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3,679,608

LOW FOAMING HARD SURFACE CLEANERS
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No Drawing. Filed Aug. 2, 1968, Ser. No. 749,597
Int. Cl. C11d 3/075

U.S. Cl. 252-526

5 Claims

ABSTRACT OF THE DISCLOSURE

Low foaming hard surface cleaner composition comprising a foaming surfactant, a sequestrant builder and, as a suds suppressor, the condensation product of a straight-chain random secondary alcohol with from 0 to about 3 moles of ethylene oxide.

FIELD OF THE INVENTION

This invention relates to a hard surface cleaner composition which has good cleaning ability and low sudsing characteristics under conditions of use on hard surfaces and when mixed into water in a bucket to form a cleaning solution. The physical form of the composition can be either liquid or solid.

PRIOR ART

Secondary alkyl ethoxylates are old having been disclosed in U.S. Pat. 2,355,823. The combination of alkyl ethoxylates and diethanolamides is disclosed in U.S. Pat. 2,831,815 which discloses that the amides improve the sudsing of alkyl ethoxylates having at least 5 ethylene oxide moieties per alkyl ethoxylate molecule. This patent, however, does not disclose that certain specific secondary alkyl ethoxylates will act as suds suppressors when mixed with amides. The combination of certain zwitterionic detergents and alkyl ethoxylates is disclosed in U.S. Pat. 3,351,557. This patent also does not disclose secondary alkyl ethoxylates specifically. None of the prior art patents disclose that there is any criticality, with respect to reduced sudsing, in selecting secondary alkyl ethoxylates for use with certain specific sudsing surfactants.

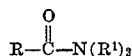
SUMMARY OF THE INVENTION

The compositions of this invention are low-foaming hard-surface cleaner compositions consisting essentially of:

(a) From about 1% to about 10% of a primary surfactant selected from the group consisting of:

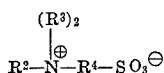
- (1) the condensation product of a straight chain primary alcohol containing from about 8 carbon atoms to about 16 carbon atoms and having an average carbon chain length of from about 10 to about 12 carbon atoms with from about 4 to about 8 moles of ethylene oxide per mole of alcohol,

- (2) an amide having the formula



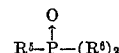
wherein R is a straight chain alkyl group containing from about 7 to about 15 carbon atoms and having an average carbon chain length of from about 9 to about 13 carbon atoms and wherein each R¹ is a hydroxyalkyl group containing from 1 to about 3 carbon atoms,

- (3) a zwitterionic surfactant having the formula



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wherein R² contains from about 8 to about 16 carbon atoms and has an average of from about 10 to about 13 carbon atoms, each R³ is selected from the group consisting of alkyl and hydroxy alkyl groups containing from 1 to about 3 carbon atoms, and R⁴ is a saturated alkylene or hydroxyalkylene group containing from 2 to about 5 carbon atoms and wherein the hydroxy group in said hydroxyalkylene group is attached to a carbon atom which is separated from the nitrogen atom by at least one methylene group,
(4) a phosphine oxide surfactant having the formula



wherein R⁵ contains from about 8 to about 16 carbon atoms and has an average of from about 10 to about 12 carbon atoms and wherein each R⁶ is selected from the group consisting of alkyl and hydroxy alkyl groups containing from 1 to about 3 carbon atoms, and

- (5) Mixtures thereof;

(b) From about 1% to about 3% of a suds suppressor and surfactant which is the condensation product of a straight chain random secondary alcohol having a chain length of from about 11 to about 15 carbon atoms and having an average length of from about 12 to about 15 carbon atoms with from 0 to about 3 moles of ethylene oxide;

- (c) From about 10% to about 50% of a sequestrant builder selected from the group consisting of alkali metal and ammonium aminopolycarboxylates, organic polyphosphonates, polymeric carboxylates, pyrophosphates and tripolyphosphates;

- (d) From 0% to about 80% of a salt selected from the group consisting of alkali metal and ammonium carbonates, sesquicarbonates, bicarbonates, borax and mixtures thereof;

- (e) From 0% to about 12% of a hydrotrope agent selected from the group consisting of alkali metal, ammonium, and triethanolammonium isopropylbenzene sulfonates, xylene sulfonates, toluene sulfonates, and benzene sulfonates, and mixtures thereof; and

- (f) The balance water, the ratio of (a) to (b) being from about 4:1 to about 0.7:1 and the ratio of the sum of (a) and (b) to (c) being from about 1:2 to about 1:10.

