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DETERGENT COMPOSITION WITH THERMO-CONTROLLED FOAMING CAPACITY
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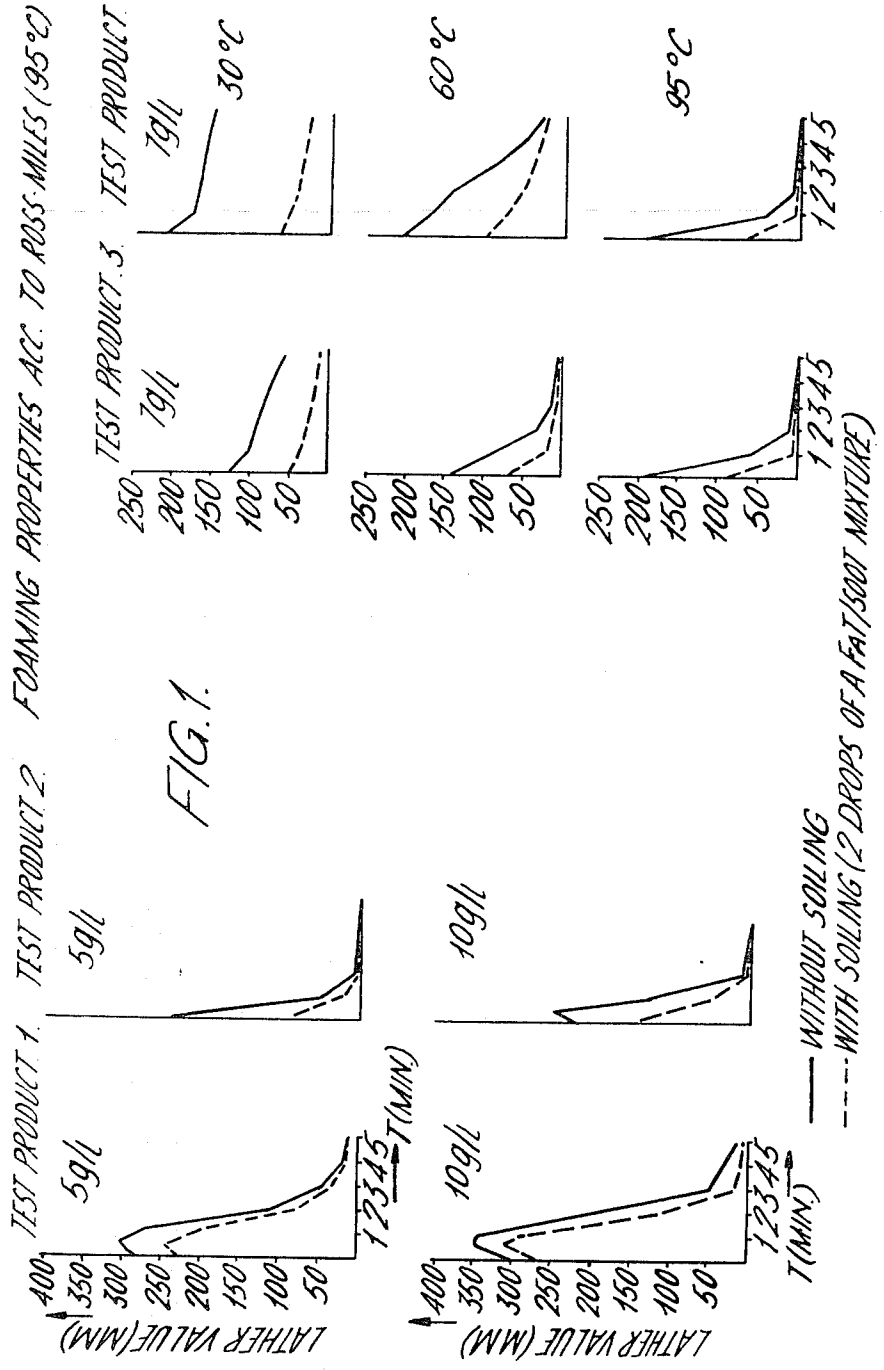


FIG. 1.

