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(54) Titre : DETERGENT POUR LAVE-VAISSELLE
(54) Title: MACHINE DISHWASHING DETERGENT

(57) **Abrégé/Abstract:**

The invention relates to a liquid to paste machine dishwashing detergent which, in addition to customary machine dishwashing detergent ingredients, comprises a crystalline, layered silicate of the formula $a A_2O \cdot b BO \cdot c C_2O_3 \cdot d D_2O_5 \cdot e SiO_2 \cdot f H_2O$, in which A is an alkali metal and/or hydrogen, B is an alkaline earth metal, C is an element from the third main group of the Periodic Table, and D is an element from the fifth main group of the Periodic Table, and the following also apply: $0 \leq a \leq 1$; $0 \leq b \leq 0.5$; $0 \leq c/e \leq 0.05$; $0 \leq d/e \leq 0.25$; $1.9 \leq e \leq 4$; $0 \leq f \leq 20$. The invention also relates to a process for the preparation of this machine dishwashing detergent and to its use.

Machine dishwashing detergent

Abstract:

The invention relates to a liquid to paste machine dishwashing detergent which, in addition to customary machine dishwashing detergent ingredients, comprises a crystalline, layered silicate of the formula



in which A is an alkali metal and/or hydrogen, B is an alkaline earth metal, C is an element from the third main group of the Periodic Table, and D is an element from the fifth main group of the Periodic Table, and the following also apply: $0 \leq a \leq 1$; $0 \leq b \leq 0.5$; $0 \leq c/e \leq 0.05$; $0 \leq d/e \leq 0.25$; $1.9 \leq e \leq 4$; $0 \leq f \leq 20$.

The invention also relates to a process for the preparation of this machine dishwashing detergent and to its use.

The invention relates to a liquid to paste machine dishwashing detergent, to a process for its preparation and to its use.

5 Solid detergents for machine dishwashing are largely supplied in powder or granular form (agglomerates). A serious disadvantage of this type of solid detergents is that there is a strong tendency towards caking or clumping due to the hygroscopicity of individual raw
10 materials when small amounts of moisture enter. This can sometimes lead to a loss in cleaning action and additionally leads the user to believe that the quality is reduced for optical reasons.

15 Liquid dishwashing detergents, as are used especially in the large-scale commercial sector, are unsuitable for use in automatic household dishwashing machines in the domestic sector primarily because of their insufficiently low viscosity and their high alkalinity,
20 since these products must be characterized as "irritant" and thus represent a great safety risk in the home. In addition, retention of the dishwashing detergent in standard domestic dosing devices is not ensured in most cases.

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Standard commercial gelatinous or thixotropic dishwashing detergents comprise greater or lesser amounts of alkali metal silicates, generally in the form of aqueous solutions (water glass), for example in the ratio $\text{Na}_2\text{O}:\text{SiO}_2$ of 1:2 to 1:3.3, which are used to achieve the desired alkalinity and as corrosion inhibitors for the glaze and decoration on porcelain.

It has, however, been found that dishwashing detergents with such decoration and glaze protection have the disadvantage that they form deposits of varying severity on the remainder of the ware, particularly on glasses; they form initially in bright tarnish colors, and subsequently in whitish-opaque bluish adherent films and can only be removed with extremely strong acids, for example a hydrofluoric acid/sulfuric acid mixture. Such dishwashing detergents are therefore unsuitable for use over a prolonged period.

The object of the invention is therefore to provide a non-solid machine dishwashing detergent which, as well as having a good cleaning action, results in less corrosion, in particular on glasses and porcelain plates, and produces fewer deposits compared with the prior art.

This object is achieved by a machine dishwashing detergent of the type mentioned in the introduction, which, in addition to other machine dishwashing detergent ingredients, comprises a crystalline, layered silicate of the formula



in which A is an alkali metal and/or hydrogen, B is an alkaline earth metal, C is an element from the third main group of the Periodic Table, and D is an element from the fifth main group of the Periodic Table, and the following

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also apply: $0 \leq a \leq 1$; $0 \leq b \leq 0.5$; $0 \leq c/e \leq 0.05$; $0 \leq d/e \leq 0.25$; $1.9 \leq e \leq e 4$; $0 \leq f \leq 20$.

