

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 992 574 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

12.04.2000 Bulletin 2000/15

(51) Int. Cl.⁷: **C11D 3/37**

(21) Application number: **98870208.0**

(22) Date of filing: **05.10.1998**

(84) Designated Contracting States:

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

Designated Extension States:

AL LT LV MK RO SI

(71) Applicant:

**THE PROCTER & GAMBLE COMPANY
Cincinnati, Ohio 45202 (US)**

(72) Inventors:

- **Cardola, Sergio (NMN)**
00064 Rome (IT)

- **Scorsini, Carla (NMN)**

00155 Rome (IT)

- **Massa, Alessandra (NMN)**

80026 Casoria (Napoli) (IT)

(74) Representative:

**Engisch, Gautier et al
BVBA Procter & Gamble Europe SPRL,
Temseleaan 100
1853 Strombeek-Bever (BE)**

(54) **Cleaning compositions**

(57) According to the present invention there is provided a cleaning composition comprising a polymeric thickening system of at least two homo or copolymers.

EP 0 992 574 A1

DescriptionField of the invention

- 5 **[0001]** The present invention relates to cleaning compositions, especially to thickened liquid cleaning compositions exhibiting effective cleaning performance and viscosity.

Background of the invention

- 10 **[0002]** Efficient cleaning performance and viscosity of the cleaning compositions are two requirements which drive consumer acceptance of cleaning products. Effective cleaning of surfaces is important, especially on greasy and oily soils and/or where the composition is thereafter diluted. However viscosity is also a key factor in the preparation of such a cleaning composition. The viscosity of the cleaning composition must be high enough to enable the cleaning compositions to remain on the surface being cleansed for a sufficiently long period of time to ensure effective cleaning. Such
15 a requirement is of particular utility in cleaning compositions intended to be applied "as is" to non-horizontal structural surfaces such as walls, windows and sanitary fittings such as sinks, baths, showers, wash basins and WCs. More particularly, viscosities of 10 cps to 4000 cps are suitable.

[0003] It is therefore an object of the present invention to provide cleaning compositions having effective cleaning performance and viscosity.

- 20 **[0004]** Thickened cleaning compositions are known in the art. The most commonly used thickener is a polycarboxylate polymer of high molecular weight i.e. in the range of 500 000 to 4 500 000. Furthermore for best results it is preferred that the polycarboxylate polymer is cross-linked. EP 834 549 and EP 812 904 both describe cleaning compositions comprising such polymeric thickeners. However the Applicant has found disadvantages in the use of such a polymeric thickeners in that whilst the polymer provides adequate increase in viscosity, the yield stress of the composition is also increased. The effect of the increase in yield stress is that the composition can become too thick such that
25 it does not spread easily on the surface and is therefore difficult to use and/or rinse. In addition it has been found that occasionally air bubbles may become trapped in the composition during manufacture which are difficult to remove and not consumer acceptable.

- 30 **[0005]** The Applicant has now found that the polymeric thickening system described herein provides thickening of the composition without the disadvantages of the previously used thickening systems as described above.

Summary of the invention

- 35 **[0006]** According to the present invention there is provided a cleaning composition comprising a polymeric thickening system comprising a polycarboxylate homo or copolymer having molecular weight in the range of from 500 000 to 4 500 000 and a polycarboxylate homo or copolymer having a molecular weight of from 500 to 10 000.

[0007] In another aspect of the invention, there is provided a method for cleaning a hard surface by applying on said surface an effective amount of a composition of the present invention.

- 40 Detailed description of the invention

Polymeric Thickening System

- 45 **[0008]** The compositions of the present invention comprise a polymeric thickening system. The benefits of using the polymers described herein versus others described in the art for example cellulosic polymers such as guar gum or xanthum gum, are that they are more stable in the presence of bleach (especially hypochlorite bleach), provide better thickening efficiency and do not elevate the yield stress value to levels that might cause flow problems.

- [0009]** The polymeric thickening system of the present invention comprises at least two polycarboxylate polymers; a high molecular weight and a low polycarboxylate homo or copolymer. By high molecular weight it is meant a polycarboxylate homo or copolymer having a molecular weight in the range of from 500 000 to 4 500 000, more preferably from
50 1 000 000 to 4 000 000.