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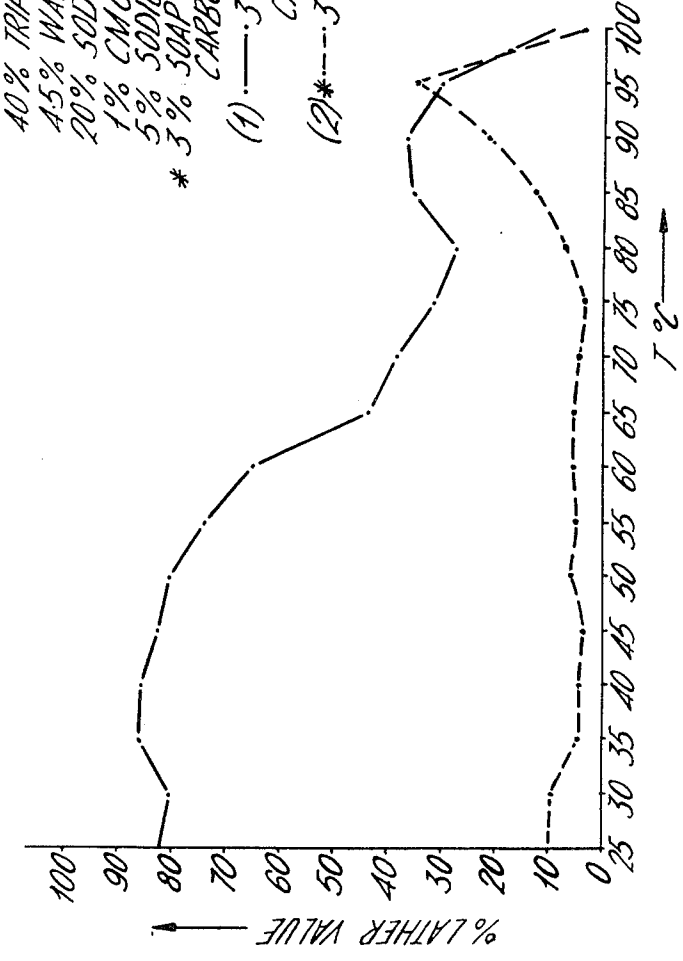
FIG. 2.

FOAMING BEHAVIOUR IN THE ROTARY FOAMING APPARATUS (WITH SOILING)

FORMULAR

12% SODIUM ALKYL BENZENE SULPHONATE
4% TALLOW FATTY ACID AMID AND-11 EO
40% TRIPOLYPHOSPHATE
45% WATERGLASS-38 Be'
20% SODIUM PERBORATE
1% CMC
5% SODIUM SULPHATE
* 3% SOAP OR SODIUM SALTS OF CYCLIC CARBOXYLIC ACIDS

(1) ——3% SODIUM SALTS OF CYCLIC CARBOXYLIC
(2)*---3% HARDENED TALLOW SOAP



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DETERGENT COMPOSITION WITH THERMO-CONTROLLED FOAMING CAPACITY

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Continuation-in-part of abandoned application Ser. No. 14,783, Feb. 26, 1970, which is a continuation of application Ser. No. 669,845, Sept. 22, 1967. This application Oct. 27, 1970, Ser. No. 84,454

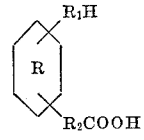
Claims priority, application Germany, Sept. 23, 1966, U 13,106

Int. Cl. C11d *1/04, 3/065, 9/32*

U.S. Cl. 252—539 4 Claims

ABSTRACT OF THE DISCLOSURE

Foaming at low washing temperature is obtained without over-foaming at high temperatures. the foam-controlling agent is an effective amount of a material selected from the group consisting of cyclized fatty acids and sodium salts of such acids, said acids being essentially obtained from cyclization of unsaturated C_{12}–C_{33} fatty acids by any suitable process known in the art, and being a mixture of acids having the formula:



wherein R represents a saturated or unsaturated six-membered carbon ring; R_1 is a hydrocarbon chain having from 0–12 carbon atoms, R_2 is a hydrocarbon chain having from 0–21 carbon atoms, the total number of carbon atoms of R_1 and R_2 being at least 5.