The machine dishwashing detergent preferably comprises from 1 to 50% by weight of the crystalline layered
5 silicate.

The machine dishwashing detergent particularly preferably comprises from 5 to 30% by weight of the crystalline layered silicate.

The crystalline layered silicate is preferably
10 essentially disodium disilicate.

The disodium disilicate is preferably layered crystalline disodium disilicate which consists of at least one of the polymorphic phases of disodium disilicate and of sodium silicates of a nonphyllosilicatic nature.

15 The layered crystalline disodium disilicate preferably consists of one or more of the following (the following data refers to percentages by weight) from 1 to 40% of alpha-disodium disilicate, up to 50% of beta-disodium disilicate, from 50 to 98% of delta-disodium disilicate and
20 up to 40% of nonphyllosilicatic sodium silicates.

In another embodiment of the invention, the layered crystalline disodium disilicate consists of one or more of the following; up to 40% of alpha-disodium disilicate, from 20 to 98% of beta-disodium disilicate, up
25 to 40% of delta-disodium disilicate and up to 50% of nonphyllosilicatic sodium silicates.

In another embodiment of the invention, the layered crystalline disodium disilicate consists of one or more of the following; from 20 to 98% of alpha-disodium
30 disilicate, up to 40% of beta-disodium disilicate up to 50%

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of delta-disodium disilicate and up to 50% of nonphyllosilicatic sodium silicates.

The definitions of alpha-, beta- and delta-disodium disilicate are known and can be found, for example, 5 in EP 0 164 514.

The crystalline layered silicate in the machine dishwashing detergent according to the invention preferably comprises up to 10 mol% of boron, based on SiO_2 .

The crystalline layered silicate in the machine dishwashing detergent according to the invention preferably comprises up to 50 mol% of phosphorus, based on SiO₂.

5

The machine dishwashing detergent preferably also comprises at least a surfactant and/or a bleach and/or a rheological additive and/or a dispersant and/or a dispersion medium.

10

The machine dishwashing detergent preferably comprises, as surfactants, block polymers of long-chain aliphatic alcohols with ethylene oxide or propylene oxide groups, modified fatty alcohol polyglycol ethers, mono- and
15 dialkylsulfates, alkanesulfonates, amine oxides and/or fatty acid methylpolyglycol esters.

The machine dishwashing detergent preferably comprises, as bleach, active chlorine carriers and/or active
20 oxygen carriers.

The machine dishwashing detergent preferably comprises, as rheological additive and/or dispersant, carboxy-
methylcellulose, polycarboxylates, phosphonates and/or
25 synthetic clays.

The machine dishwashing detergent preferably comprises, as dispersion medium, ethylene glycols, cooligomers/

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copolymers of propylene oxide and ethylene oxide and/or water.

In addition to the customary machine dishwashing
5 detergent ingredients, the machine dishwashing
detergent preferably comprises
from 2.5 to 50% by weight of crystalline layered sodium
disilicate
from 0 to 20% by weight of surfactant
10 from 0 to 40% by weight of sodium tripolyphosphate
from 0 to 20% by weight of bleach
from 0.1 to 15% by weight of rheological additive
and/or dispersant
from 50 to 80% by weight of dispersion medium
15 as other ingredients.

In addition to the customary machine dishwashing
detergent ingredients, the machine dishwashing
detergent preferably comprises
20 from 5 to 30% by weight of crystalline layered sodium
disilicate
from 0 to 20% by weight of surfactant
from 15 to 30% by weight of sodium tripolyphosphate
from 5 to 15% by weight of bleach
25 from 0.1 to 10% by weight of rheological additive
and/or dispersant
from 50 to 70% by weight of dispersion medium
as other ingredients.

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In addition to the customary machine dishwashing detergent ingredients, the machine dishwashing detergent preferably comprises

5 from 5 to 30% by weight of crystalline layered sodium disilicate

from 5 to 15% by weight of bleach

from 0 to 20% by weight of surfactant

from 0.1 to 10% by weight of rheological additive and/or dispersant

10 from 30 to 70% by weight of dispersion medium as other ingredients.

