



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 066 915**

B1

(12)

## EUROPEAN PATENT SPECIFICATION

- (45) Date of publication of patent specification: **11.11.87**      (51) Int. Cl.<sup>4</sup>: **C 11 D 3/37**  
(21) Application number: **82200602.9**  
(22) Date of filing: **17.05.82**

---

(54) **Detergent composition containing performance additive and copolymeric compatibilizing agent therefor.**

(30) Priority: **30.05.81 GB 8116607**

(43) Date of publication of application:  
**15.12.82 Bulletin 82/50**

(45) Publication of the grant of the patent:  
**11.11.87 Bulletin 87/46**

(84) Designated Contracting States:  
**AT BE CH DE FR GB IT LI NL**

(56) References cited:  
**EP-A-0 025 551**  
**EP-A-0 063 017**  
**DE-A-1 959 272**  
**FR-A-2 388 045**

(71) Proprietor: **THE PROCTER & GAMBLE COMPANY**  
**301 East Sixth Street**  
**Cincinnati Ohio 45202 (US)**

(14) **CH GB LI AT**

(71) Proprietor: **Procter & Gamble European Technical Center**  
**Temselaan 100**  
**B-1820 Strombeek-Bever (BE)**

(14) **BE DE FR IT NL**

(72) Inventor: **Koster, Robertus J.C.**  
**Berkenlaan 105**  
**B-1850 Grimbergen (BE)**  
Inventor: **Baeck, André**  
**Putsesteenweg 253**  
**B-2820 Bonheiden (BE)**

(74) Representative: **Ernst, Hubert et al**  
**PROCTER & GAMBLE EUROPEAN TECHNICAL CENTER**  
**Temselaan 100**  
**B-1820 Strombeek-Bever (BE)**

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

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

**EP 0 066 915 B1**

# 0 066 915

## Description

This invention relates to the detergent utilization of certain copolymeric ingredients in a compatibilizing functionality in conjunction with performance additives. The copolymeric ingredient is prepared from an ethylenically unsaturated carboxylic acid and an ethylenically unsaturated dicarboxylic acid. Preferred monomers are acrylic and methacrylic acids on one hand and maleic and citraconic acids on the other hand. The copolymeric agent was found to be especially suitable for enhancing the compatibility of detergent additives which are known to be sensitive to various conditions inclusive of prolonged storage, temperature, alkalinity, and/or laundry conditions. In more detail, the copolymeric compatibilizing agent is capable of procuring, in contradistinction to their art-established functionality, unexpected transfer properties in relation to specific detergent additives. These transfer properties go against the prevailing opinion according to which comparable copolymeric adjuvants serve as deposition inhibitors, and consequently diminish the physical contact between detergent ingredients and e.g. the fiber.

The use of low levels of (co)polymeric additives for detergent application has been known for a long time and has found application in commercial detergent products. European Patent Application 0009171, BASF AG, published April 2, 1980 relates to the incorporation of polymaleic acid as a builder ingredient and/or as an incrustation inhibitor in detergents. European Patent Application 0025551, BASF AG, published March 25, 1981 discloses the utilization of (meth)acrylic acid—maleic acid copolymeric ingredients as incrustation inhibitors in detergent compositions. The copolymer comprises a large majority of the (meth)acrylic acid monomer FR—A—2388045, The Procter & Gamble Company, published November 17, 1978, pertains to detergent compositions containing surface-active agents, builders and a binary system based on not more than 4% of a polyphosphonate and not more than 4% of a polymeric ingredient which can be represented by the copolymers obtained from the polymerization of (meth)-acrylic acid and maleic anhydride.

German Patent Application DOS 19 59 272, Procter & Gamble European Technical Center, published July 23, 1970, relates to solid oxygen-bleach detergent compositions containing a copolymeric ingredient based on vinyl methyl ether and maleic anhydride. The copolymeric ingredient is claimed to provide effective active oxygen regulation.

It has now been discovered that the particular copolymeric ingredient of the invention herein can be used beneficially with a view to secure very desirable performance benefits upon use in combination with particular detergent additives with the proviso that the copolymeric ingredient is preferably used in excess levels in relation to a given performance additive.

It is an object of this invention to formulate detergent compositions having desirable performance characteristics containing specific detergent additives.

It is a further object of this invention to formulate laundry products capable of providing superior overall performance in presence of specific additives.

### Brief description of the invention

It has now been discovered that markedly improved detergent compositions can be formulated containing a conventional detergent matrix in combination with detergent performance additives and a copolymeric ingredient. The performance additives are present in an amount from 0.002% to 5% by weight. The copolymeric ingredient is prepared from an ethylenically unsaturated carboxylic acid monomer having not more than five carbon atoms and from an ethylenically unsaturated dicarboxylic acid monomer having not more than six carbon atoms, whereby these monomers are copolymerized in a molar proportion of 1:4 to 4:1. The weight ratio of the copolymeric ingredient to the performance additives is from 500:1 to 1:5. Performance additives for use in combination with the copolymeric ingredients are selected from water-soluble porphine photoactivators such as mixtures of sulfonated metal phthalocyanines; and renewable polyamine or amine oxide soil release agents.

### Detailed description of the invention

The invention herein comprises at least three major parameters, namely: a conventional detergent matrix comprising surface-active agents and builders; a detergent performance additive; and a specific copolymeric ingredient. The major parameters of the invention are described in more detail hereinafter.

