facts

Safe and effective green descaling with lactic and citric acids

Jungbunzlauer

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Introduction

When it comes to purchasing cleaners and descaling agents, consumers are now just as concerned with the environmental and safety aspects as they are with the performance and price of the products. ECOCERT approved or green detergents can be one way of convincing consumers as long as the performance of the product is equal to that of classical detergents.

In addition, the industry has to deal with new regulatory requirements in terms of product labelling. These new labelling and classification requirements may change consumers buying behaviours as they now also affect home care products. Label-friendly descaling solutions containing organic acids like lactic and citric acids are already widely used in household cleaning formulations. They are well performing and eco-friendly at the same time. Thus their importance in such consumer oriented applications may further increase.

Therefore this paper provides an overview of the descaling performance of solutions of organic acids such as lactic and citric acids compared to other acids such as hydrochloric acid and sulfonic acid derivatives as well as to two current consumer products in a modified IKW test.

Green cleaning formulations – a challenge?

A clean and healthy environment is the key for human well-being and the ecological sustainability of our planet. Consumers are very aware of the major issues we are facing concerning the pollution of soil, water and air. The demand for ecologically friendly household cleaners will therefore continue to represent a strong growth market.

Standard descaling household cleaners normally contain synthetic ingredients like methanesulfonic or sulfamic acids. These products have very strong descaling properties and are therefore quite efficient. Alternatively, organic acids derived by fermentation are one possible solution as functional ingredients within a descaling cleaner formulation. At first glance, organic acids appear to be less efficient. However, this study has demonstrated that their performance is sufficient enough to meet the requirements of a standard household cleaner.

Jungbunzlauer is offering lactic and citric acid for the use as descaling agents in household cleaning formulations. These acids are produced by fermentation based on natural and renewable resources. In addition, these two Jungbunzlauer acids are ECOCERT approved as raw materials of 100% natural origin for the use in detergents.

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New classification and labelling requirements (CLP)

The Regulation (EC) No 1272/2008 on classification, labelling and packaging (CLP) will be newly effective for mixtures from 1 June 2015 onwards. This labelling change will also affect consumer household cleaning products.

According to this regulation all chemical mixtures have to be relabelled with new hazardous pictograms which are in line with the globally harmonised system of classification and labelling of chemicals (GHS). Similarly, stricter classifications in terms of hazard will also apply to mixtures and to certain chemicals – which could lead to more demanding relabelling of existing cleaning formulations.

The new symbols and classifications on product labelling may also raise consumer concerns affecting their buying decisions. According to a 2015 Mintel GNPD report, 57 – 64% of French, Italian and Spanish users of hard surface cleaners are worried about the ingredients in such products and the impact they may have on their health. The same report indicates that 23% of the consumers in UK are trying to use surface cleaners with fewer chemicals.[1]

A reformulation of cleaning products using less harmful ingredients could therefore be the consequence of these new legal requirements and resulting consumer behaviours. Lactic and citric acid are much more label friendly in a certain range of use level compared to harsh inorganic acids. They are beneficial at pH levels above 2 in particular, which is the border line for a corrosive labelling of a cleaning formulation.[2] Table 1 shows the labelling requirements for lactic and citric acid according to Regulation (EC) No1272/2008.

Table 1: Use level depending labelling requirements for lactic and citric acid according to Regulation (EC) No 1272/2008

	Acid	Acid concentration	Label
pH < 2	Any	Any	
pH > 2	Lactic Acid	≥ 3%	
		1% ≤ c < 3%	
		< 1%	No label
	Citric Acid	≥ 10%	
		< 10%	No label

In general, the first labelling criterion for all acids and mixtures is the pH. As long as the pH is below 2 the product has to be labelled as corrosive – no matter which type of acid and at which concentration it is used. In addition to this, there are also specific requirements for the single acids which can differ a lot. There are three concentration depending cases for lactic acid. At pH > 2 and concentration ≥ 3%, the lactic acid containing product has to be labelled as corrosive. At a concentration of 1% ≤ c < 3%, the product still needs an irritant marking and at concentrations < 1%, no marking is necessary. There are only two cases for citric acid. All citric acid containing products with ≥ 10% acid content have to be labelled as irritants. Below this concentration there is no labelling required.

