervescent formulations on the market in pharmaceutical, food and non-food applications. Innovative formats such as beverage tablets are becoming very popular in the food industry in particular, as they meet the need for products in a sustainable format. Removing the water from a beverage formulation significantly reduces the product's volume and weight, potentially meaning less packaging waste and reduced emissions associated with shipping.

Ensuring good storage stability and rapid dissolution with effervescent formulations is challenging, especially if hygroscopic components are included. In particular, this can be observed in beverage tablets with natural extracts and fruit powders, as these are very moisture-sensitive and tend to agglutinate. This, in turn, can affect tablet hardness, dissolution time and storage stability.

Tablet properties such as storage stability and dissolution time are influenced by factors such as particle distribution and compression force. Therefore, it is important that all added ingredients are powders with similar-sized particles to prevent segregation during production. In short, a balanced formulation is needed, consisting of an effervescent system at a sufficient concentration that dissolves quickly and other valuable ingredients.

The following recipe was developed as an example beverage tablet formulation. As typical effervescent systems use citric acid and sodium bicarbonate, the recipe includes CITROCOAT® EP as a ready-to-use effervescent compound and CITROCOAT® N for pH control.

Table 1: Recipe for effervescent beverage tablets, with ingredients and their suppliers

Ingredients	Supplier	Concentration [%]
CITROCOAT® EP	**Jungbunzlauer**	58.9
CITROCOAT® N	**Jungbunzlauer**	14.7
Natural flavour grapefruit	Takasago	13.5
Rosemary extract powder	Martin Bauer	6.38
Thyme extract powder	Martin Bauer	3.93
Rebaudioside A		1.28
Vitamin C		1.18
Vitamin B6	BASF	0.021
Vitamin B12 (0.1%)	BASF	0.049
Total		**100**

All ingredients were mixed well, and a single-punch tablet press was used to manufacture the tablets. All tablets were comparable in weight (2.0 ± 0.1 g) and tensile strength (0.24 ± 0.02 kPa). Tablets with CITROCOAT® EP required 23% less compression force to generate the same tensile strength as tablets with regular citric acid.

Additionally, tablets were dissolved in water at room temperature, without stirring, and their dissolution times were measured. Tablets containing CITROCOAT® EP dissolved 24% faster than tablets using regular citric acid.

Storage stability – and the demands this places on packaging – are important considerations for consumers. Stability was therefore tested by storing these Jungbunzlauer tablets open in a climate chamber at 30°C and 60% relative humidity together with popular beverage tablets available on the market.

After just one day of storage, obvious changes were visible in the market samples (figure 7, image B): the tablets had almost completely dissolved and had lost their structure. Bubbles were visible, indicating the release of carbon dioxide and the absorption of moisture.

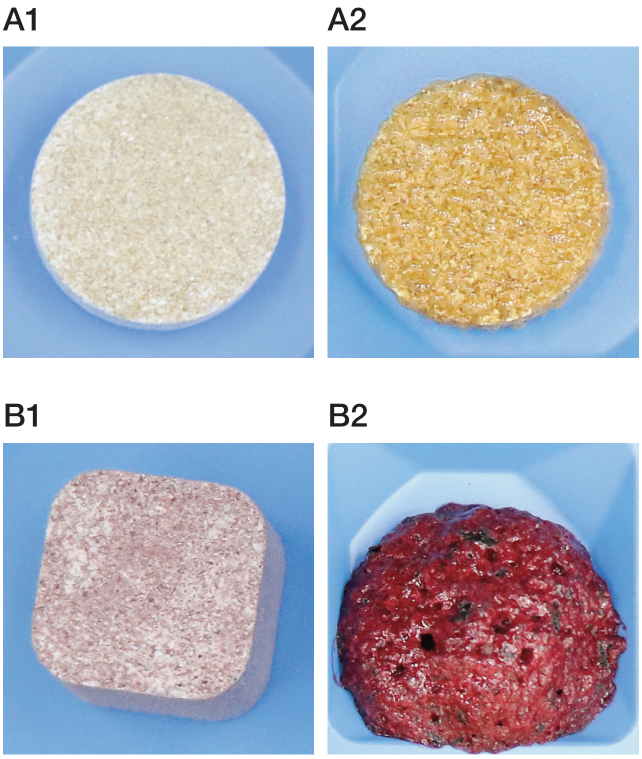

Figure 7: Beverage tablets (A: recipe with CITROCOAT® EP; B: market sample) before (1) and after (2) being stored at 30°C and 60% relative humidity for one day

The surface of the tablets with CITROCOAT® EP had darkened somewhat over the same period (figure 7, image A), indicating some moisture absorption. However, these tablets retained their shape and the absence of bubbles showed that no effervescent reaction had occurred.

Consequently, beverage tablets made with CITROCOAT® EP can be successfully stored with less packaging or more sustainable packaging, as they are more stable under harsh environmental conditions and have a longer shelf life than tablets using regular citric acid.

The versatility of CITROCOAT® EP and its advantages over regular citric acid can also be seen in novel solid formats in non-food applications, such as multipurpose cleaning tablets.

Conclusion

Jungbunzlauer's range of functional acids provides a toolbox for all kinds of applications where the stability of effervescent formulations needs to be improved or where directly compressible solutions are desired.

All functional acids tested proved to be more stable during storage than regular citric acid, thus maintaining the reactivity of the effervescent system during prolonged storage. For powder and tablet applications, where the hygroscopic nature of regular citric acid causes problems and premature reactions can occur, CITROCOAT® N and CITROCOAT® EP are the products of choice. Furthermore, dissolution was faster than with regular citric acid.

CITROCOAT® N improves the stability of powder and tablet applications where regular citric acid would cause greater moisture uptake and premature reaction. As a ready-to-use effervescent compound, CITROCOAT® EP additionally offers the advantage of a homogenous mixture and a lower segregation risk while processing, resulting in excellent reactivity.

Tableting is a complex process that involves many different factors and poses a variety of challenges for manufacturers. Citric acid DC results in significantly higher tablet hardness. CITROCOAT® EP offers similar benefits, as the binder helps to improve the compressibility of the compound.

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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 investments, 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 the protection of people and their environment.

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