In addition to the customary machine dishwashing detergent ingredients, the machine dishwashing

15 detergent preferably comprises

from 10 to 40% by weight of crystalline layered sodium disilicate

from 0 to 20% by weight of surfactant

from 15 to 30% by weight of sodium tripolyphosphate

20 from 0.1 to 15% by weight of rheological additive and/or dispersant

from 30 to 70% by weight of dispersion medium as other ingredients.

25 In addition to the customary machine dishwashing detergent ingredients, the machine dishwashing detergent preferably comprises

from 10 to 50% by weight of crystalline layered sodium disilicate

from 0 to 20% by weight of surfactant
from 0.1 to 15% by weight of rheological additive
and/or dispersant
from 30 to 70% by weight of dispersion medium
5 as other ingredients.

In the case of the abovementioned preferred
compositions, the sodium disilicate is essentially
disodium disilicate.

10

The machine dishwashing detergent according to the
invention preferably has corrosion-inhibiting
properties.

15 The machine dishwashing detergent according to the
invention particularly preferably has corrosion-
inhibiting properties on silicatic surfaces of the
ware.

20 The machine dishwashing detergent according to the
invention particularly preferably has corrosion-
inhibiting properties, in particular on glasses.

The machine dishwashing detergent according to the
25 invention preferably has increased cleaning action.

The machine dishwashing detergent according to the
invention preferably has a lower degree of deposits, in
particular on glasses.

The invention likewise relates to a process for the preparation of a machine dishwashing detergent, which comprises firstly dissolving alkali metal carrier in an
5 initial charge of aqueous medium and/or dispersion medium, then mixing in rheological additives and/or dispersants, cooling to room temperature, adding the other components and, at the end of the mixing operation, adding the crystalline layered silicate.

10

The alkali metal carrier is preferably sodium carbonate, sodium hydroxide, potassium hydroxide and/or water-soluble alkali metal silicates.

15 The components are preferably surfactants, bleaches, fillers, builders, cobuilders, phosphates, organic complexing agents, foam inhibitors, perfumes and/or dyes and/or optionally other machine dishwashing detergent ingredients.

20

The invention also relates to the use of the machine dishwashing detergent according to the invention for machine dishwashing.

25 The layered silicate present in the machine dishwashing detergent according to the invention and having the formula as described above

a A₂O • b BO • c C₂O₃ • d D₂O₅ • e SiO₂ • f H₂O,

in which A is an alkali metal and/or hydrogen, B is an alkaline earth metal, C is an element from the third main group of the Periodic Table and D is an element from the fifth main group of the Periodic Table (and the following also apply: $0 \leq a \leq 1$; $0 \leq b \leq 0.5$; $0 \leq c/e \leq 0.05$; $0 \leq d/e \leq 0.25$; $1.9 \leq e \leq 4$; $0 \leq f \leq 20$), can, in particular, also comprise calcium and magnesium ions.

10 Other ions which are preferably present are those from the third and fifth main group of the Periodic Table, including in particular boron and phosphorus. This is the case particularly when the layered silicate used is a disodium disilicate as described above and below.

15

The layered silicate can, however, also be a sodium potassium disilicate in which the sodium to potassium ratio can be varied within a wide range.

20 In accordance with the invention are likewise layered silicates of the above formula which essentially comprise alkali metals (Li, Na, K) and/or hydrogen, and which comprise small amounts of the abovementioned alkaline earth metals (Be, Mg, Ca, Sr, Ba) and elements
25 from the third main group of the Periodic Table (B, Al, Ga, In, Tl) or from the fifth main group of the Periodic Table (P, As, Sb, Bi).

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For the machine dishwashing detergent according to the invention, the abovementioned silicate is used either in a finely ground form, i.e. as powder having an average particle diameter of from 1 to 200 micrometers, or in readily dispersible form, e.g. as compressed granules which disintegrate into microscopically small particles when incorporated into the dishwashing dispersion.

