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(54) **Liquid detergent composition.**

(57) An aqueous solution of detergent compositions comprising one or more surface active agents, and a water soluble inorganic salt, organic salt or polymeric compound, with an interfacial tension to a triglyceride phase of not more than 0.5 $mN.m^{-1}$ and/or a penetrating speed in a triglyceride phase of not less than 5×10^{-9} $m.sec^{-1}$ has an outstanding cleansing power and is particularly suitable for use for washing tableware without recourse to manual labor or mechanical force.

EP 0 243 927 A2

BACKGROUND OF THE INVENTION

1) Field of the Invention

This invention relates to a detergent composition and, more specifically, a detergent composition suitable for dip washing or cleansing.

2) Prior Art

Majority of the detergents for clothes and tableware known in the art are those requiring a mechanical force for washing or cleansing. This is particularly true in the detergents for tableware, which demands manual labor of the users. This is because most of the detergents currently available in the market contain in their formulations ionic surface active agents as a major component and nonionic surface active agents as a co-surfactant. Detergency or cleansing power of these detergents is functioned by their foaming ability and their ability of emulsifying oils which are exerted by applying a mechanical force to the aqueous solution of such detergents (such solution is here and there referred to as "cleansing liquid" in this specification.) That is to say, the conventional detergents for tableware relied their cleansing power largely on the foaming ability and the stability of the emulsion system.

Because of the nuisance and complexity of everyday manual labors of washing dishes, there has been a demand for a new cleansing method and detergents therefor which do not have a dependency on the mechanical force, and is free from the undue electricity consumption and noises in the washing operation as are experienced in the conventional automatic dish washing machines.

Detergency of a surface active agent is generally considered as such phenomena as emulsification, solubilization and dispersion which are caused by the decrease of the interfacial tension functioned by the surface active agent. In the conventional detergents for tableware, however, the decrease of interfacial tension which is an important factor of cleansing has not been properly regarded, because there has been a limitation imposed by the requirement for the consideration to the least irritation or stimulant to the skin. Another reason is that the foaming ability of a detergent has customarily been adopted as a standard for the cleansing power. Thus, there has been no detergent for tableware having an appropriately reduced interfacial tension.

Likewise, there has hitherto been made no adequate studies on the penetrating action of a surface active agent into oils and fats of vegetables or animals origin, i.e.,

triglycerides, which are the major components of stains on dishes.

SUMMARY OF THE INVENTION

The present inventors have made extensive studies on the relations between the interfacial tension and/or penetrating speed of aqueous solutions of detergents and their cleansing power. As a result the inventors have found that the cleansing liquid having an interfacial tension to a triglyceride phase of not more than 0.5 $mN.m^{-1}$ and/or an penetrating speed in a triglyceride phase of not less than 5×10^{-9} $m.sec^{-1}$ are particularly effective for use for washing tableware without relying upon the manual labor. Such finding has led to the completion of this invention.

Accordingly, an object of this invention resides in an improvement in a detergent composition comprising one or more surface active agents and, as required, a water soluble inorganic salt, organic salt or polymeric compound, said improvement being characterized in that the cleansing liquid containing said detergent composition has an interfacial tension to a triglyceride phase of not more than 0.5 $mN.m^{-1}$ and/or a penetrating speed in a triglyceride phase of not less than 5×10^{-9} $m.sec^{-1}$.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a perspective illustration of a device for measuring the cleansing power, in which the numeral 1 indicates a glass sheet on which oily stains are coated and the numeral 2 indicates a holder for the slide glasses. The device is set in a container 3 containing the cleansing liquid to be tested.

Figure 2 is a drawing showing a device for measuring the penetrating speed in triglycerides. The numeral 4 indicates a stainless plate on which a thin film 5 of the mixture of beef tallow and rapeseed oil is coated. The numeral 6 indicates a drop of the aqueous solution of the detergent to be tested. The stainless plate 1 is connected to an oscilloscope 8 via electrodes 7.

DETAILED DESCRIPTION OF THE INVENTION AND PREFERRED EMBODIMENTS

The term "interfacial tension of a detergent in a triglyceride" as used in this specification is defined as the interfacial tension between the cleansing liquid and the triglyceride as measured when the triglyceride is added to and reaches the solubility equilibrium at 25°C in the cleansing liquid with the detergent concentration of 3 wt%. The penetrating speed of a detergent to a triglyceride is

calculated according to the period of time required for a 0.05 ml drop of the aqueous detergent solution of a 0.05 wt% concentration (as surface active agents) to pass through a thin film of the triglyceride of a 20 ± 3μ thickness coated and dried on a sheet of glass as described hereinafter in detail in the example.

