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(54) Title: METHOD FOR REDUCING STAIN

(57) Abstract

The invention provides a method for reducing stain which comprises applying to said stain N,N-bis (carboxymethyl)-glutamic acid or a salt thereof.

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METHOD FOR REDUCING STAIN

The invention relates to methods for reducing stain and to detergent formulations, especially for machine dish-washing.

It is known that the addition of sequestrants such as ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) to detergent compositions in concentrations above the amount required to sequester the hardness of the water in which the composition is to be used, aids reducing stain on for example, crockery.

EDTA has the drawback that it is not biodegradable. Recent legislation bans it from certain applications. There are doubts about the safety of NTA. Thus alternatives to NTA and EDTA are needed. Sodium tripolyphosphate (STPP) and tetrapotassium pyrophosphate (TKPP) have been used instead of EDTA and NTA. However, the use of these sequestrants is not permitted in some countries for environmental reasons because they may cause eutrophication.

The present invention provides a method for reducing stain which comprises applying to a stain the chelating agent N,N-bis(carboxymethyl)glutamic acid or a salt thereof (hereinafter referred to by the abbreviation GLUDA).

German Patent specification DE-A-4211713 discloses methods of producing N,N-diacetic-aminodicarboxylic acids including GLUDA. These methods include the following:

(a) reacting glutamic acid with sodium cyanide and formaldehyde under alkaline conditions; and

(b) reacting glutamic acid with hydrogen cyanide and formaldehyde under acid conditions.

GLUDA may also be obtained by reacting glutamic acid with sodium monochloroacetate under alkaline conditions or by the processes disclosed in, for example, United States Patent US-2500019 and UK Patent Specification GB1439518.

GLUDA is biodegradable and breaks down into CO_2 and H_2O without the formation of any undesirable by-products. Its superiority to EDTA and NTA in this respect is shown by the following results from the Zahn Wellens Inherent Biodegrability test (OECD 302B):

$GLUDA.Na_4$	100%
$NTA.Na_3$	99%
$EDTA.Na_3$	9%

The method of the invention is preferably applied to tannin-derived based stains, for example stains produced by hot water extracts from tannin-containing substances. Examples of such stains include stains derived from tea, coffee, cocoa, red wine or fruit extracts, for example blackcurrant or tomato juice.

The method of the invention is preferably applied to stain present on glass, steel, enamel, crockery or plastics. These materials may be, for example, in the form of cups, saucers, plates, bowls, pots or pans. The method of the invention may also optionally be applied to cutlery or fabrics.

The method of the invention is preferably carried out at a temperature of 40 to 80°C, more preferably about 60°C.

In the method of the invention, GLUDA is preferably used as an alkali metal salt or ammonium salt, more preferably the tetrasodium salt. GLUDA is generally applied in the form of an aqueous solution preferably containing up to 50% GLUDA by weight, more preferably 25 to 50 and typically 38%. It is preferably employed in association with a surfactant and/or an alkali. Suitable alkalis include sodium hydroxide.

The method of the invention is conveniently applied in machine dish-washing.

Examples of detergent formulations which are suitable for use in the method of the invention are those which comprise GLUDA in association with an alkali and/or a surfactant (particularly a low foam surfactant) and include formulations such as:

(i)	Sodium Hydroxide		7.5%
	Solution containing 38% w/w of GLUDA-Na_4		40%
	Water	to	100%
(ii)	Sodium Hydroxide		10%
	Solution containing 38% w/w of GLUDA-Na_4		40%
	Miravon B79R		1%
	Miravon B12DF		1%
	Mirataine JC.HA		6%
	Water	to	100%

(iii)	Sodium Hydroxide		20%
	Solution containing 38% w/w of GLUDA.Na_4		9%
	Miravon B79R		1%
	Miravon B12DF		1%
	Mirataine JC.HA		6.5%
	Water	to	100%

The above formulations are optionally diluted up to 300 times in use. Miravon B79R and Miravon B12DF are biodegradable low foam non ionic surfactants and Mirataine JC.HA is a low foam amphoteric surfactant.