Also suitable are, preferably, readily dispersible compounds of crystalline, layered sodium disilicate with polycarboxylates, as are described in DE-A 197 19 888. Preferred polycarboxylates are homo- or any combinations of copolymers of the monomers acrylic acid and/or maleic acid and/or vinyl acetate and/or methallylsulfonate. The preferred compound of polycarboxylate and crystalline, layered sodium disilicates consists here of from 50 to 98% by weight of said silicate and from 2 to 50% by weight of polycarboxylate.

The other dishwashing detergent components, some of which have already been mentioned above, such as fillers, alkali metal carriers, surfactants, builders, bleaches, rheological additives and dispersants, foam inhibitors and optionally perfumes and dyes and others, can be substances which are already adequately known for these purposes.

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The filler used can, for example, be sodium sulfate.

Alkali metal carriers which may be mentioned are the oxides, hydroxides, carbonates and silicates of the
5 alkali metals, preferably sodium carbonate and/or sodium hydroxide and/or potassium hydroxide or water-soluble alkali metal silicates.

Suitable surfactants are chlorine-stable block polymers
10 of long-chain aliphatic alcohols with ethylene oxide or propylene oxide groups or modified fatty alcohol polyglycol ethers or mono- and dialkylsulfates or alkanesulfonates or amine oxides or fatty acid methylpolyglycol esters.

15

Builders which can be used are monomeric, dimeric, oligomeric or polymeric alkali metal phosphates, preferably pentaalkali metal triphosphate, anhydrous and/or partially hydrated and/or hexahydrate.

20

Other suitable constituents according to the invention are organic complexing agents, such as mono-, di-, tri-, oligo- and/or polycarboxylic acids, hydroxycarboxylic acids, aminocarboxylic acids and
25 phosphonic acids, preferably in the form of their water-soluble salts. Preferred oligocarboxylic acids are citric, tartaric, maleic acid etc. These are preferably used together with the crystalline layered silicate as compressed granules.

Preferred bleaches are active chlorine carriers, such as sodium dichloroisocyanurate or sodium hypochlorite solution (chlorine bleaching liquor) and active oxygen
5 carriers, such as hydrogen peroxide, alkali metal peroxides, alkaline earth metal peroxides, alkali metal perborate, persulfate, percarbonate, perphosphate and peroxycarboxylic acids and salts thereof, such as
10 dodecaneperoxydicarboxylic acid or magnesium peroxyphthalate.

Bleach activators or bleach catalysts can also be used. A customary bleach activator is tetraacetylene-diamine. Customary bleach catalysts are complexes of
15 manganese with specific ligands, e.g. derivatives of 1,4,7-triaminocyclononane.

Preferred rheological additives and dispersion auxiliaries are carboxymethylcellulose, poly-
20 carboxylates, phosphonates or synthetic clays.

Clays which can be used according to the invention are naturally occurring activated and sometimes modified clay minerals such as bentone types from Rheox, or also
25 synthetic clay minerals such as the Laponite grades from Laporte or synthetic hectorite of the type SKS-21 from Hoechst and synthetic saponite of the type SKS-20 from Hoechst. Other suitable clays are known to the

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person skilled in the art and can be found in the manufacturer's catalogs.

In the dispersion, dissolved alkali metal silicates or
5 mono-, oligo- and polyphosphates can have a supporting
action.

The dispersion carrier (liquid component) used can be a
monomeric, oligomeric or polymeric ethylene glycol or
10 cooligomers/copolymers of propylene oxide and ethylene
oxide and/or water.

Foam in dishwashers, in most cases caused by foam-
producing surfactants or proteinaceous food residues,
15 causes a reduction in cleaning action. It is therefore
necessary to add to the dish-washing detergents a foam
suppressor or foam dampener, for example chlorine-
stable phosphoric esters, such as, for example,
triisobutyl phosphate (antifoam TIP from Clariant
20 GmbH), or known silicones, such as the SP grades from
Wacker Chemie GmbH.

The abovementioned components can be present in the
machine dishwashing detergent according to the
25 invention individually or in mixtures together with the
crystalline layered silicates, in particular sodium
disilicates (e.g. type SKS-6 from Clariant GmbH).

The consistency of the mixtures according to the invention can be adjusted, depending on the solids content, from low-viscosity/liquid to paste/gelatinous.

