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SURFACE ACTIVE AGENTS

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No Drawing. Continuation-in-part of application Ser. No. 392,592, Aug. 27, 1964. This application Mar. 4, 1968, Ser. No. 709,965

Int. Cl. C07c *41/10, 43/04, 43/14*

U.S. Cl. 260—611 4 Claims

ABSTRACT OF THE DISCLOSURE

Surface active agents having a combination of desirable properties including defoaming, good sheeting action, low foaming, caustic stability and biodegradability, which agents are prepared by ethoxylating a long chain alcohol with the chain being terminated with a benzyl group.

This application is a continuous-in-part of our copending application, Ser. No. 392,592, filed Aug. 27, 1964, and now abandoned.

This invention relates to novel surface active agents. More particularly, this invention relates to novel nonionic surface active agents possessing a unique combination of properties.

The surface active agent art is well developed and there are known various surfactants which possess properties adapting them for use as detergents. Thus, surface active agents having acceptable detergent properties find widespread use in commercial mechanical dishwashers, residential dishwashers, clothes washing machines, metal cleaning units, dairy pipe cleaning machines and so forth. For such applications a high degree of detergency must be achieved with comparatively little foam. Excessive foam results in loss of wash pressure with consequent loss in ability to remove soil. In addition to the above, a satisfactory detergent should also possess good defoaming properties, have good sheeting action and be relatively stable in the presence of caustic materials.

Surface active agents or detergents possessing several or all of the above described properties are available at at present time. However, in the past several years much attention has been directed to the biodegradability of the detergents. Non-biodegradable detergents, due to their slow degradabi'ity, pass through ordinary sewage treatment systems and appear in well waters and also create serious foaming problems in sewage treating plants and in rivers where the effluent is finally discharged. In view of this, detergent manufacturers have been subjected to considerable pressure to provide biodegradable surfactants which can be substituted for the non-biodegradable surfactants. In fact, in a growing number of political jurisdictions laws have been proposed or enacted to ban the sale or use of non-biodegradable detergents.

It is therefore a principal object of the present invention to provide novel nonionic surface active agents suitable for use as detergents and which have acceptable foaming, defoaming, sheeting and caustic stability characteristics and which are also biodegradable.

It is another object of the present invention to provide a process for producing the novel detergents disclosed herein.

In accordance with art practices and for the purposes of the present patent description, the following definitions and test procedures have been employed:

The foaming properties of a detergent relate to the tendency of the detergent itself to produce foam when utilized in a washing operation. A low foaming detergent

is one which will not foam to a degree which will impair wash action. As determined by the known Ross-Miles foam test, a low foaming detergent is one which provides an initial foam of not more than about 45 millimeters in height and not more than 15 millimeter foam height after 5 minutes.

The defoaming properties of a surfactant relate to the ability of the surfactant to control or suppress foaming caused by materials present in the washing operation other than the surfactant itself. A number of soils, notably egg and milk soils, in washing processes, will promote excessive foaming to a point where serious loss in wash pressure and soil removal occurs. The defoaming properties of a surfactant can be conveniently measured under conditions simulating practical field use. Thus, a surfactant is incorporated in a washing detergent formulation and the formulation added to a wash solution containing 0.1% by weight of whole raw egg as a soil load in a commercial dishwashing machine. The detergent formulation is added to provide a concentration of 0.2% by weight. The dishwashing machine has a pitot tube over the wash jet in the lower wash arm connecting directly to an open end mercury manometer. The pressure developed by the force of the wash water coming out of the wash jet is measured by the manometer with the extent of foaming being related to the decrease in wash pressure. A good defoamer is one which will suppress the foam produced by egg or milk soil to such an extent that the original wash pressurse is restored. The foaming and defoaming properties of the surfactant are determined in the same manner except that in this application foaming properties are determined in the absence of food soils that cause foaming, while the defoaming properties are determined in the presence of such soils.

