

DETERGENT COMPOSITION

The present invention relates to a detergent composition containing a specific amphoteric polymer. More particularly, the present invention relates to a detergent composition having a deterging capacity remarkably improved by incorporating a specific amphoteric polymer obtained by copolymerizing a cationic vinyl monomer with an anionic vinyl monomer.

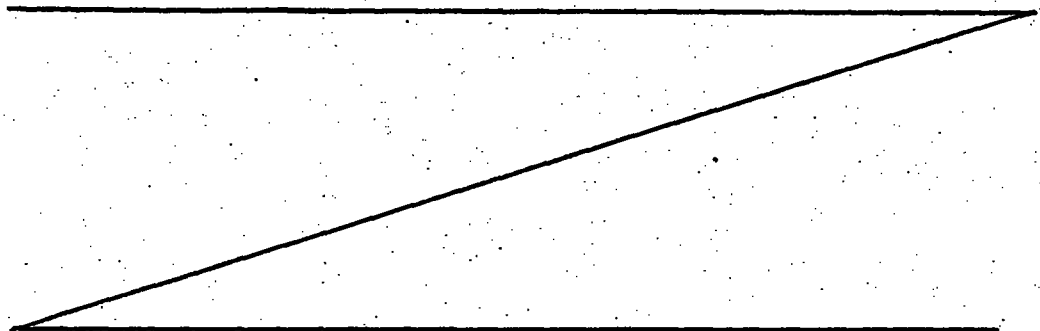
Polymers have been used as additives for detergents. For example, there have known detergent compositions containing polymers as a thickening agent,

stabilizer, protective colloid, builder, softener, encapsulating agent, hazing agent, pearling agent or skin- or hair-protecting agent. However, they have been used merely according to the properties generally known as the characteristics of the high molecular compounds.

After investigations made for the purpose of finding a new application of polymers in detergent systems, the inventors have found that, surprisingly, a specific polymer greatly improves the detergency of a detergent composition particularly in the presence of a surfactant. The present invention has been completed on the basis of this finding.

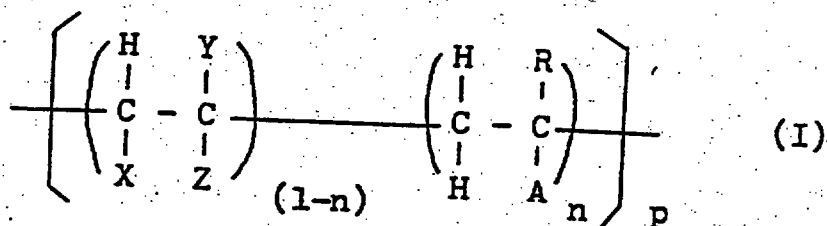
According to the invention we provide a detergent composition which comprises 0.01 to 10 percent by weight of an amphoteric copolymer obtained by co-polymerizing an anionic monomer having a polymerizable unsaturated group with a cationic monomer having a polymerizable unsaturated group in a molar ratio of 1 : 99 to 99 : 1 the balance being optional additives and a carrier for the liquid or powder detergent composition.

The above molar ratio is preferably 20-80 : 80-20. The amphoteric copolymer thus obtained is preferably one that is represented by general formula (I):



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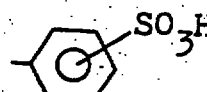
-3-



wherein:

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X: -H or -COOH

Y: -H, -CH₃, -CH₂COOH or -OHZ: -COOH, -SO₃H, -CH₂SO₃H, 

$$\text{or } -\text{CONH} \begin{array}{c} \text{CH}_3 \\ | \\ \text{C} \cdot \text{CH}_2\text{SO}_3\text{H} \\ | \\ \text{CH}_3 \end{array}$$

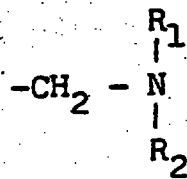
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R: -H or -CH₃

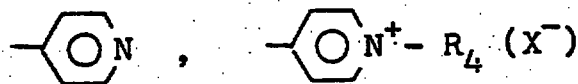
$$\text{A: } -\text{CH}_2 - \begin{array}{c} \text{R}_1 \\ | \\ \text{N}^+ - \text{R}_3 \\ | \\ \text{R}_2 \end{array} (\text{X}^-)$$

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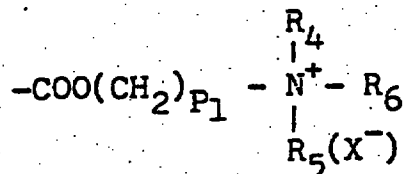
in which R₁, R₂ and R₃ each represent a C₁ to C₃ alkyl group and X⁻ represents an anion such as a halogen or diethyl sulfate.