There has been a study on the decrease in an interfacial tension relating to the technology of the enhanced oil recovery. According to the report the interfacial tension between microemulsions prepared by a surface active agent and hydrocarbons of 8 to 10 carbon contents exhibited a remarkable decrease to as low as 0.001 $mN.m^{-1}$. In contrast, there has never been a report on the reduced interfacial tension of triglycerides which are the major stains of dishes and tableware. Although it has been reported that the cleansing power of ionic and cationic surface active agents was increased by the addition of inorganic salts, the concentration of salts in the cleansing liquid studied was no more than 0.017 N (Normal). No study has ever been made on the effects of salts at the higher concentration. This is because the hardness of the cleansing liquid will go up at a higher concentration of salts, which in turn will bring about a higher Krafft point of the detergents and thence a decline in their cleansing power at

a lower temperature.

The present inventors have made studies on the higher concentrations of salts, e.g., more than 0.05 wt% of sodium chloride or sodium sulfate, in combination with conventional ionic surface active agents such as sodium alkylbenzenesulfonate and sodium alkylbenzensulfate, and as a result, have found that the cleansing liquid with such higher salts concentrations exhibited a lowered interfacial tension to triglycerides, a higher penetration in the triglycerides phase, and a greater cleansing power, e.g., 10 to 100 times of that obtained by the cleansing liquid with conventionally utilized lower salts concentrations.

The detergent composition may be prepared by incorporating the following ingredients at a prescribed ratio. That is; conventional surface active agents, including ionic, nonionic, cationic and amphoteric surface active agents; surface active materials, including, for example, oil soluble higher alcohols such as cetyl alcohol and dodecyl alcohol; inorganic salts such as sodium tripolyphosphate, sodium sulfate, magnesium sulfate and sodium carbonate; organic salts such as sodium citrate, sodium and p-toluenesulfonate; and polymeric compounds such as sodium polyacrylate and cationized cellulose. In particular, many of the detergent compositions having a

penetrating speed in a triglyceride phase of not less than 5×10^{-9} m.sec^{-1} may be prepared by the combination of an ionic surface active agent and an inorganic salt of a high concentration.

In order to explain various combinations of compounds by which a reduced interfacial tension and/or an increased penetrating speed are obtained, described below by way of examples are several of systems of surface active agents, with or without inorganic salts being added thereto, inclusive of systems of major ionic surface active agents, combined ionic/nonionic surface active agents, and cationic surface active agents. The compositions Nos. 1 - 26 were prepared according to the formulations in the tables below, and the interfacial tension and/or penetrating speed for each composition were measured and given in the tables.

It should be understood that the present invention shall by no means be limited to the compositions or components thereof, e.g. frequencies and length of branched hydrocarbon chains, given in the examples below.

(1) Compositions prepared by surface active agents conventionally used for kitchen detergents:

A. Ionic Surface Active Agent (1)

$C_nH_{2n+1}(EO)_mSO_4Na$

B. Nonionic Surface Active Agent (1)

$$C_pH_{2p+1}N(\rightarrow O)(CH_3)_2$$

C. Nonionic Surface Active Agent (2)

$$C_qH_{2q+1}(EO)_rCON(CH_2CH_2OH)_2$$

	Components									
	A			B		C			Interfacial Tension	Penetrating Speed
No.	n	m	wt%	p	wt%	q	r	wt%	($mN.m^{-1}$)	($x10^{-9}m.sec^{-1}$)
1	12	0	34	12	16	12	0	50	0.3	2.1
2	12	1	26	12	14	12	0	60	0.2	3.0
3	12	3	14	12	6	12	0	80	0.2	5.0
4	16	3	53	12	27	12	0	20	0.3	5.0
5	16	2	60	12	30	12	0	10	0.3	5.0
6	12	3	34	12	16	18	0	60	0.2	2.0
7	12	3	14	12	6	18	2	80	0.2	0.5

(2) Compositions of other typical ionic/nonionic surface active agents systems

A. Ionic Surface Active Agent (1)

$$C_nH_{2n+1}(EO)_mSO_4Na$$

D. Nonionic Surface Active Agent (3)

$$C_pH_{2p+1}(EO)_qOH$$

E. Sodium Chloride (water soluble inorganic salt)

	Components								
	A			D			E	Interfacial Tension	Penetrating Speed
No.	n	m	wt%	p	q	wt%	Conc.(N)	($mN.m^{-1}$)	($x10^{-9}m.sec^{-1}$)
8	12	3	8	12	7	92	0.3	0.4	2.0
9	12	1	14	12	7	86	0.2	0.5	1.5
10	12	0	22	12	7	78	0.05	0.4	0.2