The amount of the primary surfactant in the compositions of this invention is determined by the cleaning requirements and the type of product desired. There is usually from about 1% to about 10% of this component in the composition. When the product is in the form of a liquid, however, it is preferred that the primary surfactant range from about 2% to about 5%, more preferably from about 2% to about 3%, of the composition. Specific examples of suitable primary surfactants are given hereinafter in the examples.

There is a definite relationship between the amount of primary surfactant and the suds suppressor. There is from about 1% to about 3%, preferably from about 1% to about 2% of the suds suppressor in the composition and the ratio of primary surfactant to suds suppressor ranges from about 4:1 to about 0.7:1, preferably from about 2:1 to about 1:1, and most preferably from about 1.5:1 to about 1:1. The preferred ratio is 1.5:1. The suds suppressor keeps down the level of suds when the product is being used to clean hard surfaces in a diluted form and more importantly it suppresses sudsing when the product is being diluted in the housewife's bucket under conditions which involve higher concentrations of surfactant and greater agitation. The housewife wants a minimum amount of suds in a hard surface cleaner, especially where the housewife does not rinse the surface

after the washing step. The suds suppressor of this invention lowers the level of suds for the specific primary surfactants of this invention, but not for conventional anionic synthetic surfactants such as alkyl benzene sulfonates. Furthermore, if the corresponding primary alkyl ethoxylate is used instead of the random secondary alkyl ethoxylate, the reduction in sudsing, especially during dilution in the bucket, is much less pronounced. This is totally unexpected. These suds suppressors do not harm the cleaning effectiveness of the composition and even contribute to the cleaning effect. The preferred suds suppressor is the condensation product of a random secondary straight chain alcohol having from about 11 to about 15 carbon atoms and an average of about 13 carbon atoms with about 3 moles of ethylene oxide per mole of alcohol.

The compositions also contain a sequestering builder. Suitable builders include the alkali metal (e.g., sodium and potassium) and ammonium (including substituted ammonium, e.g., triethanolammonium) aminopolycarboxylates, organic polyphosphonates, polymeric carboxylates, pyrophosphates, and tripolyphosphates. Suitable aminopolycarboxylates are those described in U.S. Pats. Nos. 3,329,617 and 3,336,233. Suitable polyphosphonates are those described in U.S. Pats. Nos.: 3,329,617; 3,336,233; 3,332,880 and 3,213,030; copending U.S. applications: Roy, Ser. No. 266,055 filed Mar. 18, 1963 U.S. Pat. No. 3,422,021; Roy, Ser. No. 493,925 filed Mar. 18, 1963 U.S. Pat. No. 3,404,178; Quimby, Ser. No. 489,637 filed Sept. 23, 1965 U.S. Pat. No. 3,400,148; Quimby, Ser. No. 507,662 filed Nov. 15, 1965 U.S. Pat. No. 3,400,176; Quimby, Ser. No. 517,073 filed Dec. 28, 1965 U.S. Pat. No. 3,422,137; Quimby and Prentice, Ser. No. 587,417 filed Oct. 18, 1966 now abandoned; Quimby, Ser. No. 605,606 filed Dec. 29, 1966 U.S. Pat. No. 3,497,313; Curry, Ser. No. 717,999 filed Apr. 1, 1968 now abandoned; Nicholson and Campbell, Ser. No. 694,002 filed Dec. 27, 1967 now abandoned; Nicholson and Campbell, Ser. No. 694,003 filed Dec. 27, 1967 now abandoned; Prentice and Quimby, Ser. No. 694,112 filed Dec. 28, 1967 U.S. Pat. No. 3,400,151; and Prentice and Quimby, Ser. No. 694,106 filed Dec. 28, 1967 U.S. Pat. No. 3,512,862. Suitable polymeric carboxylates are disclosed in U.S.

liquid, it is desirable to have from about 2% to about 12% of a hydrotrope agent to keep the composition homogeneous under varying storage conditions. Mixtures of alkali metal, ammonium and/or triethanolammonium isopropyl benzene sulfonate and the equivalent salts of either xylene, toluene or benzene sulfonate in ratios of from about 10:1 to about 0.5:1 are preferred since they are more effective than the individual hydrotropes. The isopropyl benzene sulfonate is also effective.