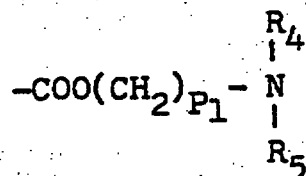
5 in which R_1 and R_2 each represent a C_1 to C_3 alkyl group,



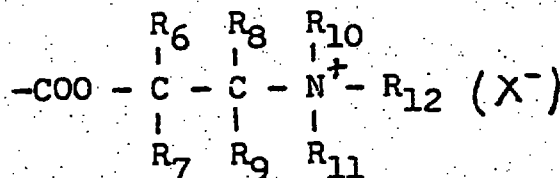
in which R_4 represents a C_1 to C_3 alkyl group,



10 in which R_4 , R_5 and R_6 each represent a C_1 to C_3 alkyl group and P_1 represents an integer of 2 to 4,

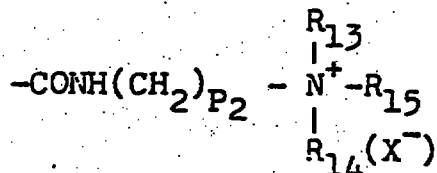


15 in which R_4 and R_5 each represent a C_1 to C_3 alkyl group and P_1 represents an integer of 2 to 4,

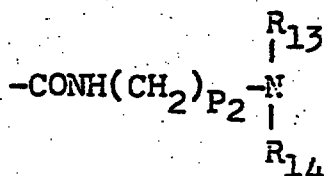


20 in which R_6 , R_7 , R_8 and R_9 each represents H

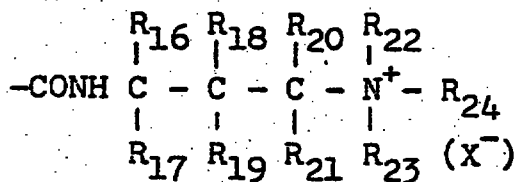
or CH₃ and R₁₀, R₁₁ and R₁₂ each represents a C₁ to C₃ alkyl group,



in which R₁₃, R₁₄ and R₁₅ each represent a C₁ to C₃ alkyl group and P₂ represents an integer of 2 to 4,



in which R₁₃ and R₁₄ each represent a C₁ to C₃ alkyl group and P₂ represents an integer of 2 to 4, or



in which R₁₆ to R₂₁ each represents H or CH₃ and R₂₂ to R₂₄ each represents a C₁ to C₃ alkyl group

n represents a number of 0.01 to 0.99, p represents an integer of 5 to 10000, and each of X, Y and Z is an alkali metal salt, ammonium salt or alkanolamine salt.

The amphoteric polymer of the above general

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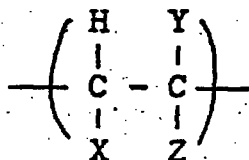
formula (I) used in the present invention may be obtained by copolymerizing a cationic monomer with an anionic monomer. Those amphoteric polymers can be produced by a well known method.

5 In the copolymerization, water is generally used as a solvent and potassium peroxodisulfate, potassium peroxodisulfate/sodium hydrogensulfite or hydrogen peroxide/ Fe^{2+} may be used as an initiator. The resulting copolymer may be used as such or after the

10 purification. The purification is effected by dialysis or reprecipitation method.

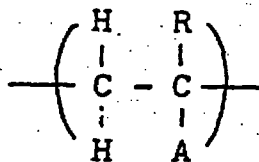
The amphoteric copolymer used in the present invention preferably comprises anionic monomer structural units of the formula:

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and cationic monomer structural units of the formula:

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randomly arranged in a molar ratio of 1-99:99-1,

preferably 20-80:80-20 to form a linear polymer having a molecular weight of 1,000 to 3,000,000. This amphoteric copolymer is produced by polymerizing a mixture of the above-mentioned anionic vinyl monomer and cationic vinyl monomer in a given ratio in the presence of a polymerization initiator in water generally under a nitrogen stream. The polymerization is carried out generally at a temperature ranging from room temperature to 90°C for 2 to 24 h to obtain the intended copolymer having a molecular weight of preferably 3,000 to 1,000,000. Either solution polymerization or bulk polymerization method may be employed. The thus obtained copolymer may be reacted with an alkali metal hydroxide, ammonia or alkanolamine to form a salt.

