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(54) LIQUID DETERGENTS COMPRISING NONIONIC SURFACTANTS

(71) We MITSUBISHI PETROCHEMICAL COMPANY LIMITED, a company organised and existing under the laws of Japan, of 5-2 Marunouchi 2-chome, Chiyoda-ku, Tokyo-to, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: 5

This invention relates, generally, to detergents which comprise nonionic surfactants, and, specifically, to liquid detergents of this type. In particular, the invention relates to a liquid detergent comprising a nonionic surfactant which is produced by a specific addition process, and has an excellent detergent performance and little odour. 5

In recent years, there has been a tendency for the commodity form of detergents to become diversified. That is, in addition to detergents of the powder type containing large quantities of builders and constituting the mainstream of detergents until recently, multiform types of detergents have appeared, e.g., those of the concentrate type wherein the content of the surfactant is increased, and those of the liquid type. 10

Detergents of the liquid type, in particular, can be simply and conveniently applied at the time of use and, moreover, have advantageous features in use such as the need for a small quantity only in each cycle of washing, each of local washing of greatly soiled local parts, high solubility in water and ease of use. Furthermore, liquid detergents have the advantage of low costs of production and distribution due to their high concentration, and of ease of formulation. 15

In a liquid detergent of this kind, there is a limit to the quantity of builders such as condensed phosphates, carbonates and silicates which can be added thereto because of the need to maintain the detergent in the liquid state. Accordingly, nonionic surfactants, which can exhibit detergency to a certain extent without the addition of builders, are being preferentially used. Examples of such nonionic surfactants are nonionic surfactants which result from the reaction between primary or secondary alcohols, each having an alkyl group of 9 to 18 carbon atoms, or of alkylphenols, and alkylene oxides. 20

However, the use of nonionic surfactants of this kind and of liquid detergents on fabrics has been accompanied by the following problems: 25

(i) Known nonionic surfactants of this kind, in general, have had low detergencies. Consequently, liquid detergents using these surfactants also have inadequate detergencies. These detergencies are particularly inferior to those of powder type detergents containing anionic surfactants and large quantities of builders. 30

(ii) Known nonionic surfactants of this kind have high melting points (solidifying points). Consequently, the use of liquid detergents which comprise these surfactants is also unavoidably accompanied by various difficulties. 35

For example, certain liquid detergents containing known nonionic surfactants of high melting points require the addition thereto of large quantities of water, or various other solvents, in order to preserve them in the liquid state even at low temperatures such as those occurring in winter in certain places. However, the addition of such large quantities of water or other solvents lowers the detergent concentration, so that the value of the commodity as a liquid detergent of high concentration is lost. 40

In addition, in the production of such detergents using high melting point surfactants, special production equipment and supplementary equipment and special operations are needed. Thus, for example, there is a need to provide heating equipment to prevent 45

solidifying of the surfactant on the piping and formulating apparatus of the detergent production equipment, and the production process procedures also increase.

5 (iii) Among the known nonionic surfactants of this kind, there are many which contain substances such as still unreacted higher alcohol, so that a detergent in which such a surfactant has been used will have a lowered commodity value because of its odour. The 5 problem of surfactant odour can be solved by removing the low-melting point fraction by a treatment such as a topping treatment, but additional expenditure is then needed for this additional process step and the equipment needed.

10 We have now found that a specific nonionic surfactant produced by a specific addition reaction between certain alkylene oxides in specified proportions and a specified saturated 10 aliphatic primary alcohol, or alcohol mixtures, has the advantages of a low melting point and a high detergency, and is, accordingly, particularly advantageous in the formulation of liquid detergents.

The present invention is based on this finding.

15 According to this invention there is provided a liquid detergent comprising a nonionic surfactant consisting of an adduct which is the products of an addition reaction between 15 propylene oxide and ethylene oxide and a saturated aliphatic primary alcohol represented by the formula ROH, wherein R designates an alkyl group having 8 to 18 carbon atoms, of which at least 30 percent by weight is a straight-chain alkyl group,

20 the propylene oxides and the ethylene oxide undergoing the addition reaction: 20

(a) in the form of a mixture thereof; or

(b) separately and alternately, each being thus added at least twice at separate instances and in separate subdivision lots; or

25 (c) in a non-simultaneous combination of (i) addition of said oxides as a mixture thereof and (ii) addition of the propylene oxide and/or ethylene oxide separately, each being added 25 once or at least twice at separate instances and in separate subdivision lots, in which addition reaction, 3 to 9 mols of the propylene oxide and 6 to 22 mols of the ethylene oxide are added, for every mol of the saturated aliphatic primary alcohol, and the addition mol ratio of the propylene oxide to the ethylene oxide is within the range of from 0.25 to 1 to 0.6 30 to 1, inclusive. 30

The nature, advantages and further features of this invention will be more clearly apparent from the following detailed description, beginning with a consideration of general aspects of the invention and concluding with specific examples of practice illustrating preferred embodiments thereof.