Unless indicated to the contrary, the "percent" indications represent "percent by weight" indications.

Qualitatively and quantitatively suitable surface-active agents for use herein are disclosed in U.S. Patent 4,192,761, column 3, line 49 to column 5, line 42. Qualitatively and quantitatively suitable detergent builder materials can also be taken from U.S. Patent 4,192,761, column 8, line 56 to column 9, line 68.

It goes without saying that the detergent matrix of the compositions of this invention can also contain other major components according to the particular needs and/or the physical state of the invention. In this respect, the compositions herein can be solid, pasty or liquid. Major amounts of pH regulators, inert fillers like sodium sulfate, water and/or organic solvents like hydrocarbons and/or lower alcohols can be applied as is well-known in the art. The detergent matrix can also contain major levels of bleaching agents, for example, oxygen bleach agents such as perborate, percarbonate, perpyrophosphate, persilicate or, more in general, all oxygen-bleach agents which are known to be suitable for use in detergent compositions in the established levels.

## 0 066 915

The copolymeric ingredient consists of an ethylenically unsaturated monocarboxylic acid monomer having not more than 5, preferably 3 or 4, carbon atoms, and an ethylenically unsaturated dicarboxylic acid monomer having not more than 6, preferably 4 carbon atoms, whereby the molar ratio of the monomers is in the range from 1:4 to 4:1 (i.e., monocarboxylic acid:dicarboxylic acid). Suitable examples of the

- 5 monocarboxylic acid monomer are: acrylic acid, methacrylic acid and vinyl acetic acid. Acrylic and methacrylic acids are preferred. Suitable examples of the dicarboxylic acid monomers are: maleic acid; fumaric acid; citraconic acid; and mesaconic acid. Preferred dicarboxylic acids are maleic acid and citraconic acid.

The copolymeric ingredient can be further defined with the aid of the calcium sequestration value.

- 10 These values can be measured by nephelometric titration methods (as described in literature  
—S. Chaberek and A. E. Martell, *Organic Sequestering Agents*, Wiley, New York, 1959;  
—R. L. Smith, *The Sequestration of Metals*, Chapman and Hall, London, 1959):  
a calcium nitrate solution is added to a solution containing sequestrant and sodium oxalate until turbidity is produced; the titration is being carried out at constant pH=10 and room temperature.

- 15 The sequestration value is expressed in mgCaCO<sub>3</sub>/gram of copolymeric ingredient.

The calcium sequestration value of the copolymeric ingredient is preferably in the range from 300—900 mgCaCO<sub>3</sub>/g.

- 10 The performance additives herein are present in an amount from 0.002% to 5%. Depending upon the particular functionality of the additive and the planned use of the final detergent composition, the preferred  
20 usage ranges for the individual additives vary from additive to additive. The term performance additive as used herein is meant to express that the specific ingredient is added either to cure a deficiency of the general detergent matrix and/or to provide special laundry and cleaning benefits.

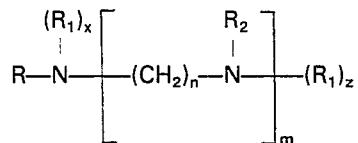
- A class of performance additives that can be utilized beneficially in combination with the copolymeric agent is represented by a photoactivator, also frequently termed a photosensitizer. The photoactivator is a porphine of a mono-, di-, tri-, or tetraaza porphine solubilized with anionic, nonionic, and/or cationic substituent groups and metal free or metallated with Zn(II), Ca(II), Cd(II), Mg(II), Sc(III), Al(III), or Sn(IV). Preferred metal-ions for the photoactivator are zinc and aluminum. The photoactivator is frequently used in low levels, e.g., in the level from about 20 ppm to 2000 ppm. In solid detergent compositions, the photoactivator is generally used in combination with a carrier material such as polyphosphates, sulfates, a.s.o. Generally, the level of such photoactivator particles (containing a carrier material) represents from 0.1% to 1% of the detergent composition. The photoactivator is believed to exhibit its activity in the direct environment of the fiber possibly in combination with perborate. The copolymeric ingredient favors this transfer of photoactivator to the fiber in presence of the other components in the laundry liquor at the applicable temperatures, e.g., laundry temperatures in the range from up to about 60°C or up to the boil.

- 35 As an example, a water-soluble photoactivator used in the specified levels can be represented by the porphine activators of European Patent Application 0003149. The weight ratio of copolymer to photoactivator performance additive is frequently in the range from 500:1 to 7:1.

- 40 The copolymeric ingredient was also found to be effective in combination with additive levels of renewable soil release agents as described in EP—A—0042187 and EP—A—0042188. The copolymeric ingredient enhances and contributes to a more quantitative deposition of the renewable soil release agent, specifically the polyamines oxidized or not and/or the oxidized monoamines.