The anionic monomer used may be any of anionic monomers having a polymerizable unsaturated group and includes acrylic acid, methacrylic acid, itaconic acid, aconitic acid, hydroxyacrylic acid, maleic anhydride, fumaric acid, vinylsulfonic acid, allylsulfonic acid, methallylsulfonic acid, styrenesulfonic acid and 2-acrylamido-2-methylpropanesulfonic acid.

The cationic monomer used may be any of cationic monomers having a polymerizable unsaturated

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group and includes 2-vinylpyridine, 4-vinylpyridine, dimethylaminoethyl methacrylate, diethylaminoethyl methacrylate, dipropylaminoethyl methacrylate, dimethylaminopropylmethacrylamide, allyldimethylamine, allyldiethylamine, allyldipropylamine, methallyldimethylamine, methallyldiethylamine, methallyldipropylamine and methylated, ethylated or propylated derivative thereof.

The detergent composition of the present invention contains from 0.01 to 10 wt. %, and preferably from 0.05 to 5 %, of the amphoteric copolymer.

The detergent composition of the present invention may contain from 1 to 50 percent by weight of a surfactant. An anionic, nonionic, cationic or amphoteric surfactant generally used in the art may be selected in the present invention suitably for the use. As the surfactant, there may be mentioned an anionic surfactant such as an alkyl sulfate, alkylbenzenesulfonate, alkylpolyoxyethylene-sulfate, α -olefinsulfonate, alkanesulfonate, alkyl glyceryl ether sulfonate, alkyl or alkenylcarboxylate, alkenylsuccinate, N-acylsarcosinate, salt of carboxymethylated alkylpolyoxyethylene or alkylphosphate salt; a nonionic surfactant such as a fatty acid diethanolamide, dimethylalkylamine oxide, alkylpolyoxyethylene or alkylarylpolyoxyethylene; cationic

surfactant such as an alkyltrimethylammonium salt, dialkyldimethylammonium salt or alkyl-(N-hydroxyethyl)-dimethylammonium salt; or an amphoteric surfactant such as an alkylimidazole derivative, dimethyl-alkylbetaine or dimethylalkylsulfobetaine. The amphoteric copolymer can be used in an amount of 0.02 to 50 wt. %, preferably 0.25 to 25 wt. %, based on the surfactant according to the present invention. The amount of the surfactant may be determined suitably according to use of the detergent. In carrying out the present invention, the surfactant may be omitted in some cases.

The detergent composition of the present invention may contain also other components such as a solvent, e.g. a monoalcohol, dialcohol, glycerol, ethylene glycol monobutyl ether or diethylene glycol monomethyl ether, a hydrotrope, e.g. a benzenesulfonic acid salt, p-toluenesulfonic acid salt, m-xylenesulfonic acid salt or urea, a chelating agent, an antiseptic, a dyestuff, a perfume, a U.V. absorber, an antioxidant, a hazing agent or thickening agent. The detergent composition of the present invention is generally in the form of a liquid prepared by adding water to the detergent composition. Further, it may be in the form of a solid.

The detergent composition of the present invention can be used as a detergent for metals, machines, ships, textiles, glasswares, foods, tablewares, fibers and domestic appliances as well as a shampoo base. The properties required of such a detergent include deterging power, foam-increasing property and rinsing properties (defoaming property, the touch, etc.). In the present invention, the larger the amount of the amphoteric polymer, the higher the capacities such as deterging power. However, an excessive amount of the amphoteric polymer might exert a harmful influence on physical properties of the product, such as stability and viscosity.

The following examples of synthesis of amphoteric polymers and the examples of the present invention will further illustrate the invention, which by no means limit the invention.