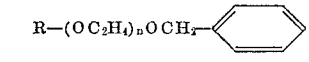
The sheeting properties of a surfactant are important when the material is used as a rinse aid and denote the combined effect of the wetting ability of the surfactant and the thinness of the surfactant film on the articles being cleaned. Wetting ability is indicated by spread of the solution on the test surface. The formation of a thin continuous film on the test surface provides minimum spotting and film residue as well as rapid drying when the article is rinsed by such a solution. In the absence of any surfactant, the water will usually tend to bead on the test surface. The sheeting properties of a surfactant can be evaluated by adding various increments of a surfactant to a commercial dishwashing machine and observing the lowest increment needed to give complete sheeting. The test is performed under fixed conditions of 140° F. water temperature and 6.5 liters of water and the "sheeting" is observed by running the machine for one minute after each addition of the surfactant, then shutting off the machine and observing the test surface through a glass window substituted for the sheet metal door. Good sheeting properties are indicated when the compound being tested produces a thin film spread evenly over the surface of the test pieces which results in rapid drying without spotting and filming.

The caustic stability of a surfactant denotes the ability of the surfactant to remain stable when in the presence of a strong caustic material. Caustic stability can be determined by mixing 2% by weight of surfactant with 98% of anhydrous commercial grade caustic. The samples are then stored in jars in a warm room maintained at 35° C. After various storage times, samples are withdrawn and tested for loss of defoaming ability. The defoaming test is carried out using a commercial dishwasher machine having a water capacity of 6.5 liters and a revolving wash arm. The revolutions per minute of the wash arm are a function of the wash pressure, the higher number of revolutions per minute, the higher the wash pressure.

The washer is filled with 6.5 liters of 140° F. water, detergent formulation (2% surfactant—98% caustic) added, and the machine operated for one minute to allow the detergent to dissolve. Mixed whole raw egg soil is added in amounts to give a concentration of 0.1% by weight and the machine operated for two minutes. The revolutions per minute are clocked to determine the wash pressure, or the wash pressure can be determined by the use of a pitot tube and a manometer as indicated above. For satisfactory caustic stability the surface active agent should not exhibit a decrease in foaming properties of more than about 15% as indicated by a decrease in wash pressure after storage in the presence of strong caustic under the conditions described for 30 days.

The biodegradability of a surfactant relates to the ease with which the surfactant is degraded or broken down by bacteria. Biodegradability may be measured in several ways. One method that pproximates conditions encountered under a practical operating situation is the so-called "River Die-Away" test. In this method a fresh sample of river water is collected and appropriate amounts of surfactant, usualy 20 to 50 parts per million, are added and the sample is stored at 20° C. for various periods of time, after which the amount of surfactant remaining is assayed. Several assay methods can be used and the assay methods employed herein are the chemical oxygen demand (C.O.D.) and measurement of the surface tension. A satisfactory biodegradable detergent is one which is about 75 to 85% degraded by microorganisms in sewage, soils, rivers or lakes within about 20–30 days and which is essentially completely degraded after 40–60 days.

The compounds of the present invention can be represented by the general formula:



wherein R is the residue of a straight-chain alcohol containing 10 to 22 carbon atoms or mixtures thereof and *n* is an integer of from 6 to 30. The alcohol from which R is obtained can be any saturated or unsaturated straight-chain alcohol or mixture of alcohols such as decyl alcohol, dodecyl alcohol, tetradecyl alcohol, cetyle alcohol, oleyl alcohol, linoleyl alcohol, palmitoleyl alcohol, arachidyl alcohol, stearyl alcohol, benhenyl alcohol, arachidonyl alcohol, myristoleyl alcohol and the like.

The compounds of the invention are prepared by ethoxylating (condensing ethylene oxide) a suitable alcohol in the presence of an alkaline catalyst such as potassium hydroxide, sodium hydroxide, sodium methoxide and the like to incorporate from 6 to 30 ethoxy units, after which the ethylene oxide chain is terminated with a benzyl group. The number of ethoxy units employed depends to some extent on the number of carbon atoms in the starting alcohol. In general, the higher alcohols require a greater number of ethoxy units in order to obtain an optimum product. Ethoxylation is conveniently accomplished by condensing an appropriate number of moles of ethylene oxide with the alcohol at a temperature in the range from about 100 to 180° C.

After addition of the desired number of ethoxy units, that is from 6 to 30 units, the chain is terminated by union with a benzyl group. This is accomplished by reacting a benzyl halide such as benzyl bromide or benzyl chloride with the ethoxylated alcohol (alkoxide) in the presence of a strongly basic agent. Representative of suitable basic agents are the alkali metals such as sodium and potassium, sodium hydroxide, potassium hydroxide, sodium methoxide, potassium methoxide, sodium carbonate, lithium hydroxide, barium hydroxide, calcium hydroxide, strontium hydroxide and the like. The benzyl halide which is employed in forming the novel compounds can be substituted with substituents which are relatively inert to the reaction components.