It is applicable in compositions essentially comprising 10–30% by weight of a water-soluble anionic detergent including soap and one to five times of said amount of a polyphosphate builder. Optionally nonionic synthetic detergents can be included.

The present application is a continuation-in-part of our copending U.S. application Ser. No. 14,783, filed Feb. 26, 1970, now abandoned which in turn is a streamlined continuation of our U.S. application Ser. No. 669,845, filed Sept. 22, 1967 (now abandoned).

Detergent compositions containing various active detergents, builders, bleaching agents and optical brighteners are known. Efforts have been made to provide detergent compositions which are low-foaming at high temperatures, i.e. over about 90° C., but have acceptable foaming characteristics at temperatures of up to about 60° C. Such compositions would be very suitable for use in drum-type washing-machines, as over-foaming at higher temperatures would be avoided. It is known that this object can be attained to some extent if the formation of foam is suppressed by the addition of foam-reducing agents, such as liquid hydrocarbons or hydrocarbons that are solid at room temperature, e.g. paraffins or waxes. A drawback

of these additives, however, is that they can adversely affect the detergency of the washing composition.

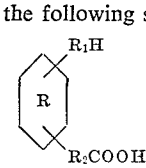
Foam suppression has also been obtained by incorporating a proportion of C_{12}–C_{33} fatty acid soap in the detergent composition. Compositions where soap is employed for this purpose generally contain about 10–30% by weight of anionic detergent, such as alkyl benzene sulphonate, alkyl sulphate, fatty alcohol sulphate and the like, as well as polyphosphate in about the same up to a fivefold amount. Frequently also a certain amount of nonionic detergent is added; detergents of this kind may include the alkylene oxide condensation products of alkyl alcohols, of alkyl phenol, of polyoxypropylene, of fatty acid amide and of other organic hydrophobic compounds. Detergent compositions of this type, the so-called mixed-active detergent compositions, further usually contain an oxygen-liberating bleaching agent, such as perborate, silicate and small quantites of optical brighteners and soil-suspending agents, such as carboxymethylcellulose.

It is known that the foam-suppressing action provided by the soap component in such detergent compositions is stronger at higher temperatures than at lower temperatures if the soap has a relatively high content of saturated molecules with at least 20 carbon atoms. However, these soaps still give a distinct suppression of foam at low and medium temperatures, which in many respects is undesirable.

It has now surprisingly been found that the adjustment of the foaming capacity of such mixed-active detergent compositions at different temperatures can be achieved far better and far more accurately as compared with conventional methods if the soap constituent of the detergent composition is wholly or partly replaced by a material selected from the group consisting of cyclized fatty acids and sodium soaps of such acids, derived from unsaturated fatty acids containing from 12 to 33 carbon atoms per molecule. Cyclized fatty acids, including aromatized fatty acids, are known in the art and several methods for their preparation are known in principle (cf. J. Am. Oil Chem. Soc., vol. 33 (Dec. 1956), pages 609–614; J.A.O.C.S., vol. 43, Aug. 1966, pages 515–518; J.A.O.C.S., vol. 36, Dec. 1959, pages 631–635; J.A.O.C.S., vol. 41, Jan. 1964, pages 60–63; J.A.O.C.S., vol. 41, Oct. 1964, pages 683–685; U.S. P. 3,005,840; U.S. P. 3,041,360; U.S. P. 3,119,850). It is, e.g., possible to subject an oil containing fatty acid with several double bonds, such as linseed oil, to the treatment described in U.S. P. 3,041,360, Example 2, and to isolate the resultant mixture of cyclic esters according to Example 1 by urea adduction. From such esters or the corresponding acids the salts used according to the invention can be recovered in a conventional way.

It is also possible in principle to produce cyclic acids by any other known cyclization reaction processes, such as the Dels-Alder reaction of unsaturated fatty acids with conjugated double bonds and an olefin.

Cyclized fatty acids are essentially composed of a mixture of acids having the following structural formula:



wherein R represents a saturated or unsaturated six-membered carbon ring, and R_1 and R_2 are hydrocarbon chains situated at 1,2; 1,3; or 1,4 positions on the nucleus.