The renewable soil release agent which frequently is used in levels from 0.1% to 1.5% is represented by polyamines having the formula:

45

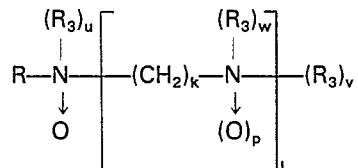


50

wherein R is an alkyl or alkenyl group having 10 to 22 carbon atoms, the R<sub>1</sub>'s, which are identical or different, are ethylene oxide or propylene oxide, R<sub>2</sub> is hydrogen, C<sub>1-4</sub> alkyl or (R<sub>1</sub>)<sub>y</sub>, where x, y, and z are numbers such that the sum (x+y+z) is in the range from 2 to 25, n is a number from 1 to 6 and m is a number from 1 to 9; or

- 55 amine oxides having the formula:

60



- 65 where R is an alkyl or alkenyl group having 10 to 22 carbon atoms, the R<sub>3</sub>'s which are identical or different are selected from C<sub>1-4</sub> alkyl, ethylene oxide and propylene oxide, k is an integer from 1 to 6, l is an

## 0 066 915

integer from 0 to 6, p is 0 or 1, u, v, and w are each 1 for alkyl substituents, and integers in the range from 1 to 10 for ethylene oxide or propylene oxide substituents such that the sum of (u+v+w) is not greater than 25, with the proviso that a 1% aqueous solution of the detergent composition has an alkaline pH (20°C).

A preferred polyamine for use herein is N-hydrogenated tallow  $C_{16}-C_{18}$ -N,N',N'-tri-(2-hydroxyethyl)-propylene-1,3-diamine. Preferred amine oxide species are  $N-C_{12-14}$ -coconutalkyl-N,N-dimethyl-N-amine oxide; N-tallow  $C_{16-18}$ -alkyl-N,N',N'-tri-(2-hydroxyethyl)-propylene-1,3-diamine-N,N'-dioxide;  $N-C_{12-14}$ -alkyl-N,N',N'-tri-(2-hydroxyethyl)-propylene-1,3-diamine-N,N'-dioxide;  $N-C_{16-18}$ -tallow-alkyl-N,N-dimethyl-N-amine oxide;  $N-C_{12-14}$ -coconutalkyl-N,N-di(2-hydroxyethyl)-N-amine oxide; or  $N-C_{16-18}$ -tallowalkyl-N,N-di-(2-hydroxyethyl)-N-amine oxide. The weight ratio of copolymer to soil release additive is 10 preferably in the range from 10:1 to 1:1.

In addition to the essential components described hereinbefore, the compositions of this invention can comprise a series of supplementary components to perfect and complement the performance advantages derived from the compositions. These additional components include brighteners, dyes, perfumes, bactericides, and antioxidants, processing aids, corrosion inhibitors, enzymes and so on. These 15 further ingredients are used for their known functionality in the art established levels, i.e., frequently in the range from 0.1% to 5%.

The following examples illustrate the invention and facilitate its understanding.

- The abbreviations for the individual ingredients have the following meaning:
- 20 LAS: Sodium salt of linear dodecyl benzene sulfonate  
TAS: Sodium salt of tallow alcohol sulfate  
FAE<sub>3</sub>S: Sodium salt of fatty alcohol ( $C_{12-18}$ ) (ethoxy)3 sulfate  
AO:  $C_{12-14}$  alkyl dimethylamine oxide  
HLAS: Linear dodecyl benzene sulfonic acid  
25 TAE<sub>11</sub>: Tallow alcohol ethoxylated with about 11 moles of ethylene oxide  
FA<sub>25</sub>E<sub>7</sub>: Fatty alcohol ( $C_{12-15}$ ) ethoxylated with about 7 moles of ethylene oxide  
FA<sub>25</sub>E<sub>4</sub>: Fatty alcohol ( $C_{12-15}$ ) ethoxylated with about 4 moles of ethylene oxide  
CFA:  $C_{12-14}$  coconut fatty acid  
HFA: Hydrogenerated  $C_{16-22}$  fatty acid  
30 STPP: Sodium tripolyphosphate  
Zeolite A: Sodium salt of zeolite 4A (average particle size between 2—6  $\mu m$ )  
NTA: Sodium salt of nitrilotriacetate  
Copolymer: AA<sup>40</sup>/MA<sup>60</sup>=copolymer of acrylic acid 40 mol-% and maleic acid 60 mol-%  
MAA<sup>50</sup>/MA<sup>50</sup>=copolymer of methacrylic acid 50 mol-% and maleic acid 50 mol-%  
35 CMC: Sodium salt of carboxymethyl cellulose  
MHPC: Sodium salt of methyl hydroxypropyl cellulose  
Silicate 1.6: Sodium silicate SiO<sub>2</sub>/Na<sub>2</sub>O=1.6  
TEA: triethanolamine  
STS: Sodium salt of toluene sulfonate  
40 EDTA: Sodium salt of ethylene diamine tetra-acetate  
Perborate: NaBO<sub>2</sub> · H<sub>2</sub>O<sub>2</sub> · 3H<sub>2</sub>O  
P.A.: Photoactivator sulfonated Zn phthalocyanine  
SRS III: oil in water emulsion  
—9% polydimethylsiloxane  
45 —1% amorphous hydrophobic silica  
—5% coconut fatty acid ethoxylated with 7 moles of ethylene oxide  
—85% water

The following granular detergent compositions are prepared by conventional spray-drying of a slurry 50 of individual ingredients and subsequent dry-mixing of this base powder with spray-drying sensitive ingredients.

Solid detergent compositions are prepared having the following formulae.