According to the present invention there is further provided a detergent composition comprising (a) N,N-bis(carboxymethyl)-glutamic acid or a salt thereof in an amount of up to 50% by weight, (b) (as alkali) an alkali metal carbonate, or bicarbonate or sesquicarbonate or cogranulates of an alkali metal carbonate and silicate, or mixtures thereof in an amount of up to 60% by weight, and (c) at least one low foam non-ionic surfactant in an amount of up to 10% by weight. This composition preferably comprises 20 to 45 weight % of (a), from 10 to 50 weight % of (b), and from 0.5 to 6 weight % of (c). Preferably (b) is a mixture of an alkali metal bicarbonate and cogranulates of an alkali metal carbonate and silicate in a bicarbonate/cogranulates ratio of 70/30 to 30/70 by weight.

Cogranulates of alkali metal carbonate and alkali metal silicate (SiO_2:M_2O = 1.5 to 3.5) preferably have a weight

ratio of carbonate/silicate of from 5/95 to 45/55, preferably from 15/85 to 35/65. They preferably contain water such that the water/dry silicate ratio is at least 33/100.

Examples of non-ionic surfactant (b) include polyoxyethylene and/or polyoxypropylene condensates of saturated or unsaturated, linear or branched chain C8-C18 aliphatic carboxylic acids containing about 5-50 ethylene oxide or propylene oxide units;

-polyoxyethylene and/or polyoxypropylene condensates of saturated or unsaturated, linear or branched chain C6-C24 aliphatic alcohols containing about 5-50 ethylene oxide or propylene oxide units;

-polyoxyethylene/polyoxypropylene block copolymers, where the polyoxyethylene part represents about 40% of the block copolymer, and having a molecular weight of about 2,000-30,000. Mixtures of any of the foregoing surfactants may optionally be used as well.

The composition according to the invention more preferably comprises from 0.5 to 6% by weight of (b).

The pH of the detergent compositions is preferably from 8 to 12, more preferably from 9 to 11. High performances are obtained even at a relatively low pH such as 9-9.5.

The detergent composition of the invention may optionally comprise other additives such as bleaching agents, high molecular mass polyoxyethylene glycols (e.g. from 0.05 to 0.5% of a polyethylene glycol having a molecular weight Mw of from 1,000,000 to 10,000,000, preferably from 3,000,000 to

7,000,000.), enzymes, loading charges, amphoteric surfactants, silicates, anti-foaming agents.

Examples of bleaching agents include halogen and peroxygen type bleaches.

Suitable halogen bleaches include di- or tri-chloro or bromo cyanuric acid and hydrosoluble salts thereof, particularly potassium and sodium dichloroisocyanurates. They are preferably used in a quantity such that they provide from 0.2 to 1.5% available chlorine

Other suitable halogen bleaches are lithium, sodium or calcium hypochlorite or hypobromite, preferably in a quantity of from 0.05 to 5% by weight, more preferably from 0.5 to 3%.

Oxygen bleaches include alkali and ammonium salts of perborates, percarbonates, persulfates, dipersulfates. They are preferably employed in a quantity of from 0.5 to 20% by weight, more preferably from 0.5 to 10% by weight. Oxygen bleaches are generally used in conjunction with an activator such as tetraacetyl ethylene diamine (TAED).

Examples of antifoaming agents include hydrocarbon oils, silicone oils and their mixtures with silica.

Suitable loading agents include inorganic salts apart from the alkali used as (b), such as alkali metal sulfates, preferably in a quantity up to 20% by weight.

As the amphoteric surfactants, alkyl mono and/or diamphoacetates, such as cocoamphoacetates, alkylamidopropylbetaines, such as cocamidopropylbetaine, alkylbetaines, or sodium alkyliminodipropionates, such as C8

or C12 iminodipropionates may be used, generally in a quantity up to 10% by weight.

Examples of silicates include sodium silicates having a molar ratio (SiO_2/Na_2O) of from about 1 to 3.3, preferably from 2 to about 3.3, can be present as anti-corrosion agents for metals, preferably in a quantity of up to 15% by weight (dry).

Enzymes may be present in a quantity of about 0.5 to 5% by weight.

Minor amounts of other addititves such as perfumes, dyes, colorants, anti-tarnish agents, soil suspending agents and hydrotropes, may be present.

The detergent compositions are generally suitable for use in automatic dishwashers.

The invention is illustrated by the following examples, wherein percentages are percentages in weight.

EXAMPLE 1

The ability of GLUDA to reduce stain caused by tea on white china cups was compared with that for NTA and other sequestrants.