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The classification and labelling requirements are similar in some cases for inorganic or sulphur based acids (table 2). However, due to their low pKa value, low concentrations of these acids already lead to pH values below 2.

Table 2: CLP labelling requirements for inorganic and sulphur based acids depending on their concentration

Acid	Categorisation	Labelling
Hydrochloric acid	c ≥ 1% corrosive	
Phosphoric acid	c ≥ 25% corrosive 10% ≤ c < 25% irritant	
Methanesulphonic acid	c ≥ 5% corrosive 1% ≤ c < 5% irritant	
Sulfamic acid	c ≥ 1% irritant	

At pH levels above 2, strong acids like methanesulfonic acid completely lose their descaling properties while the weaker lactic and citric acids still show an appropriate action. This could be beneficial for their use in surface applications like shower and bath or kitchen descaling products where the consumer might come into direct skin contact with the product.

The combination of good descaling properties and relative mildness as well as their less offensive odour, means that lactic and citric acid are already widely used in household cleaning formulations. The fact that they also find a wide application in food makes them even more suitable for green cleaner formulations.

Descaling performance of lactic and citric acid

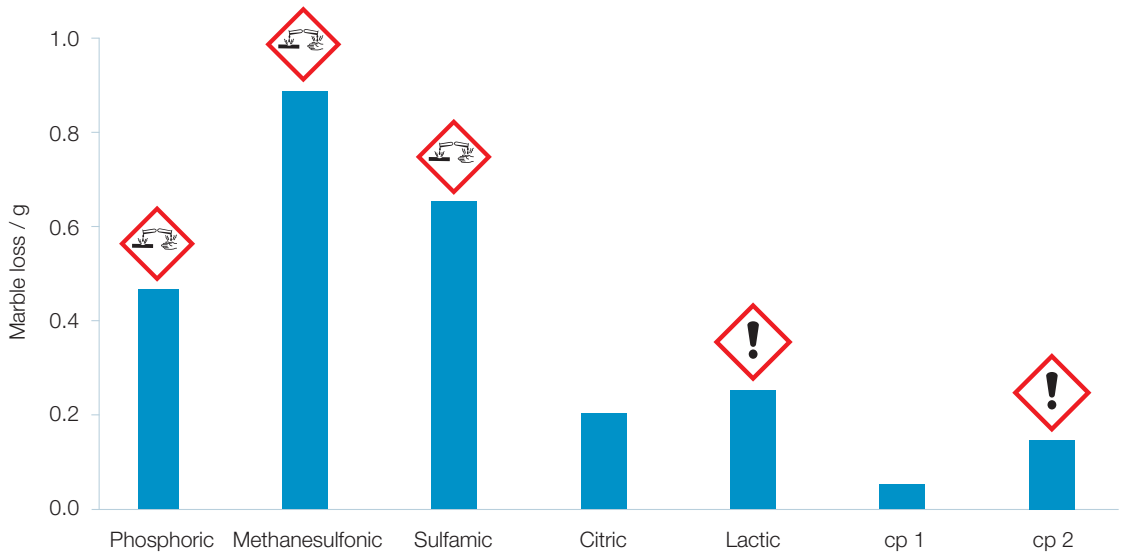
The selection of descaling agents among the numerous acids is usually done by the pKa. Solutions of strong mineral acids such as hydrochloric acid have therefore often been used. Modern descaling detergents also contain organic acids such as citric acid or acetic acid as well as sulphur based acids as methanesulfonic or sulfamic acid.

To determine the strength of a descaling solution, the weight loss of carrara marble slabs was an analysed in a modified IKW test.[3] Smaller tiles of 50 x 50 x 10 mm were used. Prior to cleaning, the slabs were degreased with ethanol and thoroughly cleaned with water. The tiles were dried at 70°C until constant weight. After cooling down, the weight was determined on an analytical balance.

