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LOW SUDSING DETERGENT AND CLEANING AGENTS

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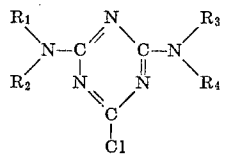
ABSTRACT OF THE DISCLOSURE

Low sudsing detergent and cleaning compositions containing a water-insoluble triazine derivative of the formula:



wherein R_1 and R_3 each represents hydrogen or an organic radical containing 1 to 24 carbon atoms and R_2 and R_4 each represent an organic radical containing 2 to 24 carbon atoms; said organic radical designating substituted or unsubstituted straight or branched chain aliphatic, cycloaliphatic or aromatic groups which may contain heteroatoms in their chains.

This invention relates to suds-suppressing additives for use in detergent and cleaning compositions. More particularly this invention relates to a class of water-insoluble triazine derivatives constituting effective suds-suppressing agents and to the detergent and cleaning compositions containing such triazine derivatives.

In copending patent applications, such as application Ser. No. 525,765, now U.S. 3,422,020, there have been proposed for use as suds-suppressing additives for incorporation into detergent and cleaning compositions, N-substituted melamines, in which each of the three primary nitrogen atoms has at least one hydrocarbon radical containing 4 to 24 carbon atoms. The alkylated melamines are usually prepared by the reaction of 1 mole of cyanuric chloride with a three molar quantity of a primary or secondary amine of relatively high molecular weight.

It has now been found that this procedure is associated with considerable disadvantages when the reaction is carried out on a technical scale. Cyanuric chloride reacts smoothly with two moles of amine with the formation of monochloro-bis-(alkylamino)-s-triazines. The replacement of the third chlorine atom with an alkylamine group, however, takes place very slowly and requires the use of relatively high temperatures or the use of pressure vessels.

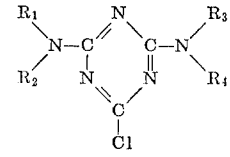
An object of the instant invention lies in the provision of a class of easily manufactured suds-suppressing agents which can be used for replacing the aforesaid melamines in detergent compositions.

Another object of the invention is the provision of a class of suds-suppressing agents having a greater effectiveness than the N-substituted melamines.

Still another object of the invention is the provision of a class of highly effective suds-suppressing compounds whereby the minimum quantity thereof required for adequate suds suppression can be considerably reduced.

A further object of the invention is the provision of novel detergent and cleaning compositions containing as suds-suppressing agent a water-insoluble triazine derivative.

In accordance with this invention low-sudsing detergent and cleaning compositions contain as suds-suppressing agents at least one water-insoluble triazine derivative of the formula:



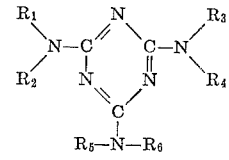
I

wherein R_1 and R_3 each represents hydrogen or an organic radical containing from 1 to 24 carbon atoms, and R_2 and R_4 each represents an organic radical containing from 2 to 24 carbon atoms. The term organic radical designates straight or branched chain aliphatic, cycloaliphatic or aromatic hydrocarbons, which may contain hetero atoms, such as nitrogen, oxygen or sulfur atoms in their chain and which may carry other substituents, such as halogen atoms for example. However, they are not to have any water-solubilizing groups.

The preparation of the compounds defined by the above Formula I and hereinafter designated chlorotriazine derivatives for brevity can be carried out by conventional methods, as for example, by the reaction of 1 mole of cyanuric chloride with a two molar quantity of a primary or secondary amine having the stated number of carbon atoms, starting from amines of the same or different constitution and carbon number. Of particular practical importance are chlorotriazine derivatives in which the radicals R_1 and R_3 are both hydrogen and the radicals R_2 and R_4 are each straight-chained saturated or unsaturated hydrocarbon radicals having a C_6 to C_{18} chain length. These preferred compounds are obtained by the reaction of one mole of cyanuric chloride with a two molar amount of an alkylamine of the stated chain length. Alkylamines having 6 to 18 carbon atoms can be prepared in the known manner, as for example, from naturally occurring fatty acid mixtures, such as coconut fatty acid, palm kernel fatty acid, tallow fatty acid, rape oil fatty acid and other fatty acids of vegetable or animal origin.