In each test the following method was used. A stock of uniform, glazed, white china cups was stained with a quantity of strong Indian tea using the same brand, concentration and method for each test. The cups were then allowed to dry. An industrial dishwasher was cleaned and de-scaled (a suitable example of a single tank machine is the Hobart AN 12 E). The sequestrant to be tested was placed in the dishwashing

machine at the concentration determined below which was usually in the range of 1 to 6gl^{-1}. The machine was cycled through one wash cycle only (an initial rinse cycle was not used). The temperature and cycle time of the dishwashing machine was adjusted to be 60° to 65°C and 45 seconds for the wash cycle and 80 to 85°C and 7 to 10 seconds for the subsequent rinse cycle. The stained cups were placed in the machine in predetermined positions and the machine was run through one wash and one rinse cycle. The cups were then removed and allowed to dry naturally. This procedure was repeated five times. The cups were assessed visually for the area of tea stain removed, not the stain intensity, relative to a set of previously agreed standard cups. The following results were obtained:

TABLE 1

SEQUESTRANT	CONCENTRATION/PPM	PERCENTAGE TEA STAIN REMOVAL
GLUDA.Na_4	50	61.1
NTA.Na_3	50	77
STPP	100	57
TKPP	100	30
Na hexam	100	18.1

In the above table STPP refers to sodium tripolyphosphate, TKPP is tetrapotassium pyrophosphate and Na hexam is sodium hexametaphosphate.

The concentrations given in the above table are overbuilt concentrations. In other words they are the

concentrations of the sequestrant in excess of that required to sequester only the water hardness in the tap water supply, as determined by titration before every test. In the above table it is important to note that NTA and GLUDA were tested at product concentrations of only 50ppm greater than the water hardness, compared to concentrations of 100ppm greater than the water hardness for the remaining, less effective sequestrants. This clearly demonstrates the superior performance of GLUDA relative to alternative sequestrants.

EXAMPLE 2

Further tests were carried out to compare the ability of GLUDA to remove tea stains with known sequestrants.

For each sequestrant tested the methodology was as follows:

The following formulation was prepared for each sequestrant:

Sodium hydroxide	7.0%
Test sequestrant	11.4% active
Deionised water to	100%

Then 25 tea-bags were added to about 11 litres of boiling water, stirred and left to stew for about an hour. 36 cups were filled with the tea and put in an oven at 60°C for about four days until dry. The cups were then dipped in a two litre aqueous solution of 0.3% of the above formulation at 60°C for seven seconds and then removed. The pH of the aqueous solution was then adjusted to 11.8 (with NaOH or HCl)

and the absorption of the solution was then measured at 400nm on a Unicam SP600 Series 2 Spectrophotometer. The stain removed was then calculated from a calibration graph. The following results were obtained:

TABLE 2

Formulation	Average Percentage Clean
Tap Water only	20%
7% NaOH only	23%
NTA.Na_3	54%
GLUDA.Na_4	53%
EDTA.Na_4	49%
KTPP	37%
Na_3 Citrate	26%
TKPP	21%

In the above table the Average Percentage Clean values are average values for the percentage clean obtained from performing three tests, KTPP is potassium tripolyphosphate and TKPP is tetrapotassium pyrophosphate.

The calibration graph was determined by completely cleaning a cup in two litres of water at 60°C for a time sufficient to remove all the tea stain. The water used did not contain sequestrant. The pH of the solution was adjusted to pH 11.8 and the absorbance was measured to determine the

100% clean value. The solution was then successively diluted and the absorbance was measured at each concentration.

The above results show that GLUDA gives results comparable to NTA and is superior to other known sequestrants, particularly EDTA.

Example 3

Further tests were carried out on crockery, glasses and cutlery using egg, margarine, tea, powder based milk, semolina and spinach stains. These stains were applied for 30 minutes and then the stained items were placed in a dishwasher following the manufacturers instructions. They were left in the dishwasher for 15 to 20 hours with the door closed before the washing machine cycle was begun according to the manufacturers instructions. Four tests were carried out using the compositions described in the following Table 3. After washing points were awarded on the basis of the appearance of each item according to the following three categories:

Clean pieces - 2
Items with minor defects - 1
Unacceptable items - 0

The total of the points awarded divided by twice the total number of items gives the percentage clean listed in Table 4.