The compositions can also be in the form of stable emulsions. For such emulsions, the hydrotrope should be omitted and an emulsion stabilizer added in amounts from about 0.5% to about 2%, preferably from about 0.8% to about 1.5%. Acrysol ASE-108, a commercial product, is preferred. The compositions can also contain numerous miscellaneous ingredients such as dyes, pigments, perfumes, ammonia, etc.

The following examples demonstrate the advantages of this invention, but should not be taken as limiting its scope.

EXAMPLE I

The compositions listed in the following table were tested for cleaning hard surfaces, the amount of suds produced on the surfaces cleaned, and the amount of suds generated when the compositions were diluted with water in a bucket. All of the compositions cleaned the surfaces well and gave acceptably low suds on the surfaces cleaned. However, the amount of suds generated in the bucket varied remarkably depending on whether a secondary alcohol ethoxylate or a primary alcohol ethoxylate was used.

The bucket sudsing values given are the average of the inches of suds produced when two tests were run on each composition. In both tests the dilution rate was $\frac{1}{4}$ cup of product in one gallon of water. The two tests are as follows: In the first the detergent composition is added first, then the water is added from a tap at a standard height and the suds measured. In the second test the water is added first, then the detergent is added and agitation is provided by repeating five times in a minute the steps of dipping a sponge into the water and then wringing it out; the suds are then measured.

Composition	1	2	3	4	5	6	7	8	9	10
The condensation product of a primary straight chain alcohol (C_8-C_{12}) containing an average of about 10 carbon atoms and about 7 moles of ethylene oxide per mole of alcohol			3	3						
Fatty acid diethanolamide containing fatty acyl groups ($C_{10}-C_{12}$) with an average of about 11 carbon atoms		3	3							
Decyldimethylphosphine oxide					3	3				
The condensation product of a primary straight chain alcohol (C_8-C_{12}) having an average of about 10 carbon atoms and about 4 moles of ethylene oxide per mole of alcohol							3	3		
3-[N-coconut ¹ alkyl-N,N'-dimethylammonio]-2-hydroxypropane-1-sulfonate									3	3
The condensation product of a coconut ¹ alcohol and about three moles of ethylene oxide per mole of alcohol	2		2				1			
The condensation product of a random secondary straight chain alcohol ($C_{11}-C_{15}$) containing an average of about 13 carbon atoms and about three moles of ethylene oxide per mole of alcohol		2		2	2			1		2
Sodium nitrilotriacetate			13	13			13	13		
Potassium pyrophosphate	13	13			13	13			13	13
Sodium carbonate	4	4	4	4	4	4	4	4	4	4
Potassium toluene sulfonate	7	7			6	6	9	4.5	9	9
Sodium cumene sulfonate								4.5		
Acrysol ASE-108			1	1						
Water										
Bucket sudsing (inches of suds)	2.9	0.7	1.9	1.25		Balance	2.4	1.2	2.6	1.6

¹ "Coconut" refers to a chain length distribution substantially as follows: 2%- C_{10} , 66%- C_{12} , 23%- C_{14} , and 9%- C_{16} .

Pat. No. 3,308,067. All of the above patents and applications are incorporated herein by reference.

Preferred sequestering builders are sodium nitrilotriacetate, potassium pyrophosphate, potassium tripolyphosphate, and sodium or potassium ethane-1-hydroxy-1,1-diphosphonate.

Sodium carbonate or other alkaline salts are added to the compositions, in amounts up to about 80% as pH buffers. In liquid compositions there should be from about 1% to about 5% sodium carbonate. Other pH buffers can be used including sodium sesquicarbonate, borax, etc., but sodium carbonate is preferred for many reasons such as availability and cost.