The reaction of the benzyl halide or substituted benzyl halide with the ethoxylated alcohol (alkoxide) is carried out at a temperature in the range from about 100 to 180° C., preferably from about 100 to 140° C. The temperature of the reaction is not particularly critical and can be varied outside of the stated range. The reaction is essentially complete at the end of about 15 minutes, although longer reaction times are preferably and generally employed to insure complete reaction After completion of the reaction, the desired product is recovered by standard procedures. Thus, the reaction mixture can be treated with water to effect a phase separation between a water layer and an organic layer. The organic layer can then be readily separated, dried, and filtered to recover the novel surface active agents of the invention.

The preparation and advantages of the surface active agents of the present invention are further illustrated by the following specific examples.

Example I

To a reactor equipped with appropriate stirrer, gas inlet, vapor trap and heater were added 334 grams (0.5 mole) of a commercial mixture of C_{12}–C_{18} carbon length straight-chain alcohols which had been ethoxylated with 10 moles of ethylene oxide (60% of the total weight). To this mixture were added, with agitation, 27.0 grams (0.5 mole) of sodium methoxide. The temperature was maintained in the range of 100° C. to 115° C. for two hours, during which time nitrogen gas was bubbled through the reaction mixture to sweep out the methanol formed upon the addition of the sodium methoxide. At the end of two hours nitrogen flow was interrupted and 63.2 grams (0.5 mole) of benzyl chloride were added slowly over a period of 15 minutes at a temperature of about 115° C. During this addition, a temperature rise was encountered. The reaction mixture was then left to mix for an additional hour before it was removed from the reactor. Water was added thereto in an mount corresponding to approximately 50% of the weight of the mixture. This mixture was heated to 80–100° C. and left stand for a period upon which an organic layer separated on top and a water layer on the bottom. The water layer was discarded. The organic layer was then heated to 150° C. to remove residual water and filtered. The resulting product was a light yellow liquid which solidified at room temperature.

Example II

To a stainless steel pressure reactor were added 0.73 gram of crushed potassium hydroxide and 133.5 grams of a commercial mixture of alcohols. This alcohol mixture consisted of 73% by weight oleyl alcohol, 7% palmitoleyl alcohol, 5% linoleyl alcohol, 3% myristoleyl alcohol, 4% myristyl alcohol, 6% cetyl alcohol and 2% stearyl alcohol. Nitrogen gas was flushed through this system and the heat applied. The reactor was left vented to the atmosphere at this time. When the temperature had reached 105° C., the reaction mixture was then again flushed with nitrogen gas, leaving a residual 20 p.s.i. of nitrogen pressure within the cylinder when it was closed. After the reactor was closed, 352.40 grams of ethylene oxide, which is equivalent to 8.0 moles, were added slowly over a period of approximately 2¼ hours. During this time the heat of reaction raised the temperature from the starting 106° C. to a final temperature of 155° C. The reaction mixture was then left under a residual pressure of 40 p.s.i. nitrogen while cooling down to room temperature. The reactor was then heated up to 60° C. to melt the ethoxylated alcohol, and it was removed from the reaction vessel.

Approximately 242 grams (0.25 mole) of the above ethoxylated alcohol mixture were added to a reactor equipped with stirrer, gas inlet, vapor trap and heater. Approximately 13.5 grams (0.25 mole) of sodium meth-

oxide were then added with agitation and the mixture heated. The temperature was maintained between 90° and 120° C. for approximately 2¼ hours, during which time nitrogen gas was bubbled through the reaction mixture to sweep out the methanol formed from the reaction. At the end of 2¼ hours the nitrogen flow was interrupted and 31.6 grams (0.25 mole) of benzyl chloride added slowly over a period of 20 minutes. The reaction mixture was then permitted to mix for an additional ½ hour. After this time water was added to the reaction mixture in an amount corresponding to 50% by weight of the mixture. A phase separation occurred with the bottom water layer being discarded. The organic top layer was heated to 150° C. to remove residual water and filtered. The resulting product was a light colored clear liquid which solidified upon standing at room temperature.

