



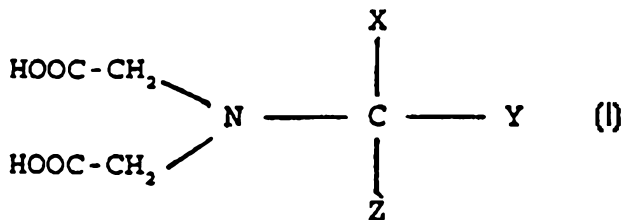
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(54) Title: ADDITIVE FOR A DETERGENT FORMULATION, DETERGENT FORMULATION COMPRISING SUCH AN ADDITIVE AND USE OF SAID FORMATION FOR CLEANING BOTTLES

(57) Abstract

An additive for a detergent formulation is described, comprising a sequestrant having formula (I), wherein: X = a COOH group or an alkyl chain comprising a COOH group; Y = an H atom; Z = an H atom, a C₁-C₃₀ alkyl group or a C₂-C₃₀ alkenyl group; and further comprising a nonionic surfactant and/or a hydrotrope. Preferably, said sequestrant is selected from the group of nitrilo triacetic acid (NTA), β-alanine diacetic acid (β-ADA), methyl glycine diacetic acid (MGDA), serine diacetic acid (SDA) and ethyl glycine diacetic acid (EGDA). Furthermore, the use of a detergent formulation containing said additive for cleaning bottles, in particular returnable plastic bottles, such as PET (polyethylene terephthalate) or polycarbonate bottles is described.



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ADDITIVE FOR A DETERGENT FORMULATION, DETERGENT FORMULATION
COMPRISING SUCH AN ADDITIVE AND USE
OF SAID FORMULATION FOR CLEANING BOTTLES

5 **Field of the invention**

The present invention relates to an additive for a
detergent formulation, a detergent formulation comprising
said additive, and to the use of said formulation for
10 cleaning bottles, in particular returnable plastic bottles
such as PET (polyethylene terephthalate) bottles,
polyethylene naphthalate (PEN), copolymers of PET/PEN
and/or returnable polycarbonate bottles.

15 **Background of the invention**

Many soft drinks are being sold in returnable bottles,
these bottles being made of either glass or plastic, in
particular PET or polycarbonate. In order to ensure product
quality it is very important that such bottles be
20 thoroughly cleaned and disinfected before being refilled
with the soft drink for example.

The use of glycine-N-N-diacetic acid (NTA) derivatives as
textile detergent builders is known from WO 94/29421.

An existing problem with such beverage bottles after they
25 have been emptied of their contents, is that fungal growth
can occur on any residue left behind.

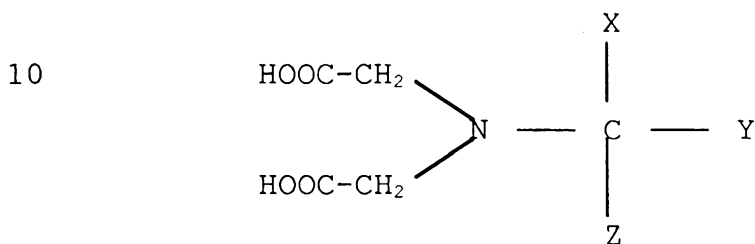
An objective of the present invention is to provide an
additive suitable for a detergent formulation, for
30 effectively removing mould from beverage bottles.

It was now surprisingly found that a combination of an
nonionic and/or a hydrotrope with a specific group of

sequestrants, as specified below, provides particularly good cleaning performance.

Definition of the invention

5 Consequently, according to a first embodiment of the present invention there is provided an additive for a detergent formulation, said additive comprising a sequestrant having the formula:



wherein:

15 X = a COOH group or an alkyl chain comprising a COOH group,

Y = an H atom

Z = an H atom or C₁-C₃₀, C₂-C₃₀ alkenyl group

and wherein the formulation further comprises one or more
20 non-ionic surfactants and/or one or more hydrotropes.

In an other aspect of the invention, there is provided a formulation comprising an additive according to the invention wherein the sequestrant is present in a wt% range
25 of 5-60, preferably 15-35, and the nonionic and/or hydrotrope in a wt% range of about 0.5-40, preferably 1-25. The formulation of the invention can additionally contain other common detergent components, including oxidizing agents, caustic, H₂O₂, hypochlorite, anti-foaming agents,
30 alkali sources, threshold agents to prevent deposition of hard water scale, structuring or emulsifying polymers, and bleaches to degrade or decolorise oxidisable stains.

According to a third aspect of the present invention, there is provided the use of the formulation of the invention as a detergent in cleaning bottles, particularly retunable
5 PET bottles, when the formulation comprises no hydrotrope, and particularly returnable polycarbonate bottles when the formulation comprises no nonionic surfactant.

According to a fourth aspect of the invention, there is
10 provided a process for washing bottles, comprising the steps of exposing bottles to a formulation or additive according to the invention, wherein the sequestrant, nonionic surfactant and/or hydrotrope and possibly any further standard detergent formulation components, such as
15 a defoamer, for example Dehypon LT104, are collectively or individually supplied into a bottle washing system

Detailed description of the invention

The C₁-C₃₀ alkyl group or the C₂-C₃₀ alkenyl group present in
20 the sequestrant according to the present invention preferably comprises one or more of the following:

- hydroxyl groups, preferably not more than five,
 - formyl groups,
 - C₁- to C₄-alkoxy groups,
 - 25 - phenoxy groups,
 - C₁-C₄ alkoxycarbonyl groups,
- and/or a phenylalkyl with 1-20 C atoms in the alkyl group, and can comprise one or more of the following:
- a five- or six-membered unsaturated or saturated
30 heterocyclic ring preferably with up to 3 hetero-atoms, most preferably selected from the group nitrogen, oxygen, and sulfur.

Furthermore the phenylalkyl group and/or the heterocyclic ring may comprise one or more of the following groups:

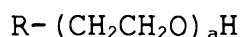
- a C₁-C₄ alkyl group,
- a hydroxyl group,
- 5 - a carboxyl group,
- a sulfo group,
- a phosphono group
- a sulphate ester
- a phosphate ester
- 10 - a C₁-C₄ alkoxy carbonyl group.

Such an additive yields good cleaning results.

The sequestrant is furthermore most preferably selected from the group consisting of Nitrilo triacetic acid (NTA),
15 β -Alanine diacetic acid (β -ADA), Methyl glycine diacetic acid (MGDA), Serine diacetic acid (SDA) and Ethyl glycine diacetic acid (EGDA), wherein MGDA and SDA yield particularly good cleaning results.