5 Machine dishwashing detergents according to the invention can either contain phosphate or be phosphate-free.

The preparation should preferably be carried out in
10 accordance with the following procedure:

alkali metal carriers, such as, for example, sodium carbonate and/or sodium hydroxide and/or sodium water glass, are firstly dissolved in an initial charge of aqueous medium or another dispersion medium, then
15 rheological additives and/or dispersants (preferably polycarboxylates and/or phosphonic acids) are mixed in, the mixture is cooled to room temperature, and the other components (for example bleach, surfactant and builder (phosphate)) are added. At the end of the
20 mixing operation, the crystalline layered silicate is added.

Admixture preferably takes place with the action of strong shear forces, e.g. with customary dispensers,
25 high-shear mixers from Haake & Kunkel (Ultraturrax(TM)) or impeller, propeller or turbine stirrers.

The machine dishwashing detergents according to the invention are notable for good cleaning capacity even

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for critical soilings such as burnt-on proteinaceous food residues. In addition, they exhibit high chlorine or active oxygen stability.

- 5 The damage to glasses and decorated porcelain plates as a result of deposits and as a result of corrosion is much to very much less than for standard commercial dishwashing detergents which correspond to the prior art. This can be seen clearly from the examples below.

10

The machine dishwashing detergents according to the invention are preferably used in domestic dishwashers, but can also be used in commercial dishwashers.

- 15 Examples below aim to provide proof of the advantageous properties of the machine dishwashing detergent according to the invention. For comparison purposes, standard commercial dishwashing detergent gels based on phosphate and a test mixture without the addition of
20 crystalline layered silicate (according to the invention) are used.

The pH of the cleaning liquors was then determined directly after the soiling had been filtered off, using
25 a glass electrode.

Machine dishwashing detergents used

	A	Commercial product 1	
5	B	Commercial product 2	
	C	Commercial product 3	
	D	Comparison	
10		22.20% by weight	of sodium tripolyphosphate, partially hydrated
		9.00% by weight	of sodium hypochlorite solution (chlorine bleach liquor, 15% active chlorine)
15		0.10% by weight	of thickener
		0.04% by weight	of silicone antifoam
		49.50% by weight	of sodium silicate (water glass, 45.5% by weight, silicon dioxide to disodium oxide ratio 2.0)
20		1.50% by weight	of sodium alkanesulfonate ([®] Hostapur SAS 60 from Clariant GmbH)
		0.80% by weight	of sodium polyacrylate
25		0.60% by weight	of phosphonate (43% of active substance)
		3.96% by weight	of sodium carbonate
		12.30% by weight	of water

	E	Comparison	
		1.0% by weight	of crystalline layered sodium disilicate (SKS-6 from Clariant GmbH)
5		25.0% by weight	of sodium tripolyphosphate granules
		9.0% by weight	of sodium hypochlorite solution
		0.2% by weight	of antifoam
10		1.5% by weight	of sodium alkylsulfate
		1.1% by weight	of sodium polyacrylate
		0.3% by weight	of phosphonic acid (60% of active substance)
		0.5% by weight	of sodium hydroxide
15		6.0% by weight	of sodium carbonate
		46.5% by weight	of sodium water glass (as in D)
		8.9% by weight	of water
20	F	Invention	
		5.5% by weight	of crystalline layered sodium disilicate (SKS-6 from Clariant GmbH)
25		22.2% by weight	of sodium tripolyphosphate, anhydrous
		9.0% by weight	of sodium hypochlorite solution
		0.4% by weight	of antifoam ([®] Entschäumer TIP from Clariant GmbH)

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	49.50% by weight	of sodium silicate (water glass, 45.5% by weight, silicon dioxide to disodium oxide ratio 2.0)
5	1.0% by weight	of sodium alkanesulfonate
	2.0% by weight	of sodium polyacrylate
	0.6% by weight	of phosphonic acid (50% of active substance)
	1.0% by weight	of sodium hydroxide
10	4.0% by weight	of sodium carbonate
	17.3% by weight	of water
	G Invention	
15	17.5% by weight	of crystalline layered sodium disilicate/copolymer compound based on acrylic acid/maleic acid (SKS-6 HD from Clariant GmbH)
20	20.0% by weight	of sodium tripolyphosphate, anhydrous
	10.0% by weight	of sodium percarbonate
	1.4% by weight	of fatty acid polyglycol ester
	0.6% by weight	of antifoam
25	49.50% by weight	of sodium silicate (water glass, 45.5% by weight, silicon dioxide to disodium oxide ratio 2.0)
	0.2% by weight	of bentonite thickener
	18.3% by weight	of water