TABLE 3

	COMPARATIVE		INVENTION	
TEST	1	2	3	4
NABION 15	24.5	24.5	24.5	24.5
PLURAFAC LF403	2	2	2	2
POLYOX COAGULANT	0	0.2	0	0.2
CITRATE	35	35	0	0
PERBORATE MONO	10	10	10	10
TAED	2	2	2	2
ESPERASE	3	3	3	3
BICARBONATE	23.5	23.3	23.5	23.3
GLUDA.Na_4	0	0	35	35
TOTAL	100	100	100	100

TABLE 4

% CLEAN	1	2	3	4
SPINACH/EGGS	91	92	86.1	94.4
SEMOLINA	91.7	87.5	97.2	95.8
SHORTENING	90.5	95.3	92.9	90.5
MILK	100	98.6	98.6	98.6
TEA	32	20,8	100	100
AVERAGE PERFORMANCE	87.8	86.3	92.5	96.4

NOTE: the average performance takes into account the relative importance of the various soils

In this Example the following additives were used:

NABION 15 (trademark) which is cogranulates of sodium carbonate and sodium silicate with a SiO_2/Na_2O ratio of 2 comprising 55% by weight of carbonate, 29% by weight of silicate and 16% by weight of water;

PLURAFAC LF403 (trademark), a nonionic surfactant which is an aliphatic alcohol oxyethylene and oxypropylene;

POLYOX COAGULANT: (trademark) a polyoxyethylene glycol with a molecular mass of 5,000,000;

CITRATE: trisodium citrate dihydrate;

PERBORATE: mono sodium perborate mono hydrate;

TAED: tetraacetyl ethylene diamine (92% active matter);

ESPERASE: a protease type enzyme, ESPERASE 4-0T (trademark) was used which has an enzymatic activity of 4.0 KNPU/g;

BICARBONATE: sodium bicarbonate was used.

CLAIMS

1. A method of reducing stain which comprises applying to said stain N,N-bis(carboxymethyl)-glutamic acid or a salt thereof.

2. A method according to claim 1 wherein the salt is an alkali metal or ammonium salt.

3. A method according to claim 1 or 2 wherein the stain is a tannin-derived stain.

4. A method according to claim 1, 2 or 3 wherein the stain is present on glass, metal, china, enamel or plastic.

5. A method according to any one of the preceding claims wherein the acid or salt is applied in association with an alkali and/or a surfactant.

6. A method according to claim 5 wherein the alkali is an alkali metal carbonate, bicarbonate, or sesquicarbonate or a cogranulate of an alkali metal carbonate and silicate, or a mixture thereof and the surfactant is at least one low foam non-ionic surfactant.

7. A method according to claim 5 or 6 wherein the alkali is an alkali metal bicarbonate.

8. A method according to claim 5 or 6 wherein the alkali is a mixture of an alkali metal bicarbonate and a cogranulate of an alkali metal carbonate and silicate in a bicarbonate/cogranulate ratio of 70/30 to 30/70 by weight.

9. A method according to any one of the preceding claims which is carried out at a temperature of from 40 to 80°C.

10. A detergent composition comprising (a) N,N-bis(carboxymethyl)-glutamic acid or a salt thereof in an amount of up to 50% by weight, (b) an alkali metal carbonate, bicarbonate, or sesquicarbonate or a cogranulate of an alkali metal carbonate and silicate, or a mixture thereof, in an amount of up to 60% by weight, and (c) at least one low foam non-ionic surfactant in an amount of up to 10% by weight.

11. A composition according to claim 10 comprising from 20 to 45 weight % of (a), from 10 to 50 weight % of (b), and from 0.5 to 6 weight % of (c).

12. A composition according to claim 10 or 11 wherein (b) is an alkali metal bicarbonate.

13. A composition according to claim 10 or 11 wherein (b) is a mixture of an alkali metal bicarbonate and a cogranulate of an alkali metal carbonate and silicate in a bicarbonate/cogranulate ratio of 70/30 to 30/70 by weight.

14. A method according to any one of claims 1 to 9 which comprises applying a composition according to any one of claims 10 to 13.

INTERNATIONAL SEARCH REPORT

International application No.
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A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB, A, 1439518 (LES PRODUITS ORGANIQUES DU SANTERRE-ORSAN ET AL), 16 June 1976 (16.06.76), page 1, line 73 - line 75; page 3, line 46 - line 64, claims 8-13	1-14
A	US, A, 4822886 (STEPHEN F. DONOVAN), 18 April 1989 (18.04.89)	1-14

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Information on patent family members

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