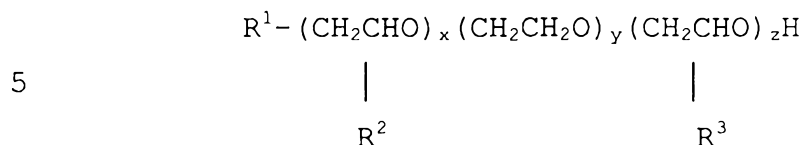
20 The non-ionic surfactant preferably comprises one or more of the following:

- polyoxyethylene or polyoxypropylene condensates of aliphatic carboxylic acids having about 8 to about 18 carbon atoms in an aliphatic chain and incorporating from
25 about 2 to about 50 ethylene oxide and/or propylene oxide units,
- polyoxyethylene or polyoxypropylene condensates of aliphatic alcohols having about from 6 to about 24 carbon atoms and incorporating from about 2 to about 50 ethylene
30 oxide and/or propylene oxide units,
- a compound of formula:



wherein R is a C₆-C₂₄ linear or branched alkyl group and a is an integer from 2 to 50,

- a compound of formula:

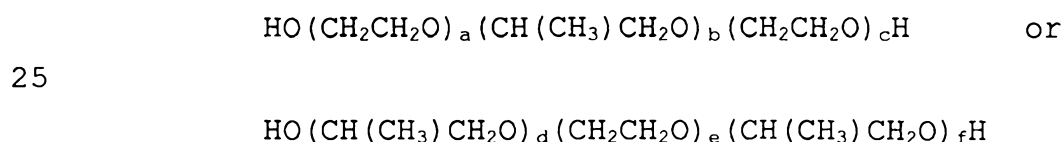


wherein R¹ is a linear alkyl group having an average of about 6 to about 18 carbon atoms, R² and R³ are each linear alkyl groups of about 1 to about 4 carbon atoms, x is an integer from 1 to 6, y is an integer from 4 to 20 and z is an integer from 4 to 25,

- polyoxyethylene or polyoxypropylene condensates of alkyl phenols having about 6 to 12 carbon atoms and incorporating from about 2 to 25 moles of ethylene oxide and/or propylene oxide,

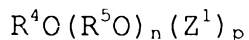
- polyoxyethylene derivatives of sorbitan mono-, di- and tri-fatty acid esters wherein the fatty acid component has between 12 and 24 carbon atoms and the polyethylene chains contain between about 4 and 30 ethylene oxide units,

- polyoxyethylene-polyoxypropylene block copolymers having the formula:



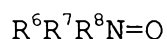
wherein a, b, c, d, e, and f are integers from 1 to 350 reflecting the respective polyethylene oxide and polypropylene oxide blocks of said polymer, wherein the polyoxyethylene component of the block polymer is at least about 10% of the block polymer,

- alkyl glycosides having formula:



wherein R^4 is a monovalent organic radical, for example a monovalent saturated aliphatic, unsaturated aliphatic or aromatic radical such as alkyl, hydroxyalkyl, alkenyl, hydroxyalkenyl, aryl, alkylaryl, hydroxyalkylaryl, arylalkyl, alkenylaryl, arylalkenyl and the like having from about 6 to about 30 carbon atoms, wherein R^5 is a divalent hydrocarbon radical containing from 2 to about 4 carbon atoms such as ethylene, propylene or butylene (most preferably the unit $(R^5O)_n$ represents repeating units of ethylene oxide, propylene oxide and/or random or block combinations thereof); n is an integer from 0 to about 12; Z^1 represents a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms (most preferably a glucose unit); and p is a number from 0.5 to about 10,

- amine oxides having formula:



20

wherein R^6 , R^7 and R^8 are saturated aliphatic groups or substituted saturated aliphatic groups, wherein preferably R^6 is an alkyl chain of about 10 to 20 carbon atoms and R^7 and R^8 are methyl or ethyl groups or both R^6 and R^7 are alkyl chains of about 6 to 14 carbon atoms and R^8 is a methyl or ethyl group.

An additive with such a non-ionic surfactant in combination with the above sequestrant yielded good cleaning results.

30 The non-ionic surfactant preferably has a hydrophilic-lipophilic balance (HLB) of about 20 or less, preferably about 10-20 and most preferably from about 14-20.

Non-ionic surfactants can be broadly defined as surface active compounds with one or more uncharged hydrophilic substituents. A major class of non-ionic surfactants are those compounds produced by the condensation of alkylene
5 oxide groups with an organic hydrophobic material which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having a desired
10 degree of balance between hydrophilic and hydrophobic elements.

The HLB value represents the hydrophilic-lipophilic balance of the molecule. The lower the HLB value the more hydrophobic the material is, and vice versa. For simple
15 alcohol ethoxylates, the HLB value may be calculated from

$$\text{HLB} = E/5 \quad (\text{I})$$

where E is the weight percentage of ethylene oxide in the molecule.

The simple straight chain alcohol ethoxylates are usually
20 well defined materials. The inventors have been able to find a relationship between HLB-value (as calculated using equation (I)) and cleaning performance (as measured by mould removal). The straight chain alcohol ethoxylates according to the present invention possess an HLB-value
25 from about 12 to 20.

For fatty esters of polyalcohols and their alkoxyates, the HLB value is given by:

$$\text{HLB} = 20 \times (1-S/A) \quad (\text{II})$$

where

30 S = saponification number of the ester, ie. the number of mg of potassium hydroxide needed to neutralise the free and bonded acid in 1 g of the substance;

A = acid value of the esterified fatty acid, ie. the number of mg of potassium hydroxide to neutralise the free acid in 1 g of the substance.

The inventors have found that an additive with such a non-ionic surfactant, exhibiting the above HLB' values, yields particularly good cleaning results for PET bottles.

The additive most preferably comprise a non-ionic surfactant selected from the group consisting essentially of Synperonic A7, Synperonic L11, Lutensol A20, Lutensol AO30, Lutensol AT80, Neodol 45-4E, Dehypon G2084, Poly-Tergent SLF18B45, Surfynol 504 and Plurafac LF231, wherein the non-ionic surfactant preferably has a cleaning score of about 3 or above, preferably about 4 or above and most preferably about 5 or above.

15

Cleaning score

The cleaning results are obtained by measuring the absorbance at λ_{\max} between 662.0 en 664.0 nm, which is a measure for the amount of methylene blue in solution. To compare the results of different batches of mould soiled strips, an internal standard was measured for every new batch of strips. This internal standard was a product containing 63.5% Trilon ES9644 (35% MGDA, ex. BASF), 7% Dissolvine NG (ex. Akzo Nobel), 1% Bayhibit AM (ex. Bayer), 4% Triton H-66 (ex. Union Carbide), 0.8% Sodium Cumene Sulfonate (40%, ex Hüls), 2% Dehypon LT104 (ex. Henkel).

