

1 Toilets are mostly cleaned with acid-containing pre-
parations which enable even limestone deposits to be rapidly
removed. In addition to liquid preparations, solid, powder-
5 form preparations above all have been successfully used in
the home because they are safer and more convenient to handle.
In addition to a solid water-soluble acid, preparations such
as these generally contain a certain proportion of water-
soluble carbonates which release carbon dioxide when the pre-
10 paration comes into contact with water, thereby promoting
dissolution of the preparation and distribution of the active
ingredients. In addition, the preparations may contain
fillers, other active components and auxiliaries.

15 The disadvantage of these powder-form lavatory cleaners
is their tendency to cake in a moist atmosphere which exists
even when the preparations are stored in plastic bottles.
One cause is presumably that the closures normally used for
these containers can never be totally liquid-tight. This
can lead to serious deterioration of the sprinkling properties
to the point where the contents of the container completely
20 cake, above all when the preparations are stored for long
periods or are exported to countries where high atmospheric
humidity frequently prevails. Although the situation may
be remedied to a certain extent by addition of standard anti-
caking agents, such as finely divided silicas, other disadvan-
25 tages, such as serious dust emission and dulling of the

1 ceramic surfaces treated through adsorption, have to be
accepted.

It has now been found that caking of the preparations
may be largely or completely avoided without other disad-
5 vantages arising by addition of cellulose powder to the
preparations.

Accordingly, the present invention relates to solid,
powder-form acidic sprinkling preparations for cleaning toilets which,
in addition to solid water-soluble acids, water-soluble
10 carbonates and, optionally, other ingredients, also contain
cellulose powder. In addition, the preparations preferably
contain inorganic salts, surfactants and perfume.

The additional use of cellulose powder in the acidic
cleaning preparations improves the flow of the powders and
increases their stability in storage, even under conditions
15 of extreme humidity, to a very considerable extent. This
is the case even when the powders are repeatedly exposed to
an alternating sequence of humid and dry atmospheric
conditions. The presence of cellulose powder does not
20 impair the cleaning power of the preparations and, although
cellulose powder is insoluble in water, the shine of the
ceramic surfaces is not affected. It is also remarkable
that the presence of cellulose powder increases the capacity
of the preparations to take up perfume and that the perfume
25 oils can be incorporated more permanently than in preparations
which do not contain cellulose powder. In addition, neither
the production nor the use of the preparations is adversely
affected by the presence of cellulose powder.

Thus, the production process may be carried out in
30 simple mixing units, the mostly coarse-grained constituents
either being mixed all at once or premixed initially being
prepared from only some of the components and the remaining
components being added in further steps. It is also possible,
particularly where very finely divided starting materials are
35 used, to agglomerate all or part of the components into

1 relatively coarse grains by build-up granulation in order
to achieve, for example, freedom from dust or higher stability
in storage of individual constituents.

5 The preparations may be applied in the usual way by
scattering or sprinkling of the powders. Where the
automatic cleaning effect obtained through the effervescence
of the powder is not used on its own, but in conjunction
with additional mechanics, the cellulose powder is capable
10 of making an advantageous contribution to the cleaning effect
as a mild abrasive component.

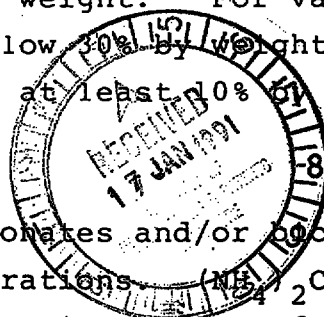
The individual ingredients, which are described in the
following, are generally used in anhydrous form:

a) Acids

15 The acids present in the preparations serve primarily
to dissolve limestone and deposits of rust on the ceramic
surfaces. Suitable acids are solid, water-soluble acids
having a pK_s -value below 5, such as for example sodium bi-
sulfate, amidosulfonic acid, tartaric acid, adipic acid,
glutaric acid, succinic acid and citric acid. The expression
20 "water-soluble" as used in the present context is intended to
signify a solubility of more than 1 g per 100 g water at 15°C.
It is preferred to use acids having a pK_s -value below 4,
more especially sodium bisulfate, amidosulfonic acid and
citric acid. The proportion of these acids in the prepar-
25 ations is between about 3 and about 90% by weight and pre-
ferably between 5 and 80% by weight. For various reasons,
the proportion of acid is below 30% by weight where organic
acids are used and generally at least 10% by weight where
inorganic acids are used.