The reaction can be carried out by mixing the cyanuric chloride, which can be suspended or dissolved in an inert solvent such as an aromatic hydrocarbon or halogenated hydrocarbon, with a twice-molar quantity of amine; one half of the amine reacting with the triazine radical and the hydrogen chloride released being bonded with the remaining amine to form a hydrochloride. After the addition of 2 moles of a strongly basic compound such as for example, caustic soda solution, the reaction is then carried to completion, with gentle heating, if desired, and the sodium chloride which develops separated by washing.

The suds-suppressing properties of the chlorotriazine derivatives thereby obtained can be further improved if they are employed in a mixture with at least one water-insoluble melamine derivative of the formula:



II

in which formula, R_1, R_3 and R_5 each represent hydrogen or a hydrocarbon radical having 1 to 24 carbon atoms and R_2, R_4 and R_6 each represent a hydrocarbon radical having 4 to 24 carbon atoms. As in the case of the chlorotriazine derivatives, the aforesaid radicals can be satuarted or unsaturated, straight or branch chained, aliphatic, cycloaliphatic or aromatic, and can

contain hetero atoms and/or be substituted by halogen atoms. Preferably the radicals R_1, R_3 and R_5 designate hydrogen and R_2, R_4 and R_6 designate straight-chained, saturated hydrocarbon radicals having 6 to 18 carbon atoms.

The compounds corresponding to Formula II shall hereinafter be referred to as melamine derivatives, can be prepared by known methods as, for example, using a method similar to that employed in the preparation of the chlorotriazine derivatives, the amount of amine and of basic compound being increased by 1 mole. However, it is more advantageous to use 2.1 to 2.9 moles of amine per mole of cyanuric chloride, so that mixtures of chlorotriazine and melamine derivatives are directly formed.

These mixtures of chlorotriazine derivatives and melamine derivatives are characterized by a synergistic intensification of action, i.e., their suds-suppressing properties exceed considerably the sum of the individual components.

The amount of the chlorotriazine derivative or of the mixtures of chlorotriazine derivative and melamine derivative which are to be used are regulated by the total quantity of the surface active or wash-active materials, and by the magnitude of the suds-suppressant effect. The quantities which have been proven advantageous in practice range from 0.1 to 20% and preferably from 0.2 to 10% of the weight of the wash-active materials. It is possible using still larger amounts, as for example, up to 50% of the weight of the wash-active materials, to achieve a substantially complete suppression of sud formation, however, in the usual detergents this is not generally necessary. If mixtures of the two suds-suppressing compounds (chlorotriazine and melamine derivatives) are used, the mixture ratio of chlorotriazine to melamine derivative amounts to from 10:1 to 1:10. An optimum effect is achieved at a ratio of chlorotriazine to melamine derivative of from 2:1 to 1:4. The afore-stated ratios represent weight ratios.

The suds inhibitors, in accordance with the invention, are suitable for use with different kinds of anionic, ampholytic, cationically active and non-ionic wash-active substances. Illustrative of the anionic substances which can be used in the detergent and cleaning compositions include alkali soaps of fatty acids, fatty acid condensation products such as derivatives of aminocarboxylic acids; surfactants of the sulfate or sulfonate type, such as primary or secondary alkylsulfates, fatty acid alkanolamide sulfates, fatty acid isoethionates, fatty acid taurides, alkyl sulfonates and olefin sulfonates, alkylbenzene sulfonates, α-sulfofatty acid esters, and others. The chlorotriazine derivatives and mixtures thereof with melamine derivatives are also effective in combination with ampholytic substances, such as the alkyl betaines, alkyl sulfobetaines and phosphate betaines, as well as cationically active surfactants such as quaternary ammonium salts. The chlorotriazine derivatives and their mixtures which the melamine derivatives can furthermore be combined with non-ionic wash-active substances, such as alkyl and acyl polyglycol ethers, alkyl phenol polyglycol ethers, fatty acid sugar esters, aminoxides, fatty acid alkanolamines and other fatty acid condensation products, and with saponines.