When the composition is in the form of a homogeneous

The compositions containing the secondary alcohol ethoxylates (2, 4, 5, 8, and 10) all gave lower bucket sudsing than the compositions containing the primary alcohol ethoxylates (1, 3, and 7) and the compositions containing no suds suppressor (6 and 9).

The above compositions clearly demonstrate the unobvious advantages, with respect to bucket sudsing, of the secondary alkyl ethoxylates as compared with the primary alkyl ethoxylates.

The following compositions give results which are substantially similar to those obtained with the preceding compositions in that the bucket sudsing is less when the compositions contain the indicated straight-chain random secondary alcohol ethoxylates rather than the correspond-

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ing primary alcohol ethoxylates and the bucket sudsing is also less for the compositions containing the straight-chain random secondary alcohol ethoxylates than for similar compositions without the secondary alcohol ethoxylates.

EXAMPLE II

Solid granular

	Percent
Ethoxylated (5 moles) primary alcohol (C ₁₀ and C ₁₂ —1:1 mixture) -----	2
Decyldi (2-hydroxyethyl)phosphineoxide -----	2
Dodecyldimethylphosphineoxide -----	2
Ethoxylated (2 moles) straight-chain random secondary alcohol (C ₁₃) -----	3
Sodium tripolyphosphate -----	26
Sodium sesquicarbonate -----	30
Borax -----	35

EXAMPLE III

Liquid

	Percent
3 - [N,N' - dimethyl - N-decylammonio]-propane-1-sulfonate -----	2
Ethoxylated (8 moles) primary alcohol (C ₈) -----	1
Ethoxylated (3 moles) straight-chain random secondary alcohol (C ₁₅) -----	2
Ammonium ethylenediaminetetraacetate -----	0.5
Triethanolammonium poly(itaconate-acrylate) (4:1 on a molar basis) (specific viscosity of 1% by weight, in dimethyl formamide at room temperature, .40) (equivalent weight, 65.8) -----	10
Sodium polyitaconate (specific viscosity of 1% by weight in dimethylformamide at room temperature, .13) (equivalent weight, 65) -----	2
Ammonium cumene sulfonate -----	2
Ammonium benzene sulfonate -----	2
Ammonium xylene sulfonate -----	2
Sodium carbonate -----	4
Water -----	Balance

EXAMPLE IV

Liquid

	Percent
Fatty acid (1:1 C ₁₁ and C ₁₃) diisopropanolamide ---	3
Ethoxylated (2 moles) straight chain random secondary alcohol (C ₁₅) -----	2
Potassium polymaleate (specific viscosity of 1% by weight in dimethylformamide at room temperature, .13) (equivalent weight as acid, 58) -----	10
Potassium ethane-1,1,2-triphosphonate -----	10
Sodium carbonate -----	2
Triethanolammonium cumene sulfonate -----	4
Water -----	Balance

EXAMPLE V

Liquid

	Percent
4 - [N,N' - di(2-hydroxyethyl)-N-dodecylammonio]-2-hydroxybutane-1-sulfonate -----	3
4 - [N,N' - diethyl - N - undecylammonio]-butane-1-sulfonate -----	1
Ethoxylated (2.5 moles) straight-chain random secondary alcohol (C ₁₄) -----	1.5
Potassium ethane-1-hydroxy-1,1,2-triphosphonate --	3
Ammonium ethane-2-hydroxy-1,1,2-triphosphonate --	3
Tripotassium ethane-1-hydroxy-1,1-diphosphonate --	3
Sodium carbonate -----	3
Potassium cumene sulfonate -----	3
Potassium toluene sulfonate -----	3
Water -----	Balance

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EXAMPLE VI

Solid

	Percent
5 3-[N,N'-dimethylol-N-alkyl(1:1:1 C ₁₁ , C ₁₃ and (C ₁₅) ammonio]-2-hydroxypropane-1-sulfonate -----	3
Ethoxylated (7 moles) primary alcohol (1:1:1 C ₉ , C ₁₁ and C ₁₃) -----	3
Ethoxylated (3 moles) straight-chain random secondary alcohol (C ₁₁ —C ₁₅ ; C ₁₃ average) -----	3
10 Sodium tripolyphosphate -----	15
Sodium nitrilotriacetate -----	15
Trisodium ethane-1-hydroxy-1,1-diphosphonate ----	15
Sodium sesquicarbonate -----	30
Borax -----	16

