

19



Europäisches Patentamt
European Patent Office
Office européen des brevets

11

Publication number:

**0 266 904
A2**

12

EUROPEAN PATENT APPLICATION

21

Application number: **87308797.7**

51

Int. Cl.4: **C11D 3/386 , C11D 3/28 ,
C11D 3/33**

22

Date of filing: **05.10.87**

The title of the invention has been amended
(Guidelines for Examination in the EPO, A-III,
7.3).

30

Priority: **07.10.86 GB 8624050**

43

Date of publication of application:
11.05.88 Bulletin 88/19

84

Designated Contracting States:
CH DE ES FR GB IT LI NL SE

71

Applicant: **UNILEVER PLC**
Unilever House Blackfriars P.O. Box 68
London EC4P 4BQ(GB)

84

GB

71

Applicant: **UNILEVER NV**
Burgemeester s'Jacobplein 1 P.O. Box 760
NL-3000 DK Rotterdam(NL)

84

CH DE ES FR IT LI NL SE

72

Inventor: **Frankena, Hidde**
Parkweg 154
NL-3134 VS Vlaardingen(NL)

74

Representative: **Green, Mark Charles et al**
Unilever PLC Patent Division P.O. Box 68
Unilever House Blackfriars
London EC4P 4BQ(GB)

54

Machine dish washing composition containing dipicolinic acid.

57

Machine dishwashing compositions comprise low or zero phosphate, using dipicolinic acid derivatives as the builder, and are also provided with enzymes to increase performance. Other conventional ingredients may also be included.

EP 0 266 904 A2

MACHINE DISHWASHING COMPOSITIONS

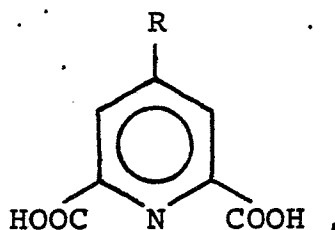
The present invention relates to machine dishwashing compositions which contain low levels of phosphate salts or which are completely phosphate-free and particularly to such compositions of the enzymatic type.

In the general detergent art it has been well established that, although for ecological reasons it is desirable to formulate compositions containing low or zero phosphate contents, alternative compounds capable of matching all the properties of phosphate salts are difficult to find. Over the last two decades numerous well-known alternatives have been proposed, including the zeolites, sodium nitrilotriacetate and citrates, to be employed either alone or in various combinations with each other.

A more unconventional example of a phosphate salt substitute is dipicolinic acid (2,6-pyridinedicarboxylic acid) or a salt thereof, the usefulness of which in fabric-washing compositions has been described in British Patent No 1 342 095. In German Patent Specification No 26 19 668 dipicolinic acid has been described for use in combination with a relatively soluble magnesium salt in hand-dishwashing formulations having a high-foaming behaviour under both soft and hard water conditions and in the United States Patent No 3 956 159 dipicolinic acid has also been described as suitable stabiliser for peroxygen bleaches. In European Patent Specification 0 082 564 a machine dishwashing composition comprising dipicolinic acid as a sequestrant is described, although no mention of enzymes as co-additives is made.

It has been found that the dipicolinic acid-containing compositions should comprise enzymes to improve performance, and it has now been discovered that contrary to what would be expected from the literature (Aldrich Chemie, Benelux, 1984 - Aldrich is a registered trade mark of Aldrich Chemie SA/NV), the use of dipicolinic acid does not inhibit enzymic action on soils.

Accordingly, the present invention provides a machine dishwashing composition comprising a carboxylic acid derivative of pyridine or a water-soluble or water-dispersible salt thereof having the general formula:



in which R is a hydrogen atom, a halogen atom, a hydroxyl group, an amino group, a carboxyl group or a short-chain alkyl group, together with an enzyme.

In the machine washing of dishes, compositions are in general formulated so as to provide a cleaning solution which removes soils, burnt materials, amylaceous products, dyes and the like, but without corrosive attack on dishware made of glass, china and metal. Moreover, formulations should be such that the formation of films and spots on the cleaned surfaces is prevented or avoided.

To the above purpose, conventional machine dishwashing compositions in general contain a significant amount of inorganic, relatively alkaline salts, such as alkali metal phosphates, alkali metal silicates and alkali metal carbonates, a bleaching system providing active chlorine or oxygen and, optionally, ingredients such as proteolytic and/or amylolytic enzymes, and nonionic surfactants for foam-reduction and wetting.

