



(11) **EP 1 061 123 B2**

(12) **NEW EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the opposition decision:
14.02.2007 Bulletin 2007/07

(51) Int Cl.:
C11D 3/20 (2006.01)

(45) Mention of the grant of the patent:
30.06.2004 Bulletin 2004/27

(21) Application number: **00303177.0**

(22) Date of filing: **14.04.2000**

(54) **Automatic dish-washing machine cleaning process and compositions relating thereto**

Verfahren und Zusammensetzungen zum Reinigen von Geschirrspülmaschinen

Procédé et compositions pour le nettoyage de lave-vaisselles

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

(30) Priority: **28.05.1999 EP 99304182**

(43) Date of publication of application:
20.12.2000 Bulletin 2000/51

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AT BE CH DE DK ES FI FR GR IT LI LU MC NL PT SE

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(56) References cited:
EP-A- 0 256 148 **EP-A- 0 612 843**
GB-A- 1 396 678 **US-A- 4 392 977**

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

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Description**Technical Field**

5 [0001] The present invention is in the field of machine dishwashing. More specifically, the invention encompasses a cleaner for automatic dishwashing machines.

Background of the Invention

10 [0002] The present invention relates to a composition used to clean dish washing machines. Such cleaning compositions are frequently used by the consumer to clean the dish washer itself and so remove deposits after the machine has been used to clean crockery.

[0003] Conventional cleaning machine cleaning products are put in the machine's dispenser and/or sprinkled on the base of machine. However, it has been found that occasionally conventional dish washer cleaning formulations tend to coagulate in the sieve in the bottom of the machine thus forming a solid mass that can block the machine and pump.

15 [0004] The present invention relates to a composition for cleaning dish washers in which the problem of co-agulation is mitigated.

Description of the Invention

20 [0005] Accordingly the present invention provides a granular automatic dish washing machine cleaner comprising at least 50% wt of the total composition of a fully hydrated organic acid and at least 0.5 % wt of the total composition of a surfactant

25 [0006] The present invention also provides the use of citric acid monohydrate in a dish washing machine cleaner to prevent mass solidification.

Detailed Description of the Invention

30 [0007] The compositions of the present invention comprise a fully hydrated organic acid as an essential element. Suitable fully hydrated organic acids include, for example, carboxylic acids, such as citric and succinic acids, polycarboxylic acids, such as polyacrylic acid, and also acetic acid, boric acid, malonic acid, adipic acid, fumaric acid, lactic acid, glycolic acid, sulphamic acid, tartaric acid, tartronic acid, malonic acid, their derivatives and any mixtures of the foregoing.

35 [0008] Suitable water-soluble monomeric or oligomeric carboxylates can be selected from a wide range of compounds but such compounds preferably have a first carboxyl logarithmic acidity/constant (pK_1) of less than 9, preferably of between 2 and 8.5, more preferably of between 2.5 and 7.5.

[0009] Polycarboxylic acids containing four carboxy groups include oxydisuccinic acids, 1,1,2,2-ethane tetracarboxylic acids, 1,1,3,3-propane tetracarboxylic acids and 1,1,2,3-propane tetracarboxylic acids. Polycarboxylic acids containing sulfo substituents include the sulfosuccinic derivatives, and the sulfonated pyrolysed citric acids.

40 [0010] Of the above, the preferred polycarboxylic acids are hydroxycarboxylic containing up to three carboxy groups per molecules, more particularly citric acid monohydrate.

[0011] It is preferable if the partially/fully hydrated acids have an average particle size from 0.8 to 3 d_m (RR)/mm, more preferably from 1.4 to 2.5 d_m (RR)/mm.

[0012] It is also preferable if the 95 % of the particles have a particle size greater than 1mm and less than 3mm.

45 [0013] The organic acid is present at a level of at least 50 wt% of the total formulation, more preferably at a level greater than 70 wt%, most preferably at a level from 85 wt% to 98 wt%.