In addition to the above-named surface active compounds, the detergent and cleaning agents according to the invention may also contain the customary fillers and additives. These include the washing alkalies, particularly, the pyrophosphates, polyphosphates and phosphates of higher condensation, silicates, carbonates, bicarbonates, borates and hydroxides of alkalies; oxygen-yielding bleaches or bleaches containing active chlorine, particularly sodium perborate. Other suitable additives are the known complex compound formers, such as aminopolycarboxylic acids such as aminotriacetic acid, ethylenediaminotetraacetic acid and diethylenetriaminopentaacetic acid, and also aminopolyphosphonic acids

such as aminotri-(methylenephosphonic acid) or ethylenediaminotetra-(methylenephosphonic acid) and hydroxyalkyldiphosphonic acids such as 1-hydroxyethylenediphosphonic acid. In place of the free acids their alkali or ammonium salts can also be used. Other components suitable for inclusion in the compositions of the invention include oxygen stabilizers such as magnesium silicate, and neutral salts such as sodium sulfate, dirt dispersing agents, particularly cellulose derivatives, optical brighteners and perfumes and dyes. The detergent compositions in liquid or paste form can also contain hydrotropic materials such as alkylbenzenesulfonates of low molecular weight, urea and organic solvents. The chlorotriazine derivatives and the mixtures thereof with melamine derivatives exert their suds suppressing action even in the presence of the above-named additives.

The particular advantage associated with the chlorotriazine derivatives and the mixtures thereof with melamine derivatives is to be appreciated from the fact that, even in low concentration, they exhibit a considerable suds-suppressing action both in hard and in soft water, with all of known wash-active substances, without in any way diminishing their wash activity. The additives according to the invention do not adversely affect the pulverluent properties of the detergents and/or cleaning composition, and they can be easily incorporated into the detergent concentrates as produced for spray drying or into ready-to-use liquid detergents.

It is especially advantageous to add the melamine derivatives to the solid detergent components or to a solid component of the detergent composition. This can be done, for example, by mixing the finely divided chlorotriazine derivative or the liquid, melted or dissolved (organic solvents) melamine derivatives with the powdered or granulated detergent or a portion thereof, such as for example, with the sodium perborate, or by spraying the liquid components onto the dry materials.

The composition of the detergents in which the suds inhibitors according to the invention are utilized can vary within wide limits. For example, solid or powdered low-sudsing detergents can contain the following principal components:

	Percent
Anionic, ampholytic or non-ionic wash-active substances or mixtures thereof	5–60
Suds inhibitors	0.1–3
Inorganic salts, such as anhydrous phosphates, alkali silicates and alkali carbonates	0–90
Per compounds	0–25
Dispersing agents of high molecular weight, such as carboxymethylcellulose	0.1–5
Dyes and perfumes as well as optical brighteners	0–1

plus stabilizing agents for per compounds, complex compound formers, inorganic neutral salts and moisture

Liquid detergents can contain the following as principal components:

	Percent
Anionic, ampholytic or non-ionic wash-active substances and mixtures thereof	5–50
Suds inhibitors	0.1–3
Anhydrous phosphates, preferably in the form of potassium salts	0–35
Solubilizers, particularly alkylbenzenesulfonates with low alkyl groups	0–10
Dyes and perfumes as well as optical brighteners	0–1

and in addition complex compound formers, water, and, if desired, organic solvents.

The action of the chlorotriazine and melamine derivatives, however, it is not limited to the detergent compositions and quantity ratios given above or in the following examples.

The following examples will further illustrate this invention but the invention is not restricted to these examples.

EXAMPLES

The detergent as used in the following examples had the following composition (the recited amounts are in percent by weight):

	Percent
n-Dodecylbenzenesulfonate (Na salt)	9.0
Ethoxylated oleyl alcohol (10 glycol ether groups)	2.5
Soda soap (50% tallow, 50% coconut oil)	2.0
Pentasodium triphosphate	40.0
Water glass	4.0
Magnesium silicate	2.5
Sodium perborate	20.0
Sodium cellulose glycolate	1.0
Sodium sulfate	10.0
Suds inhibitors	0.3–0.5
Optical brighteners and perfumes	0.4
Balance, water.	

The suds inhibitors which were employed were chlorotriazine and melamine derivatives which had been obtained by the reaction of cyanuric chloride with the corresponding amounts of primary N-alkylamines of different chain length. The moieties R_1, R_3 and R_5 each designates hydrogen, and the moieties R_2, R_4 and R_6 each had chain lengths as follows:

Alkyl from first runnings	Coconut alkyl	Tallow alkyl
2% C_6	8% C_8	40% C_{16}
43% C_8	6% C_{10}	60% C_{18}
27% C_{10}	47% C_{12}	(Unsaturated.)
28% C_{12}	18% C_{14}	
	10% C_{16}	
	11% C_{18}	

In Examples 4 to 8, mixtures of separately prepared chlorotriazine and melamine derivatives were used, while

the mixtures used in Examples 9 to 11 were obtained by the reaction of 1 mole of cyanuric chloride with an amount of the alkylamine of between 2 and 3 moles.