30 b) Carbonates

Ammonium or alkali carbonates and/or carbonates are
preferably used in the preparations. $(NH_4)_2CO_3$ and, above
all, Na_2CO_3 and $NaHCO_3$ are particularly preferred. The
quantity of carbonates in the preparations is always selected
35 so that, after complete evolution of the CO_2 , enough acid



1 is still available for the removal of deposits of lime and
rust. Accordingly, the preparations preferably contain
only so much carbonate that no more than 80% and more
especially no more than 50% by weight of the acid equivalents
5 present are used up in the evolution of the CO_2 . The
proportion of carbonates is normally between about 1 and
about 25% by weight and preferably between about 3 and about
20% by weight. Where organic acids are used, they are
generally present in quantities of no more than 10% by
10 weight, whereas where inorganic acids are used they are
mostly present in the preparations in quantities of at
least 5% by weight.

c) Cellulose powder

The starting material for the cellulose powders suitable
15 for use in accordance with the invention are celluloses
freed from lignin and other impurities, more especially
bleached celluloses, from which the powders are obtained by
mechanical size-reduction. The nature of the chemical pre-
treatment of the cellulose is unimportant as long as it is
20 ensured that the purified cellulose still has those proper-
ties of the native cellulose which are of importance in
the context of the invention, i.e. the celluloses should
still have the fibrous structure of the native material
which is made up of partly crystalline fibrils and they
25 should be insoluble in water and should not swell to the
point of gelatinization. In particular, chemically non-
modified celluloses are used as starting material.

The particle size of the cellulose powder is primarily
determined by the requirements that no noticeable residues
30 should remain in the lavatory bowl after use of the prepar-
ations. Accordingly, the size of the particles should
generally not exceed 1000 μm and preferably should not
exceed 600 μm . Since the preparations should not emit any
troublesome dust on application, the lower limit to the
35 fiber length is 1 μm and preferably 5 μm . Particularly

1 preferred cellulose powders are those of which more than 90%
of the particles are between 5 and 300 μm in size and more
especially between 10 and 200 μm in size. The emission of dust
may also be favorably influenced by using finely divided
5 cellulose powder in agglomerated form, i.e. as granulate.

The proportion of cellulose powder in the preparations
may be between about 2% by weight and about 85% by weight
and is preferably between 5 and 30% by weight and more pre-
ferably between 5 and 15% by weight.

10 d) Builders (salts)

In addition to the compulsory constituents a) to c),
the preparations may contain inorganic salts in quantities
of up to 90% by weight as builders or fillers. Suitable
builders or fillers are the alkali and ammonium salts of
15 mineral acids, providing they do not impair the acidic
reaction of the preparations, more especially sodium sulfate
and sodium chloride. The proportion of salts in the prepar-
ations is preferably at least 5% by weight and up to 75%
by weight, the proportion of salts being in particular above
20 60% by weight when organic acids are present in the prepar-
ations.

e) Surfactants

To support their cleaning effect, the preparations may
contain anionic or nonionic surfactants in quantities of
25 up to 5% by weight, preferably in quantities of from 0.05 to
5% by weight and more preferably in quantities of no more than
1% by weight.

The anionic surfactants used in the preparations according
to the invention are in particular those of the sulfate and
30 sulfonate type, for example alkyl sulfates (sulfuric acid semi-
esters of long-chain alcohols), ether sulfates (sulfuric acid
semi-esters of ethylene oxide adducts with long-chain
alcohols), alkylbenzene sulfonates, olefin sulfonates, alkane
sulfonates and α -sulfofatty acid esters. The anionic sur-
35 factants are predominantly used in the form of their sodium

1 salts. Particularly preferred anionic surfactants are
the alkylbenzene sulfonates, the olefin sulfonates and the
alkyl sulfates.