Each marble tile was used only once. The slab was completely submersed in a beaker in the cleaning solution (125 mL) at the given temperature for 10 minutes. After being thoroughly cleaned with water, the tile was washed with ethanol and dried at 70°C to constant weight. The difference in weight was identified by the same analytical balance. The determination of the descaling power of each solution is carried out.

The loss in weight for different acids and two market benchmarks is shown in figure 1. The good performance of corrosive labelled solutions is clearly visible.

Figure 1: Performance of 2% solutions (w/w of active substance) of different acids and undiluted consumer products (cp1 is an acidic bathroom cleaner. cp2 is a dedicated scale removing agent) at room temperature. The corresponding labels due to the new GHS classification are shown.



Based on pure performance criteria, the effect of a hydrochloric acid solution (2%, marble loss: 2.9 g, not shown) is by far the best of all tested acids, yet it has to be labelled as corrosive. Methanesulfonic acid (0.9 g) and sulfamic acid (0.7 g) follow in the midfield.

However, with regard to consumer safety and less aggressive cleaners, the less strict labelled organic acids still maintain a good and well acceptable level of performance.

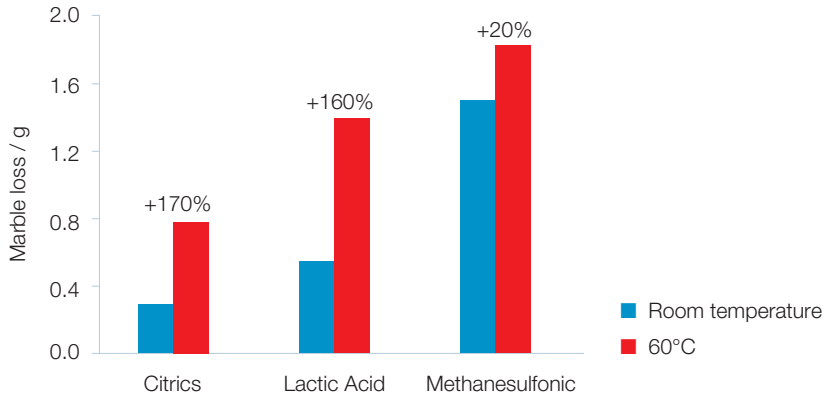
2% Lactic acid (0.3 g) and 2% citric acid (0.2 g) dissolve more marble than the undiluted consumerproduct (cp 2), which is a well-known descaler brand labelled as an irritant.

Scale problems in regions with hard water occur particularly in hot water applications such as coffee machines and water kettles. Increasing the temperature has a major effect on the scale removal strength of organic acids as citric and lactic acids.

The performance at 60°C is more than twice the activity of room temperature for a 3% solution. Interestingly, the strength of methanesulfonic acid is also improved, yet in a far smaller scale around 20% for 3% solutions.

In figure 2, the performance difference between room temperature and 60°C for 3% solutions of methanesulfonic, lactic and citric acids is shown.

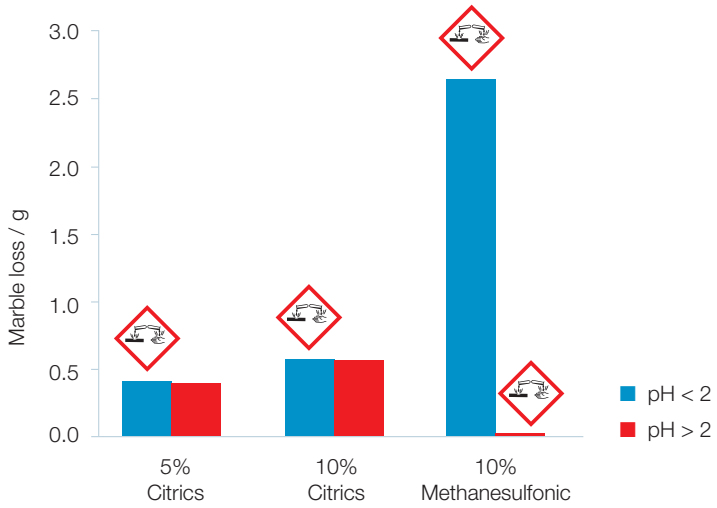
Figure 2: The performance of 3% solutions of citric, lactic and methanesulfonic acid at room temperature and 60°C. The increase of the temperature results in only 20% more descaling power for methanesulfonic acid. On the other hand, the performance of lactic acid is increased 1.6 fold.