	H	Invention	
		10.0% by weight	of crystalline layered sodium disilicate
5		10.0% by weight	of sodium perborate monohydrate
		0.1% by weight	of silicone antifoam
		0.9% by weight	of sodium alkanesulfonate
		5.0% by weight	of sodium carbonate
10		15.0% by weight	of sodium tripolyphosphate, partially hydrated
		15.0% by weight	of sodium polyphosphate hexahydrate
		1.5% by weight	of bentonite
15		42.5% by weight	of water
	I	Invention	
		30.0% by weight	of crystalline layered sodium disilicate granules
20		4.0% by weight	of sodium carbonate
		1.0% by weight	of sodium hydroxide
		0.5% by weight	of phosphonic acid, 50% strength
		1.0% by weight	of sodium copolymer (Sokalan CP5, BASF)
25		1.5% by weight	block polymer (Genapol 2909, Clariant GmbH)
		1.5% by weight	of protease enzyme
		1.5% by weight	of amylase enzyme

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10.0% by weight of sodium perborate monhydrate
49.0% by weight of water

Example 1 (formation of deposits on ware)

5

Using glasses and decorated porcelain plates of varying provenance, composition and shape, the mixtures D to H according to the invention were tested for irreversible damage compared with the commercial products B and C.

10 Porcelain plates and cups, and stainless steel cutlery was used as ballast to make up the prescribed amount of ware of 12 place settings. The test method is in accordance with DIN V ENV 12875-1: April 1998, Mechanische Geschirrspülmaschinenbeständigkeit von

15 Haushaltswaren [Mechanical Dishwasher Stability of Household Goods], Part 1. The amount of test detergent added deviates from the draft standard, in each case 40 g of liquid test mixture were added in the washing cycle and 3 ml of rinse-aid were added in the rinse-aid

20 cycle of the test dishwasher.

Method 1: Determination of deposits on the ware

After 125 wash cycles, the crockery is assessed visually in the daylight and in a so-called "black box"

25 (black box with diffused artificial light) using the point evaluation table below.

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Method 2: Corrosion determination on glasses

The number of washing cycles after which the first visible sign of clouding appears is determined.

Grade	Daylight	"Black box"
0	No clouding	No clouding
1	No clouding	Very weak clouding/iridescence
2	No clouding	Weak clouding/iridescence
3	Very weak clouding/iridescence	Significant iridescence
4	Weak clouding/iridescence	-----
5	Significant clouding	-----

5

The arithmetic mean, calculated from the total of the evaluations and number of glasses, gives the grade for the damage which has occurred.

10 Method 1

Product	Prior art			According to the invention			
	B	C	D	E	F	G	H
PH (10g/l)	11.5	11.7	11.3	11.4	11.7	11.4	11.2
Grading of the deposits on glasses	5.0	5.0	5.0	4.0	1.0	0.5	0.0

Method 2

Product	Prior art			According to the invention			
	B	C	D	E	F	G	H
Number of wash cycles	20	25	25	30	125	375	>400

A comparison of machine dishwashing detergents according to the invention and commercial products according to the prior art or the test product according to the prior art with regard to the grades according to Methods 1 and 2 shows that the products according to the invention produce significantly less damage as a result of deposits and as a result of corrosion.

Example 2 (cleaning action)

The cleaning action of the machine dishwashing detergents A to I was determined in accordance with DIN standard draft 44990 and the IKW method in three Miele G 688 SC domestic dishwashers. The test products according to the invention, the comparative product according to the prior art and the commercial products according to the prior art were used in the same amount of 40 g of dishwasher detergent and 3 ml of rinse-aid. Evaluation was carried out after washing by visual assessment of the ware. The test result is given as a percentage (100% = clean). The table below gives the results of the tests and the pH of the wash liquor.