55

60

65

**0 066 915**

	Ingredients	Composition (% by weight)		
		I	II	III
5	LAS	10.0	5.0	7.0
	TAS	—	3.0	—
10	FAE <sub>3</sub> S	3.0	—	—
	TAE <sub>11</sub>	1.0	1.0	2.7
	HFA	—	4.0	3.5
15	STPP	—	60.0	28.0
	NTA	—	—	4.0
20	Na <sub>2</sub> CO <sub>3</sub>	20.0	—	—
	Copolymer MAA <sup>40</sup> /MA <sup>60</sup>	1.7	1.4	0.3
	CMC	1.0	1.0	0.8
25	MHPC	—	0.5	—
	Silicate 1.6	18.0	3.0	8.0
30	MgSO <sub>4</sub>	1.0	—	0.5
	Na <sub>2</sub> SO <sub>4</sub>	5.2	9.5	4.2
	NaOH	1.1	0.9	0.2
35	STS	1.4	—	—
	EDTA	0.2	0.3	0.3
40	Perborate	25.0	—	30.0
	P.A.	0.007	0.003	0.002
	Enzyme (proteolytic)	0.3	0.6	0.2
45	Brightener, perfume, H <sub>2</sub> O		Balance to 100	

50

55

60

65

**0 066 915**

	Ingredient	IV	V	VI	Composition (% by weight)	VII
5	LAS	7.0	4.5	7.0		4.5
	TAS	—	2.5	—		2.5
	A.O.	0.5	0.3	0.8		1.0
10	TAE <sub>11</sub>	2.7	—	2.7		—
	FA <sub>25</sub> E <sub>7</sub>	—	2.0	—		2.0
15	CFA	—	2.0	—		2.0
	HFA	3.5	4.0	3.5		4.0
	STPP	31.0	24.0	16.0		8.0
20	Zeolite A	—	—	16.0		16.0
	NTA	—	4.0	—		6.0
25	Copolymer AA <sup>40</sup> /MA <sup>60</sup>	—	1.5	—		1.5
	MAA <sup>55</sup> /MA <sup>45</sup>	—	—	1.3		—
	AA <sup>50</sup> /MA <sup>50</sup>	2.0	—	—		—
30	CMC	0.8	0.8	1.0		1.0
	Silicate 1.6	5.0	5.0	2.0		2.0
35	MgSO <sub>4</sub>	—	0.5	0.5		1.0
	Na <sub>2</sub> SO <sub>4</sub>	7.4	10.5	8.5		11.6
	NaOH	1.3	1.0	0.8		1.0
40	EDTA	0.2	0.3	0.3		0.2
	Perborate	32.0	28.0	30.0		28.0
45	Enzyme (proteolytic)	0.2	0.2	0.3		0.2
	Brightener, perfume, water			balance to 100		

50

55

60

65

0 066 915

A liquid detergent composition is made by mixing the following individual ingredients.

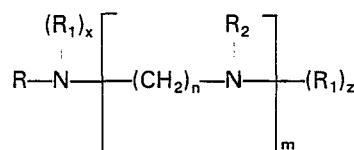
5	Ingredient	Composition (% by weight)
	HLAS	VIII 13.5
10	TAE <sub>11</sub>	20.0
	FA <sub>25</sub> E <sub>4</sub>	10.0
	Copolymer MAA <sup>50</sup> /MA <sup>50</sup>	0.5
15	TEA	7.7
	P.A.	0.002
20	Enzyme (proteolytic)	0.8
	SRS III	1.0
	1—2 propylene glycol	2.0
25	Ethanol	11.0
	Brightener, perfume, dye, H <sub>2</sub> O	balance to 100

30 Claims

1. A detergent composition with a conventional matrix on basis of surface-active agents, builders, performance additives and a copolymeric ingredient, characterized in, that the performance additive is present in an amount from 0.002% to 5% by weight, and is selected from:

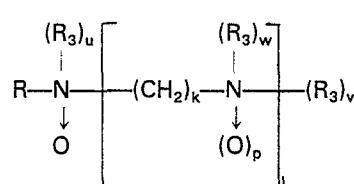
35 present in an amount from 0.002% to 5% by weight, and is selected from:  
(a) a water-soluble photoactivator from the group of porphine or mono-, di-, tri-, or tetraaza porphine solubilized with anionic, nonionic, and/or cationic substituent groups and metal free or metallated with Zn(II), Ca(II), Cd(II), Mg(II), Sc(III), Al(IV) or Sn(IV); and

(b) a soil release agent which is a polyamine having the formula



45 wherein R is an alkyl or alkenyl group having 10 to 22 carbon atoms, the R<sub>1</sub>'s, which are identical or different, are ethylene oxide or propylene oxide, R<sub>2</sub> is hydrogen C<sub>1-4</sub> alkyl or (R<sub>1</sub>)y, where x, y, and z are numbers such that the sum (x+y+z) is in the range from 2 to 25, n is a number from 1 to 6 and m is a number from 1 to about 2; or

number from 1 to about 9; or  
an amine oxide having the formula:



60 wherein R is an alkyl or alkenyl group having 10 to 22 carbon atoms, the R<sub>3</sub>'s which are identical or different are selected from C<sub>1-4</sub> alkyl, ethylene oxide and propylene oxide, k is an integer from 1 to 6, l is an integer from 0 to 6, p is 0 or 1, u, v, and w are each 1 for alkyl substituents, and integers in the range from 1 to 10 for ethylene oxide or propylene oxide substituents such that the sum of (u+v+w) is not greater than 25, and that the copolymeric ingredient consists of an ethylenically unsaturated monocarboxylic acid monomer having not more than 5, preferably 3 or 4, carbon atoms, and an ethylenically unsaturated dicarboxylic acid monomer having not more than 6, preferably 4, carbon atoms, whereby the molar ratio of

# 0 066 915

the monomers is in the range from 1:4 to 4:1; and whereby the weight ratio of the copolymer to the performance additive is in the range of from 500:1 to 1:5.

