

Recommendations for the quality assessment of acidic toilet cleaners

Quality recommendations issued by Industrieverband Körperpflege- und Waschmittel e.V. (IKW – The German Cosmetics, Toiletries, Perfumes and Detergents Association), Department of Cleaning and Maintenance Products, Frankfurt am Main (version 1999)

Foreword to these recommendations

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Objective

The companies belonging to the IKW publish their expert knowledge of the products they manufacture. This is done in the form of quality recommendations. The IKW requested the expert committee »Cleaning and Maintenance Products« (Fachausschuss Putz und Pflegemittel – FP) to draft the recommendations given in this paper. The FP committee is composed of experts from competing companies. This ensures the neutrality of the committee. The »Recommendations for the quality assessment of acidic toilet cleaners« are to enable a qualified assessment of such products by the companies themselves, consumers and test institutes. Quality standards for these products need to be laid down if the expectations of consumers and manufacturers are to be fulfilled.

Environment

This clearly defined objective is directly linked with efforts of manufacturers of cleaning and maintenance products to develop optimal quality standards for their goods.

The manufacturers of cleaning and maintenance products see the realisation of this aim as an integral part of the international initiative »Responsible Care«. Basically this initiative stands for the commitment to continuously improve health and environmental protection which obviously includes the pursuit of a lasting and future oriented – sustainable – development. Furthermore natural resources are to be used in a sparing and efficient manner so that the needs of the present generation are taken into account without impairing significantly the development options of future generations.

Against this backdrop the quality recommendations issued in this paper serve to encourage company staff to act responsibly towards man and the environment in the development and manufacture of products whilst meeting the expectations of consumers in terms of efficacy, safety healthy and environmentally compatible products.

Assessment of test results

These quality standards determine what qualities are relevant to a given product and to what extent these qualities must be present. It should be noted that each finished product has a certain spectrum of quality character-

istics largely oriented to consumer expectations, and for individual products some properties will be emphasised whilst others properties are less important. Moreover the desired combination of product characteristics is subject to constant change, depending on the latest technical possibilities and new consumer habits. Quality recommendations must not impair such developments. Therefore for each product only an overall result is valid to determine whether the product meets the quality requirements or not. Emphasis on isolated test criteria is inadmissible and may be misleading.

Legal provisions and voluntary agreements

Regarding composition, packaging and labelling inter alia the valid provisions of following statutory requirements must be observed wherever applicable:

- The German foodstuffs and commodities act (Lebensmittel- und Bedarfsgegenständegesetz – LMBG)
- The German chemicals act (Chemikaliengesetz – ChemG)
- The German dangerous substances ordinance (Gefahrstoffverordnung – GeFStoffV)
- The German detergents and cleaning products act (Wasch- und Reinigungsmittelgesetz – WRMG)
- The German surfactant ordinance (Tensidverordnung – TensV)
- The German ordinance on pre-packaged products (Fertigpackungsverordnung – FPV)
- The German ordinance on the trans-

port of dangerous goods by road (Gefahrgutverordnung Straße – GGVS)

- The German ordinance on the transport of dangerous goods by rail (Gefahrgutverordnung Eisenbahn – GGVE)
- The EU recommendation of 13 September 1989 regarding the labelling of detergents and cleaning products as well as voluntary agreements
- Ban of APEO of 14 January 1986
- Procedural rules for communicating particulars pursuant to §9 of the German detergents and cleaning products act (WRMG) of 5 December 1988

Further development

The expert committee for »Cleaning and Maintenance Products« is aware that the further development of the products themselves and changes in raw materials and consumer habits may necessitate a further development of the recommendations.

The recommendations submitted here replace the 1993/94 version. The new recommendations take into account the changed market situation.

Definition

Acidic toilet cleaners are liquids, powder products or granules for the cleaning of toilet bowls, urinals and bidets. To clean these objects (from soiling/dirt, deposits of limescale and rust and the like), they contain acids or acid salts, surfactants and possibly also disinfectants and perfumes.

WC cleaners are marketed in plastic bottles or plastic pouches.

Furthermore the quality of products in other forms intended for special applications in toilets (e.g. tablets) can be assessed on the basis of these recommendations. The assessment can be adapted accordingly.