F. Ionic Surface Active Agent (2)

sodium di-(2-ethylhexyl)sulfosuccinate

D. Nonionic Surface Active Agent (3)

$C_pH_{2p+1}(EO)_qOH$

E. Sodium Chloride (water soluble inorganic salt)

	Components						
	F	D			E	Interfacial Tension	Penetrating Speed
No.	wt%	p	q	wt%	Conc.(N)	($mN.m^{-1}$)	($x10^{-9}m.sec^{-1}$)
11	95	12	3	5	0.001 - 0.005	0.5	6.0
12	82	12	3	18	0.05	0.5	7.0
13	76	12	3	24	0.08	0.4	4.5
14	86	12	7	14	0.2	0.5	3.0

(3) Compositions comprising ionic surface active agents and water soluble inorganic salts

A. Ionic Surface Active Agent

$C_nH_{2n+1}(EO)_mSO_4Na$

E. Sodium Chloride (water soluble inorganic salt)

	Components				
	A			E	Penetrating Speed
No.	n	m	wt% (*)	Conc.(N)	($x10^{-9}$ m.sec^{-1})
15	12	0	0.05	0.2	8.0
16	12	0	0.02	0.4	6.0
17	12	0	0.015	0.8	5.0
18	12	1	0.05	0.4	7.0
19	12	1	0.02	0.7	6.0
20	12	1	0.015	0.9	5.0
21	16	2	0.05	0.3	6.0
22	16	2	0.02	0.5	5.0
23	16	2	0.015	0.9	5.0

(*) concentration in the cleansing liquid

(4) Compositions comprising cationic surface active agents and water soluble inorganic salts

G. Cationic Surface Active Agent

$C_pH_{2p+1}N(CH_3)_3.Cl$

E. Sodium Chloride (water soluble inorganic salt)

	Components			
	G		E	Penetrating Speed
No.	p	wt%(*)	Conc.(N)	($x10^{-9}$ m.sec^{-1})
24	12	0.05	0.3	7.0
25	12	0.02	0.5	5.0
26	12	0.015	0.8	5.0

(*) concentration in the cleansing liquid

Among the above compositions of this invention, particularly preferred are those having the interfacial tension to a triglyceride phase of not more than 0.5 $mN.m^{-1}$ and the penetrating speed in a triglyceride phase of not less than $5x10^{-9}$ $m.sec^{-1}$.

Various additives may be incorporated in the composition of the present invention to the extent they are compatible with the purpose of this invention. Such additives may be those conventionally employed in detergent compositions and include fluorescent whiteness improvers, bactericides, antideposition agents, colorants, perfumes, foam controlling agents, enzymes, solubilizers and the like.

The composition of this invention exhibits a high cleansing power with a moderate mechanical force, or even without any mechanical force, and without using an alkali

agent. Therefore, the composition can be utilized not only as a detergent for tableware and dishes, but also as detergents or cleansing agents of a variety of articles including clothes, various housefurnishings, bathtubs, and the like. The detergent composition can be applicable to an industrial purposes as well.

The present invention will be described in more detail by way of the example, which shall not be construed as limiting the scope of the invention.

Example 1

Compositions comprising ionic surface active agents, nonionic surface active agents and inorganic salts as shown in Table 1 were prepared, and the cleansing power, interfacial tension and penetrating speed in a triglycerides phase were measured on each of the compositions. The results are shown in the same Table 1.

Test Method:

Cleansing Power

(1) Preparation of stains specimens

Stains made of beef tallow and rapeseed oil of a weight ratio of 9/1 dissolved in chloroform to a concentration of 40 wt% were put on slide glasses and air-dried. Each 6 pieces of the slide glasses were weighed in

advance (weight: W_1). The amounts of stains put on the glasses were so adjusted that the average weight on each of the pieces may be 0.140 ± 0.010 g (W_2).

(2) Cleansing

Each set of 6 slide glasses stained as above was dipped for 3 minutes and at 25 ± 1 °C in 700 ml of the surface active agent test solution of a 0.05 wt% concentration contained in the apparatus as shown in the attached Figure 1.

(3) Rinsing

Each slide glass having been subjected to cleansing as above was dipped in water for rinsing at the same temperature for 1 minute.

(4) Drying

The rinsed slide glasses were air-dried for overnight, after which it was submitted to the evaluation.