2. The detergent composition in accordance with Claim 1 wherein the copolymeric ingredient is comprised of (meth)-acrylic acid and maleic acid monomers.

5 3. The detergent composition in accordance with Claim 1 wherein the photoactivator is present in an amount from 20 ppm to 2000 ppm and wherein the weight ratio of copolymer to photoactivator is in the range from 500:1 to 7:1.

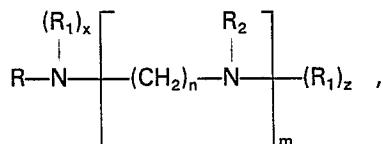
10 4. The detergent composition in accordance with Claim 1 wherein the soil release agent is present in an amount from 0.1% to 1.5% by weight in a weight ratio of copolymer to performance additive in the range from 10:1 to 1:1, whereby a 1% aqueous solution of the detergent composition has an alkaline pH (20°C).

## Patentansprüche

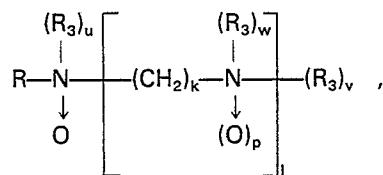
15 1. Eine Reinigungsmittelzusammensetzung mit einer üblichen Matrix auf Basis von grenzflächenaktiven Mitteln, Gerüststoffen, wirkungsfördernden Zusätzen und einem Copolymerbestandteil, dadurch gekennzeichnet, daß der wirkungsfördernde Zusatz in einer Menge von 0,002 Gew.-% bis 5 Gew.-% vorliegt und ausgewählt ist aus:

20 (a) einem wasserlöslichen Photoaktivator aus der Porphin- oder Mono-, Di-, Tri- oder Tetraazaporphingruppe, der mit anionischen, nichtionischen und/oder kationischen Substituentengruppen löslich gemacht und metallfrei oder mit Zn(II), Ca(II), Cd(II), Mg(II), Sc(III), Al(III) oder Sn(IV) metallisiert ist; und

(b) einem Schmutzfreisetzungsmittel, das ein Polyamin der Formel



30 30 worin R eine Alkyl- oder Alkenylgruppe mit 10 bis 22 Kohlenstoffatomen ist, die Reste R<sub>1</sub>, welche gleich oder verschieden sind, Ethylenoxid oder Propylenoxid sind, R<sub>2</sub> Wasserstoff, C<sub>1-4</sub>-Alkyl oder (R<sub>1</sub>)<sub>y</sub> ist, wobei x, y und z Zahlen derart sind, daß die Summe (x+y+z) im Bereich von 2 bis 25 liegt, n eine Zahl von 1 bis 6 ist, und m eine Zahl von 1 bis etwa 9 ist; oder eine Aminoxid der Formel:



35 40 45 50 worin R eine Alkyl- oder Alkenylgruppe mit 10 bis 22 Kohlenstoffatomen ist, die Reste R<sub>3</sub>, die gleich oder verschieden sind, aus C<sub>1-4</sub>-Alkyl, Ethylenoxid und Propylenoxid ausgewählt sind, k eine ganze Zahl von 1 bis 6 ist, l eine ganze Zahl von 0 bis 6 ist, p 0 oder 1 ist, und u, v und w für Alkylsubstituenten jeweils 1 sind, und der artige ganze Zahlen im Bereich von 1 bis 10 für Ethylenoxid- oder Propylenoxidsubstituenten darstellen, daß die Summe von (u+v+w) nicht mehr als 25 beträgt, ist;

und daß der Copolymerbestandteil aus einem ethylenisch ungesättigten Monocarbonsäuremonomer mit nicht mehr als 5, vorzugsweise 3 oder 4, Kohlenstoffatomen, und einem ethylenisch ungesättigten Dicarbonsäuremonomer mit nicht mehr als 6, vorzugsweise 4, Kohlenstoffatomen besteht, wobei das Molverhältnis der Monomeren im Bereich von 1:4 bis 4:1 liegt; und wobei das Gewichtsverhältnis des Copolymers zum wirkungsfördernden Zusatz im Bereich von 500:1 bis 1:5 liegt.