SPECIALITIES

Product characterisation	Testing
1. Details on packaging	
1.1 Product designation, including brand name	
1.2 Manufacturer and/or distributor	Pursuant to statutory requirements
1.3 Labelling of dangers/warnings/ingredients	Pursuant to statutory requirements
1.4 Instructions for use (statements by manufacturer)	Check accuracy of statements, to the extent that they are not covered by subsequent testing, pursuant to statutory requirements
2. General physical/chemical properties	
2.1 Form	Organoleptic evaluation (fine-grained, coarse-grained, clear, turbid)
2.2 Colour	Organoleptic evaluation
2.3 Odour	Organoleptic evaluation
2.4 Reaction (pH value)	Acidity, to be determined in 1% aqueous solution with an electric pH meter. For liquid products: also with undiluted product
2.5 Stability	
2.5.1 Storage stability	No major changes in product properties after 1 year of storage in temperatures at which the product is usually exposed. Test: 14 days of alternating temperatures + 5 oC / + 30 oC, alternating every 12 hours
2.5.2 Heat stability	No major changes in product properties on cooling to 20°C following 3 months of storage at 40 oC.
3. Composition	
3.1 Acidity	5 g of toilet cleaner are dissolved in distilled water and filled up to 100 ml in a measuring flask. 25 ml of this solution are titrated with 1/2 n of sodium hydroxide solution using methyl orange as indicator. Acidity is expressed in mol NaOH/kg.
Calculation: % HCl = $\frac{\text{Consumption ml} \times \text{normal.NaOH} \times \text{mol mass} \times \text{content of measuring flask} \times 100\%}{\text{weighted-in quantity} \times \text{applied ml} \times 1000 \text{ (equivalent)}}$	
Molarity calculation: Mol NaOH/kg = $\frac{\% \text{ HCl} \times 10}{\text{Mol mass (NaOH)}}$	
3.2 Active oxygen content (AO)	10 g of toilet cleaner are weighed into a (wide-mouth) Erlenmeyer flask, precise to the second decimal point. Add ca. 2 g of potassium iodide, analytically pure (Merck product no. 5043), 25 ml of distilled water and 10 ml of sulphuric acid, analytically pure (for foam inhibition use – if necessary – some drops of isopropanol, analytically pure) and titrate immediately with a solution of Na ₂ S ₂ O ₃ (0.1 n) solution to pale yellow. Add freshly produced starch solution and titrate to colourless. The result is expressed in % of active oxygen.

Product characterisation		Testing
Calculation: % AO =		$\frac{\text{Consumption ml x normal thiosulphate x mol mass of O}_2 \times 100\%}{\text{weighted-in quantity x 1000 (equivalent)}}$
3.3	Water-insoluble shares	Determination by dissolving 10 g of toilet cleaner in 1 l of distilled water. Filter off after the end of the reaction, and dry the residue at 150°C to constant weight.
4.	Foam volume	
4.1	Independent foam formation - solid products	90 ml of water (temperature 20°C) are poured over 10 g of toilet cleaner in a 250, 500 or 1000 ml mixing cylinder (depending on the expected foam volume) pursuant to German standard DIN 12686; the volume of foam formed when the foam maximum is reached – is registered immediately, after 5 minutes and after 10 minutes.
4.2	Foam volume - solid products	One hour after the test in 4.1 the liquid remaining in the cylinder is shaken 10 times; then the foam volume is registered immediately, after 5 minutes and after 10 minutes.
4.3	Foam volume - liquid products	10 g of toilet cleaner are dissolved in a 1000 ml mixing cylinder pursuant to DIN 12686 in 90 ml of water (temperature 20°C) and shaken 10 times; then the foam volume is registered immediately, after 5 minutes and after 10 minutes.
5.	In-use test values	
5.1	Covering of toilet surface	The product should cover the surface evenly.
5.2	Solubilizing power regarding limescale (calcium carbonate)	
5.2.1	Liquid products	<p>The test object is a slab of white Carrarra marble sized 75x150x5mm. Slabs of this quality can be obtained e.g. from A. Wessel GmbH & Co. Marmorwerk KG, Postfach 15 03 26, Karlsruher Str. 32, D-40229 Düsseldorf (quoting »IPP Test, Type Bianco CD«).</p> <p>Prior to testing the marble slabs are degreased with ethanol. Any residues are removed under running water with a plastic brush. Then the slab is dried at 105°C for at least 1 hour to constant weight. After cooling down, the slab is weighed out on an analytical balance (precision +/- 1 mg).</p> <p><i>Note:</i></p> <p>It must be ensured that tests take place in a temperature range from 20 to 23°C, i.e. ambient temperature and the temperature of products and marble supports must be in this range.</p> <p>At least 250 ml of the cleaner is transferred to a cuvette. Then the test slab is totally immersed for 10 seconds in the cleaner solution.</p> <p>Subsequently the test slab is immediately removed and placed vertically in a stand intended for this purpose. Here it is essential to make sure that the adhering product can run off and no pool forms at the base of the marble slab. Exposure time in the vertical position is 10 minutes.</p>

**Slabs of this quality can be obtained e.g. from
Müller & Wolf Naturstein
Peter-Busch-Straße 24
41363 Jüchen-Hochneukirch
Tel.: +49(0)2164 2378
<https://mueller-wolf.gmbh/>
(quoting "IPP Test, Type Bianco CD)**

Product characterisation

Testing

The thus treated marble slab is then rinsed under running water, and adhering residues are brushed off with a plastic brush, followed again by drying to 105°C to constant weight and weighing.