Dish-washing detergent	A	B	C	D	E	F	G	H	I
pH of wash liquor	10.1	10.6	10.6	10.4	10.5	10.5	10.5	10.2	10.5
% cleaning action at 50°C wash temperature	79	76	74	76	79	86	89	86	92

The results show that the machine dishwashing detergents according to the invention have a clearly
5 better cleaning action compared with those from the prior art.

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CLAIMS:

1. A liquid to paste machine dishwashing detergent which, in addition to other machine dishwashing detergent ingredients, comprises a crystalline, layered silicate of
5 the formula



in which A is an alkali metal and/or hydrogen, B is an alkaline earth metal, C is an element from the third main group of the Periodic Table, and D is an element from the
10 fifth main group of the Periodic Table, and the following also apply : $0 \leq a \leq 1$; $0 \leq v \leq 0.5$; $0 \leq c/e \leq 0.05$; $0 \leq d/e \leq 0.25$; $1.9 \leq e \leq 4$; $0 \leq f \leq 20$.

2. The machine dishwashing detergent as claimed in claim 1, which comprises from 1 to 50% by weight of the
15 crystalline, layered silicate.

3. The machine dishwashing detergent as claimed in claim 1 or 2, which comprises from 5 to 30% by weight of the crystalline layered silicate.

4. The machine dishwashing detergent as claimed in
20 any one of claims 1 to 3, wherein the crystalline layered silicate is essentially disodium disilicate.

5. The machine dishwashing detergent as claimed in claim 4, wherein the disodium disilicate is layered crystalline disodium disilicate which consists of at least
25 one of the polymorphic phases of disodium disilicate and of sodium silicates of a nonphyllosilicatic nature.

6. The machine dishwashing detergent as claimed in claim 5, wherein the layered crystalline disodium disilicate comprises one or more of the following: from 1 to 40% of

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alpha-disodium disilicate, up to 50% of beta-disodium disilicate, from 50 to 98% of delta-disodium disilicate and up to 40% of nonphyllosilicatic sodium silicates.

7. The machine dishwashing detergent as claimed in claim 5, wherein the layered crystalline disodium disilicate comprises one or more of the following: up to 40% of alpha-disodium disilicate, from 20 to 98% of beta-disodium disilicate, up to 40% of delta-disodium disilicate and up to 50% of nonphyllosilicatic sodium silicates.
- 10 8. The machine dishwashing detergent as claimed in claim 5, wherein the layered crystalline disodium disilicate comprises one or more of the following: from 20 to 98% of alpha-disodium disilicate, up to 40% of beta-disodium disilicate, up to 50% of delta-disodium disilicate and up to 15 50% of nonphyllosilicatic sodium silicates.
9. The machine dishwashing detergent as claimed in any one of claims 1 to 8, wherein the crystalline layered silicate comprises up to 10 mol% of boron, based on SiO_2 .
10. The machine dishwashing detergent as claimed in 20 any one of claims 1 to 9, wherein the crystalline layered silicate comprises up to 50 mol% of phosphorus, based on SiO_2 .
11. The machine dishwashing detergent as claimed in any one of claims 1 to 10, which also comprises a 25 surfactant, a bleach, a rheological additive, a dispersant, a dispersion medium, or mixtures thereof.
12. The machine dishwashing detergent as claimed in any one of claims 1 to 11, which comprises, as surfactants, block polymers of long-chain aliphatic alcohols with 30 ethylene oxide or propylene oxide groups, modified fatty

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alcohol polyglycol ethers, mono- and dialkylsulfates, alkanesulfonates, amine oxides and/or fatty acid methylpolyglycol esters.

13. The machine dishwashing detergent as claimed in
5 any one of claims 1 to 12, which comprises, as bleach, active chlorine carriers, active oxygen carriers or both.

14. The machine dishwashing detergent as claimed in
any one of claims 1 to 13, which comprises, as rheological
additive or dispersant, carboxymethylcellulose,
10 polycarboxylates, phosphonates, synthetic clays or mixtures thereof.