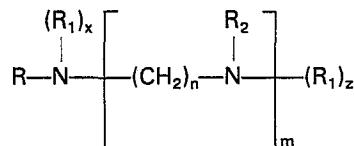
55 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160 165 170 175 180 185 190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275 280 285 290 295 300 305 310 315 320 325 330 335 340 345 350 355 360 365 370 375 380 385 390 395 400 405 410 415 420 425 430 435 440 445 450 455 460 465 470 475 480 485 490 495 500 505 510 515 520 525 530 535 540 545 550 555 560 565 570 575 580 585 590 595 600 605 610 615 620 625 630 635 640 645 650 655 660 665 670 675 680 685 690 695 700 705 710 715 720 725 730 735 740 745 750 755 760 765 770 775 780 785 790 795 800 805 810 815 820 825 830 835 840 845 850 855 860 865 870 875 880 885 890 895 900 905 910 915 920 925 930 935 940 945 950 955 960 965 970 975 980 985 990 995 1000 1005 1010 1015 1020 1025 1030 1035 1040 1045 1050 1055 1060 1065 1070 1075 1080 1085 1090 1095 1100 1105 1110 1115 1120 1125 1130 1135 1140 1145 1150 1155 1160 1165 1170 1175 1180 1185 1190 1195 1200 1205 1210 1215 1220 1225 1230 1235 1240 1245 1250 1255 1260 1265 1270 1275 1280 1285 1290 1295 1300 1305 1310 1315 1320 1325 1330 1335 1340 1345 1350 1355 1360 1365 1370 1375 1380 1385 1390 1395 1400 1405 1410 1415 1420 1425 1430 1435 1440 1445 1450 1455 1460 1465 1470 1475 1480 1485 1490 1495 1500 1505 1510 1515 1520 1525 1530 1535 1540 1545 1550 1555 1560 1565 1570 1575 1580 1585 1590 1595 1600 1605 1610 1615 1620 1625 1630 1635 1640 1645 1650 1655 1660 1665 1670 1675 1680 1685 1690 1695 1700 1705 1710 1715 1720 1725 1730 1735 1740 1745 1750 1755 1760 1765 1770 1775 1780 1785 1790 1795 1800 1805 1810 1815 1820 1825 1830 1835 1840 1845 1850 1855 1860 1865 1870 1875 1880 1885 1890 1895 1900 1905 1910 1915 1920 1925 1930 1935 1940 1945 1950 1955 1960 1965 1970 1975 1980 1985 1990 1995 2000 2005 2010 2015 2020 2025 2030 2035 2040 2045 2050 2055 2060 2065 2070 2075 2080 2085 2090 2095 2100 2105 2110 2115 2120 2125 2130 2135 2140 2145 2150 2155 2160 2165 2170 2175 2180 2185 2190 2195 2200 2205 2210 2215 2220 2225 2230 2235 2240 2245 2250 2255 2260 2265 2270 2275 2280 2285 2290 2295 2300 2305 2310 2315 2320 2325 2330 2335 2340 2345 2350 2355 2360 2365 2370 2375 2380 2385 2390 2395 2400 2405 2410 2415 2420 2425 2430 2435 2440 2445 2450 2455 2460 2465 2470 2475 2480 2485 2490 2495 2500 2505 2510 2515 2520 2525 2530 2535 2540 2545 2550 2555 2560 2565 2570 2575 2580 2585 2590 2595 2600 2605 2610 2615 2620 2625 2630 2635 2640 2645 2650 2655 2660 2665 2670 2675 2680 2685 2690 2695 2700 2705 2710 2715 2720 2725 2730 2735 2740 2745 2750 2755 2760 2765 2770 2775 2780 2785 2790 2795 2800 2805 2810 2815 2820 2825 2830 2835 2840 2845 2850 2855 2860 2865 2870 2875 2880 2885 2890 2895 2900 2905 2910 2915 2920 2925 2930 2935 2940 2945 2950 2955 2960 2965 2970 2975 2980 2985 2990 2995 3000 3005 3010 3015 3020 3025 3030 3035 3040 3045 3050 3055 3060 3065 3070 3075 3080 3085 3090 3095 3100 3105 3110 3115 3120 3125 3130 3135 3140 3145 3150 3155 3160 3165 3170 3175 3180 3185 3190 3195 3200 3205 3210 3215 3220 3225 3230 3235 3240 3245 3250 3255 3260 3265 3270 3275 3280 3285 3290 3295 3300 3305 3310 3315 3320 3325 3330 3335 3340 3345 3350 3355 3360 3365 3370 3375 3380 3385 3390 3395 3400 3405 3410 3415 3420 3425 3430 3435 3440 3445 3450 3455 3460 3465 3470 3475 3480 3485 3490 3495 3500 3505 3510 3515 3520 3525 3530 3535 3540 3545 3550 3555 3560 3565 3570 3575 3580 3585 3590 3595 3600 3605 3610 3615 3620 3625 3630 3635 3640 3645 3650 3655 3660 3665 3670 3675 3680 3685 3690 3695 3700 3705 3710 3715 3720 3725 3730 3735 3740 3745 3750 3755 3760 3765 3770 3775 3780 3785 3790 3795 3800 3805 3810 3815 3820 3825 3830 3835 3840 3845 3850 3855 3860 3865 3870 3875 3880 3885 3890 3895 3900 3905 3910 3915 3920 3925 3930 3935 3940 3945 3950 3955 3960 3965 3970 3975 3980 3985 3990 3995 4000 4005 4010 4015 4020 4025 4030 4035 4040 4045 4050 4055 4060 4065 4070 4075 4080 4085 4090 4095 4100 4105 4110 4115 4120 4125 4130 4135 4140 4145 4150 4155 4160 4165 4170 4175 4180 4185 4190 4195 4200 4205 4210 4215 4220 4225 4230 4235 4240 4245 4250 4255 4260 4265 4270 4275 4280 4285 4290 4295 4300 4305 4310 4315 4320 4325 4330 4335 4340 4345 4350 4355 4360 4365 4370 4375 4380 4385 4390 4395 4400 4405 4410 4415 4420 4425 4430 4435 4440 4445 4450 4455 4460 4465 4470 4475 4480 4485 4490 4495 4500 4505 4510 4515 4520 4525 4530 4535 4540 4545 4550 4555 4560 4565 4570 4575 4580 4585 4590 4595 4600 4605 4610 4615 4620 4625 4630 4635 4640 4645 4650 4655 4660 4665 4670 4675 4680 4685 4690 4695 4700 4705 4710 4715 4720 4725 4730 4735 4740 4745 4750 4755 4760 4765 4770 4775 4780 4785 4790 4795 4800 4805 4810 4815 4820 4825 4830 4835 4840 4845 4850 4855 4860 4865 4870 4875 4880 4885 4890 4895 4900 4905 4910 4915 4920 