The cyclized fatty acids used in the present invention comprise essentially a mixture of acids having the above structural formula, in which the number of carbon atoms of R_1 is from 0–12, that of R_2 from 0–21, and the total number of carbon atoms of R_1 and R_2 is at least 5. Very satisfactory results are obtained by using cyclized fatty acids, their salts or mixtures thereof having not more than 24 carbon atoms in the molecule, corresponding with a sum of R_1 and R_2 of between 5 and 17, and comprising a high proportion of cyclized compounds having 18 carbon atoms in the molecule, such as those derived from linseed oil fatty acids, wood oil fatty acids or linoleic acid. These cyclized fatty acids generally comprise the ortho-substituted compounds in predominant amounts.

Subsequently, the products thus obtained may or may not be subjected to total or partial hydrogenation.

The invention therefore provides a detergent composition comprising essentially 10–30% by weight of water-soluble anionic detergents including soap, and one to five times of said amount of a polyphosphate builder, in which there is incorporated as a foam-controlling agent an effective amount of a material selected from the group consisting of cyclized fatty acids and sodium soaps of such acids, said acids being essentially obtained from cyclization of unsaturated C_{12}–C_{33} fatty acids by any suitable process known in the art.

The cyclized material used as detergent component according to the invention not only shows the advantage, as was surprisingly found, of having a good foaming capacity at low temperatures and an effective foam-suppression at elevated temperatures, but moreover they are excellent detergents, which are at least equal to the soaps usually incorporated in detergent compositions.

The foam-suppressing action at elevated temperatures provided by the cyclized material used according to the invention is so good that in most cases the desired foam-suppression at elevated temperatures can be achieved by substituting the cyclized material of the invention for only part of the soap portion normally contained in such detergent compositions.

In many cases it is advisable to replace only part of the soap portion of the detergent composition by the cyclized material according to the invention because their foaming capacity at low and medium temperatures, i.e. at temperatures up to about 60° C., is so much superior to that of the long-chain fatty acid soap that a detergent composition in which the soap component is entirely replaced by the substances of the invention would produce too much foam in the low temperature range, in spite of the practically complete suppression of foam at elevated temperatures. According to the invention the cyclized acids or their salts are therefore preferably introduced into these detergent compositions in such an amount that the soap component is replaced by the cyclic acids or their salts for 20–70%, in particular for about 45–55%.

For practical purposes it suffices indeed to use the mixture of cyclized material directly obtained from the cyclization or aromatization of oils, fats and/or fatty acids, without previously isolating it from any non-cyclic constituents.

Detergent compositions according to the invention may contain the usual additives such as optical brighteners or other colorants, perborate stabilizers, perfume, etc.

The use according to the invention is cyclized fatty acids and their salts is not restricted to the washing of laundry, but they may also be advantageously applied in any other cleaning process in which it is desired that at elevated temperatures less foam is produced than in the low and medium temperature ranges.

The superiority of the agent according to the invention is shown by the following examples:

EXAMPLE 1

Linseed oil was cyclized according to the process of U.S. Pat. No. 3,041,360, Example 2, and from the reaction

mixture the cyclized acids and their esters were isolated, totally hydrogenated and saponified with caustic soda according to Example 1 of the same patent specification. The sodium salts of cyclized acids thus obtained predominantly contain 18 carbon atoms and are predominantly ortho-substituted.

The detergency of this mixture was determined in a Tergotometer, in one instance in comparison with a soap of hardened tallow fatty acid where both soaps had been incorporated in the builder as the only active detergents, and in a second instance where these soaps had been combined with sodium alkyl benzene sulphonate and nonionic. The compositions and detergent actions of the test products 1–4 are enumerated in Table I below:

Composition 4 is a composition within the invention, compositions 1–3 are outside the invention and are tabulated only for comparative purposes.

Conditions of testing

Dosage: Test products 1 and 2: 10 g./l.; test products 3 and 4: 7 g./l.
Water hardness: 15° German hardness
Bath ratio: 1:50
Temperatures: 30°, 60° and 95° C.
Washing times: At all temperatures and dosages 15 min.
Soiling: Cotton fabric with artificial soil of the following composition:

	G./l. water
Filter gel	10
China ink	1
Iron oxide black	0.5
Iron oxide yellow	0.75
Groundnut oil	20
Emulsifier	12
Carboxymethyl guaran	12.5

One washing took place at each temperature. An evaluation of the washing results shows that sodium salts of cyclized linseed oil fatty acids have practically the same detergency as sodium soap of hardened tallow fatty acid, both when used as the only active detergent and when used in combination with alkyl benzene sulphonate and a condensation product from tallow fatty acid amide and 11 moles ethylene oxide.