- [0010]** Most preferred high molecular weight polymers for use herein contain from 0.5% to 4% by weight of a cross-linking agent, wherein the cross-linking agent tends to interconnect linear strands of the polymers to form the resulting cross-linked products. Suitable cross-linking agents include the polyalkenyl polyethers. Preferred homo- polymers
55 include the polyacrylate polymers. Preferred copolymers comprise acrylic acid monomers in combination with other monomers for maleic acid, maleic anhydride, nethacrylic acid, succinic acid, vinyl ester and/or mixtures thereof. Preferred monomers of the homo or copolymeric species contain a carboxylic group. The molecular weight of the carboxylate group-containing monomers typically varies from 25 to 200, preferably from 50 to 150, more preferably from 75 to

125. Further, other monomers may be present in the monomeric mixture, if desired, such as ethylene and propylene, which act as diluents.

[0011] Preferred high molecular weight polycarboxylate polymers for use herein are the polyacrylate polymers. Especially preferred polymers are those of the polyacrylate type including those sold under the trade names Carbopol® (especially Carbopol® ETD 2691 available from Goodrich), Acrisol® ICS-1, Polygel®, and Sokalan®. Preferred polyacrylate copolymers are those containing acrylic acid and alkyl (C₅-C₁₀) acrylate as monomers, (commercially available under the tradename Carbopol® 1623, Carbopol® 695 from BF Goodrich). Most preferred are copolymers of acrylic acid and maleic anhydride, (commercially available under the tradename Polygel® DB, Polygel® DV, Polygel® DA) and copolymers of acrylic acid and vinyl ester (commercially available under the tradename Polygel® DR from 3V Sigma)..

[0012] Mixtures of any of the high molecular weight polycarboxylate polymers, herein before described, may also be used.

[0013] The second component of the polymeric thickening system is a low molecular weight polycarboxylate homo or copolymer. By low molecular weight it is meant a polycarboxylate polymer having a molecular weight of from 500 to 10 000, more preferably from 800 to 6000, most preferably from 1000 to 4000.

[0014] Preferred low molecular weight homo-polymers are not cross-linked and are most preferably polyacrylates. Most preferred copolymers comprise acrylic acid in combination with at least one other type of monomer. An especially preferred low molecular weight polymer is Polygel® W30 available from 3V sigma.

[0015] The ratio of high molecular weight to low molecular weight polymer is preferably from 50:1 to 1: 10, more preferably from 30:1 to 1:1, most preferably from 10:1 to 5:1.

[0016] The compositions of the present invention are shear thinning, meaning viscosity is lowered with increasing shear rates. Viscosity is measured using any currently available, suitable viscosity measuring equipment. Viscosity of the composition is preferably in the range of from 10 cps to 4000 cps, more preferably from 50 to 1000cps, most preferably from 100 to 550cps when measured using a Carrimed Rheometer at 25 °C and a shear rate of from 10 to 100 s⁻¹.

[0017] The polymeric thickening system is preferably present at a level of from 0.1% to 10%, more preferably from 0.5% to 5% and most preferably from 0.7 to 2%.

Surfactant

[0018] A highly preferred, but optional component of the cleaning composition described herein is a surfactant. The surfactant may be selected from anionic, non-ionic, cationic, amphoteric, zwitterionic surfactants or mixtures thereof.

[0019] In a preferred aspect of the present invention, the cleaning composition comprises an anionic surfactant system as described in more detail in the Applicants copending patent application. The anionic surfactant system consists of at least one linear short-chain and one branched long chain anionic surfactant. The anionic surfactants are selected from sulphates, sulphonates, alkoxyated sulphates (preferably propoxylated, more preferably ethoxylated), phosphates or mixtures thereof. The short chain surfactants has from 5 to 9 carbon atoms whereas the long chain surfactant has from 10 to 16 carbon atoms.

[0020] A preferred short-chain surfactant is C7-9 Empimin available from Albright and Wilson. A preferred long-chain surfactant is C12-13 branched sulphate based on Isalchem 123 available from Albright and Wilson.

[0021] In another preferred aspect, the surfactant system additionally comprises a branched short-chain anionic surfactant. A suitable such anionic surfactant is 2 ethyl hexyl sulphate available from Albright and Wilson under the tradename Empicol 0585/A.

Optional components

[0022] The compositions according to the present invention may comprise a number of optional ingredients such as bleaching agents, fatty acids, radical scavengers, antimicrobial compounds, builders, chelants, buffers, bactericides, solvents, enzymes, hydrotropes, colorants, bleach activators, soil suspenders, dye transfer agents, brighteners, anti dusting agents, dispersants, dye transfer inhibitors, pigments, perfumes and dyes.