4925 4930 4935 4940 4945 4950 4955 4960 4965 4970 4975 4980 4985 4990 4995 5000 5005 5010 5015 5020 5025 5030 5035 5040 5045 5050 5055 5060 5065 5070 5075 5080 5085 5090 5095 5100 5105 5110 5115 5120 5125 5130 5135 5140 5145 5150 5155 5160 5165 5170 5175 5180 5185 5190 5195 5200 5205 5210 5215 5220 5225 5230 5235 5240 5245 5250 5255 5260 5265 5270 5275 5280 5285 5290 5295 5300 5305 5310 5315 5320 5325 5330 5335 5340 5345 5350 5355 5360 5365 5370 5375 5380 5385 5390 5395 5400 5405 5410 5415 5420 5425 5430 5435 5440 5445 5450 5455 5460 5465 5470 5475 5480 5485 5490 5495 5500 5505 5510 5515 5520 5525 5530 5535 5540 5545 5550 5555 5560 5565 5570 5575 5580 5585 5590 5595 5600 5605 5610 5615 5620 5625 5630 5635 5640 5645 5650 5655 5660 5665 5670 5675 5680 5685 5690 5695 5700 5705 5710 5715 5720 5725 5730 5735 5740 5745 5750 5755 5760 5765 5770 5775 5780 5785 5790 5795 5800 5805 5810 5815 5820 5825 5830 5835 5840 5845 5850 5855 5860 5865 5870 5875 5880 5885 5890 5895 5900 5905 5910 5915 5920 5925 5930 5935 5940 5945 5950 5955 5960 5965 5970 5975 5980 5985 5990 5995 6000 6005 6010 6015 6020 6025 6030 6035 6040 6045 6050 6055 6060 6065 6070 6075 6080 6085 6090 6095 6100 6105 6110 6115 6120 6125 6130 6135 6140 6145 6150 6155 6160 6165 6170 6175 6180 6185 6190 6195 6200 6205 6210 6215 6220 6225 6230 6235 6240 6245 6250 6255 6260 6265 6270 6275 6280 6285 6290 6295 6300 6305 6310 6315 6320 6325 6330 6335 6340 6345 6350 6355 6360 6365 6370 6375 6380 6385 6390 6395 6400 6405 6410 6415 6420 6425 6430 6435 6440 6445 6450 6455 6460 6465 6470 6475 6480 6485 6490 6495 6500 6505 6510 6515 6520 6525 6530 6535 6540 6545 6550 6555 6560 6565 6570 6575 6580 6585 6590 6595 6600 6605 6610 6615 6620 6625 6630 6635 6640 6645 6650 6655 6660 6665 6670 6675 6680 6685 6690 6695 6700 6705 6710 6715 6720 6725 6730 6735 6740 6745 6750 6755 6760 6765 6770 6775 6780 6785 6790 6795 6800 6805 6810 6815 6820 6825 6830 6835 6840 6845 6850 6855 6860 6865 6870 6875 6880 6885 6890 6895 6900 6905 6910 6915 6920 6925 6930 6935 6940 6945 6950 6955 6960 6965 6970 6975 6980 6985 6990 6995 7000 7005 7010 7015 7020 7025 7030 7035 7040 7045 7050 7055 7060 7065 7070 7075 7080 7085 7090 7095 7100 7105 7110 7115 7120 7125 7130 7135 7140 7145 7150 7155 7160 7165 7170 7175 7180 7185 7190 7195 7200 7205 7210 7215 7220 7225 7230 7235 7240 7245 7250 7255 7260 7265 7270 7275 7280 7285 7290 7295 7300 7305 7310 7315 7320 7325 7330 7335 7340 7345 7350 7355 7360 7365 7370 7375 7380 7385 7390 7395 7400 7405 7410 7415 7420 7425 7430 7435 7440 7445 7450 7455 7460 7465 7470 7475 7480 7485 7490 7495 7500 7505 7510 7515 7520 7525 7530 7535 7540 7545 7550 7555 7560 7565 7570 7575 7580 7585 7590 7595 7600 7605 7610 7615 7620 7625 7630 7635 7640 7645 7650 7655 7660 7665 7670 7675 7680 7685 7690 7695 7700 7705 7710 7715 7720 7725 7730 7735 7740 7745 7750 7755 7760 7765 7770 7775 7780 7785 7790 7795 7800 7805 7810 7815 7820 7825 7830 7835 7840 7845 7850 7855 7860 7865 7870 7875 7880 7885 7890 7895 7900 7905 7910 7915 7920 7925 7930 7935 7940 7945 7950 7955 7960 7965 7970 7975 7980 7985 7990 7995 8000 8005 8010 8015 8020 8025 8030 8035 8040 8045 8050 8055 8060 8065 8070 8075 8080 8085 8090 8095 8100 8105 8110 8115 8120 8125 8130 8135 8140 8145 8150 8155 8160 8165 8170 8175 8180 8185 8190 8195 8200 8205 8210 8215 8220 8225 8230 8235 8240 8245 8250 8255 8260 8265 8270 8275 8280 8285 8290 8295 8300 8305 8310 8315 8320 8325 8330 8335 8340 8345 8350 8355 8360 8365 8370 8375 8380 8385 8390 8395 8400 8405 8410 8415 8420 8425 8430 8435 8440 8445 8450 8455 8460 8465 8470 8475 8480 8485 8490 8495 8500 8505 8510 8515 8520 8525 8530 8535 8540 8545 8550 8555 8560 8565 8570 8575 8580 8585 8590 8595 8600 8605 8610 8615 8620 8625 8630 8635 8640 8645 8650 8655 8660 8665 8670 8675 8680 8685 8690 8695 8700 8705 8710 8715 8720 8725 8730 8735 8740 8745 8750 8755 8760 8765 8770 8775 8780 8785 8790 8795 8800 8805 8810 8815 8820 8825 8830 8835 8840 8845 8850 8855 8860 8865 8870 8875 8880 8885 8890 8895 8900 8905 8910 8915 8920 8925 8930 8935 8940 8945 8950 8955 8960 8965 8970 8975 8980 8985 8990 8995 9000 9005 9010 9015 9020 9025 9030 9035 9040 9045 9050 9055 9060 9065 9070 9075 9080 9085 9090 9095 9100 9105 9110 9115 9120 9125 9130 9135 9140 9145 9150 9155 9160 9165 9170 9175 9180 9185 9190 9195 9200 9205 9210 9215 9220 9225 9230 9235 9240 9245 9250 9255 9260 9265 9270 9275 9280 9285 9290 9295 9300 9305 9310 9315 9320 9325 9330 9335 9340 9345 9350 9355 9360 9365 9370 9375 9380 9385 9390 9395 9400 9405 9410 9415 9420 9425 9430 9435 9440 9445 9450 9455 9460 9465 9470 9475 9480 9485 9490 9495 9500 9505 9510 9515 9520 9525 9530 9535 9540 9545 9550 9555 9560 9565 9570 9575 9580 9585 9590 9595 960