Particularly suitable nonionic surfactants are the
5 adducts of 10 to 100 and preferably 5 to 60 moles ethylene
oxide (EO) with 1 mole of an aliphatic or alkylaromatic
 C_{10} - C_{20} compound from the group comprising alcohols, alkyl
phenols, fatty acids and fatty acid amides. The adducts
of 20 to 50 moles EO with primary alcohols of natural or
10 synthetic origin and with secondary alcohols and with alkyl
phenols are particularly suitable. Among these, particular
preference is attributed to the adducts of 20 to 50 moles
EO with C_{12} - C_{18} fatty alcohols.

f) Perfume

15 The preparations according to the invention often contain
a small proportion of perfume. In selecting this constituent,
it is generally more important than with the other ingredients
to ensure that incompatibilities with other constituents,
particularly the acid, are avoided. However, the sensitivity
20 of the perfume to chemical attack is distinctly reduced by
the presence of the cellulose powder in the preparations
according to the invention. The perfume content is normally
no more than 1% by weight and preferably between 0.05 and 0.3%
by weight.

25 g) Other optional constituents

Other optional constituents include, above all,
antimicrobial agents, polishes, bleaches, dyes and dust
inhibitors. The content of these constituents is generally
no more than 60% by weight and preferably no more than 30%
30 by weight.

Antimicrobial agents, for example phenols, are intended
to impart a germ-inhibiting effect to the preparations in
addition to their cleaning effect. They are used in
quantities of up to 10% by weight and preferably in quantities
35 of from 0.5 to 5% by weight.

1 Polishes are added to enhance the cleaning effect.
Suitable polishing constituents are acid-stable types, such
as aluminium aluminas and glass powders in a fineness which
does not lead to surface scratching, even in the event of
5 frequent application. The polishes may be present in a
quantity of up to 50% by weight and preferably in a quantity
of from 5 to 15% by weight.

The addition of bleaches also enhances the cleaning
effect and, in addition, has a disinfecting effect. The
10 bleaches used are either active oxygen carriers, such as
perborate or persulfate, or active chlorine carriers, such
as sodium dichloroisocyanurate. The bleaches may be used
in quantities of up to 10% by weight and preferably in
quantities of from 0.5 to 5% by weight.

15 The dyes used are preferably water-soluble types with
no affinity for ceramic surfaces. Food-quality dyes are
primarily used taking ecological considerations into account.
The proportion of dyes in the preparations may be up to 1%
by weight and is preferably between 0.005 and 0.5% by weight.

20 Finally, dust inhibitors are used to bind fine dusts
which may be present in some of the individual constituents.
The dust inhibitors are preferably liquid, chemically substan-
tially inert substances, for example paraffin oils, silicone
oils, terpene or polyether alcohols. These substances are
25 preferably sprayed onto the premix of the other constituents,
quantities of up to 3% by weight and preferably from 0.05 to
0.5% by weight, based on the preparation as a whole, being
sufficient.

E X A M P L E S

30 The preparations described in the following in terms
of their composition were prepared as follows:

Cellulose, sodium chloride, sodium sulfate and the sur-
factant were introduced into and mixed in a tumble mixer or
35 Drais mixer, the perfume being sprayed in through a nozzle.

1 The other components were then added. The dust inhibitor
was sprayed in last. The preparations of Examples 1 to 3
were packed in 1 kg capacity plastic bottles fitted with a
sprinkler head while the preparations of Examples 4 and 5
5 were packed in containers fitted with a child-proof sprinkling/
pouring closure.

Unless otherwise indicated, the figures in the following
represent percentages by weight. In the case of the
cellulose powder, the upper limit to the fiber length is
10 indicated.

	1.	<u>Powder-form lavatory cleaner of high Na bisulfate content</u>	
		Sodium bisulfate, beads	64.632
		Sodium carbonate	5.000
		Sodium carbonate, granulated, coarse	10.000
15		Sodium chloride, granulated	10.000
		Triphenylmethane dye	0.003
		Olefin sulfonate C ₁₅₋₁₈ , Na salt	0.065
		Paraffin oil, Bp. 364-431°C	0.300
		Cellulose powder, granulated,	10.000
20		125 µm (Technocel 100)	
	2.	<u>Powder-form lavatory cleaner of low Na bisulfate content</u>	
		Sodium bisulfate, beads	10.000
		Sodium bicarbonate, granulated, coarse	5.000
		Sodium chloride, granulated	39.100
25		Cellulose powder, 20 µm	15.000
		Perfume	0.100
		Lauryl sulfate-Na	0.500
		Paraffin oil	0.300
	3.	<u>Powder-form lavatory cleaner containing amidosulfonic acid</u>	
30		Amidosulfonic acid	10.000
		Sodium bicarbonate, granulated	5.000
		Sodium chloride	34.000
		Sodium sulfate, anhydrous	40.000
		Tallow fatty alcohol + 50 EO	0.500
35		Cellulose powder, 500 µm (Diacel 500)	10.000