[0023] A highly preferred optional ingredient according to the present invention is a hypochlorite bleaching agent, preferably an alkali metal hypochlorite. Advantageously, the compositions of the invention are stable in the presence of this bleaching agent. Although alkali metal hypochlorites are preferred other hypochlorite compounds may also be used herein and can be selected from calcium and magnesium hypochlorite. A preferred alkali metal hypochlorite for use herein is sodium hypochlorite. Compositions according to the present invention may comprise hypochlorite bleaching agents such that the content of active chlorine in the compositions is from 0.1% to 4%, preferably from 0.5% to 2% by weight.

[0024] Another optional component of the present invention is an alkali metal salt of a C₈-C₁₈ fatty acid. Said fatty acids are used as suds suppressors. Suitable fatty acids for use herein can be any C₈-C₁₈ fatty acid, preferably fully

saturated, preferably a sodium, potassium or lithium salt, more preferably the sodium salt. Suitable fatty acids may be selected from caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid and mixtures of fatty acids suitably hardened, derived from natural sources such as tallow, coconut oil, ground oil and babassu oil. Other suitable suds suppressors include C10-18 alkoxyated capped alcohols. Most preferably however the suds suppressor consists of a mixture of fatty acid, preferably coconut fatty acid (e.g. Prifac 5900 available from Unichem) and alkoxyated capped alcohol, preferably C12-14 ethoxy butoxy methyl ether (e.g. Plurafac LF231 available from BASF). Compositions according to the present invention comprise from 0.1% to 2%, preferably less than 0.6% by weight of the composition of fatty acids.

[0025] A further optional component of the present invention is a radical scavenger. Said radical scavengers are used as stabilisers. A suitable radical scavenger for use herein is the aromatic molecule containing a carboxylic group ring substitution. Suitable examples of radical scavengers for use herein include the meta and para-chlorobenzoic acid, benzoic acid, meta- ortho- and para-methoxybenzoic acid, meta nitrobenzoic acid, para bromobenzoic acid, salicylic acid, 5-sulphosalicylic acid, 3,5-dimethyl salicylic acid and paratoluic acid. Of the above materials, ortho-methoxybenzoic acid is preferred. Compositions according to the present invention comprise from 0.01% to 1.5% by weight, preferably from 0.1% to 0.8% by weight and more preferably from 0.2% to 0.5% by weight of the composition of radical scavengers.

[0026] An optional requirement of the compositions according to the present invention is that the pH is greater than 10, preferably greater than 11, more preferably greater than 12. This is achieved by the addition of from 0.4% to 2% of a caustic alkali. Suitable caustic alkalis for use herein include sodium and potassium hydroxide. Compositions according to the present invention comprising hypochlorite preferably have a pH greater than 12 for hypochlorite stability.

[0027] The compositions according to the present invention are preferably aqueous and preferably comprise from 80% to 95%, more preferably from 85% to 90% of water.

[0028] The compositions according to the present invention are prepared by methods well known in the art such as the methods described in GB 1 329 086 with the exception of the polymer being pre-dispersed in an acidic water solution of pH 3 and then neutralised up to pH 7 before starting adding the other components. The compositions according to the present invention can then be prepared by mixing all of the ingredients in a non-metallic apparatus at room temperature or in warm water. If fatty acid is used, it is melted before being added to the mixture. Preferably, the surfactant blend is first prepared by adding the short chain surfactant to the long chain surfactants. Other optionals such as perfume and the alkali metal hypochlorite are then added whilst stirring. Colourants, if present, are added after all the other ingredients have been mixed.

[0029] The compositions according to the present invention preferably have a viscosity of from 10 cps to 4000 cps, more preferably from 50 cps to 2000 cps, most preferably from 150 cps to 1000 cps measured with a Carrimed Rheometer at a temperature of 25°C and a shear rate of 15-100 s⁻¹. Where the composition is in a sprayed form, the viscosity of said spraying compositions is preferably of from 15 cps to 40 cps.

[0030] The compositions of the present invention may be used for a variety of cleaning purposes such as cleaning hard surfaces whereby said compositions thickened nature results in longer adhesion to the surface than non-thickened compositions. By "hard surface" it is meant herein any surface like bathroom, sanitary fittings such as sinks, showers, wash basins and WCs, kitchen, sinks, cooker tops, table tops, refrigerators, walls, windows and the like.