EXAMPLE VII

Liquid

	Percent
20 3 - [N,N' - dimethyl - N-coconut * alkylammonio]-2-hydroxypropane-1-sulfonate -----	2
Ethoxylated (7 moles) primary coconut * alcohol --	2
Straight-chain random secondary alcohol (C ₁₁ —C ₁₅ ; C ₁₃ average) -----	1.5
25 Sodium nitrilotriacetate -----	5
Potassium tripolyphosphate -----	10
Potassium cumene sulfonate -----	4
Potassium toluene sulfonate -----	4
Sodium carbonate -----	4
30 Water -----	Balance

*"Coconut" refers to a chain length distribution substantially as follows: 2%-C₁₀, 66%-C₁₂, 23%-C₁₄, and 9%-C₁₆.

EXAMPLE VIII

Liquid

	Percent
3-[N,N' - dimethyl-N-decylammonio]-propane-1-sulfonate -----	2
Ethoxylated (5 moles) n-decyl alcohol -----	3
Ethoxylated (2 moles) straight-chain random secondary alcohol (C ₁₄) -----	1
Potassium pyrophosphate -----	15
Potassium xylene sulfonate -----	6
Sodium carbonate -----	3
45 Water -----	Balance

EXAMPLE IX

Solid

	Percent
50 Fatty acid (C ₁₀) di(isopropanol)amide -----	3
Fatty acid (C ₁₀) dimethanolamide -----	3
Fatty acid (C ₁₁) dimethylamide -----	3
Ethoxylated (1 mole) straight-chain random secondary alcohol (C ₁₄) -----	3
55 Sodium methylene-diphosphonate -----	2
Potassium tripolyphosphate -----	4
Potassium carbonate -----	10
Sodium ethylene-1,1-diphosphonate -----	2
60 Potassium benzylmethylidene diphosphonate -----	1
Sodium N-(2 - hydroxyethyl)-ethylenediaminetriacetate -----	2
Sodium N-(2-hydroxyethyl)-nitrilo diacetates -----	2
Potassium isopropylidene diphosphonate -----	1
65 Potassium ethylidene diphosphonate -----	1
Sodium orthophosphate -----	4
Potassium ethane-2-carboxy-1,1-diphosphonate ----	1
Potassium hydroxymethanediphosphonate -----	1
Ammonium propane-1,1,3,3-tetraphosphonate -----	1
70 Ammonium propane-1,2,2,3-tetraphosphonate -----	1
Ammonium propane-1,1,2,3-tetraphosphonate -----	1
Ammonium carbonyldiphosphonate -----	2
Sodium hexametaphosphate -----	5
Sodium sesquicarbonate -----	10
75 Borax -----	Balance

7 EXAMPLE X

Liquid	Percent
5-[N-(3 - hydroxypropyl)-N-(2-hydroxypropyl)-N-tri-decylammonio]-3-hydroxypentane-1-sulfonate	1 5
Decyl (3 - hydroxypropyl) (2 - hydroxypropyl)phos- phine oxide	1
Octyldiethylphosphine oxide	1
Ethoxylated (1.5 moles) straight-chain random second- ary alcohol (C ₁₅)	1 10
Triethanol ammonium toluene sulfonate	6
Potassium pyrophosphate	12
Water	Balance

All parts, ratios, and percentages herein are by weight unless otherwise specified.