35 The surfactant of this invention suitable in liquid detergents for use on fabrics is a nonionic surfactant which has been produced by causing propylene oxide and ethylene oxide to undergo an addition reaction, by any one of the specific procedures (a), (b) and (c) 35 set forth above, with a saturated aliphatic primary alcohol represented by the general formula (1) set forth above, the number of addition mols of the propylene oxide and the ethylene oxide relative to the latter alcohol satisfying the above-described specific 40 conditions. 40

Higher alcohols

45 The starting higher alcohol used for the production of the nonionic surfactant of this invention is a saturated aliphatic primary alcohol represented by the general formula (1) set 45 forth above. Examples of such higher alcohols are: higher alcohols obtained by processing natural oils and fats such as coconut oil alcohol, sperm oil alcohol, and tallow alcohol; synthetic primary alcohols having 8 to 18 carbon atoms obtained by synthesis, such as oxo alcohols, and Ziegler alcohols; and mixtures of two or more of these alcohols.

50 Furthermore, the alkyl in this starting higher alcohol may be a straight-chain alkyl group, or a mixture of straight-chain and branched chain alkyls, but, in the case of a mixture, the content of the straight-chain alkyl group must be higher than 30 percent by weight as 50 specified above in connection with the above general formula (1). We have found that a nonionic surfactant of the above-stated kind obtained from a higher alcohol wherein this content is less than 30 percent by weight does not exhibit sufficient detergency. 55

Addition reaction

60 In order to produce the nonionic surfactant of this invention by adding propylene oxide and ethylene oxide to this starting higher alcohol, the propylene oxide and the ethylene 60 oxide are caused to undergo an addition reaction essentially by:

(a) reacting these oxides in the mixed state; or (b) reacting these oxides alternately and separately, each in two or more cycles of addition in separate subdivided lots; or (c) 65 carrying out a non-simultaneous combination of: (i) the reaction of the two oxides in the mixed state, and (ii) the reaction of the propylene oxide and/or ethylene oxide separately, 65 each being added once or at least twice at separate instances and in separate subdivision

lots.

In particular, in the latter process (c), various modes of procedure as possible. For example, the addition reaction with the two oxides in the mixed state and the addition reaction of the oxides separately may be carried out beginning with either reaction in time sequence. More specifically, prior to and/or after the addition reaction with the oxides in the mixed state, a reaction with one of the oxides by itself, or reactions of the two oxides separately and alternately, may be carried out, and the reaction with the oxides in the mixed state may be carried out two or more times in subdivided lots of the mixture with interspersions between these reaction subdivisions of reactions of one oxide by itself, or reactions of the two oxides separately and alternately. Furthermore, cycles of the reaction of the oxides in the mixed state may be interspersed between two or more cycles of the reaction of one oxide by itself, or of the two oxides separately and alternately.

In accordance with this invention, it is possible to cause the propylene oxide and/or ethylene oxide to undergo an addition reaction with the addition thereto of a very small quantity (e.g. a number of percentages by weight), each, of other epoxides such as butylene oxide and styrene oxide.

The nonionic surfactant of this invention is an adduct produced by the specific addition process described above. In this process, moreover, the propylene oxide is added in a quantity of 2 to 10 mols, preferably 3 to 9 mols, and the ethylene oxide is added in a quantity of 5 to 25 mols, preferably 6 to 22 mols, for each mol of the higher alcohol, and, at the same time, the addition mol ratio of propylene oxide/ethylene oxide is (0.2 to 0.7)/1, preferably (0.25 to 0.6)/1.