[0014] A surfactant system comprising a surfactant selected from nonionic, anionic, cationic, ampholytic and zwitterionic surfactants and mixtures thereof is also present in the composition.

50 [0015] Typically the surfactant is a low to non foaming nonionic surfactant, which includes any alkoxyated nonionic surface-active agent wherein the alkoxy moiety is selected from the group consisting of ethylene oxide, propylene oxide and mixtures thereof, is preferably used to improve the detergency without excessive foaming especially preferred are ethoxylated and/or propoxylated straight chain alcohols.

[0016] However, an excessive proportion of nonionic surfactant should be avoided. Normally, an amount of 10% by weight or lower, preferably 7% by weight or lower, most preferably 5% by weight or lower and preferably 0.1 % by weight or higher, more preferably 0.5% by weight or higher is quite sufficient.

55 [0017] Examples of suitable nonionic surfactants for use in the invention are the low- to non-foaming ethoxylated straight-chain alcohols of Plurafac LF series ex BASF, Synperonic series ex ICI; of the Lutensol® LF series, supplied by the BASF Company and of the Triton® DF series, supplied by the Rohm & Haas Company.

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[0018] Other surfactants such as anionic surfactant may be used but may require the additional presence of an antifoam to suppress foaming. If an anionic surfactant is used it is advantageously present at levels of 2 wt% or below.

[0019] It is advantageous if a flow aid is present in the composition suitable flow aids include Aluminium silicate (Alusil), Calcium silicate (Calflow) and silicas.

5 [0020] Bleach material may optionally be incorporated in composition for use in processes according to the present invention, but preferably are not present.

[0021] The bleach material may be a chlorine- or bromine-releasing agent or a peroxygen compound. Peroxygen based bleach materials are however preferred.

10 [0022] Further optional ingredients that may be present include crystal-growth inhibitors, threshold agents; perfumes and dyestuffs and the like.

pH of wash liquor

15 [0023] Preferably the dish washing machine cleaner has gives a pH of 3 or less in a 1% aqueous solution at 20°C. More preferably the composition has a pH from 1 to 2 in a 1% aqueous solution at 20°C.

Product Form

20 [0024] The dish washing composition is granular. Granular in the context of the present invention includes both powdered material and tablets.

Method of Using the Composition.

25 [0025] The cleaning composition may be added to the machine via the dispenser drawer or sprinkled directly into the base of the dish washer. It is particularly advantageous if the composition is added directly to the base of the machine, as this leads to an effective dosing level.

[0026] Dishwash compositions according to the present invention may be dosed in the wash liquor at levels of from 30 g/l to 2.5 g/l.

30 [0027] The invention will now be illustrated by the following non limiting Examples. Examples of the invention are illustrated by a number, comparative Examples are illustrated by a letter.

[0028] All percentages are on a weight basis.

EXAMPLE I

35 [0029]

Table 1

	WT/%	
	1	A
Citric acid monohydrate	92.1	-
Citric acid Anhydrous		92.1
Starch based flow aid	5.5	5.5
Perfume	0.2	0.2
Nonionic surfactant ¹	2.0	2.0
minors	to 100	to 100
Particle Size	1.8 mm	1.8 mm
1) Nonionic surfactant, ex BASF (LF 403)		

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55 [0030] The compositions were tested in a robotised Miele G5953C (total water hardness 17°FH, including temporary hardness of 9°FH).

[0031] The compositions were dosed at a level of 120 g/wash by sprinkling the powder in the base of the machine near the sieve; the main wash time was 20 minutes; the drying time with open door was 10-20 minutes; the washing temperature was up to 65°C.