Packaging form of the compositions

[0031] The compositions herein may be packaged in a variety of suitable detergent packaging known to those skilled in the art. The liquid compositions herein may desirably be packaged in manually operated spray dispensing containers, which are usually made of synthetic organic polymeric plastic materials. Accordingly, the present invention also encompasses liquid cleaning compositions of the invention packaged in a spray dispenser, preferably in a trigger spray dispenser. Indeed, said spray-type dispensers allow to uniformly apply to a relatively large area of a surface to be cleaned the liquid cleaning compositions suitable for use according to the present invention; thereby contributing to the cleaning properties of said compositions. Such spray-type dispensers are particularly suitable to clean vertical surfaces. Surprisingly, the spraying of a liquid composition containing a polycarboxylate polymer, contrary to compositions which do not contain the polycarboxylate polymer, has been seen beneficial for preventing or reducing inhalation of the composition by the user as said composition is sprayed.

[0032] The present advantage is preferably observed where the cleaning composition is as defined hereinbefore. Accordingly, the use of a polycarboxylate polymer in a liquid cleaning composition is provided, said composition being in a sprayed form, for preventing or reducing inhalation of said composition by the user as said composition is sprayed. Preferably, the liquid cleaning composition is as defined hereinbefore.

[0033] Suitable spray-type dispensers to be used according to the present invention include manually operated foam trigger-type dispensers sold for example by Specialty Packaging Products, Inc. or Continental Sprayers, Inc. These types of dispensers are disclosed, for instance, in US-4,701,311 to Dunnining et al. and US-4,646,973 and US-

4,538,745 both to Focarracci. Particularly preferred to be used herein are spray-type dispensers such as T 8500® or T 8900® commercially available from Continental Spray International or T 8100® commercially available from Canyon, Northern Ireland. In such a dispenser the liquid composition is divided in fine liquid droplets resulting in a spray that is directed onto the surface to be treated. Indeed, in such a spray-type dispenser the composition contained in the body of said dispenser is directed through the spray-type dispenser head via energy communicated to a pumping mechanism by the user as said user activates said pumping mechanism. More particularly, in said spray-type dispenser head the composition is forced against an obstacle, e.g. a grid or a cone or the like, thereby providing shocks to help atomise the liquid composition, i.e. to help the formation of liquid droplets.

[0034] The present invention further encompasses a method for cleaning a hard surface by applying on said surface an effective amount of a composition of the invention. The said composition may be applied in its neat form or after having been diluted with water. Preferably said composition is diluted up to 200 times its weight of water, preferably into 50 to 150 times its weight of water and more preferably 75 to 95, before it is applied to said surface. When the composition is diluted prior to use (to reach a total active level in the order of 1.2%), the composition will still advantageously provide effective cleaning performance. In the preferred embodiment of the method of the present invention wherein said composition is applied to a hard-surface to be cleaned in its diluted form, it may not be necessary to rinse the surface after the composition has been applied.

Examples

[0035] The examples provided below are not intended to be limiting and merely provide an example of the sort of formulation that is envisaged by the Applicant. All amounts are listed in % weight of the total composition.

	A % w/w	B % w/w	C % w/w
High MW polymer #1	1.0	-	1.0
Low MW polymer	0.1	0.1	0.1
High MW polymer #2	-	1.5	-
Heptyl-nonyl sulfate (Empimin LN from A&W)	1.5	1.5	3.0
Capped nonionic alcohol (Plurafac LF231 from BASF)	-	-	0.1
Coconut fatty acid (Prifac 5900 from Unichema)	-	-	0.1
2 ethyl-hexyl sulfate (Empicol 0585/A from A&W)	1.5	1.5	-
C12-C13 branched sulfate (based on Isalchem123)	1.0	1.0	1.0
Citrus Bleach PCMF perfume	0.3	0.3	0.2
Hypochlorite	1.0	1.0	1.0
Caustic	1.0	1.0	1.0
Green dye	0.0058	0.0058	0.0058
Periodic acid	0.01	0.01	0.01
Sodium silicate	0.4	0.4	0.4
Demineralized water	Balance	Balance	Balance
High MW polymer #1 is Polygel DR from 3Vsigma High MW polymer #2 is Carbopol ETD2691 from Goodrich Low MW polymer is Polygel W30 from 3Vsigma			

Claims

1. A cleaning composition comprising a polymeric thickening system comprising a first polycarboxylate homo or copolymer having molecular weight in the range of from 500 000 to 4 500 000 and a second polycarboxylate homo or copolymer having molecular weight in the range of from 500 to 10 000.