The specific nonionic surfactant of this invention as described above has highly desirable properties such as excellent detergent performance, e.g. high detergency and a very low solidification point, whereby it will not solidify, even at low temperatures such as those encountered in winter. Moreover, the residual quantity of the low volatility component of unreacted alcohol and the like is very small, and the surfactant is almost odourless even when it has not been subjected to treatment such as topping. In contrast, a nonionic surfactant of mixed polyalkylene glycol type which does not satisfy any of the above-described conditions is unsatisfactory with respect to one or more of the above-described properties as will be apparent from the examples and comparison examples set forth hereinafter.

As can be deduced from its production process and other circumstances, the nonionic surfactant of this invention can be considered to have any one of a number of possible structures. For example, one possible structure is that wherein the polyalkylene glycol chain added to the higher alcohol is in a form wherein the propylene oxide and the ethylene oxide are added substantially at random. In another possible structure, the polyalkylene glycol chain is in a form wherein propylene glycol chains and ethylene glycol chains are essentially added alternately in block form, and, moreover, the blocks are added in a dispersed state in two or more positions. In still another possible structure, the polyalkylene glycol chain is in a form wherein chains of random structure and chains of block-form structure suitably coexist.

The nonionic surfactant of this invention is produced by causing propylene oxide and ethylene oxide to undergo an addition reaction by a specific process as described above with a higher alcohol represented by the general formula (1), set forth hereinbefore, with the use *inter alia* of conventional acidic or alkaline catalysts.

In the case of the procedure (a), wherein a random adduct is obtained by carrying out the addition reaction with the propylene oxide and the ethylene oxide in a mixed state, the two oxides may be introduced into the reaction system in a previously mixed state, or they may be separately but simultaneously introduced into the reaction system and thus mixed in the reaction system to undergo the reaction. In the case of the procedure (b), wherein an adduct in block form is obtained by the oxides being caused to undergo an addition reaction separately and alternately, each by itself and in two or more separate addition cycles, the oxides must be introduced into the reaction system separately, each in two or more separate cycles, and, moreover, alternately in a time sequence. In the case of the procedure (c), wherein an addition reaction with the oxides in the mixed state and an addition reaction of each oxide by itself are carried out together, a method of introducing the oxide in accordance with the joint mode of reaction is used.

In each case, the total quantity of the propylene oxide and the ethylene oxide introduced is, of course, so adjusted that the desired addition mol number and addition mol ratio are obtained, as indicated just below.

Products

The nonionic surfactant of this invention has a specific addition mol number, specific addition mol ratio, and specific polyalkylene glycol chain structure obtained by the addition

reaction according to the specific process described above. Since this nonionic surfactant has a low melting point (solidifying point), it remains in liquid form even at low temperatures, and, moreover, since it is almost odourless, a liquid detergent for fabrics in which this surfactant is used as the predominant component has excellent washing power, and remains in a stable liquid form even when it has not been diluted with a large quantity of a solvent or water, that is, even at a high surfactant concentration.

Furthermore, the liquid detergent does not solidify or become cloudy or milky even at low temperatures and, moreover, has little or no odour, so that its commodity value is high. Still another advantageous feature of the liquid detergent is that its desudsing characteristic after washing is good, and rinsing is extremely easy. A further desirable feature of the detergent is that, since the melting point of the surfactant is low, heating equipment for maintaining the surfactant in the liquid state during the production of the detergent is not needed, and the production operation is also simple, whereby production costs can be kept low.

By utilizing its advantageous features, the nonionic surfactant according to this invention can be effectively used as the predominant component, or formulating ingredient, of liquid detergents in various fields of detergents.

For example, when the surfactant of the invention is used in liquid detergents for clothing and household fabrics, the detergents are remarkably superior to known liquid detergents in characteristics such as odour, liquidity, detergency, and desudsing property, as mentioned hereinbefore. Furthermore, the nonionic surfactant of the invention can be advantageously applied to liquid detergents for use in kitchens, bathrooms, and other home, industrial or social uses. This surfactant can be used in detergents for a wide range of processes in the textile industries such as detergents for raw wool, detergents for woolen fabrics, detergents for scouring cotton and detergents for washing out surplus dyes after dyeing.

In the fields of machinery and metal industries, also, detergents in which this surfactant is used have been found to be advantageous. Examples of such detergents are those for cleaning metal surfaces prior to painting, those for removing oily grime from machine parts, and those for cleaning the interiors and exteriors of vehicles.