The difference in cleaning performance between the internal standard and another observation is significant when the calculated difference is larger than the confidence intervals around the measured averages. This can be transformed into a formula where every significant difference will result in an increase or decrease of the

cleaning score, compared to the internal standard. The cleaning score can be calculated according to equation (III).

$$\text{Cleaning score} = \frac{(X_i - X_s)}{\sigma \times T_{(\alpha=0.1;v)}} + V_i$$

Where:

- 10 X_i = Measured absorbance of the internal standard
(corrected for the blanc; i.e. measured
absorbance of an unsoiled strip);
- X_s = Measured absorbance of the sample (corrected for
the blanc; i.e. measured absorbance of an
15 unsoiled strip);
- σ = Average deviation of the measurement. Following
the procedure described above, the average
deviation was found to be 0.18;
- $T_{(\alpha=0.1;v)}$ = Students value for a two tail test at 80%
20 confidence level with v degrees of freedom;
- V_i = Value of internal standard (equals 4 for the
internal standard described above).

This definition of the cleaning score leads in this study
25 to a range from 0 to 11 depending on σ , in which the higher
the value the better the mould removal performance.
Table 1 shows a selection of preferred non-ionics.

Table 1 Straight chain primary alkanol ethoxylates: H-
 $(CH_2)_n - (OCH_2CH_2)_m - OH$

n m	10	12	14	16/18(avg:17)
3	aq: not soluble HLB: 9.1 (theor) Dehydol D3 Dobanol 91-2.5 Ethylan CD 103 Ethylan CD 913 Genapol Z030X Synperonic 91-2.5	aq: not soluble HLB: 8.3 (theor) Dobanol 23-3 Elfapur LT30SL Ethylan CD123 Genapol LA-030 Remcopal 121 Rolfor LA 3 Synperonic L3 Volpo L3 Special	aq: not soluble HLB: 7.6 (theor) Dobanol 25-3 Elfapur LP 25 S Elfapur LP 25 SL Ethylan D253 Renex 703 Synperonic A3	aq: not soluble HLB: 6.8 (theor) Atlas G-70140 Volpo N3
7	cl.pnt HLB: 13.2(theor) Ethylan CD 107 Ethylan CD 916 Synperonic 91-7	cl.pnt: HLB: 12.5 (theor) Ethylan CD 127 Dobanol 23-6.5 Elfapur LT65SLN Genapol LA-070 Genapol LA-079 Synperonic L7 Volpo T7	cl.pnt: 48°C HLB: 11.8 (theor) Dobanol 25-7 Dobanol 45-7 Renex 711 Synperonic A7	cl.pnt: HLB: 10.9 (theor) Eumulgin WM7 Rolfor CO 7
11	cl.pt approx 95°C HLB: 15.1 (theor)	cl.pnt: HLB: 14.4 (theor) Sellig LA11 100M8 Synperonic L11	cl.pnt > 100°C (5% aq) HLB: 13.9 (theor) Dobanol 45-11 Elfapur LP110SLN Ethylan CD 4511 Renex 720 Synperonic A11	cl.pnt > 100°C HLB: 13.1(theor) Britex CS 110 Genapol T-110 Lutensol AT11 Marlipal 1618/11 Rolfor HT 11 Simulsol 56 Synperonic TAE11
20	cl.pnt > 100°C HLB: 17.0 (theor) Synperonic 91-20	cl.pnt >100°C HLB: 16.5 Sellig LA11 100 Sellig LA11 50	cl.pnt >100°C (5% aq) HLB: 16.1 (theor) Renex 720 Synperonic A20	cl.pnt 90°C (1% in 5% NaCl) HLB 15.5 (theor) Atlas G-4938 Brij 58 (C16) Brij 78 (C18) Britex S 200 Ethylan CS20 Genapol T-200 Sellig SU 25 100 Volpo CS 20

There are many more primary alkanol ethoxylates
e.g. $n=10, m=4$; $n=10, m=5$; $n=10, m=6$; $n=10, m=8$...
 $n=11, m=3, 4, 5, 6, 7, 8, 9, 10, 11, \dots, 80$
 $n=20, m=3, \dots, 80$

5

The hydrotrope can comprise a hydrophilic-substituted aromatic hydrocarbon, and/or the alkali metal salt thereof, optionally having an alkyl or aryl side chain and preferably comprises the sodium salt of a sulfonated aromatic hydrocarbon and is most preferably selected from the group consisting essentially of: sodium benzoate, sodium 3-hydroxy-2-naphtoate, sodium xylene sulphonate, phosphate esters, sodium decyl diphenyl oxide, sodium dimethyl naphthalene sulphonate, sodium salts of linear alkyl benzene sulphonate, having from about C_8 to C_{12} in the alkyl portion, as well as mixtures thereof, wherein the hydrotrope is most preferably Triton H66 also being a solubilizing agent. An additive comprising this hydrotrope yielded particularly good cleaning results.

20 An hydrotrope is preferable to a non-ionic surfactant when cleaning polycarbonate bottles, since non-ionic surfactants are thought to damage these.

The invention will now be described by way of the following examples and results, referring to figures 1-2 and the tables.

Experimental

30 Standard soiling

The standard soiling was made by mixing Tomato juice and a solution of *Aspergillus niger*.

Preparation of standard soilingMaterials

- Aspergillus niger ATC 6275
- Czapek Dox agar (code CM97 ex Oxoid)
- 5 - D-Glucose monohydrate
- 10% Lactic acid solution SR 021 K
- Bacto Pepton L37 (ex Oxoid)
- Sodium chloride

10 Procedures

Aspergillus niger was grown on 2 plates containing Czapek Dox agar with 2% glucose and 10 ml lactic acid (10%) per litre agar. The mould was grown for 5 days at 25°C. Subsequently, the moulds were taken from the plate
15 with two times 9 ml of a sterile solution containing 1 g/l Pepton and 8.5 g/l NaCl per plate. The mould solution was added (=18 ml) to 300 gr of tomato juice (Zontomaatje ex Riedel) and homogenised.

20 **Preparation of ref-PET strips**Materials

- New ref-PET bottles
- Sodium hydroxide

25 Procedure

The bottom and the neck were cut from a 1.5 ltr ref-PET bottle. The middle of the bottle was used to cut pieces of 70 x 25 mm from the length direction of the bottle. The strips were then treated with 1.5% caustic of
30 59°C for 15 minutes. The strips were rinsed with water to remove the caustic and the strips were dried.