The difference in performance between methanesulfonic and lactic acid is significantly reduced at higher temperatures. Taking the labelling aspect into focus, lactic acid has an advantage since its solutions that contain active matter below 3% only have to be signed with the irritant logo according to the new CLP regulation.

The new CLP regulation also stipulates that existing cleaner formulations have to be relabelled due to their low pH. As of June 2015, every solution below a pH of 2 has to be labelled as corrosive. This has a huge impact on performance. If the pH is adjusted to a value slightly above 2, some strong acids lose their performance. In figure 3, the maintained descaling power of citric acid solutions in comparison to methanesulfonic acid at elevated pH is displayed. A higher pH is the key factor for consumer safety.[4]

Figure 3: Solutions of citric acid (5% and 10%) and methanesulfonic acid (5%) without and with pH correction (NaOH) to a value of 2.04. The corresponding GHS labels are given above the bars.



Conclusion

The trend towards more green cleaners means that products containing sustainable ingredients will continue to grow in popularity. Jungbunzlauer lactic and citric acid have clearly demonstrated their good descaling properties. Particularly in the case of higher pH, there is a clear advantage compared to other descaling agents such as methanesulfonic acid. In regard to the new CLP classification and labelling requirements, these advantages could become even more important as standard household products are deeply affected. Consumer concerns regarding health consequences may also be raised by the new markings and they may therefore switch to less critical products.

Depending on the targeted performance, formulators of household cleaners have the choice on which acid to use at which use level. For the best descaling performance to be achieved, it is recommended that lactic acid be used at concentrations higher than 5%. If a less critical product labelling is required (e.g. irritant) then a lactic acid concentration slightly below 3% would provide a good descaling performance. Citric acid is recommended in formulations which should have no labelling at all. In these cases, up to 10% of citric acid can be used when the formulation is buffered to a pH of slightly above 2 as the tests have shown that there is almost no loss in descaling performance compared to the un-buffered acid.

It has also been shown that there is a descaling performance increase of more than 150% at higher temperatures for both lactic and citric acids. This allows a very efficient use of these acids in applications like coffee machine or kettle descaling solutions. Lactic and citric acid are also less corrosive to different materials which enable a sufficient and broad use in various applications.

The good biodegradability as well as the fermentation based manufacturing process of lactic and citric acids make them very suitable for the use in green cleaning formulations. Finally, this is also supported by the ECOCERT approval of both Jungbunzlauer substances as raw materials of 100% natural origin for the use in detergents.

References

[1] http://www.gnpd.com/sinatra/gnpd/editorial&search_id=BA9tOBoRPn/[Category Insight: Hard Surface Care; February 2015]

[2] Regulation (EC) No 1272/2008 on classification, labelling and packaging of substances and mixtures

[3] IKW, “Recommendations for the Quality Assessment of Bathroom Cleaners”, SOFW 2003, 129, 42–49

[4] A. Johnson, G. Nole, M. Rozen, J. DiNardo, “Skin tolerance of AHAs: a comparison of lactic and glycolic acids and the role of pH”, Cosmet. Derm. 1997, 10, 38–45

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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. Due to continuous investments, state-of-the-art manufacturing processes and comprehensive quality management, we are able to assure outstanding product quality. Our mission “From nature to ingredients®” commits us to the protection of people and their environment.

Jungbunzlauer lactic and citric acids are produced by fermentation and therefore are a good alternative to synthetic chemicals used in cleaning applications. They are providing efficiency in the removal of all kind of scale deposits. Jungbunzlauer lactic acid is offered as aqueous solution of 80% and 88% concentration. Jungbunzlauer citric acid is offered mainly in crystalline form but is also available as a 50% aqueous solution.

The Authors

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

Frithjof Raab – Technical Service Manager Lactics, Jungbunzlauer International AG
frithjof.raab@jungbunzlauer.com

Discover more on
www.jungbunzlauer.com

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

www.jungbunzlauer.com

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