1	Perfume	0.200
	Paraffin oil	0.300
4.	<u>Powder-form lavatory cleaner containing citric acid</u>	
	Citric acid anhydrate, granules	9.000
5	Sodium bicarbonate, granulated, coarse	5.000
	Sodium sulfate, anhydrous	30.000
	Sodium chloride, granulated	50.384
	Lauryl sulfate-Na	0.500
	Perfume (spruce note)	0.100
10	Food-quality dyes: E 104	0.015
	E 131	0.001
	Cellulose powder, 20 μ m	5.000
5.	<u>Powder-form lavatory cleaner containing</u>	
	<u>citric acid and antimicrobial agent (Kathon)</u>	
15	Citric acid anhydrate, granules	20.000
	Sodium bicarbonate, granulated, coarse	7.000
	Sodium sulfate, anhydrous	30.000
	Sodium chloride, granulated	29.584
	Sodium alkylbenzene sulfonate	0.600
20	Perfume (acid-stable apple note)	0.300
	Kathon 886 MW	3.000
	Kathon 893	1.500
	Cellulose powder, granulate 125 μ m	8.000
	(Technocel 100)	
25	Dye E 104	0.015
	E 131	0.001

6. - 13. Flow testing after exposure to high humidity

The test was carried out with quantities of 100 g of the preparations listed in Table 1 which were placed in open powder bottles and stored in an atmosphere cell for 7 days at 40°C/90% relative humidity. The first assessment was made after cooling to room temperature, the second assessment after drying for 24 hours at 40°C. Flow was assessed in marks of 1 (flow unaffected) to 5 (powder

completely caked).

The extraordinary positive effect of the cellulose powder is clearly apparent from Table 1.

Table 1

Composition of the preparations	6	7+	8	9+	10	11+	12	13+
Sodium bisulfate, beads	60.000	60.000	10.000	10.000	-	-	-	-
Citric acid anhydrate, granules	-	-	-	-	9.000	9.000	-	-
Amidosulfonic acid	-	-	-	-	-	-	10.000	10.000
Sodium bicarbonate, granulated, coarse	20.000	20.000	5.000	5.000	5.000	5.000	5.000	5.000
Sodium chloride	19.690	14.590	54.084	44.084	54.184	49.184	54.084	39.084
Sodium sulfate, anhydrous	-	-	30.000	30.000	30.000	30.000	30.000	30.000
Cellulose granulate 100 μ m	-	5.000	-	10.000	-	-	-	15.000
Cellulose powder 20 μ m	-	-	-	-	-	6.000	-	-
Olefin sulfonate C ₁₅₋₁₈	0.050	0.050	-	-	-	-	-	-
Lauryl sulfate-Na	-	-	0.500	0.500	0.500	0.500	0.500	0.500
Acid-stable apple perfume	0.050	0.050	-	-	-	-	-	-
Acid-stable spruce perfume	-	-	0.100	0.100	0.100	0.100	0.100	0.100
Pyrogenic silica (Aerosil 200)	-	-	-	-	1.000	-	-	-
Paraffin oil	0.200	0.300	0.300	0.300	0.200	0.200	0.300	0.300
Quinoline Yellow 70 E 104	-	-	0.015	0.015	0.015	0.015	0.015	0.015
Patent Blue 80 E 131	-	-	0.001	0.001	0.001	0.001	0.001	0.001
Triphenylmethane dye	0.010	0.010	-	-	-	-	-	-
1st assessment (mark)								
after 7 days at 40°C/90% rel.H.	3	1	5	2	5	1	3	1
2nd assessment (mark)								
after drying for 24h/40°C	5	1	5	1	5	1	5	1

+ according to the invention

1 14. - 17.. Storability test, original pack

5 The preparations listed in Table 2 were mixed as described before Examples 1 to 5, placed in 1 kg portions in plastic containers fitted with a pouring and sprinkling closure and stored in an atmosphere cell at 30°C/80% relative humidity. The assessment was made after cooling to room temperature following a period of storage of 14 days.