Applying the soiling to the strips

Strips were taken and submerged for 75% vertically in the standard soiling (tomato juice with *Aspergillus niger*). The strips were then taken out of the solution and held 5-10 sec. vertically. In this way the excess soiling can drip off the strips. The strips were placed with the bold side up in a petri dish and put together with other strips in a plastic bag in an incubator at 25°C. After 5 days the plastic bag was removed and the strips, in closed petri-dishes, were restored in the incubator for 2 more days. After this the strips were ready for a quality check before use.

Quality check and cleaning procedure

The standard soiled strips were taken and washed for 10 minutes in 1.5% caustic to check the quality of the soiling.

Materials

- Beaker broad model 2000 ml
- Magnetic stirrer (25 mm X 5 mm triangle shaped)
- Temperature and rotation controlled stirrer
- Stripholder
- Chronograph

25

Chemicals

- Methylene blue solution (0.10%), TNO procedure COP for ref-PET, V18 method A
- Acetic acid (1.00%)
- Caustic solution (1.50%) + additive (0.2%)

Conditioning procedure

- Take the petri dishes with the standard soiled strips out of the incubator.
- Take 4 soiled strips from the petri dishes and 2
5 unsoiled and place them in the strip holder.
- Heat a 1000 ml 1.50% caustic solution up to 59°C± 1°C and set the stirring speed to 600 rpm. Place the strip holder with the 4 soiled ref-PET strips and 2
10 clean ref-PET strips for exactly 10.0 minutes in the caustic solution.
- Rinse the strips (3 times 5 sec) in 1000 ml of demineralised water.
- Wait 1 minute.
- After this the strips are dyed for 20 seconds in a
15 0.10% methylene blue solution.
- Wait 1 minute.
- The strips are again rinsed for 3 times 5 sec. in 1000 ml of fresh demineralised water.
- Wait 1 minute.
- 20 - Put the 4 dyed strips in a closable can with 25 g of 1.00% acetic acid. Repeat this for the two blank strips. Shake the dye from the strips.
- Filtrate 10 ml of the solution (within 24 hrs) over a
25 0.45 µm filter and discard the first 5 ml. Put the other 5 ml in a 1 cm cuvet.
- Measure the absorption at λ_{\max} (between 662.0 and 664.0 nm) against 1.00 % acetic acid.
- Carry out the above steps with another 3 x 6 strips in the same cleaning solution.

Investigation of additives and formulations according to the present invention

To assess the mould removal performance of various bottlewashing additives, PET strips standardly
5 soiled with a tomato juice contaminated with a common mould species (*Aspergillus niger*) were used. After conditioning, as above, these strips were soaked in an alkaline medium (1.5% caustic in 8.5 DH water) for 10 minutes. The method to quantify the soil residue, as detailed above was used to
10 determining the cleaning score for the various additives and formulations, results of which are shown in the following tables.

Table 2

Sequestrant (Trade or development name)	Supplier	Level in formulation (w%)	Cleaning Score
EDTA, tetra sodium salt (Trilon E39, 39% solution)	BASF	80.0	3
Potassium tripolyphosphate (50% solution)	Budenheim	27.2	1
MGDA, tri sodium salt (Trilon ES9964, 35% solution)	BASF	63.5	4
SDA, tri sodium salt	BASF	24.2	4

15

The results shown in table 2 were obtained using formulations that, in addition to the sequestrant listed,

contained sodium gluconate (7%), Bayhibit AM (1% of a 50% solution), Triton H66 (4% of a 50% solution), sodium cumene sulfonate (0.8% of a 40% solution), and Dehypon LT104 (2%). These formulations were dosed at a 0.2% level in water of 5 8.5DH hardness, containing 1.5% NaOH. The mould soiled strips were soaked in these solutions for 10 min at 59°C.

The results shown in tables 3-8 were obtained using formulations that, in addition to the surfactant, contained Trilon ES9644 (63.5% of a 35% solution), sodium 10 gluconate (7%), Bayhibit AM (1% of a 50% solution), Triton H66 (4% of a 50% solution), and sodium cumene sulfonate (0.8% of a 40% solution). These formulations were dosed at a 0.2% level in water of 8.5DH hardness, containing 1.5% NaOH. The mould soiled strips were soaked in these 15 solutions for 10 min at 59°C (see above).

The formulations in table 3 exhibited good cleaning scores.

Table 3

Trade name (Nonionic surfactant)	Supplier	Alkyl chain	EO	HLB calculated using (I)	Cleaning Score
Synperonic A7	ICI	C10	7	11.8	4
Synperonic L11	ICI	C12-14	11	14	5
Lutensol A20	BASF	C13-15	20	16.2	5
Lutensol AO30	BASF	C13-15	30	17	5
Lutensol AT80	BASF	C13-15	80	18.5	6

On the other hand, straight chain alcohol ethoxylates with lower HLB-values exhibited a lesser cleaning score, as shown by table 4:

5 Table 4

Trade name (Nonionic surfactant)	Supplier	Alkyl chain	EO	HLB calculated using (I)	Cleaning Score
Neodol 45-4E	Shell	C14-C15	4	8.9	1

Also some capped non-ionic surfactants showed good cleaning scores, as shown by table 5:

10

Table 5

Trade name (Nonionic surfactant)	Supplier	Alkyl chain (s / b)	EO	PO	Cap	Cleaning Score
Dehypon G2084	Henkel	C16-20 (b)	8	-	Butyl	4
Dehypon LT104	Henkel	C12-C18 (s)	10	-	Butyl	4
Poly-Tergent SLF18B45	Olin	C20-C30 (s)	20	1	Octyl	5

Additional nonionics that showed good performance are shown in table 6:

Table 6

Trade name (Nonionic surfactant)	Supplier	Technical information by supplier	Cleaning Score
Surfynol 504	Air Products	Ethoxylated tetramethyldecynediol	4
AG 6202	Akzo-Nobel	Low-foaming alkylpolyglucoside with C12 alkyl chain	4
Plurafac LF231	BASF	Alkali-stable, low-foaming fatty alcohol alkoxylate	4

Many nonionic surfactants however did not exhibit good cleaning scores in combination with sequestrant types, as shown by table 7:

Table 7

Trade name (Nonionic surfactant)	Supplier	Alkyl chain	EO	PO	Cleaning Score
Dehypon LS24	Henkel	C12-14	2	4	2
Dehypon LS36	Henkel	C12-14	3	6	1
Dehypon LS45	Henkel	C12-14	4	5	2
Dehypon LS54	Henkel	C12-14	5	4	2
Dynol 604	Air Products	ethoxylated acetylenic diols			2

The following formulations were investigated according to the cleaning procedure and yielded the following results, Table 8:

Table 8

Component	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %	wt %
Trilon ES9644 (35% MGDA) ex. BASF	63.5		63.5	63.5	63.5	63.5	63.5	63.5	63.5	63.5	63.5	63.5
SDA (ex. BASF)		24.2										
Dissolvine NG (Na gluconate) (Appendix 2) ex AkzoNobel	7	7	7			7	7	7	7	7	7	7
Bayhibit AM (Appendix 3) ex. Bayer	1	1	1	1	1	1	1	1	1	1	1	1
Triton H-66 (50%) (Appendix 5) ex. Union Carbide	4	4	4			4	4	4	4	4	4	4
Sodium Cumene Sulfonate (40%) (Appendix 4) ex. Huls	0.8	0.8	0.8			0.8	0.8	0.8	0.8	0.8	0.8	0.8
Dehypon LT104 (Appendix 6) ex. Henkel	2	2	10	10								
Poly-Tergent SLF18B45 ex. Olin					2							
AG 6202 ex AkzoNobel						2						
Synperonic L11 ex. ICI								2				
Lutensol A20 ex. BASF										2		
Lutensol AO30 ex. BASF											2	
Keltrol F (Appendix 1) ex. Kelco				0.5								
Water	rest	rest	rest	rest	rest	rest	rest	rest	rest	rest	rest	rest
Cleaning score	4	4	4	4	4	5	4	5	4	5	5	5

The cleaning score (as given in the last row of this table) is a measure for the cleaning performance of these formulations. The higher the score the better the performance.

5

Functionality of components:

- Dissolvine NG (Na gluconate) - transition metal ion sequestrant
- Bayhibit AM - threshold agent, prevents deposition of inorganic scales
- Triton H-66 - hydrotrope or solubilising agent
- Sodium Cumene Sulfonate - hydrotrope or solubilising agent
- Keltrol F - structurant that stabilises nonionic in water emulsions (suspends-non-ionic)

10

15

20 (See Appendices 1-6 for product specifications)

For reference purposes, the mould removal performance of a few current commercial formulations were tested under the same conditions. The results are shown in table 9.

25

Table 9

Detergent trade name	Supplier	Cleaning score
Stabilon Flussig	Henkel-Ecolab	1
SU860	DiverseyLever	2

Investigation of mould removal from PET bottles

Procedure for pre-washing PET bottles

New 1.5 litre PET bottles were washed/rinsed
5 according to the following procedure:

- 30 min soaking in 1.5% NaOH at 58-60°C; empty the bottles
- 5 min delay
- 10 - 15 min rinsing / soaking in fresh tapwater (rinse 1)
- 5 min delay
- 15 min rinsing / soaking in fresh tapwater (rinse 2)
- 5 min delay
- 15 min rinsing / soaking in fresh tapwater (rinse 3)
- 15 - store bottles bottom-up in crates for 1 - 2 hours
- post - rinse with 0.5 litre demineralised water per bottle
- storage of the bottles bottom-up in crates for 30 - 60 min
- 20 - wipe outside of the bottles until dry with absorbing paper
- store the bottles, in upright position and allow the remaining bit of water to evaporate (at least 24 hours) before further use of the bottle.

25

Procedure for mould-soiling of pre-washed PET bottles

The pre-washed PET bottles were "mould-soiled" as follows:

- grow *Aspergillus niger* on 2 plates containing Czapek
30 Dox Agar with 2% glucose and 10 ml lactic acid (10%) per litre agar.
- grow the mould for at least 7 days at 25°C.

- take the moulds from the plate with 9 ml of a sterile solution containing 1 g/L Peptone and 8.5 g/L NaCl per plate.
- add twice 9 ml of the mould suspension to 300 g of
5 tomato juice (Zontomaatje ex Riedel, the Netherlands) and homogenate with glass pearls.

Application of this soil onto the inside surface of the (1.5 litre, transparent colourless) pre-washed ref-PET bottle was carried out within 6 hours after preparation
10 of the soil. 5 g of soil was used to cover the inner wall/bottom up to 1/3 of the height of each bottle.

The soiled bottles stoppered by a wad of cotton wool were stored for 6 weeks at room temperature in order to allow the fungi to grow/sporulate and to allow the
15 tomato juice to dry.

Test procedure for cleaning PET bottles

The performance of a series of (n) cleaning solutions, 70 litres, was compared by taking n sets of
20 m standard mould-soiled bottles.

A method, mimicking the conditions and mechanical action in an industrial bottlewasher was used. Each detergent solution was used to clean several sets of (maximum 4) bottles:

- 25 t = 0 min: immerse (soak) 4 bottles in (70 l) detergent solution (58-60°C).
- t = 3 min: take bottles out of solution and empty them
- t = 4 min: immerse bottles in first (fresh) water bath
- t = 6 min: take bottles out of first water bath and
30 empty them
- t = 7 min: immerse bottles in second (fresh) water bath

t = 9 min: take bottles out of second water bath and empty them

After this cleaning procedure, the bottles were stored, overnight, bottom-up in crates for further evaluation.

Per cleaning solution, the n (e.g. 12) cleaned bottles were coded according to their ranking (1 = cleanest, n = dirtiest. The result is m (e.g. 4) crates containing n (e.g. 12) ranked bottles each.

Table 10

1-1	1-2	1-3	= = etc = = >	4-1	4-2	4-3
1-4	1-5	1-6		4-4	4-5	4-6
1-7	1-8	1-9		4-7	4-8	4-9
1-10	1-11	1-12	= = etc = = >	4-10	4-11	4-12

15 Procedure for evaluation of the cleaning result

After cleaning (procedure see:), the (nxm) bottles (coded 1-1, 1-2, ..1-m, 2-1, ..., n-m) were ranked 1, 2, ..., nxm-1, nxm (1: best cleaning result; nxm (e.g.48): worst cleaning result).

The sum of all rankings is: S (= e.g.
1+2+.....+47+48 = 1176).

Per cleaning solution: T = sum (total) of
rankings

5 The best possible result for T is: B (e.g.
1+2+...+11+12 = 78)

The worst possible result for T is: W(e.g.
37+38+...+47+48 = 510)

10 In some cases, the average ranking was taken such
that "S" remained constant (e.g. 2x13.5 instead of 13 and
14, or 3x46 instead of 45, 46, and 47).

The relative cleaning performance, P, is given
as:

15

$$P = 10 \times (W - T) / (W - B)$$

(10 = best relative performance, 0 = worst relative
performance)

20 Table 11 below shows the formulation tested,
whilst figure 1 shows the relative performance of a number
of formulations according to the present invention.