According to a more limited aspect of the invention it has been found that it is possible to formulate machine dishwashing compositions of equal or superior efficiency to conventional compositions based on inorganic salts, bleach, enzymes and optionally a nonionic surfactant, in which the conventional phosphate component is substantially substituted by the pyridine derivative defined above.

Surprisingly, dipicolinic acid proves not only to be an acceptable alternative to phosphate salts, but, contrary to many of the conventional phosphate replacers in machine dishwashing compositions, it exhibits a cleaning efficiency on a large number of soils, which is superior to the cleaning efficiency of phosphate-containing compositions.

The purpose of introducing the pyridine derivative is to reduce or avoid the use of phosphates while retaining the performance which they provide and so the compositions of the invention comprise less than 6% by weight, preferably less than 4% by weight calculated as phosphorus, of phosphates, or are substantially phosphorus-free.

5 The compositions may also include one or more alkaline salts, bleaches and nonionic surfactants, either singly or in combination.

Desirably the pyridine derivative comprises 5 to 50% by weight of the composition, preferably 15 to 30% by weight.

It is preferred that R is a hydrogen atom.

10 The pyridine derivative will generally be used in its salt form, in particular in the form of its alkali metal salt, such as the sodium salt. If so desired, also the ammonium or substituted ammonium salts of the pyridine derivative may be used.

The machine dishwashing compositions according to the invention may comprise one or more salts suitable to provide adequate alkalinity and buffering capacity. Thus, they may comprise organic and/or 15 inorganic builder and filler salts such as the alkali metal salts of silicate, in particular metasilicate, carbonate, borate, citrate, carboxymethyloxysuccinate, nitrilotriacetate and ethylenediaminetetraacetate, as well as polyelectrolytes such as polyacrylate, polymethacrylate, and polyamaleate. Polyelectrolytes may be present at 0-20% by weight. Examples include Sokalan CP5, Sokalan CP7, Gantrez and Builder U. Molecular weights may range from 1 000-5 000 000. Also combinations of the above salts among themselves or with 20 inert filler salts such as sodium sulphate are possible.

The amount of the above salts may vary between 10 and 90% by weight of the composition, and normally lies between 30 and 70% by weight.

The compositions according to the invention may further comprise a bleach component, which may be of both the oxygen-and chlorine-releasing type. Suitable chlorine-releasing bleaches include the well-known 25 alkali metal hypochlorites and chlorinated cyanuric acid salts. Because the compositions also contain one or more enzymatic components, these should either be protected against attack by such chlorine-releasing bleaches, eg by encapsulating them, or, and this is preferred, oxygen-releasing bleaches should be used. Particularly preferred in the present invention is the use of a peroxygen salt such as sodium perborate tetrahydrate or monohydrate, percarbonate and persulfate. It may also be advantageous to combine such a 30 persalt with a bleach activator therefor.

The activators for peroxygen salts are organic compounds which react with the peroxygen salt in solution to form an organic peroxygen acid as the effective bleaching agent. Numerous examples of such activators are known in the art. Preferred activators for use in the present invention are tetraacetylenediamine, tetraacetylglucuril, glucosepentaacetate and xylose tetraacetate.

35 The peroxygen salt is normally included in an amount of up to 25% by weight, in particular of from 3 to 15% by weight of the total composition.

Where also an activator for the bleach is included, the ratio between the peroxygen salt and the activator lies in the range of from 8:1 to 1:1, preferably 4:1 to 1.5:1.

40 Although optional, the compositions of the present invention preferably also comprise a surfactant which should be of essentially nonionic character. In particular, low-to non-foaming nonionic surfactants selected from the group consisting of alkoxyated nonionic surfactants wherein the alkoxy moiety consists of ethylene oxide, propylene oxide and/or butylene oxide or mixtures thereof may be used.

45 Examples of suitable and preferred low-to non-foaming nonionics for use in the present invention are the ethoxylated straight-chain alcohols sold under the trade names of Synperonic LF/RA 30 and Synperonic LF/RA 40 by the ICI Company, Lutensol LF 403 and Lutensol LF 1300 by the BASF Company, and Triton DF 12 by the Rohm & Haas Company.