Synthesis Example 1

600 g of ion-exchanged water, 55 g of dimethylaminoethyl methacrylate, 30 g of methacrylic acid and 0.3 g of potassium peroxodisulfate were charged in a 1 l flask provided with a stirrer, thermometer, reflux condenser and nitrogen gas inlet. The polymerization reaction was carried out at 70°C under a nitrogen stream for 6 h. Then, the reaction mixture

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was cooled to room temperature and poured into 3000 g of acetone. An amphoteric polymer thus precipitated was filtered out. The weight of the polymer after drying under reduced pressure was 83 g. The rate of polymerization was 98 %.

Synthesis Example 2

An anionic monomer and a cationic monomer as shown in Table 1 were copolymerized in a molar ratio of 1:1 in the same manner as in the above Synthesis Example 1. The synthesis conditions were as follows:

Ion exchanged water	600 ml
Monomers	0.5 M
Temperature	70°C
Reaction time	6 h
Initiator	$K_2S_2O_8$

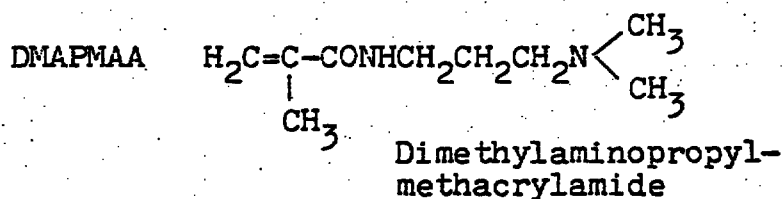
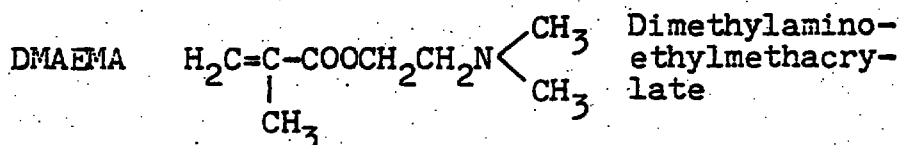
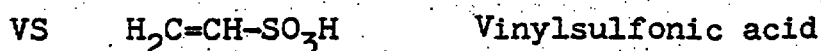
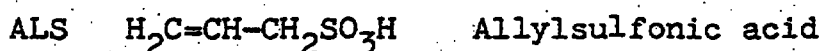
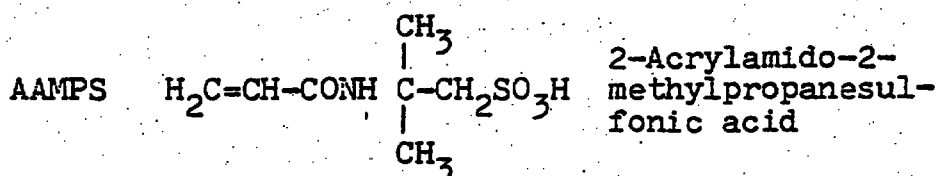
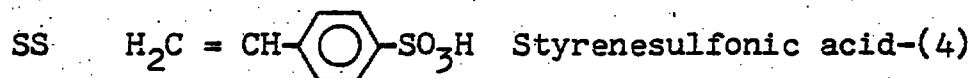
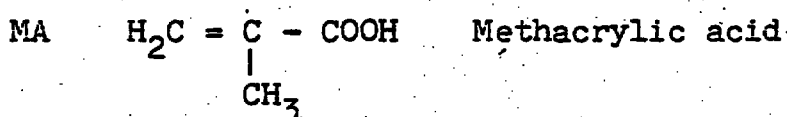
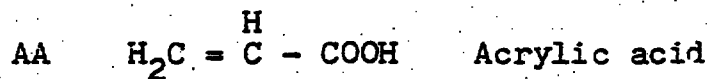
Table 1

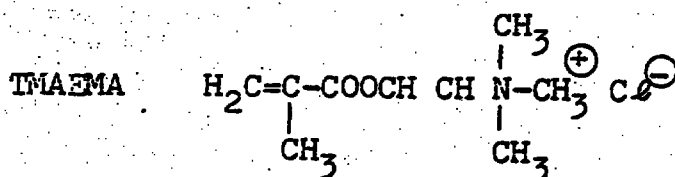
<u>Synthesis No.</u>	<u>Anionic monomer</u>	<u>Cationic monomer</u>
1	AA	DMAEMA
2	AA	TMAEMA
3	AA	EDMAEMA
4	MA	TMAEMA
5	MA	EDMAEMA
6	SS	TMAEMA
7	SS	TMAPMAA