Table 11

Test no.	1	3	4					
	No adjunct	MGDA/4E	MGDA/11E	BEST POSSIBLE				WORST POSSIBLE
Adjunct composition (%m/m)					RANKING			
				Test no.	1	2	3	
					No adju	MGD	MGDA/11E	
MGDA-Na3 (35%)		63.50	63.50					
Na-Gluconate		7.00	7.00	1	8	2	1	19
Bayhibit AM (50%)		1.00	1.00	2	10	7	3	20
Triton HG6 (50%)		4.00	4.00	3	16	13	4	21
SCS (40%)		0.80	0.80	4	18	14	5	22
Nedol 45-4E		2.00		5	22	15	6	23
Synperonic L11			2.00	6	24	17	9	24
				7	25	19	11	25
				8	26	21	12	26
%NaOH (pH 8.2)	1.5	1.5	1.5	9	27	23	20	27
% adjunct		0.2	0.2					
pH (roomtemp)	>13	>13	>13					
				45	176	131	71	207
				5	1.91	4.69	8.40	378

Procedure for mould-soiling of pre-washed PC bottles

Grow *Aspergillus niger* (ATCC 16404) on 2 plates containing Malt Extract Agar. Grow the mould for 5 days at 25°C . Take the moulds from the plate with 10 ml of milk per plate. Add the 2x10 ml mould contaminated milk to 200 g yoghurt/milk mixture (150 g yoghurt Campina "halfvol" and 50 g milk Campina "halfvol") and homogenate with glass pearls.

Application of this soil onto the inside surface of the (1.0 litre, transparent colourless) pre-washed PC bottle should occur within 6 hours after preparation of the soil. An amount of 10 g mould contaminated milk/yoghurt is used to cover the inner wall/bottom up to 1/2 of the height of the bottle. The bottles are, loosely, closed by means of a wad of cotton wool.

The soiled bottles are incubated for at least 6 weeks at 30°C in order to allow the fungi to grow/sporulate and to allow the milk/yoghurt to dry.

20 Cleaning procedure for mould-soiled PC bottles

The performance of a series of (n) cleaning solutions, 70 litres, is compared by taking n sets of m standard mould-soiled bottles. Soiling of the bottles must have taken place at least 6 weeks before, according to the procedure for mould-soiling of pre-washed PC bottles.

The cleaning procedure for polycarbonate (PC) bottles comprises a combination of soaking in a 70 litre bath filled with detergent solution during 10 min at 79-81°C, and spraying with the same cleaning solution into the bottle according to the spraying program given below.

1. 15 sec spraying, followed by 10 sec delay

2. 15 sec spraying, followed by 10 sec delay
3. 15 sec spraying, followed by 10 sec delay
4. 15 sec spraying, followed by 10 sec delay
5. 15 sec spraying

5

For this detergent rinse, the bottles (one by one) are placed, bottom-up, vertically over a nozzle. Through this nozzle, a jet of cleaning liquid is directed exactly to the middle of the bottom of the bottle. The flow is adjusted to 1750-2000 ml per five pulses of 15 seconds each. Nozzle: NF2000 (BSP BETE), supplied by Spraybest, angle=)°, max flow = 20 l/min
Total contact time = 5 x 15 s = 75 s = 1 min 15 s
Flow rate = 1.4-1.6 l/min

15 After the cleaning procedure, the bottles are rinsed by immersing them in cold tapwater directly followed by emptying. The bottles are stored, bottom-up in crates for further evaluation.

Per cleaning solution, the n (e.g. 12) cleaned bottles are coded according to their ranking in the same way as described in the procedure for PET bottles.

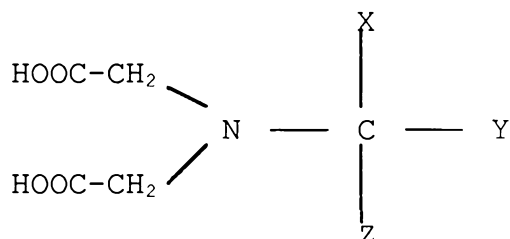
Table 12 below shows the formulation tested, whilst figure 2 shows the results thereof.

Table 12 Cleaning of milk-mould soiled polycarbonate (PC) bottles

	1	2	3	4		1	2	3	4	
	BW 68	BW 62	BW 65	BW 69	BEST POSSIBLE	RANKING				WORST POSSIBLE
MGDA-Na3 (35%) Bayhibit AM (50%) Triton H66(50%)	1.00	63.50 1.00	63.50 1.00 4.00	1.00 4.00	1	7	5	1	4	13
					2	12	6	2	11	14
					3	14.5	8	3	13	15
					4	16	9.5	9.5	14.5	16
					10	49.5	28.5	15.5	42.5	58
					5	1.77	6.15	8.85	3.23	136
					5					136

CLAIMS

1. Additive for a detergent formulation, said additive comprising a sequestrant having the formula:



wherein:

X = a COOH group or an alkyl chain comprising a COOH group,

Y = an H atom

Z = an H atom, a C₁-C₃₀ alkyl group or a C₂-C₃₀ alkenyl group,

and wherein the formulation further comprises a non-ionic surfactant and/or a hydrotrope.

2. Additive according to claim 1, wherein the C₁-C₃₀ alkyl group, or the C₂-C₃₀ alkenyl group, comprises one or more of the following:

- hydroxyl groups, preferably not more than five,
- formyl groups,
- C₁- to C₄-alkoxy groups,
- phenoxy groups,
- C₁-C₄ alkoxycarbonyl groups.

3. Additive according to claims 1 or 2, wherein the C₁-C₃₀ alkyl group, or the C₂-C₃₀ alkenyl group, comprises one or more of the following:

- a phenylalkyl, with 1 to 20 C-atoms in the alkyl group.

4. Additive according to any of the previous claims, wherein the C₁-C₃₀ alkyl group, or the C₂-C₃₀ alkenyl group, comprises one or more of the following:

- a five- or six-membered unsaturated or saturated heterocyclic ring preferably with up to 3 hetero-atoms, most preferably selected from the group nitrogen, oxygen, and sulfur.

5. Additive according to claims 3 or 4 wherein the phenyl-group and/or the heterocyclic ring comprise one or more of the following groups:

- a C₁-C₄ alkyl group,
- a hydroxyl group,
- a carboxyl group,
- a sulfo group,
- a phosphono group
- a sulphate ester
- a phosphate ester
- a C₁-C₄ alkoxy carbonyl group.

6. Additive according to any of the previous claims, wherein the sequestrant is selected from the group consisting of, Nitrilo triacetic acid (NTA), β -Alanine diacetic acid (β -ADA), Methyl glycine diacetic acid (MGDA), Serine diacetic acid (SDA) and Ethyl glycine diacetic acid (EGDA).