The amount of the nonionic surfactant should be such that detergency and wetting are improved, and excessive foaming due to certain proteinaceous soils is reduced or suppressed. In general, amounts will be between 0.2 and 10% by weight, in particular between 0.5 and 5% by weight of the total composition.

50 The compositions according to the present invention should be substantially free from other types of surfactants, such as anionic or cationic surfactants.

The enzymes may be of the amyolytic, proteolytic and lipolytic type or mixtures thereof. The amyolytic enzymes for use in the present invention can be those derived from bacteria or fungi. Preferred amyolytic enzymes are those described in British Patent Specification No 1 296 839, cultivated from the 55 strains of Bacillus licheniformis NCIB 8061, NCIB 8059, ATCC 6334, ATCC 6598, ATCC 11 945, ATCC 8480 and ATCC 9945 A. A particularly preferred enzyme is an amyolytic enzyme produced and distributed

under the trade name Termamyl by Novo Industri A/S. Copenhagen, Denmark. These amylolytic enzymes are generally sold as granules and may have activities from about 2 to 10 Maltose units/milligram. The amylolytic enzyme is normally included in an amount of from 0.1 to 5% by weight, in particular of from 0.3 to 1.5% by weight.

5 The composition may, and preferably does, also contain a proteolytic enzyme. Examples of suitable proteolytic enzymes are the subtilisins which are obtained from particular strains of B subtilis and B. licheniformis, such as those commercially available under the trade names Maxatase, supplied by Gist-Brocades NV, Delft, Netherlands, and Alcalase, supplied by Novo Industri A/S, Copenhagen, Denmark. Particularly preferred are the proteases obtained from a strain of Bacillus having maximal activity throughout
10 the pH range of 8-12, being commercially available under the trade names of Esperase and Savinase, sold by Novo Industri A/S. The preparation of these and analogous enzymes is described in the British Patent No 1 243 784.

These proteolytic enzymes are generally sold as granules and may have enzyme activities of from about 500 to 1700 glycine units/milligram. The proteolytic enzyme is normally included in an amount of
15 from 0.1 to 5% by weight, in particular of from 0.3 to 1.5% by weight.

The compositions may further contain useful additives conventional in the machine dishwashing art, such as enzyme-stabilising agents, hydrotropes, perfumes, colouring agents, germicides, soil-suspending agents, aminopolyphosphonic acids and the alkali metal or alkaline earth metal salts thereof, anti-corrosion agents such as fatty acids, benzotriazole and so on.

20 The products of the present invention should be formulated such that they provide in the wash liquor a pH in the range of from 7 to 12.5, preferably of from 9.5 to 12.0 at a use concentration of about 3 grams/litre in water.

The products of the invention may be in powder, gel or liquid form.

The invention will now be further illustrated by way of examples.

25

Example 1

30 Machine dishwashing formulations having the following composition were prepared by conventional granulating and mixing procedures:

	<u>% by weight</u>
35 Sodium metasilicate pentahydrate	65
Sodium perborate monohydrate	7
¹ Savinase	1
40 ² Termamyl	1
³ Synperonic RA 40	1
Builder salt	25

45

1 a protease sold by Novo Industri A/S

2 an amylase also sold by Novo Industri A/S

3 (Trade mark) an ethoxylated, straight-chain alcohol,
50 nonionic surfactant sold by Imperial Chemical
Industries PLC

The builder salts used are shown below with the designations used for them in the following tables:

55 Sodium carbonate/calcite carb/calc
Sodium Zeolite 4 zeol
Sodium dipicolinate DPA

Sodium citrate cit
 Sodium nitrilotriacetate NTA
 Sodium carboxymethyloxymalonate CMOM
 Sodium carboxymethyloxysuccinate CMOS

5 These formulations were used to wash porcelain (porc) and stainless steel (st st) dishes soiled with potato, bambix, custard and egg yolk, and to wash other articles soiled with tea, coffee, custard, egg yolk, milk and lipstick. The articles were soiled in such a way that their total surfaces were covered (2.5 gms soil per article). They were then stored at 30°C and 55% relative humidity for 24 hours. The washing was performed in two machines, a MIELE G542 and a THOMSON BRANDT T 12 G1 using the washing
 10 programmes outlined below:

MIELE G542 universal 55° programme-rewash

-mainwash, heating for 12 minutes to 55°C

15 -cold rinse

-final rinse, 60°C

Total time: 65 minutes

20 THOMSON BRAND T 12 G1, eco 50°C programme-main wash (heating for 2 minutes to 47°C)

-cold rinse

-final rinse, 58°C

Total time : 62 minutes

25

The various formulations were added to the machines to produce a dosage of 2 grams/litre, using water of 15° French Hardness (no salt).