In the paper and pulp industries, the surfactant can be used as a depitching agent and as a deinking agent. Other applications include those of emulsifiers and dispersants for substances such as agricultural chemicals, dyes, synthetic resins, and paints and the like.

The nonionic surfactant of this invention is essentially applicable to a great variety of fields in which nonionic surfactants known heretofore have been used and, of course, is not limited to the above-recited applications, which have been set forth merely as illustrative examples.

Any of various anionic surfactants and various nonionic surfactants can be added, depending on the case, to a liquid detergent in which the nonionic surfactant of this invention is used. Examples of the anionic surfactants are alkylbenzene sulphonates, higher alcohol sulphate salts, higher alcohol ethoxylate sulphate salts, alkenylsulphonates, fatty acid salts and sulphofatty acid esters. Examples of the nonionic surfactants are polyalkyleneglycol ethers or esters of higher alcohols, alkylphenols, higher fatty acids, higher alkylamines, fatty amides and partial esters of polyhydroxyalcohols.

The nonionic surfactant of this invention, similarly to other known nonionic surfactants of the polyalkylene glycol type, is stable with respect to hard water, and does not become cloudy or milky, precipitate, or suffer a lowering of its detergency, even in water in which ions such as Ca ions are present. Accordingly, by using the surfactant of this invention in combination with an alkylbenzene sulphonate, an alkyl sulphate, or the like, which are unstable in hard water, these other surfactants can be stabilized in hard water.

Furthermore, various additives can be formulated into a detergent in which the nonionic surfactant of this invention is used. Examples of such additives are: inorganic builders such as silicates and sulphates; chelating agents such as condensed phosphates, nitrilotriacetates, ethylene diamine tetraacetates, and citrates; solubilizing agent such as urea, xylene sulphonate and ethanol; optical brighteners; resoiling prevention agents; foam stabilizers; perfumes; and colouring matters.

In order more fully to indicate the nature and various features and advantages of this invention, the following specific examples of practice, constituting preferred embodiments of the invention, and the following comparison examples are set forth, it being understood that the examples of preferred practice are presented as illustrative only, and that they are not intended to limit the scope of the invention. Throughout these examples, all quantities expressed in percentages are by weight.

Example 1

A synthetic higher alcohol, "Dobanol (trade mark) 23", a product of Mitsubishi Petrochemical Co. Ltd., Japan, was charged into an autoclave provided with an agitation device. "Dobanol" is a mixed alcohol in which of the alkyl group is 43 percent C₁₂ and 57 percent C₁₃ is 78 percent straight-chain alkyl and is 22 percent branched-chain alkyl, with branching at the β position, and has an average molecular weight of 194. KOH was added, as a catalyst in a quantity of 1 percent relative to the higher alcohol. The resulting mixture was preheated to a temperature of 130°C while gaseous nitrogen was introduced into the system. 4 mols of propylene oxide and 15 mols of ethylene oxide for each mol of the higher alcohol were also introduced into the system by the various modes of introduction set forth below, under a pressure of 3 to 5 kg/cm², gage, in each case, to effect the addition reaction in each case. As a result, the various surfactants described below were produced.

Surfactant 1a:

Specific quantities of propylene oxide (hereinafter referred to as PO) and ethylene oxide (hereinafter referred to as EO) were mixed beforehand, and reaction was carried out as this mixture was continuously introduced under a specific pressure into the reaction vessel, whereupon a random adduct was obtained.

Surfactant 1b:

Specific quantities of PO and EO were introduced separately and alternately in the sequence: PO-EO-PO-EO-PO-EO, each of the PO and EO being thus added in lots of 1/3rd of its total quantity, thereby to effect an addition reaction. As a result, an alternate block adduct was obtained.

Surfactant 1c:

First, 3 moles of the EO per mol of the higher alcohol were introduced alone into the reaction system. Then, the remaining 12 mols of the EO and 4 mols of the PO; per mole of the higher alcohol, were introduced in a premixed state into the system, and thus caused to react together. As a result, a block-random combination adduct was obtained.

Surfactant 1d:

First, the total specific quantity of the PO was introduced into the reaction system to produce an addition reaction. Then, the total specific quantity of the EO was introduced to cause an addition reaction. As a result, a block adduct was obtained.

Surfactant 1e:

First, the total specific quantity of the EO was introduced into the reaction system so as to effect an addition reaction. Thereafter, the total specific quantity of the PO was introduced to effect an addition reaction. As a result, a block adduct was obtained.