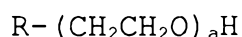
7. Additive according to any of the previous claims, wherein the non-ionic surfactant comprises one or more of the following:

- polyoxyethylene or polyoxypropylene condensates of aliphatic carboxylic acids having about 8 to about 18

carbon atoms in an aliphatic chain and incorporating from about 2 to about 50 ethylene oxide and/or propylene oxide units,

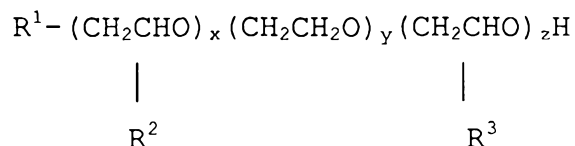
- polyoxyethylene or polyoxypropylene condensates of aliphatic alcohols having about from 6 to about 24 carbon atoms and incorporating from about 2 to about 50 ethylene oxide and/or propylene oxide units,

- a compound of formula:



wherein R is a C₆-C₂₄ linear or branched alkyl group and a is an integer from 2 to 50,

- a compound of formula:



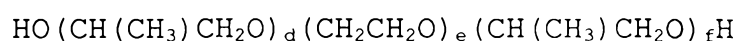
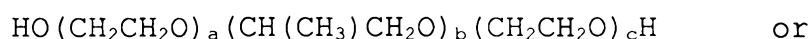
wherein R¹ is a linear alkyl group having an average of about 6 to about 18 carbon atoms, R² and R³ are each linear alkyl groups of about 1 to about 4 carbon atoms, x is an integer from 1 to 6, y is an integer from 4 to 20 and z is an integer from 4 to 25,

- polyoxyethylene or polyoxypropylene condensates of alkyl phenols having about 6 to 12 carbon atoms and incorporating from about 2 to 25 moles of ethylene oxide and/or propylene oxide,

- polyoxyethylene derivatives of sorbitan mono-, di- and tri-fatty acid esters wherein the fatty acid component has between 12 and 24 carbon atoms and the

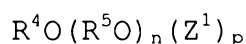
polyethylene chains contain between about 4 and 30 ethylene oxide units,

- polyoxyethylene-polyoxypropylene block copolymers having the formula:



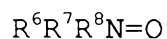
wherein a, b, c, d, e, and f are integers from 1 to 350 reflecting the respective polyethylene oxide and polypropylene oxide blocks of said polymer, wherein the polyoxyethylene component of the block polymer is at least about 10% of the block polymer,

- alkyl glycosides having formula:



wherein R^4 is a monovalent organic radical, for example a monovalent saturated aliphatic, unsaturated aliphatic or aromatic radical such as alkyl, hydroxyalkyl, alkenyl, hydroxyalkenyl, aryl, alkylaryl, hydroxyalkylaryl, arylalkyl, alkenylaryl, arylalkenyl and the like having from about 6 to about 30 carbon atoms, wherein R^5 is a divalent hydrocarbon radical containing from 2 to about 4 carbon atoms such as ethylene, propylene or butylene (most preferably the unit $(\text{R}^5\text{O})_n$ represents repeating units of ethylene oxide, propylene oxide and/or random or block combinations thereof); n is an integer from 0 to about 12; Z^1 represents a moiety derived from a reducing saccharide containing 5 or 6 carbon atoms (most preferably a glucose unit); and p is a number from 0.5 to about 10,

- amine oxides having formula:



wherein R^6 , R^7 , and R^8 are saturated aliphatic groups or substituted saturated aliphatic groups, wherein preferably R^5 is an alkyl chain of about 10 to 20 carbon atoms and R^7 and R^8 are methyl or ethyl groups or both R^6 and R^7 are alkyl chains of about 6 to 14 carbon atoms and R^8 is a methyl or ethyl group.

8. Additive according to any of the previous claims, wherein the non-ionic surfactant has a hydrophylic-lipophylic balance of between about 5-20, preferably about 10-20 and most preferably from about 14-20.

9. Additive according to any of the previous claims, wherein the non-ionic surfactants are selected from the group consisting essentially of Synperonic A7, Synperonic L11, Lutensol A20, Lutensol A030, Lutensol AT80, Neodol 45-4E, Dehypon G2084, Poly-Tergent SLF18B45, Surfynol 504 and Plurafac LF231 and or any chemically similar nonionics.

10. Additive according to any of the previous claims, wherein the non-ionic surfactant has a cleaning score of about 3 or above, preferably about 4 or above and most preferably about 5 or above.

11. Additive according to any of the previous claims wherein the hydrotrope comprises a hydrophilic-substituted

aromatic hydrocarbon, and/or the alkali metal salt thereof, optionally having an alkyl or aryl side chain.

12. Additive according to claim 11 wherein the hydrotrope comprises the acid or water soluble form of a sulphonated or phosphonated aromatic hydrocarbon or a sulphate or phosphate ester of an aromatic hydrocarbon.

13. Additive according to claim 12 wherein the hydrotrope is selected from the group consisting essentially of:

- sodium benzoate, sodium 3-hydroxy-2-naphtoate, sodium xylene sulphonate, sodium decyl diphenyl oxide, sodium dimethyl naphthalene sulphonate, sodium salts of linear alkyl benzene sulphonate, having from about C₈ to C₁₂ in the alkyl portion, as well as mixtures thereof.

14. Additive according to any of the previous claims wherein the hydrotrope is also a solubilising agent.

15. Additive according to claim 14, wherein the hydrotrope is preferably Triton H66 (an alkali metal salt of a phosphate ester).

16. Additive according to any of the previous claims, further comprising a structurant to aid in solubilising the non-ionic surfactant.