The suds inhibitors were mixed in the dry state with the perborate, and the latter mixture was then admixed with the spray-dried wash powder.

The sudsing was tested under close to actual conditions in a fully automatic household washing machine (AEG "Lavamat nova 64"). This machine was provided with a circular viewing window through which the suds level could be observed and evaluated by means of markings applied thereon. The following scores were used with respect to the suds levels:

Score:	Suds level
0	No suds.
1	¼ of viewing window.
2	½ of viewing window.
3	¾ of viewing window.
4	¼ of viewing window.
5	Suds in the filler opening.
6	Heavy suds overflow.

The washing machine was loaded with 3 kg. of clean laundry. The detergent concentration amounted to 7.5 g./l. in both wash cycles, and the tap water hardness was 16° dH. The results, reported in each instance as averages of three individual measurements, are set out in the following tables. The results show that the chlorotriazine derivatives effectively prevent oversudsing of the wash water, and mixtures thereof with melamine derivatives do so to an even greater extent. Detergents without the additives according to the invention oversudsed in all temperature ranges.

In a second experimental series, Examples 1 to 3 and 9 to 11 were repeated using softened water (2° dH.). Within the limits of error, no change took place in the sudsing action, establishing that the suds suppression is independent of the water hardness.

TABLES

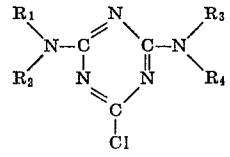
	Suds inhibitor	Percent	Sudsing scores at — 30° C.	40° C.	50° C.	60° C.	80° C.	90° C.	95° C.
1	Chlorotriazine deriv. (R_2R_4=first runnings)	0.5	4	4	3	0	4	4	4
2	Chlorotriazine deriv. (R_2R_4=coconut)	0.5	4	4	3	1	4	5	4
3	Chlorotriazine deriv.	0.5	3	4	1	0	4	5	4
4	(a) Chlorotriazine deriv. (b) Melamine deriv. ($R_2R_4R_6$=coconut)	0.23 0.07	4	4	3	1	4	4	4
5	(a) Chlorotriazine deriv. (b) Melamine deriv. ($R_2R_4R_6$=coconut)	0.18 0.12	4	4	2	1	3	3	4
6	(a) Chlorotriazine deriv. (b) Melamine deriv. ($R_2R_4R_6$=coconut)	0.13 0.17	4	4	1	1	0	0	1
7	(a) Chlorotriazine deriv. (b) Melamine deriv. ($R_2R_4R_6$=coconut)	0.08 0.22	4	4	3	0	0	0	2
8	(a) Chlorotriazine deriv. (b) Melamine deriv. ($R_2R_4R_6$=coconut)	0.01 0.29	4	4	4	2	5	5	5
9	Chlorotriazine deriv. Melamine deriv. ($R_2R_4R_6$=tallow)	0.08 0.22	4	4	4	0	1	0	0
10	Chlorotriazine deriv. Melamine deriv. ($R_2R_4R_6$=coconut)	0.13 0.17	4	3	0	1	0	0	1
11	Chlorotriazine deriv. Melamine deriv. ($R_2R_4R_6$=first runnings)	0.14 0.16	4	4	0	0	0	0	0

The suds inhibitors which were employed in the following Examples 12 to 20 were chlorotriazine and melamine derivatives in which the moieties R_1, R_3 and R_5 each represents hydrogen and R_2, R_4 and R_6 each designates coconut alkyl. The sulfobetaine was prepared by reacting N-dimethyl-N-alkylamine with propane sultone. The sudsing was tested under the same conditions used in the foregoing examples. The results are set out in the following table.