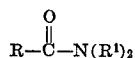
What is claimed is:

1. A low-foaming hard-surface cleaner composition consisting essentially of:

(a) from about 1% to about 10% of a primary surfac-
tant selected from the group consisting of:

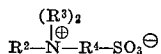
- (1) the condensation product of a straight chain
primary alcohol containing from about 8 to
about 16 carbon atoms and having an average
carbon chain length of from about 10 to about
12 carbon atoms with from about 4 to about 8
moles of ethylene oxide per mole of alcohol,

(2) an amide having the formula



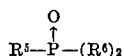
wherein R is a straight chain alkyl group con-
taining from about 7 to about 15 carbon atoms
and having an average carbon chain length of
from about 9 to about 13 carbon atoms and
wherein each R¹ is a hydroxyalkyl group con-
taining from 1 to about 3 carbon atoms,

(3) a zwitterionic surfactant having the formula



wherein R² contains from about 8 to about 16
carbon atoms and has an average of from about
10 to about 13 carbon atoms, each R³ is selected
from the group consisting of alkyl and hydroxy
alkyl groups containing from 1 to about 3 car-
bon atoms, and R⁴ is selected from the group
consisting of a saturated alkylene group and a
saturated hydroxyalkylene group containing
from 2 to about 5 carbon atoms and wherein
the hydroxy group in said hydroxy alkylene
group is attached to a carbon atom which is
separated from the nitrogen atom by at least
one methylene group,

(4) a phosphine oxide surfactant having the for-
mula



wherein R⁵ contains from about 8 to about 16
carbon atoms and has an average of from about
10 to about 12 carbon atoms and wherein each
R⁶ is selected from the group consisting of alkyl
and hydroxy alkyl groups containing from 1 to
about 3 carbon atoms, and

(5) mixtures thereof;

(b) from about 1% to about 3% of a suds suppressor
and surfactant which is the condensation product of
a mixture of straight-chain random secondary alco-
hols having a chain length of from about 11 to about
15 carbon atoms, said alcohols having an average
chain length of from about 12 to about 15 car-
bon atoms with about 3 moles of ethylene oxide;

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(c) from about 10% to about 50% of a sequestrant
detergency builder selected from the group consist-
ing of alkali metal and ammonium aminopolycar-
boxylates, organic polyphosphonates, polymeric car-
boxylates, pyrophosphates and tripolyphosphates;

(d) from 0% to about 80% of a salt selected from the
group consisting of alkali metal and ammonium
carbonates, sesquicarbonates, bicarbonates, borax,
and mixtures thereof;

(e) from 0% to about 12% of a hydrotrope agent
selected from the group consisting of alkali metal,
ammonium, and triethanolammonium isopropylben-
zene sulfonates, toluene sulfonates, xylene sulfonates,
and benzene sulfonates and mixtures thereof; and

(f) water, the ratio of (a) to (b) being from about
4:1 to about 0.7:1 and the ratio of the sum of (a)
and (b) to (c) being from about 1:2 to about 1:10.

2. The composition of claim 1 wherein the sequester-
ing detergency builder is selected from the group consist-
ing of sodium nitrilotriacetate, potassium pyrophosphate,
potassium tripolyphosphate, and sodium or potassium
ethane-1-hydroxy-1,1-diphosphonate.

3. The composition of claim 1 in the form of a homo-
geneous liquid containing

- (1) from about 2% to about 5% of component (a);
- (2) from about 1% to about 2% of component (b);
- (3) from about 10% to about 20% of component (c);
- (4) from about 1% to about 5% sodium carbonate;
- (5) from about 2% to about 12% of component (e);

and
(6) the balance water, and the ratio of component (a)
to component (b) is from about 2:1 to about 1:1.

4. The composition of claim 3 wherein the sequester-
ing detergency builder is selected from the group consist-
ing of sodium nitrilotriacetate, potassium pyrophosphate,
potassium tripolyphosphate, and sodium or potassium
ethane-1-hydroxy-1,1-diphosphonate.

5. The composition of claim 3 wherein there is from
about 2% to about 3% of component (a) and the ratio
of component (a) to component (b) is from about 1.5:1
to about 1:1.

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LEON D. ROSDOL, Primary Examiner

A. I. RADY, Assistant Examiner

U.S. Cl. X.R.

252—527, 540, 545, 546, 559

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,679,608 Dated July 25, 1972

Inventor(s) Harry Julius Aubert and Edward Carroll Gemperle

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 3, lines 43 and 44, "3,512,862" should read
-- 3,496,222 --.

Signed and sealed this 23rd day of January 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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