Example III

To a stainless steel pressure reactor were added 0.73 gram of crushed potassium hydroxide and 133.5 grams of a commercial mixture of alcohols. This alcohol mixture consisted of 73% by weight oleyl alcohol, 7% palmitoleyl alcohol, 5% linoleyl alcohol, 3% myristoleyl alcohol, 4% myristyl alcohol, 6% cetyl alcohol and 2% stearyl alcohol. Nitrogen gas was flushed through this system and the heat applied. The reactor was left vented to the atmosphere at this time. When the temperature had reached 105° C., the reaction mixture was then again flushed with nitrogen gas, leaving a residual 20 p.s.i. of nitrogen pressure within the cylinder when it was closed. After the reactor was closed, 352.40 grams of ethylene oxide, which is equivalent to 8.0 moles, were added slowly over a period of approximately 2¼ hours. During this time the heat of reaction raised the temperature from the starting 106° C. to a final temperature of 155° C. The reaction mixture was then left under the residual pressure of 40 p.s.i. nitrogen while cooling down to room temperature. The reactor was then heated up to 60° C. to melt the ethoxylated alcohol, and it was removed from the reaction vessel.

Approximately 175 grams (0.18 mole) of the above ethoxylated alcohol mixture were added to a reactor equipped with stirrer, gas inlet, vapor trap and heater. Approximately 4.14 grams (0.18 mole) of sodium metal were then added over a period of approximately 1¾ hours while maintaining a flow of nitrogen gas through the system and maintaining the temperature between 100° and 125° C. After addition of sodium, a mixing period of 2 hours at a temperature range of 100°–125° C. with nitrogen gas bubbling through was maintained. At the end of the 2-hour period, 24.7 grams (approximately 0.18 mole) of benzyl chloride were added slowly over a 15 minute period while maintaining the temperature between 100° and 135° C. After the benzyl chloride addition was completed, a one-hour mixing period was maintained after which 50% by weight water was added to the mixture and the temperature raised to 85°–95° C. to permit phase separation. The lower water layer was discarded while the top organic layer was heated to 150° C. to remove residual water and it was then filtered. The resulting material was a light yellow liquid which solidified upon standing at room temperature.

Example IV

To a pressure reactor were added 2.00 grams of crushed potassium hydroxide and approximately 185.14 grams of an alcohol mixture containing approximately 30% decanol, 40% dodecanol and 30% tetradecanol. Nitrogen gas was flushed through the system and the system left vented to the atmosphere while heat and agitation were applied. When a temperature of 110° C. was obtained, an additional flushing with nitrogen was conducted, leaving a residual pressure of 15 p.s.i.g. when the system was closed. After closing the system, the addition of 704 grams (16 moles) of ethylene oxide was begun slowly over a period of 2½ hours. During this time the temperature rose from approximately 110° C. to 170° C., after which time the reaction had been completed. The reactor contents were then stirred continually as the temperature was left to cool to approximately 60° C. At this time the contents were removed from the reactor.

Approximately 222.3 grams (0.25 mole) of the above ethoxylated alcohol mixture were added to a reactor equipped with a stirrer, gas inlet, vapor trap and a heater. Approximately 5.75 grams (0.25 mole) of sodium metal were then added slowly over a period of approximately 2 hours while maintaining a temperature of 100–125° C. and a nitrogen flow. This mixture was agitated with a nitrogen blanket for one hour at a temperature of 80–110° C. The nitrogen flow was turned off and 31.6 grams (0.25 mole) of benzyl chloride added slowly over a period of 15 minutes at a temperature of 100–120° C. This was followed by a one hour heating period, after which 50% by weight of water was added and the mixture heated to 85–95° C. A phase separation occurred and the bottom aqueous layer was discarded. The upper organic layer was heated to 150° C. to remove the residual water and then filtered. The resulting product was a light yellow colored clear liquid which solidified upon standing at room temperature.

Example V

To a pressure reactor were added 2.00 grams of crushed potassium hydroxide and approximately 185.14 grams of an alcohol mixture containing approximately 30% decanol, 40% dodecanol and 30% tetradecanol. The mixture was flushed with nitrogen gas and the reactor vented to the atmosphere. Agitation was started and heat applied. When a temperature of 110° C. was obtained, the system was again flushed with nitrogen leaving 10 p.s.i.g. pressure within the reactor when it was closed to the atmosphere. The addition of 880 grams (20 moles) of ethylene oxide was accomplished over a period of approximately 2 hours and the temperature rose from 110° C. to 165° C. The reactor was then left to cool while agitation was continued. When the temperature reached 60° C. the contents were removed from the reactor.