Tests of solidifying point and cotton fabric washing power were carried out on each of the five kinds of surfactants produced in the above-described manner. The results were as set forth in Table 1 below:

TABLE 1

Surfactant	1a	1b	1c	1d	1e
Solidifying point (°C)	-2.9	-2.9	-2.7	25.6	15.3
Washing power (%)	85.5-89.4	85.4-86.0	85.0-88.3	84.4-87.0	87.9-90.4
Remarks	Present Invention			Comparison	

NOTE: The test methods were as follows.

1) Solidifying point..... according to Japanese Industrial Standards, JIS K 8004 - 1961.

2) Detergency test..... on cotton fabric.

An artificial contaminant simulating grime due to skin fat was rubbed with a sponge onto a white cotton broadcloth to prepare a cotton fabric soiled with the artificial skin fat grime, which was adjusted to a surface reflectance of 25 ± 2 percent. This artificial contaminant comprised a mixture of 8.4 percent of myristic acid, 8.4 percent of oleic acid, 8.4 percent of tristearin, 8.4 percent of triolein, 4.4 percent of cholesterol, 1.0 percent of cholesterol

stearate, 5.5 percent of paraffin, 5.5 percent of squalene, 49.5 percent of baked clay and 0.5 percent of carbon black.

Each of the surfactants was dissolved in tap water (hardness : CaCO_3 48 ppm) to form an 0.05-percent aqueous solution thereof, and an aqueous solution of a detergent was prepared.

By means of a Tergotometer (trade mark) Model 7243, manufactured by the United States Testing Company, and with 800 ml of each detergent aqueous solution, five sheets (each measuring 5 cm \times 5 cm) of the above-described cotton fabric soiled with the artificial contaminant were simultaneously washed. The washing temperature was 25°C., and the washing time was 10 minutes. Rinsing was carried out in two cycles, each cycle being carried out with 800 ml of tap water for 3 minutes.

The detergency in each case was calculated by the following equation:

$$\text{Detergency} = \frac{R_w - R_s}{R_o - R_s} \times 100,$$

where:

R_o is the reflectance (%) of the fabric before soiling;

R_s is the reflectance (%) of the soiled fabric prior to washing; and

R_w is the reflectance (%) of the soiled fabric after washing.

The above-described detergency test was carried out four times on each of the above-described surfactants (detergents), and the average detergency in each case was taken as the detergency value.

As is apparent from the results set forth in Table 1 above, the surfactants of this invention (1a, 1b, and 1c) have remarkably lower solidifying points than the other surfactants (1d and 1e), while there is almost no difference between their detergencies.

Example 2

Three kinds of synthetic higher primary alcohols with the distributions of number of carbon atoms and the straight-chain proportions shown in Table 2 were respectively used as starting materials, and, to each of these alcohols, 3 mols of PO and 9 mols of EO for every mol of the higher alcohol were added in the mixed state and caused to react. The reaction was carried out with the addition to the higher alcohol of 1 percent, relative to the higher alcohol, of KOH as a catalyst, and by preheating the higher alcohol and the catalyst, and then adding thereto the mixture of the PO and EO, in the specified quantities and under a pressure of 3 to 5 kg/cm², gauge. As a result, a random adduct was obtained in each case.

Similarly, as described above in Example 1, the solidifying point and the detergency of an 0.05-percent aqueous solution of each of the adducts (surfactants) thus obtained were measured, whereupon the results shown in Table 2 were obtained.

TABLE 2

	Surfactant		2a	2b	2c	
5	Alkyl group structure of starting material higher alcohol					5
10	Distribution of number of carbon atoms	C ₁₂	54	43	47	10
		C ₁₃	—	57	53	
15		C ₁₄	29	—	—	15
		C ₁₅	—	—	—	
		C ₁₆	10	—	—	
20		C ₁₇	—	—	—	20
		C ₁₈	7	—	—	
25	Straight chain proportion					25
	Straight chain	(%)	100	78	4	
30	β-position branch	(%)	0	22	96	30
30	Properties of formed surfacant					
35	Solidifying point	(°C)	−4.0	−15.0	−17.4	35
	Detergency of 0.05 % aqueous solution	(%)	83.8	84.5	78.1	
40	Remarks		Present Invention		Compa- rison	40

45 As is apparent from the results set forth in Table 2, the surfactants of this invention (2a and 2b) have excellent detergency, whereas the surfactant (2c) wherein the straight chain proportion of the starting material higher alcohol deviates from the limiting value has a very low detergency.