2. A cleaning composition according to claim 1 wherein the first polycarboxylate polymer is a polyacrylate polymer
3. A cleaning composition according to any of the preceding claims wherein the first polymer is cross-linked.
- 5 4. A cleaning composition according to any of the preceding claims wherein the second polycarboxylate polymer is a polyacrylate polymer which is not cross-linked.
5. A cleaning composition according to any of the preceding claims wherein both the first and second polymers are copolymers containing at least two monomer types, wherein at least one of the monomers is acrylic acid.
- 10 6. A cleaning composition according to any of the preceding claims wherein the ratio of the first to the second polymer is 50:1 to 1: 10.
7. A cleaning composition according to any of the preceding claims wherein the viscosity of the composition is in the range of from 10 cps to 4000 cps measured as described herein.
- 15 8. A method of cleaning a surface by applying a composition according to any of the preceding claims to the surface and optionally subsequently rinsing.

20

25

30

35

40

45

50

55



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 87 0208

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO 96 27000 A (KAY CHEMICAL CO) 6 September 1996 * page 8, paragraph 4 * * page 10, paragraph 3 * * claims 1,8,19; examples; tables 1-8 * ---	1-8	C11D3/37
X	EP 0 517 313 A (COLGATE PALMOLIVE CO) 9 December 1992 * formulation E * * claims 1,7,12; example 5; table 1 * ---	1-6,8	
X	EP 0 517 309 A (COLGATE PALMOLIVE CO) 9 December 1992 * formulation E * * page 11, line 29 - line 35; claims 1-4; table 1 * -----	1-6,8	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C11D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22 January 1999	Examiner Loiselet-Taisne, S
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03/82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 87 0208

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-01-1999

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9627000	A	06-09-1996	AU 5174696 A	18-09-1996
			BR 9607133 A	25-11-1997
			CA 2213129 A	06-09-1996
			CN 1176657 A	18-03-1998
			EP 0813592 A	29-12-1997
EP 0517313	A	09-12-1992	US 5252242 A	12-10-1993
			US 5205953 A	27-04-1993
			AU 1727192 A	10-12-1992
			CA 2069966 A	08-12-1992
			EP 0517308 A	09-12-1992
			EP 0517310 A	09-12-1992
			EP 0517311 A	09-12-1992
			EP 0517312 A	09-12-1992
			EP 0517314 A	09-12-1992
			FI 922495 A	08-12-1992
			NZ 242825 A	26-10-1994
			PT 100549 A	30-09-1993
			AU 1617092 A	10-12-1992
			CA 2070025 A	08-12-1992
			EP 0517309 A	09-12-1992
			FI 922496 A	08-12-1992
			GR 92100227 A	28-04-1993
			NZ 242822 A	27-09-1994
			PT 100547 A	30-09-1993
			TR 26584 A	15-03-1995
			AU 1616892 A	10-12-1992
			CA 2070093 A	08-12-1992
			FI 922497 A	08-12-1992
			GR 92100228 A	28-04-1993
			NZ 242829 A	22-12-1994
			PT 100548 A	30-09-1993
			TR 26143 A	15-02-1995
			AU 1616792 A	07-01-1993
			CA 2070086 A	06-01-1993
			FI 922499 A	06-01-1993
			GR 92100245 A	24-05-1993
			NZ 242833 A	26-10-1994
			PT 100550 A	30-09-1993
			US 5368766 A	29-11-1994
			US 5298180 A	29-03-1994
EP 0517309	A	09-12-1992	AU 1617092 A	10-12-1992
			CA 2070025 A	08-12-1992
			EP 0517308 A	09-12-1992
			EP 0517310 A	09-12-1992

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 87 0208

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

22-01-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0517309	A	EP 0517311 A	09-12-1992
		EP 0517312 A	09-12-1992
		EP 0517313 A	09-12-1992
		EP 0517314 A	09-12-1992
		FI 922496 A	08-12-1992
		GR 92100227 A	28-04-1993
		NZ 242822 A	27-09-1994
		PT 100547 A	30-09-1993
		TR 26584 A	15-03-1995

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82