(5) Evaluation

Each set of 6 slide glasses dried as above was weighed to obtain its weight (W_3). The cleansing rate was determined according to the following equation.

$$\text{Cleansing Rate} = (W_3 - W_1)/(W_2 - W_1) \times 100$$

The results obtained were grouped as follows according to the rate of the cleansing:

Results	Cleansing Rate
Good	80 - 100 %
Modest	60 - 80 %
Poor	Below 60 %

Interfacial Tension

Triglyceride (rapeseed oil) was added to the aqueous solution with prescribed concentration of the detergents, (3 wt% as surface active agents) and the mixture was left over at 25 °C until the solubility equilibrium was obtained, upon which the interfacial tension between the cleansing liquid and rapeseed oil was measured by the Spinning Drop type tester [SPD-100, Produce of Miyamoto Manufacturing Co.]

Penetrating Speed in Triglyceride

(1) Preparation of the test specimen

The mixture of beef tallow and rapeseed oil (weight ratio 9/1) was used as a stain specimen, which was heated and fluidized at a temperature of above the melting points of oils and coated on a stainless plate (150 x 200 mm) using a barcorder in the amount such that the thickness of the stain after drying may be 20 ± 3 μ.

(2) Measurement of penetrating speed

The test specimen prepared according to (1) above was connected to the oscilloscope as shown in Figure 2, onto

which a 0.05 ml drop of the test detergent liquid (0.05 wt% as the surface active agent) at the point A of Figure 2. The period of time required for the drop of the liquid to penetrate the oil phase was measured, from which the penetrating speed was determined according to the following equation.

The Penetrating Speed = (Thickness of solid triglycerides phase < $20 \pm 3\mu$ >)/(The required for penetration)

Notes for Table 1:

1. The compositions of the products are expressed by wt%.
2. Asterisks for components mean that the products are balanced by that components.
3. Characters G, M and P for the cleansing power stand for "Good", "Modest" and "Poor" results of cleansing as defined above.

Table 1

Components	Inventive Products				Comparative Products			
	1	2	3	4	5	6	7	8
Sodium dodecylbenzenesulfonate	-	10	19	-	15	-	-	18
Sodium α-olefinsulfonate (Average length of hydrocarbon chains: C = 14)	-	-	-	8	-	-	-	5
Sodium polyoxyethylene(4.0) laurylsulfate	4	-	-	-	4	15	25	-
Lauryldimethylamineoxide	2	1	-	4	2	2	-	-
Palm core fatty acid diethanolamido	24	19	7	18	2	5	-	-
Glycerolmonostearate (HLB = 2.8)	-	-	4	-	-	-	-	-
Lauric acid	-	-	-	-	-	-	-	4
Sodium sulfate	-	-	-	-	-	-	-	*
Water	*	*	*	*	*	*	*	-
Cleansing power (0.05 wt% as surface active agents)	G	G	G	G	P	P	P	M
Interfacial tension ($mN.m^{-1}$)	0.2	0.4	0.2	0.2	1.4	3.3	2.1	3.6
Penetrating speed ($x10^{-9}m.sec^{-1}$)	0.3	2.1	0.2	0.8	0.9	1.0	3.0	4.7

Example 2

The composition as shown in Table 2 were prepared and their cleansing power was evaluated. The evaluation was made by 30 house wives who actually used the detergent compositions at their home according to the following method of cleansing. The results were grouped according to the criteria as described below:

(The method of cleansing)

Cleansing liquids of various compositions (detergent concentration: 0.15%) were prepared and an aliquot of each cleansing liquids (3 - 6 liter) were put into a conventional tub. After the homogeneous solution of the detergent was obtained, the objects to be washed was dipped and left over for 30 to 60 minutes to effect the cleansing.

(Criteria of the evaluation)

+ 2 Excellent (cleansing may be completed merely by rinsing with water after dipping in the cleansing liquid)

+ 1 Good (cleansing may be completed by slightly washing to rinse with water after dipping in the cleansing liquid)

0 Modest (thorough washing is necessary after having been dipped in the cleansing liquid)

- 1 Not Good (the amount of the oil stains does not

decrease much after dipping in the cleansing liquid)

- 2 Bad (no change of oil stains upon dipping in the cleansing liquid was observed)

The results of the evaluation are shown in Table 2.

Table 2

Components	Inventive Products		Comparative Products
	9	10	11
Sodium di-(2-ethylhexyl)-sulfosuccinate	-	25	-
Sodium polyoxyethylene(p=4.0) lauryl-ethersulfate	4	-	15
Lauryldimethylamineoxide	2	-	2
Coconut oil fatty acid diethanolamido	24	-	5
Ethanol	-	-	3
Water	balance	-	balance
Sodium sulfate	-	balance	-
Interfacial tension ($mN.m^{-1}$)	0.2	0.3	2.5
Penetrating speed ($x10^{-9}m.sec^{-1}$)	3.0	6.0	2.2
Cleansing power (Average value by the evaluation by 30 house wives)	+1.4	+ 1.8	- 0.8

Example 3

The compositions comprising ionic surface active agents, nonionic surface active agents and inorganic salts as shown in Table 3 were prepared, and the cleansing power

and the penetrating speed in a triglycerides phase were measured in the same manner as Example 1. The results are shown in the same Table 3, for which all the notes for Table 1 are applicable.