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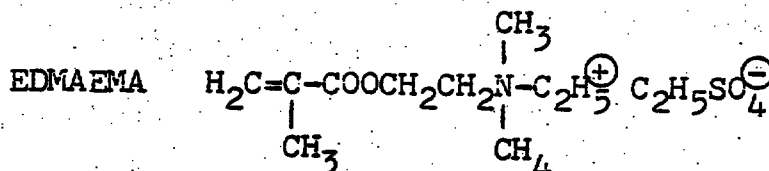
<u>Synthesis No.</u>	<u>Anionic monomer</u>	<u>Cationic monomer</u>
8	AAMPS	EDMAEMA
9	AAMPS	EVPI
10	AAMPS	TMAPMAA
11	ALS	EDMAEMA
12	VS	EDMAEMA
13	VS	DMAEMA

wherein:

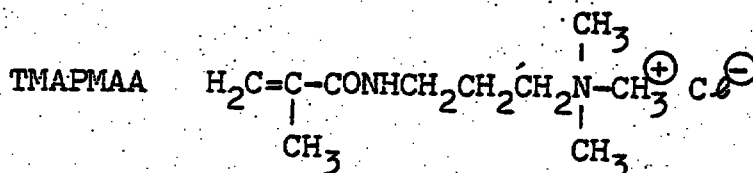




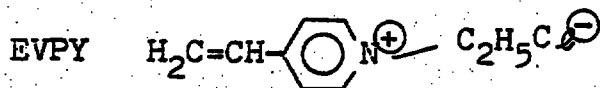
DMAEMA quaterized with
methyl chloride



DMAEMA quaterized with
diethyl sulfate



DMAEMA quaterized with methyl chloride



4-Vinylethylpyridinium
chloride

In the following examples wherein detergent compositions containing polymers of Synthesis Nos. 1 to 13 shown in Table 1 were tested, the properties of the detergents were examined according to the following methods:

[Test methods]

a) Detergency

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0.1 % of Sudan III (a red dyestuff) used as an indicator was added to beef tallow. 5 g of the mixture was applied to each porcelain dish (diameter: 25 cm) and rubbed with a sponge impregnated with 10 g of a detergent and 20 g of water. Detergency of the detergent is represented by the number of dishes cleaned with the sponge until the beef tallow could no more be removed completely.

b) Foaming power:

A foaming power of 0.5 % detergent solution containing 0.1 % of a commercially available butter as a dirt was measured. 40 cc of the butter-containing detergent solution was charged in a glass cylinder having a diameter of 5 cm and the solution was stirred by means of a rotary stirrer for 10 min. Immediately thereafter, the height of the foam was measured.

c) Water repellency:

A commercially available 200 ml glass was washed well with a cleanser. After confirming that the glass could not repel water any more, the glass was rinsed with ion-exchanged water and dried. 150 ml of 1 % aqueous detergent solution was charged in the glass, stirred by means of a rotary stirrer for 30 min and poured out. 200 ml of city water

was charged in the glass, left to stand for 30 sec, and then poured out. This procedure was repeated three times. Water repellency after the pouring of water for the fourth time and the state of the glass after left to stand for one day were observed.

d) Rinse:

100 cc of 0.25 % aqueous detergent solution (temp.: 20°C) was placed in a 500 cc separatory funnel and shaken given times. Then, the solution was poured out and the amount of the foam was measured. Thereafter, 50 cc of rinsing water (20°C) was poured thereinto and the separatory funnel was rotated slowly 10 times. This procedure was repeated until the foam disappeared to determine the number of times of rinse.

Example 1

A liquid detergent of the following composition was prepared:

Sodium straight-chain alkyl-benzenesulfonate.	20 wt. %
Coconut fatty acid diethanol-amide	5 wt. %
Polymer	1 wt. %
Water	balance

Detergency and foaming power of the detergent were measured to obtain the results

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shown in Table 2.