Approximately 266.2 grams (0.25 mole) of the above ethoxylated alcohol mixture was added to a reactor equipped with an appropriate stirrer, gas inlet, vapor trap and heater. This mixture was heated to 100° C. and the addition of approximately 5.75 grams (0.25 mole) of sodium metal was started. The addition was performed slowly over a period of approximately 2 hours while maintaining a flow of nitrogen through the mixture and a temperature range of 100° C.–115° C. The mixture was then allowed to mix for an additional one hour. The nitrogen flow was then stopped and approximately 31.6 grams (0.25 mole of benzyl chloride was added slowly over a period of about 15 minutes while maintaining the temperature between 100–140° C. When the addition was completed the mixture was agitated for an additional 15 minutes. To the mixture was added 50% by weight of water, followed by heating at 85–90° C. after which a phase separation occurred. The bottom aqueous layer was discarded and the top organic layer was heated to 150° C. to remove any residual water and then filtered. The resulting product was a light yellow colored clear liquid which solidified on cooling at room temperature.

Example VI

To a pressure reactor was added approximately 2.00 grams of crushed potassium hydroxide and 185.14 grams of an alcohol mixture containing approximately 30% decanol, 40% dodecanol and 30% tetradecanol. The reactor was flushed with nitrogen gas and then left vented while heat and agitation were applied. When the temperature reached 119° C. the reactor was again flushed with nitrogen leaving a pressure of 10 p.s.g. when the reactor was closed to the atmosphere. The addition of approximately 616 grams (14 moles) of ethylene oxide was started

and added slowly over a period of approximately 1½ hours. During this time the temperature rose from 119° C. to 165° C. The reactor was then allowed to cool while continuing agitation and when the temperature reached approximately 60° C. the contents were removed from the reactor.

Approximately 200.8 grams (0.25 mole) of the above ethoxylated alcohol mixture was adde to a reactor equipped with an appropriate stirrer, gas inlet, vapor trap and heater. The mixture was heated to 115° C. and to the mixture was added approximately 5.75 grams (0.25 mole) of sodium metal over a period of approximately one hour while maintaining a nitrogen flow through the mixture and a temperature range of 100–115° C. The mixture was maintained at 115° C. for an additional one hour. After this time the nitrogen flow was stopped and approximately 31.6 grams (0.25 mole) of benzyl chloride was added over a period of about 15 minutes while maintaining the temperature between 100–140° C. After completion of the addition the mixture was maintained at the above temperature for about 30 minutes. To the mixture was added 50% by weight of water followed by heating at 85–90° C. after which a phase separation occurred. The bottom aqueous layer was discarded and the upper organic layer was heated to 150° C. to remove any residual water, then filtered. The resulting product was a light yellow colored clear liquid which solidified on cooling at room temperature.

Example VII

To a stainless steel reactor were added 2.0 grams of crushed potassium hydroxide and 225 grams of technical grade oleyl alcohol. The reactor was then swept with nitrogen gas and the heat applied. The reactor was left vented to the atmosphere. When the reaction temperature reached 102° C., the reactor was once again swept out with nitrogen gas, but this time sealed to the atmosphere, leaving a residual pressure of 10 p.s.i. nitrogen gas. The addition of 1055 grams (24 moles) of ethylene oxide was begun slowly. The addition of the ethylene oxide took approximately 2½ hours, during which time the temperature rose from 102° C. to 162° C. The reaction mixture was left then to agitate and cool down to approximately 60° C. temperature, after which time it was removed from the reactor.

Approximately 328.2 grams (0.25 mole) of the above ethoxylated oleyl alcohol were added to a reactor equipped with a stirred, gas inlet, vapor trap and heater. Approximately 5.75 grams (0.25 mole) of sodium metal were then added batchwise while maintaining nitrogen flow through the mixture and a temperature of about 110°–115° C. The mixture was then left to mix for an additional 2 hours at the above temperature. At the end of 2 hours, the nitrogen flow was disrupted and 31.6 grams (0.25 mole) of benzyl chloride added batch-wise, while maintaining the temperature between 100° and 140° C. When the addition had been completed, the reaction was left to mix for about one hour and then treated with 50% by weight water. This was followed by heating to 85°–90° C. to cause a phase separation. The bottom water layer was discarded and the top organic layer heated to 150° C. to remove the residual water and filtered. The resulting product was a light yellow colored liquid, which solidified upon standing at room temperature.