# 0 066 915

caractérisée en ce que l'additif augmentant la performance est présent à la teneur de 0,002 % à 5% en poids et est choisi parmi

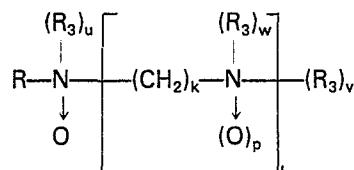
- a) un photo-activateur hydrosoluble du groupe de la porphine ou de la mono-, di-, tri- ou tétraazaporphine solubilisée par des groupes substituants anioniques, non ioniques et/ou cationiques et
- 5 exempt de métal ou métallée avec Zn(II), Ca(II), Cd(II), Mg(II), Sc(III), Al(III) ou Sn(IV) et
- b) un agent éliminant les salissures qui est une polyamine répondant à la formule

10



dans laquelle R est un groupe alkyle ou alcényle ayant 10 à 22 atomes de carbone, les R<sub>1</sub> qui sont identiques ou différents, sont de l'oxyde d'éthylène ou de l'oxyde de propylène, R<sub>2</sub> est l'hydrogène, un alkyle en C<sub>1</sub> à C<sub>4</sub> ou (R<sub>1</sub>), où x, y et z sont des nombres tels que la somme (x+y+z) est comprise dans la gamme de 2 à 25, n est un nombre de 1 à 6 et m est un nombre de 1 à environ 9; ou un oxyde d'amino répondant à la formule

20



25

dans laquelle R est un groupe alkyle ou alcényle ayant 10 à 22 atomes de carbone, les R<sub>3</sub> qui sont identiques ou différents sont choisis parmi un alkyle en C<sub>1</sub> à C<sub>4</sub>, l'oxyde d'éthylène et l'oxyde de propylène, k est un nombre entier de 1 à 6, l est un nombre entier de 0 à 6, p est 0 ou 1, u, v et w sont chacun 1 pour les substituants alkyle et des nombres entiers de 1 à 10 pour les substituants oxyde d'éthylène ou oxyde de propylène de manière que la somme de (u+v+w) ne soit pas supérieure à 25, et que le constituant copolymérique consiste en un acide monocarboxylique monomère éthyléniquement insaturé n'ayant pas plus de 5, de préférence 3 ou 4 atomes de carbone et en un acide dicarboxylique monomère éthyléniquement insaturé n'ayant pas plus de 6, de préférence 4 atomes de C, moyennant quoi le rapport molaire des monomères se situe dans la gamme de 1:4 à 4:1 et le rapport pondéral du copolymère à l'additif augmentant la performance est compris dans la gamme de 500:1 à 1:5.

2. Composition détergente selon la revendication 1, dans laquelle le constituant copolymérique comprend de l'acide (meth)-acrylique et de l'acide maléique comme monomères.

3. Composition détergente selon la revendication 1, dans laquelle le photo-activateur est présent en quantité de 20 ppm à 2000 ppm et le rapport pondéral de copolymère à photo-activateur se situe dans la gamme de 500:1 à 7:1.

4. Composition détergente selon la revendication 1, dans laquelle l'agent éliminant les salissures est présent à la teneur de 0,1% à 1,5% en poids dans un rapport pondéral de copolymère à additif augmentant la performance s'étendant de 10:1 à 1:1, moyennant quoi une solution aqueuse à 1% de la composition détergente possède un pH alcalin (à 20°C).

45

50

55

60

65