Table 2

<u>Polymer</u>	<u>Number of dishes cleaned</u>	<u>Foaming power (m/m)</u>
Not used	2	55
Synthesis No. 1	4 - 5	75
" No. 3	7 - 8	80
" No. 4	7	95
" No. 6	6	85
" No. 8	5 - 6	80
" No. 10	5	85
" No. 12	7 - 8	90

It is understood from Table 2 that the detergency and foaming power were remarkably improved by the incorporation of the polymer.

Example 2

A liquid detergent of the following composition was prepared:



Polymer 0.5 wt. %

Ethanol 2 wt. %

Water balance

Water repellency of the detergent was examined

to obtain the results shown in Table 3.

Table 3

<u>Polymer</u>	<u>Water repellency</u>
Not used	observed
Synthesis No. 2	not observed
" No. 3	not observed
" No. 5	not observed

Example 3

[Test of preference for foams]

Preference for foams were examined by a panel comprising 30 female testers. In the test, the preference for foams was examined by a pair comparison method using detergent compositions A and B in the same manner as in the deterging power test. The compositions tested are shown in Table 4 and the test results are shown in Table 5.

Criteria:

- +2: A was preferred.
- +1: A was relatively preferred.
- 0: Preferences for A and B were equal.
- 1: B was relatively preferred.
- 2: B was preferred.

(29)

Table 4

<u>Components</u>	<u>Composition No.</u>			<u>Comparative Example 4</u>
	<u>Present invention</u>			
	<u>1.</u>	<u>2</u>	<u>3</u>	
Sodium alkyl ether sulfate *	20	20	20	20
Coconut fatty acid diethanolamide.	5	5	5	5
Ethanol	5	5	5	5
Polymer				
Synthesis No. 3	0.3			
" No. 11		0.3		
" No. 13			0.3	
Water	bal- ance	bal- ance	bal- ance	balance

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Table 5

<u>Combination (A and B)</u>	<u>Marks</u>					<u>Judgment</u>
	<u>+2</u>	<u>+1</u>	<u>0</u>	<u>-1</u>	<u>-2</u>	
Compositions Nos. 1 vs. 4	9	12	7	2	0	No. 1 was preferred to No. 4 (+28)
Compositions Nos. 2 vs. 4	4	7	16	3	0	No. 2 was preferred to No. 4 (+12)
Compositions Nos. 3 vs. 4	7	9	10	4	1	No. 3 was preferred to No. 4 (+17)

(Note) * Average carbon chain length: 12, ethylene oxide
(3 mol) adduct.

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Example 4

Rinsing tests of the compositions of the present invention and polymer-free comparative compositions were carried out. The compositions are shown in Table 6 and the test results are shown in Table 7.

Table 6

Component

Composition No.

	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>	<u>12</u>	<u>Comp. 13</u>	<u>Ex. 14</u>
Alkyl ether sulfate(Na)	20	20	20	20	20	20	20	20	20	20
Straight-chain alkyl-benzenesulfonate (Na)										
Polymer										
Synthesis No. 2	0.5									
" No. 4		0.5								
" No. 7			0.5							
" No. 9				0.5						
Water	bal- ance	bal- ance	bal- ance	bal- ance	bal- ance	bal- ance	bal- ance	bal- ance	bal- ance	bal- ance

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Table 7

<u>Composition No.</u>	<u>Amount of Foam (ml)</u>	<u>Number of times of rinse</u>
No. 5	350	3
6	350	3 - 4
7	400	3 - 4
8	350	3
9	300	3
10	350	4
11	350	4
12	350	3 - 4
13	400	5 - 6
14	400	6

CLAIMS:

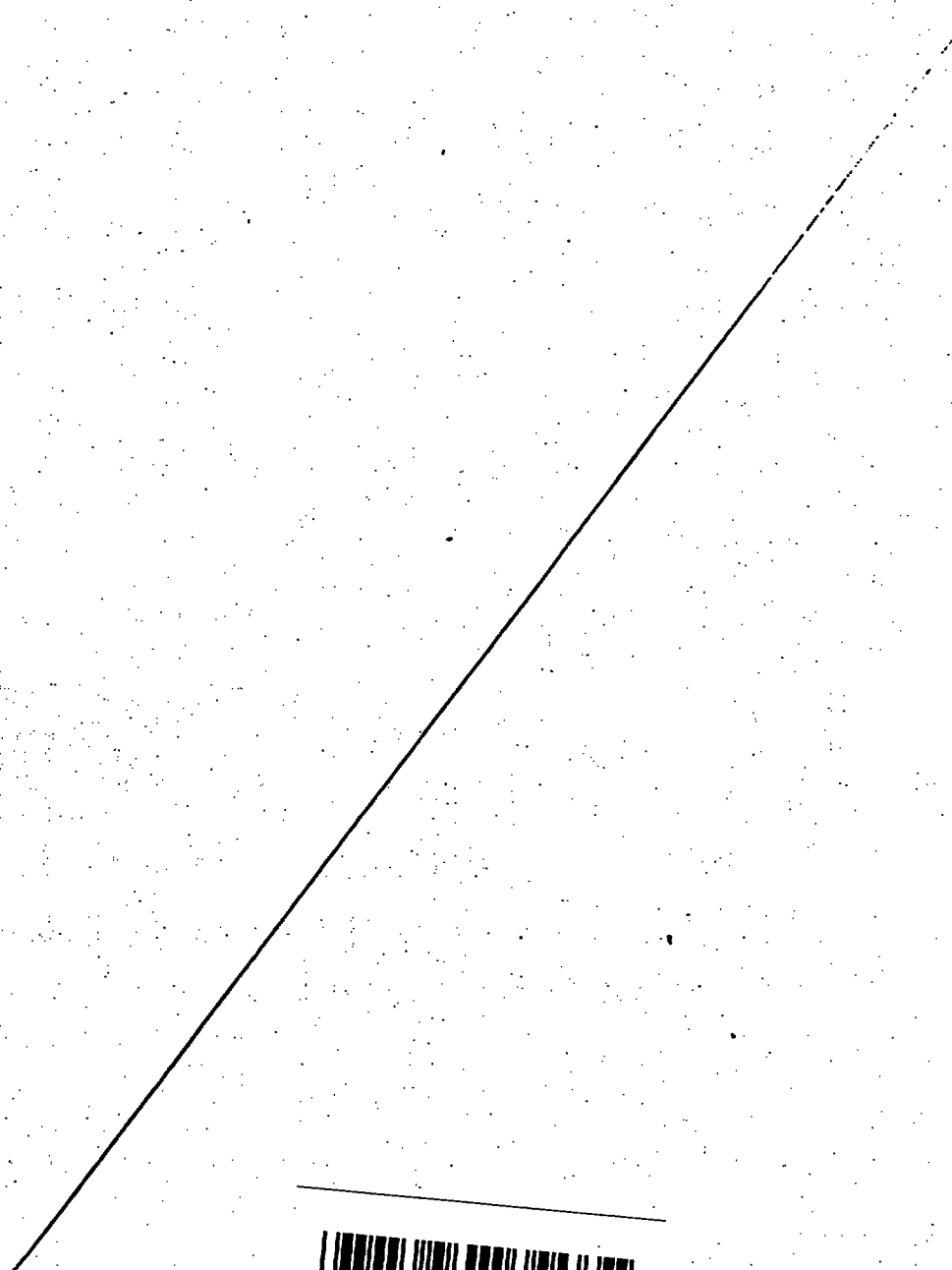
1. A detergent composition which comprises 0.01 to 10 percent by weight of an amphoteric copolymer obtained by co-polymerizing an anionic vinyl monomer having a polymerizable unsaturated group with a cationic vinyl monomer having a polymerizable unsaturated group in a molar ratio of 1 : 99 to 99 : 1, the balance being optional additives and a carrier for the liquid or powder detergent composition.
2. A detergent composition as claimed in Claim 1 which comprises 0.05 to 5% by weight of the said amphoteric copolymer.
3. A detergent composition as claimed in Claim 1 or claim 2 which further comprises from 1 percent by weight to 50 percent by weight of a surfactant.
4. A detergent composition as claimed in Claim 3, in which the said amphoteric copolymer is contained in an amount of 0.02 to 50 percent by weight, based on the surfactant.
5. A detergent composition as claimed in Claim 4 in which the said amphoteric copolymer is contained in an amount of 0.25 to 25 percent by weight, based on the surfactant.