TABLE I

Test product	1	2	3	4
Percent:				
Alkyl benzene sulphonate			12.0	12.0
Tallow fatty acid amide—11 E.O			4.0	4.0
Soap from hardened tallow fatty acid	40.0		3.0	
Sodium salts of cyclized linseed oil fatty acids		40.0		3.0
Sodium tripolyphosphate	40.0	40.0	40.0	40.0
Water glass	6.0	6.0	6.0	6.0
Carboxymethylcellulose, 100%	1.0	1.0	1.0	1.0
Sodium sulphate			21.0	21.0
Water	13.0	13.0	13.0	13.0
Total	100.0	100.0	100.0	100.0
Dosage, g./l.	10	10	7	7
Percent detergent action:				
30° C	31.5	32.0	35.5	34.5
60° C	37.0	36.0	38.5	38.5
95° C	48.5	49.5	47.0	47.5

EXAMPLE 2

Determination of the lather behaviour

For a determination of the lather behaviour under static conditions in the Ross-Miles apparatus both with and without soiling the mixtures were used as defined in Table I of Example 1, of which mixture 4 represents a detergent composition according to the invention.

The water used had a hardness of 15° C. (German hardness measurements were taken at temperatures of 30°, 60° and 95° C.). The soiling amounted to 2 drops

of a fat/soot mixture of the following composition (in 100 ml. solution):

70 parts tallow
15 parts paraffin oil
5 parts palmitic acid
5 parts cetyl alcohol
5 parts flame soot

The results of the foam tests in the Ross-Miles apparatus are graphically shown in FIG. 1.

A comparison of the foaming characteristics shows that the test product **2**, in which the soap is replaced by the saturated cyclized material according to the invention, produces distinctly less foam at 95° C. than test product **1**. This result is obtained in tests with soiling as well as without soiling and at both dosages.

From a comparison of the foam-curves for the test products **3** and **4** it appears that sodium salts of cyclized fatty acids control foam at high temperatures, but, unlike sodium soap from hardened tallow fatty acid, do not give a low foam at lower temperatures. Thus, the foaming behaviour in these tests is as desired for detergent compositions that are intended to be used in drum-type washing machines.

EXAMPLE 3

The foaming behaviour under dynamic conditions was investigated in a rotary foaming apparatus, analogous to that described by H. Bloching, W. Fries and H. J. Heitland in "Seifen, Ole, Wachse," 91, 25, 1965, page 913. The object of the investigation was a mixture of 12% sodium alkyl benzene sulphonate, 4% condensation product from tallow fatty acid amide with 11 moles ethylene oxide, 40% sodium tripolyphosphate, 4.5% water glass—38° Bé, 20% sodium perborate, 1% sodiumcarboxymethylcellulose, 5% sodium sulphate, 3% sodium salts of cyclized linseed oil fatty acids of Example 1; remainder: water, brighteners, perfume, stabilizers.

The foaming behaviour of this mixture is shown in FIG. 2 as graph 1.

For comparison also the foaming behaviour was determined of a product of the same composition, which instead of the cyclized material contained the same amount, i.e., 3%, of hardened tallow soap. The lather values measured are shown by graph 2 of FIG. 2.

It will be seen that under the conditions of the rotary foaming apparatus, which correspond closely to conditions in drum-type washing machines, the foaming capacity of the composition containing sodium salts of cyclized fatty acids according to the invention is appreciably higher at the lower temperature range, whereas at elevated temperatures the foaming capacity does not exceed that of a conventional detergent composition containing tallow soap as anti-foaming agent.

Furthermore, it was found in these tests that the foam stability of the detergent composition with the sodium salts of cyclized fatty acids at high temperatures was distinctly lower than that of the detergent composition with tallow soap. This was especially shown by the fact that the foam of the detergent composition according to the invention collapsed after a short boiling, whereas that of the composition containing tallow soap began to build up.