Example 3

50 An oxo primary higher alcohol ("Dobanol 23" (trade mark) product of Mitsubishi Petrochemical Co. Ltd., Japan, which is a mixture of alcohols of 12 and 13 atoms of carbon, with an average molecular weight of 194 and straight-chain alcohol content of 78 percent) was used as a starting material, and a mixture of 4 mols of PO and 15 mols of EO per mol of the alcohol was caused to undergo an addition reaction with the alcohol according to the process set forth in Example 2, whereupon a surfactant in the form of a random adduct was produced.

55 Similarly, an alcohol produced by the reduction of coconut oil (which was a mixture of alcohols of 12, 14, 16 and 18 carbon atoms, with an average molecular weight of 202, and a straight-chain alcohol content of 100 percent) was used as a starting material, and a mixture of 3 mols of PO and 9 mols of EO per mol of the alcohol was caused to undergo an addition reaction with the alcohol according to the process specified in Example 2, whereupon a surfactant in the form of a random adduct was produced.

60 The surfactants thus obtained (3a and 3b) were subjected to tests for odour, viscosity, solidifying point, detergency and sudsing. The results were as set forth in Table 3. For reference, the results of the same tests carried out under the same conditions on known surfactants are also shown in Table 3.

TABLE 3

	Surfactant	3a	3b	Known product A*1	Known product B*2	Known product C*3	
5	Odour *4	o	o	x	o	Δ	5
10	Viscosity (cst 30°C)*5	95.4	68.7	54.6	43.3	49.4	10
	Solidifying point (°C)	-2.9	-4.0	24.2	15.5	7.0	
15	Detergency on cotton cloth (%) (0.05% aqueous solution)	87.2	83.8	78.2	74.2	68.4	15
20	Sudsing property*6 (cm)						20
	Immediately after	9.3	7.2	11.5	14.7	12.0	
25	5 min. after	2.5	3.5	10.4	12.9	8.5	25

In Table 3:

- *1 denotes a product prepared by adding a known process EO to the same oxo alcohol ("Dobanol (trade mark) 23, Mitsubishi Petrochemical) as that used in Example 3, in a quantity ratio of 9 mols per mol of the alcohol; 30
- *2 denotes a topped product of an EO adduct of an oxo higher alcohol of 9 to 11 carbon atoms (8 mols of EO added per mol of alcohol);
- *3 denotes a product produced by adding EO by a known process to a secondary alcohol of 12 to 14 carbon atoms, in a quantity ratio of 9 mols per mol of the alcohol; 35
- *4 odour, was evaluated according to the following three ranks by five odour testers, smelling 0.05-percent aqueous solutions of the samples maintained at 50°C, 40
- o, almost no odour,
Δ, odour of medium strength, and
x, strong odour;
- *5 viscosity, was measured as kinematic viscosity at 30°C by the method of JIS K 2283; and 40
- *6 sudsing, was measured as foam height immediately after, and 5 minutes after, foaming or sudsing of 0.05-percent solutions in tap water (hardness of the tap water, CaCO₃, 48 ppm) of the samples, using the method of JIS K 3362, the foam height immediately after foaming being a measure of sudsing property, and the foam height 5 minutes after foaming being a measure of the stability of the foam. 45

As is apparent from the results set forth in Table 3 above, the surfactants 3a and 3b according to this invention, in comparison with the known other surfactants, exhibit less odour and have lower solidifying points, whereby they are in the liquid state even at low temperatures, and clearly superior detergencies. Furthermore, the sudsing properties of these surfactants 3a and 3b of this invention are lower, and the foam upon being left standing decreases rapidly, whereby it will be seen that the rinsing after washing is greatly facilitated. 50

55

Example 4

To the same oxo higher primary alcohol ("Dobanol 23") as that used in Example 3, was added 1 percent relative to the alcohol of KOH as a catalyst. This alcohol and KOH were preheated to 130 to 140°C, and different proportions of PO and EO were then respectively continuously introduced into separate lots, under a pressure of 3 to 5 kg/cm², so as to produce 9 kinds of surfactants with different proportions of added PO and EO. 60