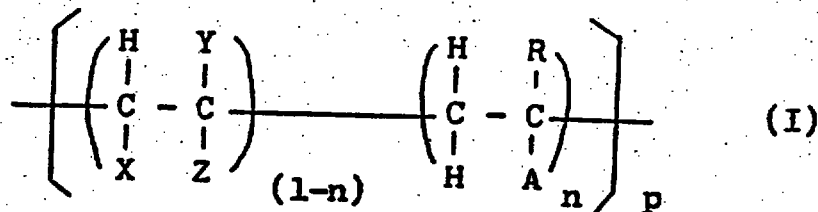
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6. A detergent composition as claimed in any preceding claim, wherein the amphoteric copolymer has the general formula :



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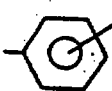


wherein:

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X: -H or -COOH

Y: -H, -CH₃, -CH₂COOH or -OH

Z: -COOH, -SO₃H, -CH₂SO₃H, 

or $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{CONH} \text{C} \cdot \text{CH}_2\text{SO}_3\text{H} \\ | \\ \text{CH}_3 \end{array}$

10

R: -H or -CH₃

A: $-\text{CH}_2 - \begin{array}{c} \text{R}_1 \\ | \\ \text{N}^+ - \text{R}_3 \\ | \\ \text{R}_2 \end{array} (\text{X}^-)$

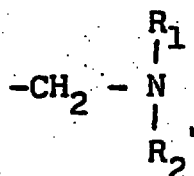
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in which R₁, R₂ and R₃ each represent a C₁ to C₃ alkyl group and X⁻ represents an anion such as a halogen or diethyl sulfate ,



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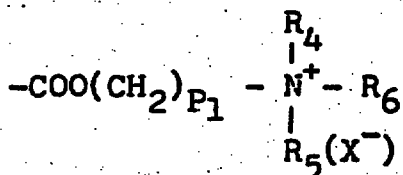


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in which R_1 and R_2 each represent a C_1 to C_3 alkyl group,

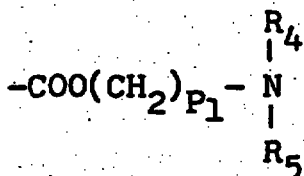


in which R_4 represents a C_1 to C_3 alkyl group,



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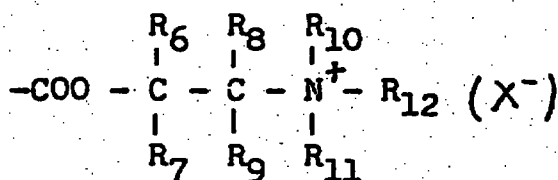
in which R_4 , R_5 and R_6 each represent a C_1 to C_3 alkyl group and P_1 represents an integer of 2 to 4,



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in which R_4 and R_5 each represent a C_1 to C_3 alkyl group and P_1 represents an integer of 2 to 4,

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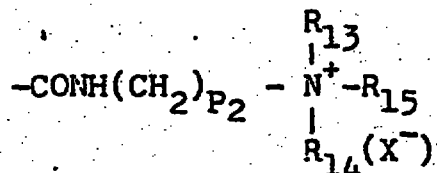


in which R_6 , R_7 , R_8 and R_9 each represents a



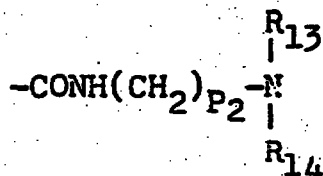
or CH_3 and R_{10} , R_{11} and R_{12} each represents a C_1 to C_3 alkyl group,

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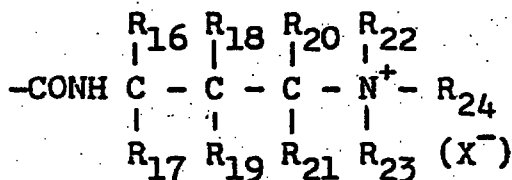
in which R_{13} , R_{14} and R_{15} each represent a C_1 to C_3 alkyl group and P_2 represents an integer of 2 to 4,

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in which R_{13} and R_{14} each represent a C_1 to C_3 alkyl group and P_2 represents an integer of 2 to 4, or

15



in which R_{16} to R_{21} each represents H or CH_3 and R_{22} to R_{24} each represents a C_1 to C_3 alkyl group

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$\underline{n}$ represents a number of 0.01 to 0.99, $\underline{p}$ represents an integer of 5 to 10000, and each of X, Y and Z is an alkali metal salt, ammonium salt or alkanolamine salt.