Example VIII

A commercial mixture of alcohols as employed in Example IV was ethoxylated with 16 moles of ethylene oxide. Approximately 16.0 pounds of this ethoxylated material were added to a reactor equipped with stirrer, gas inlet, vapor trap and heater. Approximately 0.41 pound of sodium metal was then added batch-wise, while maintaining a nitrogen flow and a temperature between about 100° and 140° C. The mixture was then left to mix for an additional 2 hours at the above temperature. At the end of 2 hours, the nitrogen flow was disrupted and 2.28 pounds of benzyl chloride were added batch-wise, while maintaining the temperature between 120° and 165° C. When the addition had been completed, the reaction was left to mix for about 2 hours and then treated with 50% by weight water, followed by heating to 85°–95° C. to cause a phase separation. The bottom water layer was discarded and the top organic layer heated to 150° C. to remove residual water and filtered. The resulting product was a light yellow colored liquid, which solidified upon standing at room temperature.

Typical chemical and physical properties of the surface active agents of the invention are shown below in Table I.

TABLE I

Surfactant (product of)	Alcohol: Chain length distribution	Alcohol: Saturated	Alcohol: Unsaturated	Moles ethylene oxide added	Benzylating agent: NaOMe	Benzylating agent: Na	Hydroxyl No.	Refractive index	Cloud point 1% soln. in distilled water,° C.	Surface tension, dynes/cm., 0.1% soln. in distilled water	Ross-Miles foam height in mm.: Initial	Ross-Miles foam height in mm.: 5 mi.
Example IV	C_{10}–C_{14}	X		16		X	5.5	1.4727	27.5	38.6	35	3
Example VI	C_{10}–C_{14}	X		14		X	16.2	1.4722	24.7	36.4	30	4
Example V	C_{10}–C_{14}	X		20		X	10.3	1.472	38.3	40.2	37	5
Example I	C_{12}–C_{18}	X		10	X		14.9	1.4718	None	32.7	10	5
Example II	C_{14}–C_{18}		X	16	X		5.4	1.4743	30.0	37.5	26	12
Example III	C_{14}–C_{18}		X	16		X	6.8	1.4750	26.5	37.3	25	10
Example VII	C_{12}–C_{20}		X	24		X	6.7	1.515	45.5	42.8	45	20
Prior art surfactant W							21.1	1.4555	30.0	41.2	2	2
Prior art surfactant X							44.5	1.4925	27.5	35.6	23	1
Prior art surfactant Y							43.7		[1] 47.0		23	15
Prior art surfactant Z							72.8	1.4550	[1] 30.9			
Prior art surfactant V									65.0	31.0	110	25

[1] 10% solution in distilled water.

Table II gives the results of sheeting tests comparing products of the invention with several prior art commercial surface active agents which have found use as detergents. The procedure utilized for evaluating the sheeting properties was as disclosed heretofore.

TABLE II

Product	Minimum amount of product to give sheeting (ml.)	Sheeting results
Example IV	0.5	Excellent sheeting.
Prior art surfactant Y	0.5	Do.
Prior art surfactant X	0.5	Do.
Prior art surfactant W	2.0	Poor sheeting.

The above results indicate that the products of this invention are equal or better to known detergents with respect to sheeting properties and that the present products are useful as additives to a final rinse in commercial washing machines.

In Table III there are summarized the results of defoaming tests on the products of the invention compared

with several prior art detergents. In these tests various surfactants were incorporated in a wash formulation having the makeup as shown below and tested in a dishwashing machine as heretofore described.

color or develop odors and gave no indication of any change.

In Table V, the biodegradability of the products of the invention are compared with several prior art surfactants.

TABLE V.—BIODEGRADABILITY BY RIVER DIE-AWAY METHOD AT 20° C.