Table 3

Components	Inventive Products			Comparative Products				
	12	13	14	15	16	17	18	19
Sodium dodecylbenzenesulfonate	-	-	-	-	15	-	-	18
Sodium di-(2-ethylhexyl) sulfosuccinate	-	-	15	-	-	-	-	-
Sodium α-olefinsulfonate (Average length of hydrocarbon chains: C = 14)	-	-	-	-	-	-	-	5
Sodium polyoxyethylene(0.5) tetradecylsulfate	15	-	-	9.5	-	-	-	-
Sodium polyoxyethylene(1.0) stearylsulfate	-	15	-	-	-	-	-	-
Sodium polyoxyethylene(4.0) laurylsulfate	-	-	-	-	4	15	25	-
Lauryldimethylamineoxide	-	-	-	-	2	2	-	-
Coconut fatty acid diethanolamido	-	-	-	-	2	5	-	-
Polyoxyethylene(7.0) branched-alkyl(C_{12-14})ether (HLB = 14.5)	-	-	-	5.5	-	-	-	-

... Continued ...

Table 3 (continued)

Components	Inventive Products			Comparative Products				
	12	13	14	15	16	17	18	19
Lauric acid	-	-	-	-	-	-	-	4
Sodium sulfate	-	*	*	*	-	-	-	*
Magnesium sulfate	*	-	-	-	-	-	-	-
Water	-	-	-	-	*	*	*	-
Cleansing power (0.05 wt% as surface active agents)	G	G	G	P	P	P	P	M
Penetrating speed ($x10^{-9}m.sec^{-1}$)	5.0	5.7	6.0	3.0	0.9	1.0	3.0	4.7

Example 4

The composition as shown in Table 4 were prepared and their cleansing power was evaluated in the same manner as described in Example 2. The evaluation was made by 30 house wives who actually used the detergent compositions at their home. The results are shown in the same Table 4.

Table 4

	Inventive Products	Comparative Products
Components	20	21
Sodium di-(2-ethylhexyl)-sulfosuccinate	15	-
Sodium polyoxyethylene(p=4.0) lauryl-ethersulfate	-	15
Lauryldimethylamineoxide	-	2
Coconut oil fatty acid diethanolamido	-	5
Ethanol	-	3
Water	-	balance
Sodium sulfate	balance	-
Penetrating speed ($x10^{-9}m.sec^{-1}$)	6.0	2.2
Cleansing power (Average value by the evaluation by 30 house wives)	+1.8	- 0.8

Having now fully described the invention, it will be apparent to one of the ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the invention as set forth herein.

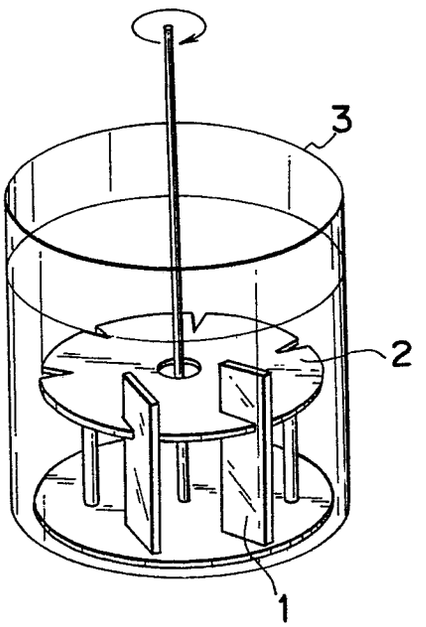
WHAT IS CLAIMED IS:

1. In a detergent composition comprising one or more surface active agents, and, as required, a water soluble inorganic salt, organic salt or polymeric compound, the improvement characterized in that the cleansing liquid containing said detergent composition has an interfacial tension to a triglyceride phase of not more than 0.5 $mN.m^{-1}$ and/or a penetrating speed in a triglyceride phase of not less than 5×10^{-9} $m.sec^{-1}$.

2. A detergent composition as claimed in claim 1, wherein the concentration of said salt in the aqueous solution of said composition is above 0.017 N (Normal) when the concentration of the surface active agent is 0.05 wt%.

1/2

Figure 1



2/2

Figure 2