15. The machine dishwashing detergent as claimed in
any one of claims 1 to 14, which comprises, as dispersion
medium, ethylene glycols, cooligomers/copolymers of
15 propylene oxide and ethylene oxide, water or mixtures thereof.

16. The machine dishwashing detergent as claimed in
any one of claims 1 to 15 which, in addition to the other
machine dishwashing detergent ingredients, comprises one or
20 more of the following:

from 2.5 to 50% by weight of crystalline layered
sodium disilicate

up to 20% by weight of surfactant

up to 40% by weight of sodium tripolyphosphate

25 up to 20% by weight of bleach

from 0.1 to 15% by weight of rheological additive,
dispersant or both

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from 50 to 80% by weight of dispersion medium as other ingredients.

17. The machine dishwashing detergent as claimed in any one of claims 1 to 15 which, in addition to the other 5 machine dishwashing detergent ingredients, comprises one or more of the following:

from 5 to 30% by weight of crystalline layered sodium disilicate

up to 20% by weight of surfactant

10 from 15 to 30% by weight of sodium tripolyphosphate

from 5 to 15% by weight of bleach

from 0.1 to 10% by weight of rheological additive, dispersant or both

15 from 50 to 70% by weight of dispersion medium as other ingredients.

18. The machine dishwashing detergent as claimed in any one of claims 1 to 15 which, in addition to the other machine dishwashing detergent ingredients, comprises one or 20 more of the following:

from 5 to 30% by weight of crystalline layered sodium disilicate

from 5 to 15% by weight of bleach

up to 20% by weight of surfactant

25 from 0.1 to 10% by weight of rheological additive, dispersant or both

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from 30 to 70% by weight of dispersion medium as other ingredients.

19. The machine dishwashing detergent as claimed in any one of claims 1 to 15 which, in addition to the other 5 machine dishwashing detergent ingredients, comprises one or more of the following:

from 10 to 40% by weight of crystalline layered sodium disilicate

up to 20% by weight of surfactant

10 from 15 to 30% by weight of sodium tripolyphosphate

from 0.1 to 15% by weight of rheological additive, dispersant or both

15 from 30 to 70% by weight of dispersion medium as other ingredients.

20. The machine dishwashing detergent as claimed in any one of claims 1 to 15 which, in addition to the other machine dishwashing detergent ingredients, comprises one or more of the following:

20 from 10 to 50% by weight of crystalline layered sodium disilicate

up to 20% by weight of surfactant

from 0.1 to 15% by weight of rheological additive, dispersant or both

25 from 30 to 70% by weight of dispersion medium as other ingredients.

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21. The machine dishwashing detergent as claimed in any one of claims 1 to 20, which has corrosion-inhibiting properties.

22. The machine dishwashing detergent as claimed in
5 any one of claims 1 to 21, which has corrosion-inhibiting properties on silicatic surfaces of the ware.

23. The machine dishwashing detergent as claimed in any one of claims 1 to 22, which has corrosion-inhibiting properties on glasses.

10 24. The machine dishwashing detergent as claimed in any one of claims 1 to 23, which has increased cleaning action.

25. The machine dishwashing detergent as claimed in
15 any one of claims 1 to 24, which has a lower degree of deposits.

26. The machine dishwashing detergent as claimed in claim 25 wherein the lower degree of deposits is on glasses.

27. A process for the preparation of a machine
dishwashing detergent as claimed in any one of claims 1 to
20 26, which comprises firstly dissolving alkali metal carrier in an initial charge of aqueous medium, dispersion medium or both, then mixing in rheological additives, dispersants or both, cooling to room temperature, adding additional components and, at the end of the mixing operation, adding
25 the crystalline layered silicate.

28. The process as claimed in claim 27, wherein the alkali metal carrier is sodium carbonate, sodium hydroxide, potassium hydroxide, water-soluble alkali metal silicates or a mixture thereof.

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29. The process as claimed in claim 27 or 28, wherein the additional components are surfactants, bleaches, fillers, builders, cobuilders, phosphates, organic complexing agents, foam inhibitors, perfumes, dyes, other
5 machine dishwashing detergent ingredients or a mixture thereof.

30. The use of the machine dishwashing detergent as claimed in any one of claims 1 to 27 for machine dishwashing.

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