Table 2

Example	1	A
Consecutive No. of runs before pump breakdown	No breakdown	10

Claims

- 5
- 10 1. A granular automatic dish washing machine cleaner comprising:
- a) at least 50% wt of the total composition of a fully hydrated organic acid and;
b) at least 0.5 wt of the total composition of a surfactant
- 15 2. An automatic dish washing machine cleaner according to claim 1 in which the fully hydrated organic acid is citric acid monohydrate.
3. An automatic dish washing machine cleaner according to claim 1 or claim 2 in which the surfactant is a nonionic surfactant.
- 20 4. An automatic dish washing machine cleaner according to claim 3 in which the nonionic surfactant is an ethoxylated and/or propoxylated straight-chain alcohol.
- 25 5. An automatic dish washing machine cleaner according to any preceding claim in which the pH of a 1% aqueous solution at 20°C is 3 or less.
6. An automatic dish washing machine cleaner according to any preceding claim which further comprises a flow aid.
- 30 7. A process for cleaning a dish washing machine comprising adding a machine dish washing cleaner as claimed in any preceding claim to a machine dish washer.

Patentansprüche

- 35 1. Granuläres Reinigungsmittel für eine automatische Geschirrspülmaschine, umfassend:
- a) zumindest 50 Gew.-% der Gesamtzusammensetzung einer vollständig hydratisierten, organischen Säure und
b) zumindest 0,5 Gew.-% der Gesamtzusammensetzung eines oberflächenaktiven Stoffes.
- 40 2. Reinigungsmittel für eine automatische Geschirrspülmaschine nach Anspruch 1, wobei die vollständig hydratisierte, organische Säure Zitronensäuremonohydrat ist.
3. Reinigungsmittel für eine automatische Geschirrspülmaschine nach Anspruch 1 oder Anspruch 2, wobei der oberflächenaktive Stoff ein nicht-ionischer oberflächenaktiver Stoff ist.
- 45 4. Reinigungsmittel für eine automatische Geschirrspülmaschine nach Anspruch 3, wobei der nicht-ionische oberflächenaktive Stoff ein ethoxylierter und/oder propoxylierter, geradkettiger Alkohol ist.
- 50 5. Reinigungsmittel für eine automatische Geschirrspülmaschine nach einem der vorherigen Ansprüche, wobei der pH einer 1%igen wässrigen Lösung bei 20 °C 3 oder weniger ist.
6. Reinigungsmittel für eine automatische Geschirrspülmaschine nach einem der vorherigen Ansprüche, das ferner einen Fließverbesserer umfaßt.
- 55 7. Verfahren zur Reinigung einer Geschirrspülmaschine, umfassend die Zugabe eines Reinigungsmittels für eine Geschirrspülmaschine wie in einem der vorherigen Ansprüche beansprucht, zu einer Geschirrspülmaschine.

Revendications

1. Nettoyant granulaire pour lave-vaisselle automatique comprenant :

- 5 a) un acide organique partiellement ou totalement hydraté à hauteur d'au moins 50 % en poids de la composition totale, et
b) un tensioactif à hauteur d'au moins 0,5 % en poids de la composition totale.

10 2. Nettoyant pour lave-vaisselle automatique selon la revendication 1, dans lequel l'acide organique entièrement hydraté est de l'acide citrique monohydraté.

3. Nettoyant pour lave-vaisselle automatique selon la revendication 1 ou la revendication 2, dans lequel le tensioactif est un tensioactif non ionique.

15 4. Nettoyant pour lave-vaisselle automatique selon la revendication 3, dans lequel le tensioactif non ionique est un alcool en chaîne droite éthoxylé et/ou propoxylé.

5. Nettoyant pour lave-vaisselle automatique selon l'une quelconque des revendications précédentes, dans lequel le pH d'une solution aqueuse à 1 % et à 20°C est de 3 ou inférieur.

20 6. Nettoyant pour lave-vaisselle automatique selon l'une quelconque des revendications précédentes, comprenant en outre un matériau d'aide à l'écoulement.

25 7. Procédé de nettoyage d'un lave-vaisselle automatique comprenant le fait d'ajouter un nettoyant pour lave-vaisselle tel que revendiqué dans l'une quelconque des revendications précédentes, dans un lave-vaisselle.

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