10 As can be seen from Table 2, exposure to these atmospheric conditions seriously affects flow in the case of preparations containing no added cellulose powder and also in the case of preparations containing standard anticaking agents, such as precipitated silica or pyrogenic silica. Only product 17 according to the invention remained unaffected in its flow.

Table 2

Composition of preparation	14	15	16	17+
Citric acid anhydrate, granules	9.000	9.000	9.000	9.000
Sodium bicarbonate, granulated, coarse	5.000	5.000	5.000	5.000
Sodium sulfate, anhydrous	30.000	30.000	30.000	30.000
Sodium chloride	55.184	52.184	54.184	54.184
Lauryl sulfate-Na	0.500	0.500	0.500	0.500
Acid-stable spruce perfume	0.100	0.100	0.100	0.100
Quinoline Yellow 70 E 104	0.015	0.015	0.015	0.015
Patent Blue 80 E 131	0.001	0.001	0.001	0.001
Paraffin oil	0.200	0.200	0.200	0.200
Cellulose granulate 100 μ m	-	-	-	5.000
Precipitated silica (Sident 3) -	-	3.000	-	-
Pyrogenic silica (Aerosil 200) -	-	-	1.00	-

<u>Assessment (mark)</u>	Flow seriously affected by agglomeration (3)	Flow unaffected
After storage for 14 days at 30°C/80% rel. humidity		

+ According to the invention

CLAIMS

1. A solid, powder-form acidic sprinkling preparation for cleaning toilets containing solid water-soluble acid and water-soluble carbonate, characterized in that it also contains cellulose powder.
2. A preparation as claimed in Claim 1, characterized in that it contains from 2 to 85% by weight of a cellulose powder having particle sizes of from 1 to 1000 μm .
3. A preparation as claimed in Claim 2, characterized in that it contains from 5 to 30% by weight of a cellulose powder in which more than 90% of the particles are between 5 and 300 μm and preferably between 10 and 200 μm in size.
4. A preparation as claimed in any of Claims 1 to 3, characterized in that the cellulose powder is incorporated in granulated form.
5. A preparation as claimed in any of Claims 1 to 4, characterized in that it additionally contains alkali or ammonium salts of mineral acids, anionic or nonionic surfactants and perfume.
6. A preparation as claimed in Claim 5 containing
from 3 to 90% by weight of solid water-soluble acid
having a pK_s - value below 5,
from 1 to 25% by weight of alkali and/or ammonium carbonate
and/or bicarbonate,
from 2 to 85% by weight of cellulose powder having particle
sizes of from 1 to 1000 μm ,
from 5 to 90% by weight of alkali and/or ammonium salts of
mineral acids,
from 0.05 to 5% by weight of anionic or nonionic surfactants,
from 0.05 to 1% by weight of perfume and
from 0 to 60% by weight of additives from the group comprising
antimicrobial agents, polishes, dyes,
bleaches and dust inhibitors,
with the proviso that the quantities of acid and carbonate
are selected so that less than 80% and preferably less than
50% of the acid equivalents are consumed in the release of CO_2 .



* C L M S *

7. A preparation as claimed in Claim 6 containing
from 3 to 30% by weight solid, water-soluble organic acid,
from 1 to 10% by weight Na_2CO_3 and/or NaHCO_3 ,
from 5 to 30% by weight cellulose powder,
from 60 to 90% by weight Na_2SO_4 and/or NaCl ,
from 0.05 to 1% by weight anionic and/or nonionic surfactants,
from 0.05 to 0.3% by weight perfume and
from 0 to 30% by weight additives.
8. A preparation as claimed in Claim 6 containing
from 10 to 80% by weight solid, water-soluble inorganic acid,
from 5 to 25% by weight Na_2CO_3 and/or NaHCO_3 ,
from 5 to 30% by weight cellulose powder,
from 5 to 75% by weight Na_2SO_4 and/or NaCl ,
from 0.05 to 1% by weight anionic and/or nonionic surfactants,
from 0.05 to 0.3% by weight perfume and
from 0 to 30% by weight additives.
9. A process for the production of solid, acidic sprinkling
preparations for cleaning toilets containing solid, water-
soluble acid and water-soluble carbonate, characterized in
that cellulose powder is added during mixing or granulation
of the preparation.