EXAMPLES 4–7

Similar good results were also found with compositions in the following examples.

EXAMPLE 4

10% sodium alkyl benzene sulphonate
5% tallow fatty alcohol polyglycol ether
3% sodium salts from totally hydrogenated cyclized linseed oil fatty acids
2% technical sodium stearate
40% sodium tripolyphosphate
20% sodium perborate
6% sodium silicate
1% sodium carboxymethylcellulose
13% water and residual salt

EXAMPLE 5

12% sodium alkyl benzene sulphonate
4% tallow fatty alcohol polyglycol ether
2% sodium salts from non-hydrogenated cyclized linseed oil fatty acids
1% technical sodium stearate
40% sodium tripolyphosphate
20% sodium perborate
6% sodium silicate
1% sodium carboxymethylcellulose
14% water and residual salt

EXAMPLE 6

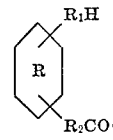
12% sodium alkyl benzene sulphonate
4% fatty acid amide polyglycol ether
3% sodium salts from hydrogenated cyclized wood-oil fatty acids
40% sodium tripolyphosphate
6% sodium silicate
1% sodium carboxymethylcellulose
21% sodium sulphate
13% water and residual salt

EXAMPLE 7

12% sodium alkyl benzene sulphonate
3% nonyl phenol polyglycolether
2% salts from non-hydrogenated cyclized wood-oil fatty acids
2% sodium stearate, technical
40% sodium tripolyphosphate
20% sodium perborate
6% sodium silicate
1% sodium carboxymethylcellulose
14% water and residual salt

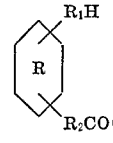
What is claimed is:

1. A detergent composition comprising from about 10 to about 30% by weight of alkyl benzene sulphonate, and 1 to about 5 times of said amount of a polyphosphate builder, in which there is incorporated as a foam-controlling agent a material selected from the group consisting of cyclized fatty acids and sodium salts of such acids, said acids being essentially obtained from cyclization of unsaturated C_{12}–C_{33} fatty acids, and being a mixture of isomers having the formula:



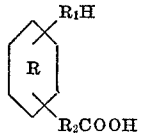
wherein R is a saturated or unsaturated six-membered hydrocarbon ring; R_1 is an aliphatic hydrocarbon chain having from 0–12 carbon atoms, R_2 is an aliphatic hydrocarbon chain having from 0–21 carbon atoms, the total number of carbon atoms of R_1 and R_2 being at least 5; wherein said foam controlling agent is present in an amount effective to cause foam suppression of the detergent composition at high temperatures.

2. A detergent composition according to claim **1** wherein the foam controlling agent is a material selected from the group consisting of cyclized fatty acids and sodium salts of such acids, said acids being obtained from the cyclization of linseed oil and being a mixture of isomers having the formula:



wherein R is a saturated six-membered hydrocarbon ring; R_1 and R_2 are aliphatic hydrocarbon chains having a total number of carbon atoms of between 5 and 17, wherein said foam controlling agent is present in an amount effective to cause foam suppression of the detergent composition at high temperatures.

3. A detergent composition according to claim 1, in which the foam controlling agent is a material selected from the group consisting of cyclized fatty acids and sodium salts of such acids, said acids being obtained from the cyclization of wood oil and being a mixture of isomers having the formula:



wherein R is a saturated or unsaturated six-membered hydrocarbon ring; R_1 and R_2 are aliphatic hydrocarbon chains having a total number of carbon atoms of between 5 and 17, wherein said foam controlling agent is present in an amount effective to cause foam suppression of the detergent composition at high temperatures.

4. A detergent composition according to claim 1, in which the foam controlling agent is a material selected from the group consisting of hydrogenated cyclized linseed oil fatty acids, hydrogenated cyclized wood oil fatty acids, and sodium salts of such acids.

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HERBERT B. GUYNN, Primary Examiner

U.S. Cl. X.R.

252—99, 108, 109, 110, 121, 132, 135, 321, 531, 532, 540