17. Additive of claim 16, wherein the structurant is Keltrol FTM.

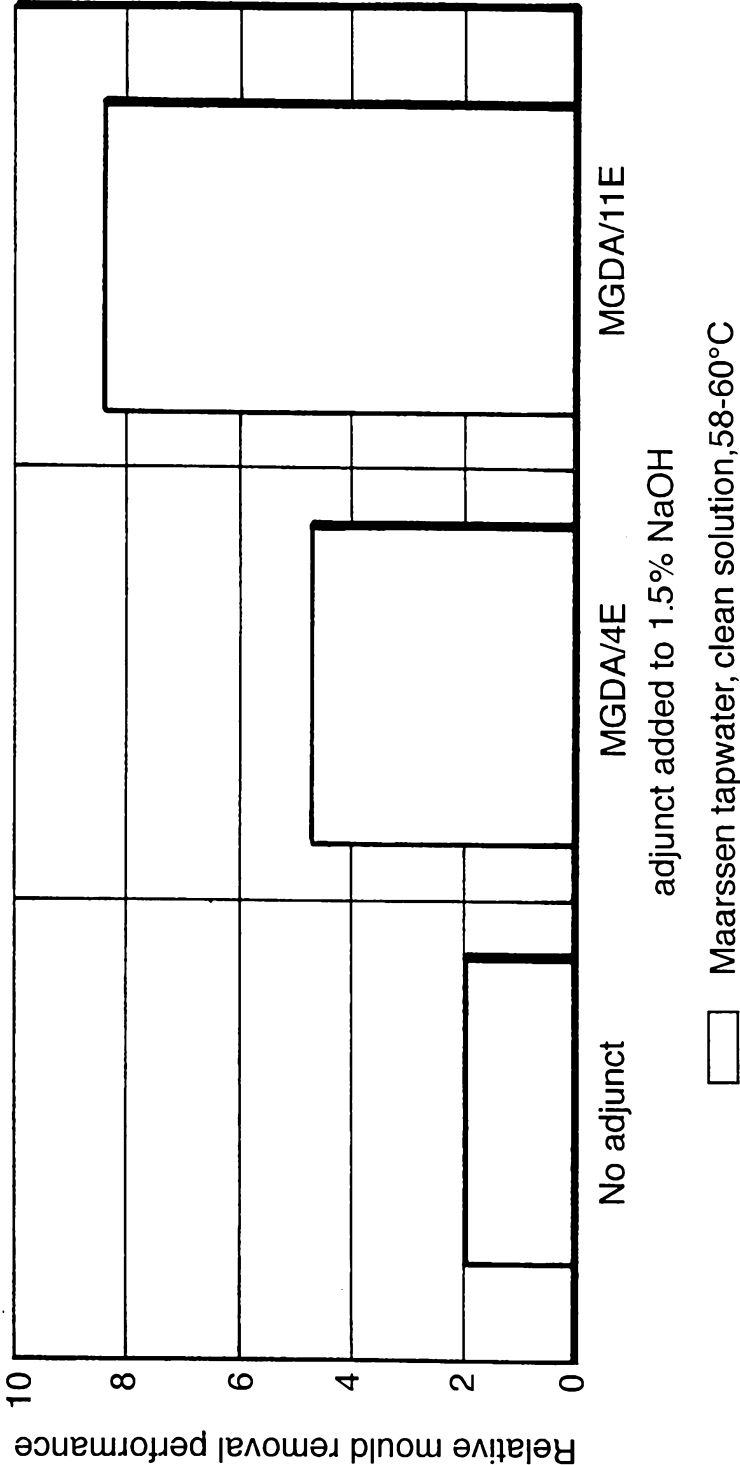
18. Additive according to any of the previous claims, further comprising a defoamer, for example Dehypon LT 104.

19. Formulation comprising an additive according to any of the previous claims wherein the sequestrant is present in a wt% range of about 5-60, preferably about 15-35, and the non-ionic and/or hydrotrope in a wt% range of about 0.5-40, preferably 1-25.

20. Use of the formulation according to claim 19 as a detergent in cleaning bottles, particularly returnable PET bottles, when the formulation comprises substantially no hydrotrope, and particularly returnable polycarbonate bottles when the formulation comprises substantially no non-ionic surfactant.

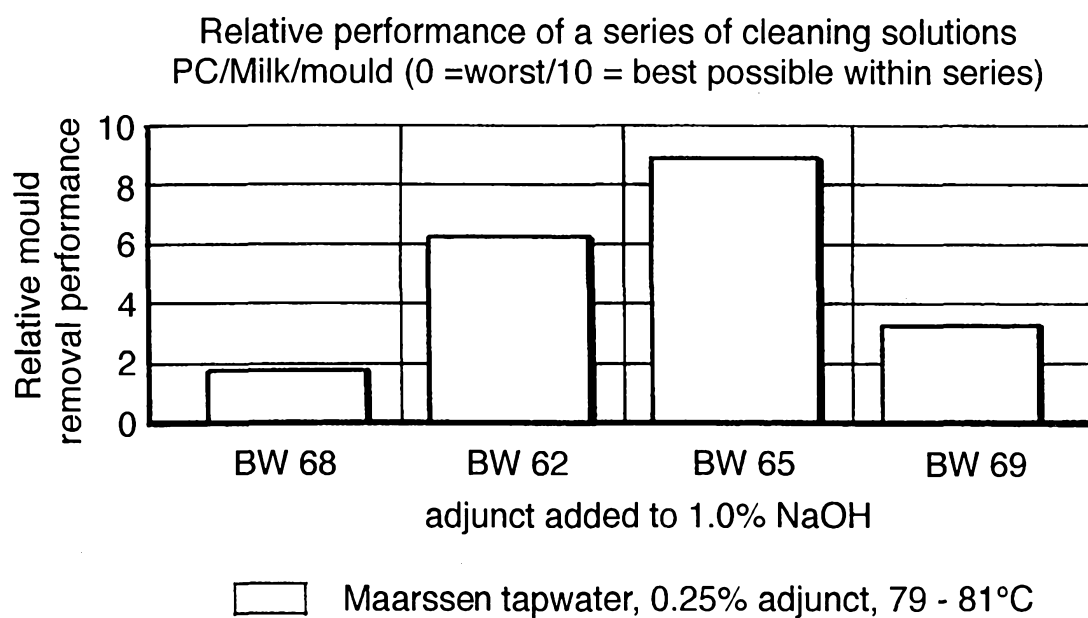
21. Process for washing bottles comprising the steps of exposing bottles to a formulation or additive according to any of the previous claims, wherein the sequestrant, non-ionic surfactant and/or the hydrotrope and possibly any further standard detergent formulation components, such as a defoamer, for example Dehypon LT104, are collectively or individually supplied into a bottle washing system.

Fig.1.
Relative performance of a series of cleaning solutions
PET/Tom.juice/A.niger (0=worst/10=best possible within series)



2/2

Fig.2.



INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 98/03695

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D3/33 C11D1/72 C11D1/722 C11D1/66 C11D1/14

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)

IPC 6 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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	DE 42 40 695 A (BASF AG) 9 June 1994 * page 3, lines 16-19; claims 1-6; examples 1,2 *	1,2, 6-10, 19-21
X	EP 0 287 885 A (BASF AG) 26 October 1988 * page 9, lines 50-52; pages 12-14; claims 1-8 *	1-10, 16, 18, 19
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search

12 October 1998

Date of mailing of the international search report

11/11/1998

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Ainscow, J

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/03695

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	EP 0 191 187 A (DEGUSSA) 20 August 1986 see claim 1; examples 1-6 ----	1,6-10, 16,18,19
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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