The quantity of dissolved calcium carbonate is determined by the difference in weight. To determine the solubilizing power of a product with regard to lime, 5 tests – each with new marble slabs – are conducted. The same cleaner solution can be used in these tests. However it must be ensured that before starting each test the cleaning solution which can be highly viscous, is thoroughly mixed. More than 5 tests with the same product are not permitted.

Assessment:

The quantity of dissolved calcium carbonate is related to a standard toilet cleaner of the following composition:

Standard toilet cleaner:

	% by weight
Citric acid monohydrate	active 4.00
Hostapur SAS 60 (Hoechst)	active 1.00
Rheozan (Rhodia)	approx. 0.23
Tap water	ad 100.00

Preparation:

Have tap water ready, slowly add Rheozan and stir with the dissolver for 30 minutes until completely dissolved. Then add citric acid and alkane sulphonate. Do not use for at least 12 hours after preparation.

The following physico-chemical parameters must be complied with:

Viscosity
550 mPas +/-50
(Brookfield 20°C, spindle, 2.20 RPM)

alternatively 450 mPas +/-30
(small sample adapter 20°C, spindle 31, 20 RPM)

Note:

Viscosity adjustment by adding Rheozan.

Assessment:

Calculation of the lime dissolution index (Kalklöseindex - KLI):

weight of lime dissolved by test product (in mg)*

weight of lime dissolved by standard toilet cleaner (in mg)

* (In German: Kalklösevermögen = KLV)

The lime dissolution index (KLI) should be at least 0.7. Values of more than 1.3 have been found unnecessary in practice.

5.2.2 Powder products

Tests are also conducted with white Carrara marble (supply source cp. 5.2.1). Pre-treatment of slabs identical with liquid products. 5 l of a 20 % solution of the powder product are prepared with tap water. Dissolution of the product: Dissolve over 10 minutes, stir during the process (room temperature).

Product characterisation	Testing
5.3 Compatibility of materials	<p><i>Note:</i> It must be ensured that tests take place in a temperature range from 20 to 23°C, i.e. ambient temperature and the temperature of products and marble supports must be in this range.</p>
5.3.1 Porcelain surfaces	<p>950 ml of the cleaner solution are transferred to a 1 l beaker (high form). Immersion time is 10 minutes. Then the test slab is removed, residues are brushed off under running water with a plastic brush and dried to constant weight. The quantity of dissolved calcium carbonate is determined by weighing the difference.</p>
	<p>To determine the solubilizing power of a product with regard to lime, 5 tests are conducted with 5 different marble slabs and fresh cleaner solution in each test.</p>
	<p><i>Assessment:</i> The quantity of dissolved calcium carbonate is related to the described standard toilet cleaner in a 20 % solution.</p>
	<p>Calculation of the lime dissolution index (Kalklöseindex - KLI):</p>
	<p>$\frac{\text{weight of lime dissolved by test product (in mg)*}}{\text{weight of lime dissolved by standard toilet cleaner 20\% (in mg)}}$</p>
	<p>*(In German: Kalklösevermögen = KLV)</p>
	<p>The lime dissolution index (KLI) should be at least 0.7. Values of more than 1.3 have been found unnecessary in practice.</p>
	<p>Tiles used in testing: Tiles for sanitary ceramics quality as made by the company Villeroy&Boch in »edelweiß-matt« (~ edelweiss white matted) and »alpinweiß-glänzend« (~ alpine white shiny). Circa 1 g of product is dotted on these tiles.</p>
	<p><i>Note:</i> It must be ensured that tests take place in a temperature range from 20 to 23°C, i.e. ambient temperature and the temperature of products and marble supports must be in this range.</p>
	<p>For liquid products, a concentrated solution of the toilet cleaner is used. Powder products are tested with a 10 % solution of the toilet cleaner.</p>
	<p>The applied products are washed off after 24 hours, and possibly occurred changes to the porcelain material are visually assessed.</p>
	<p><i>Grades:</i> 1 = no change 2 = middle value 3 = major change</p>