The odour, the unreacted alcohol content, the solidifying point, the cloud point of a 1-percent aqueous solution and the detergency with respect to cotton cloth of a 0.05-percent aqueous solution of each of these surfactants were respectively measured. The results were as set forth in Table 4 as follows: 65

TABLE 4

Surfactant *1	Number of mols added		Odor	Content of unreacted higher alco- hol (% by weight)	Solidifying point (°C)	Cloud point of 1-% aque- ous solution (°C) *2	Detergency (%) of 0.05-% aqueous so- lution *3
	PO	EO					
4a (E)	3	11	0	0.1 or lower	-7.0	60.5	67.2
4b (E)	7	15	0	"	-30 or lower	59.8	69.3
4c (E)	5	20	0	"	-0.2	76.5	68.5
4d (CE)	1	9	x	0.4	12.5	66.1	59.0
4e (CE)	12	20	0	0.1 or lower	-30 or lower	-	52.0
4f (CE)	2	4	x	0.75	-25	(insoluble in water)	57.0
4g (CE)	5	27	0	0.1 or lower	13.5	86.5	65.0
4h (CE)	2	13	0	"	12.4	79.8	68.1
4i (CE)	7	7	0	"	-30 or lower	37.2	51.0

In Table 4:

- *1 (E) denotes a surfactant of an example of this invention, while (CE) denotes a surfactant which is not according to this invention but is used for the purpose of comparison;
- *2 measured according to the method specified in ASTM D 2024;
- *3 same as in Tables 1, 2 and 3 except for the use of soiled cloth adjusted to a surface reflectivity of 15 to 20 percent. Accordingly, a proper comparison of the detergency data of Table 4 and those of Tables 1, 2 and 3 is not possible.
- The results indicated in Table 4 may be summarized as follows.
- The surfactants *4a*, *4b* and *4c* in respect of which the ratios of the number of mols added of PO and EO and those of PO/EO are within the limiting values of this invention, have little odour and have low solidifying points and high detergencies.
- In contrast, the surfactant *4d* in respect of which the number of mols added of PO is below the lower limiting value of this invention, has a strong odour and a high solidifying point, solidifying readily at room temperature.
- The surfactant *4e*, in respect of which the number of mols added of PO is above the upper limiting value of this invention, clearly has an inferior detergency.
- The surfactant *4f*, in respect of which the number of mols added of EO is below the lower limiting value of the invention, is insoluble in water, and, moreover, has a strong odour.
- The surfactant *4g* in respect of which the number of mols added of EO is above the upper limiting value of the invention, has a high solidifying point, and readily solidifies at room temperature.
- The surfactant *4h*, in respect of which the number of mols added of PO and EO is below the lower limiting value of this invention, has a high solidifying point and readily solidifies at room temperature.
- The surfactant *4i*, in respect of which the number of mols added of PO and EO is above the upper limiting value of this invention, has a very poor detergency.

WHAT WE CLAIM IS:

1. A liquid detergent comprising a nonionic surfactant consisting of an adduct which is the products of an addition reaction between propylene oxide and ethylene oxide and a saturated aliphatic primary alcohol represented by the formula ROH, wherein R designates an alkyl group having 8 to 18 carbon atoms, of which at least 30 percent by weight is a straight-chain alkyl group, the propylene oxide and the ethylene oxide undergoing the addition reaction:
 - (a) in the form of a mixture thereof; or
 - (b) separately and alternatively, each being thus added at least twice at separate instances and in separate subdivision lots; or
 - (c) in a non-simultaneous combination of
 - (i) addition of said oxides as a mixture thereof and
 - (ii) addition of the propylene oxide and/or ethylene oxide separately, each being added once or at least twice at separate instances and in separate subdivision lots, in which addition reaction, 3 to 9 moles of the propylene oxide and 6 to 22 moles of the ethylene oxide are added, for every mol of the saturated aliphatic primary alcohol, and the addition mol ratio of the propylene oxide to the ethylene oxide is within the range of from 0.25 to 1 to 0.6 to 1, inclusive.
2. A nonionic surfactant according to claim 1, and substantially as hereinbefore described and designated by the numbers *1a*, *1b*, *1c*, *2a*, *2b*, *3a*, *3b*, *4a*, *4b* and *4c* in the specific Examples.

ELKINGTON AND FIFE,
Chartered Patent Agents,
High Holborn House,
52/54 High Holborn,
London WC1V 6SH.
Agents for the Applicants.