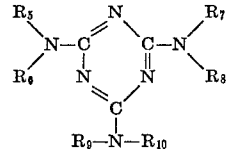
	Examples								
	12	13	14	15	16	17	18	19	20
Components (amounts in percent per weight):									
Chlorotriazine derivative	0.2	0.2	0.2	0.3	0.3	0.3	0.2	0.2	0.4
Melamine derivative	0.3	0.3	0.3	0.4	0.4	0.4	0.3	0.3	0.6
n-Dodecylbenzol sulfonate (Na salt)				5	5			3	
C_{14}-C_{18}-olefine sulfonate (Na salt)	10				5	5	5	3	
C_{13}-C_{17}-paraffine sulfonate (Na salt)		10							5
Coconut fatty alcohol sulfate (Na salt)			10					1	
C_{12}-C_{18}-alkyl sulfobetaine				5		5			5
Coconut soap (Na salt)					5		5		
Ethoxylated coconut fatty alcohol (10 glycol ether groups)						5			5
Nonylphenolpolyglycolether (10 glycol ether groups)							5	3	
Aminotriazetate (Na salt)	10	10	10	20			25		10
Ethylendiaminotriazetate (Na salt)					20	5	5		
Sodium cellulose glycolate	2	2	2	2			3	3	
Pentasodium triphosphate	40	40	40	30	10		15	50	10
Sodium silicate	5	5	5	5	10		5	4	
Sodium perborate	20	20	20	20	25		25	20	
Sodium sulfate	12.5	12.5	12.5	12.3	12	78.3		5	
Water					7.3		6.5	7.5	64
Suds level:									
Maximum	3	3	3	2	3	3	1	2	3
Minimum	0	0	0	0	0	0	0	0	0

We claim:

1. Low sudsing detergent, consisting essentially of at least one compound selected from the group consisting of anionic, ampholytic, cationic and non-ionic detergents and of 0.1 to 20 wt. percent, calculated on the weight of the detergents, of a suds inhibitor mixture consisting essentially of a water-insoluble triazine derivative of the formula



and a water-insoluble melamine derivative of the formula



wherein R_1, R_3, R_5, R_7 and R_9 represent hydrogen or hydrocarbon radicals with 1 to 24 carbon atoms, R_2 and R_4 represent hydrocarbon radicals with 2 to 24 carbon atoms and R_6, R_8 and R_{10} represent hydrocarbon radicals with 4 to 24 carbon atoms and wherein the weight ratio of triazine derivative to melamine derivative ranges from about 10:1 to 1:10.

2. Low sudsing detergents according to claim 1, wherein R_1, R_3, R_5, R_7 and R_9 represent hydrogen and R_2, R_4, R_6, R_8 and R_{10} represent a straight-chain, saturated or unsaturated hydrocarbon radical with 6 to 18 carbon atoms.

3. A detergent composition according to claim 1 wherein said mixture contains said triazine and melamine derivative in a ratio of 2:1 to 1:4.

4. A detergent composition in solid pulverulent form consisting essentially of 5–60% of at least one member selected from the group consisting of anionic, ampholytic, and non-ionic detergents;

0.1–3% of the suds-inhibitor mixture of claim 1

0–90% of an inorganic salt selected from the group consisting of pyrophosphates, polyphosphates, silicates, carbonates, bicarbonates and borates of alkalies

0–25% of a perborate

0.1–5% of carboxymethylcellulose as dispersing agent.

5. A detergent composition in liquid form consisting essentially of

5–50% of at least one member selected from the group consisting of anionic, ampholytic, and non-ionic detergents

0.1–3% of the suds-inhibitor mixture of claim 1

0–35% of an anhydrous phosphate

0–10% of a lower alkyl benzene sulfonate as solubilizer

0–1% of a member selected from the group consisting of dyes, perfumes, and optical brighteners.

6. A detergent composition comprising:

	Percent
n-Dodecylbenzenesulfonate (Na salt)	9.0
Ethoxylated oleyl alcohol (10 glycol ether groups)	2.5
Soda soap (50% tallow, 50% coconut oil)	2.0
Pentasodium triphosphate	40.0
Water glass	4.0
Magnesium silicate	2.5
Sodium perborate	20.0
Sodium cellulose glycolate	1.0
Sodium sulfate	10.0
Suds inhibitor mixture according to claim 1	0.3–0.5
Optical brighteners and perfumes	0.4

Balance water.

References Cited

UNITED STATES PATENTS

2,956,898	10/1960	Fleck	260—249.8X
3,422,020	1/1969	Schmadel et al.	252—152X
3,429,881	2/1969	Knüsli et al.	260—249.8
3,436,394	4/1969	Saul	260—249.8

OTHER REFERENCES

Schwartz and Perry: vol. 1, 1949, Surface Active Agents, p. 380.

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252—152