Product	Surface tension, dynes/cm., 20° C.					Chemical oxygen demand [1] (mgs./liter)				
	Initial	11 days	22 days	40 days	60 days	Initial	11 days	22 days	40 days	60 day
Prior art surfactant Z	39.2	51.0	51.3		51.1	90.6				85.4
Prior art surfactant X	37.7		44.5		[2] 44.5	71.1				[2] 64.0
Prior art surfactant W	45.1	45.5	45.9	43.6	45.7	83.0			82.6	82.6
Product of Example IV	41.6	51.7		69.2	68.9	80.9	56.0	34.3	31.0	12.1
Product of Example I	41.6	59.0	63.2			79.7	56.2	16.0		
Prior art surfactant T	40.0	65.1	66.1	69.3	71.0	64.7	43.6	23.8	21.0	
Prior art surfactant U	43.7	46.0	49.1	49.4	51.6	68.8			48.4	
Prior art surfactant V	46.1	46.2		44.5	46.0	72.2				39.3

[1] COD for water 16 mgs./liter. [2] 50 days.

Wash formulation	Percent by weight
Light ash (sodium carbonate)	22.23
Sodium hydroxide	19.47
Dense ash (sodium carbonate)	21.65
Sodium tripolyphosphate, granular	21.65
Sodium pyrophosphate, granular	12.98
Surfactant	2.02
	100.00

TABLE III

Surfactant in above formulation	Wash pressure millimeters of mercury		
	Water only	Water and detergent	Water, detergent and egg soil
Prior art surfactant X	60	60	48
Prior art surfactant W	60	60	54
Product of Example IV	60	60	60

Many surfactants are not stable when blended with caustic in large amounts as is desired in detergent formulations prepared for use, for example, in washing bottles and the like. It is desired that the surface active agents possess a high degree of caustic stability to permit them to be blended with large amounts of caustic in detergent formulations with the formulations being capable of storage for extended periods of time. In the following reported tests the caustic stability was evaluated by comparing the loss in defoaming properties after storage at 35° C. for various time periods as shown.

TABLE IV

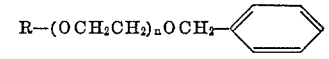
Product (2% on caustic, stored at 35° C.)	Defoaming values (r.p.m. of wash arm after various days of storage)			
	0 days	6 days	10 days	30 days
Prior art surfactant W	94	78	10	0
Prior art surfactant X	92	89	91	85
Product of Example IV	97	91	95	95

The above data indicates the superior defoaming and caustic stability of the products of the invention. The product W breaks down in less than 10 days. It was also observed that product X turned from colorless to bright yellow after several days and gave a pungent musty odor, whereas the product of the present invention did not dis-

It will be apparent from the foregoing description that the present invention provide novel nonionic surface active agents possessing a unique combination of properties. The novel surface active agents of the present invention possess excellent detergent properties, good foaming and defoaming properties and good sheeting characteristics. In addition, the novel surfactants are relatively stable to caustic and, very significantly, are biodegradable in nature.

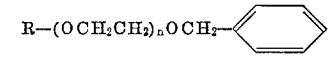
We claim:

1. Compounds of the formula



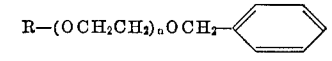
wherein R represents the residue of an unsubstituted straight-chain saturated or olefinic alcohol containing from 10 to 22 carbon atoms and *n* is an integer of 6 to 30.

2. Compounds of the formula



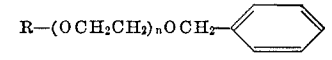
wherein R represents the residue of an unsubstituted straight-chain saturated or olefinic alcohol containing from 10 to 22 carbon atoms and *n* is an integer of 10 to 20.

3. Compounds of the formula



wherein R represents the residue of an unsubstituted straight-chain olefinic alcohol containing 18 carbon atoms and *n* is an integer of 24.

4. Compounds of the formula



wherein R represents the residue of an alcohol selected from the group consisting of decyl alcohol, dodecyl alcohol, tetradecyl alcohol, cetyl alcohol, oleyl alcohol, linoleyl alcohol, palmitoleyl alcohol, arachidyl alcohol, stearyl alcohol, behenyl alcohol, arachidonyl alcohol, myristoleyl alcohol and mixtures thereof and *n* is an integer of 6 to 30.

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BERNARD HELFIN, *Primary Examiner.*

U.S. Cl. X.R.

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