The following tables show the percentage of the surfaces of the articles from which the soil had not been removed. The quantity tabulated is Δ , defined as

30 $\Delta = \% \text{ of soil remaining using test formulations, less } \% \text{ remaining using a control formulation containing sodium tripolyphosphate of otherwise identical constituents.}$

A negative value of Δ therefore shows an advantage for the test compositions in cleaning performance.

35

40

45

50

55

Table 1Δ, MIELE G542

	<u>Soil</u>	<u>carb/ calc</u>	<u>zeol</u>	<u>DPA</u>	<u>cit</u>	<u>NTA</u>	<u>CMOM</u>	<u>CMOS</u>
	Egg yolk	51	36	-5	31	-6	-6	50
15	Tea (cup)	5	20	-5	20	-5	-5	20
	Tea (saucer)	-10	15	-10	15	-10	-10	15
	Tea (spoon)	-20	5	-20	0	-20	-20	0
	Lipstick	0	0	-40	0	-25	0	0
20	Custard	0	4	1	0	16	0	1
	Custard	10	35	8	30	-3	-7	3
	st st							
25	Custard	-38	-16	-42	-34	-16	-42	-40
	spoon							

No differences were found on potato, breakfast cereal, coffee, egg (yolk) and milk removal.

Table 2Δ, THOMSON BRANDT T 12 G1

	<u>Soil</u>	<u>carb/ calc</u>	<u>zeol</u>	<u>DPA</u>	<u>cit</u>	<u>NTA</u>	<u>CMOM</u>	<u>CMOS</u>
	Egg yolk	48	79	-9	66	-1	-7	79
	Tea (cup)	5	10	-5	5	-5	-5	5
45	Tea (saucer)	-5	15	-20	0	0	0	0
	Tea (spoon)	5	20	-10	10	0	-5	5
	Lipstick	0	0	-5	0	0	0	0
50	Custard	1	6	0	0	0	0	0
	Custard	0	2	1	7	-4	-4	-2
	st st							
55	Custard	-34	6	-14	4	26	12	-20
	spoon							

No differences were found on potato, breakfast cereal, coffee, egg (yolk) and milk removal.

Example 2

Tests were carried out to demonstrate the effect of amylolytic and proteolytic enzymes in the presence of DPA. Conditions: Miele G542 Universal 55°C

5 Dosage: 20 gram/machine
Standard Evaluation Soil
Water hardness: 15°FH
No salt

	<u>Substrate</u>	<u>Residual soil %</u>	
		<u>Without enzymes</u>	<u>With enzymes</u>
	Potato	84	1
15	Cereal	19	1
	Egg yolk (porc)	56	32
	Egg yolk (st st)	100	100
	Custard (porc)	90	86
20	Custard (st st)	91	43
	Custard (spoon)	80	20
	Lipstick	68	48

25 The results show that, contrary to teaching, there is a beneficial effect of adding DPA and enzymes together.

30 **Claims**

1. A detergent cleaning composition adapted for use in automatic dishwashing machines comprising a dipicolinic acid or a salt thereof, characterised in that it further comprises an effective amount of an enzyme.

35 2. A composition according to claim 1, characterised in that the enzyme is of the amylolytic, proteolytic or lipolytic type or mixtures thereof.

3. A composition according to claim 1 or claims 2, characterised in that the enzyme is present at from 0.1 to 10% by weight.

4. A composition according to any one of claims 1 to 3, characterised in that the composition comprises less than 6% by weight, calculated as phosphorous, of phosphates.

40 5. A composition according to any one of claims 1 to 4, characterised in that it further comprises a bleach component of the oxygen-or chlorine-releasing type.

6. A composition according to any one of claims 1 to 5, characterised in that it further comprises a surfactant of an essentially nonionic character.

45 7. A composition according to any one of claims 1 to 6, characterised in that the composition has a pH of between 9.5 and 12 at a concentration of 3 grams/litre in water.

50

55