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[54] FOAM-CLEANING ADDITIVES, COMPOSITION AND METHODS

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[63] Continuation-in-part of Ser. No. 540,212, Apr. 5, 1966, abandoned.

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[58] **Field of Search**.....252/99, 117, 118, 137, 138, 252/142, 156, 152, 161, 98

[56] **References Cited**

UNITED STATES PATENTS

3,274,117	9/1966	Stein et al.	252/161
3,247,121	4/1966	Hendricks	252/117
3,110,677	11/1963	Karabinos et al.	252/99
3,037,887	6/1962	Brenner et al.	134/22

FOREIGN PATENTS OR APPLICATIONS

921,036	3/1963	Great Britain	252/152

OTHER PUBLICATIONS

" Alkanolamides in ' Soft' Detergents" by E. A. Knaggs, Reprint from Soap & Chemical Specialties, Dec., 1964 & Jan. 1965, 8 pages

McCutcheon' s Detergents and Emulsifiers, 1963 Annual, p. 140

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[57] **ABSTRACT**

The invention disclosed is for a new improved foamable industrial cleaning composition having either a highly acid or highly basic character and containing an effective foam generating and stabilizing assistant.

5 Claims, No Drawings

FOAM-CLEANING ADDITIVES, COMPOSITION AND METHODS

The application for U.S. Letters Patent is a continuation-in-part of copending application Ser. No. 540,212, filed Apr. 5, 1966, now abandoned.

The present invention relates to a new improved foamable industrial cleaning composition having either a highly acid or highly basic character and containing an effective foam generating and stabilizing assistant. The invention also provides a method for assisting generation of foam in highly acid and highly alkaline industrial cleaning solutions.

Foam cleaning is well known and may be effected by pumping a foamable cleaning solution through a mechanical system wherein air is mixed with the cleaning solution to produce a foam. The foam, when applied to a surface to be cleaned, clings thereto and thus increases the contact time of liquid-cleaning agents with the soiled surface. Rapid drying and runoff of the liquid cleaner are prevented by surface clinging, thereby dramatically improving the cleaning effectiveness. To be effective, foam cleaning should possess the following advantages:

I. Reduce the amount of solution required for cleaning;

II. Prevent splashing such as that experienced in spray cleaning;

III. Make possible application of a cleaning solution in difficult to reach areas such as into duct work, piping, underside and otherwise difficult to reach parts of machinery and equipment where spray cleaning is impractical;

IV. Prevent irritating vapors of liquid solutions from distilling into the air; and

V. Dramatically reduce the cost of labor, time and materials.

Spray cleaning of open surfaces such as exteriors of trucks, tractor trailers, aircraft, and the interiors of factories, storage tanks and other open areas is widely used because less labor is required to apply the cleaning liquids to the open surfaces. In general, relatively mild cleaning compositions are used in these spray cleaning operations. Many of the most active cleaning compositions, however, contain strong chemicals such as strong acids or bases, volatile irritants, or other chemicals which cannot be used in spray cleaning open surfaces because they are hazardous to operating personnel. These strong noxious chemicals, through distillation, mist, or overspray offer potential danger to the eyes, nose, and skin of the operating personnel.

Foam cleaning is effected by pumping high-foam cleaning solutions through a mechanical system in which gases such as air are mixed with a liquid cleaning solution to produce a foam. Desirably, a stable, copious foam is produced which foam "dry" clings to surfaces to be cleaned; increases the contact time of liquid cleaning agents with the surfaces; prevents rapid drying and runoff of the liquid cleaner; and avoids splashing, overspray, misting, and distillation of irritating vapors of the liquid solutions into the air.

Foam cleaning compositions containing strong acids to eliminate scale from wall surfaces have been disclosed previously such as by Brenner et al. in U.S. Pat. No. 3,037,887. In the process of Brenner et al. the vessel to be treated is filled with foam containing a strong acid and other chemicals, and additional foam is passed through the closed vessel until the vessel walls have been descaled. In the closed vessel, no hazards to operating personnel are present, and the foam is employed to decrease the volume of cleaning solution required since it is necessary to entirely fill the closed vessel with the cleaning solution to effect descaling. In practice, the stability of a foam cleaning composition such as that of Brenner et al. is questionable since it is necessary to continue to deliver and disperse incoming foam at a rate in excess of the foam collapse rate.

Practically all foamable cleaning compositions which are potentially capable of producing a stable foam may contain a slightly alkaline additive based on an amine, sodium or potassium neutralized alkyl-benzene sulfonates, with or without high-foaming nonionic surface active agents, organic foam stabilizers and related materials.

The foam produced is often not stable or dry enough to be effective in foam cleaning. Low or high concentrations of acidic materials such as phosphoric acid, citric acid, sulfamic acid, sodium bisulfate, or acid phosphate salts, when formulated with tridecyl or dodecyl benzene sulfonic acid, may foam through foam-generating equipment but the foam typically is neither stable nor sufficiently copious to be effective in foam cleaning.

High concentrations of highly alkaline salts, especially caustic soda, have not been previously formulated with neutralized alkyl benzene sulfonic acids. The solubility of these foam producing chemicals is quite low in highly alkaline solutions, they readily fall out of solution, and are not effective when passed through foam-generating equipment. Thus, highly alkaline solutions heretofore have not been used as effective foam cleaning materials. Most standard foam stabilizers are not high alkaline and high-caustic stable; or have been found to be insufficiently stable to retain a stabilizing function in foaming such cleaning solutions.

It has now been found that by practice of the present invention, there is provided a particular combination of ingredients which compose a foamable industrial cleaning composition having the especially unique capability of inducing generation of copious, stable foams while containing either a highly alkaline or highly acid additive. The present industrial cleaning composition contains a small but effective amount of a particular foaming assistant which is useful in generating a copious and stable cleaning foam. The foaming assistant is effective for assisting in the generation of a copious stable foam while in the presence of either a highly alkaline or highly acid additive in an industrial cleaning composition.

The present invention is based upon the discovery of a particular blend of ingredients eminently suitable for use as a foaming assistant for industrial cleaning compositions containing either a highly alkaline or highly acid additive. Accordingly, in one embodiment hereof, the foam assistant consists essentially of a (A) a C_8 to C_{20} alkyl substituted aryl sulfonic acid or an alkali metal salt thereof; (B) from about 0.15 to about 1.0 part by weight, per part by weight of the said sulfonic acid or sulfonate salt, of an ethoxylated fatty acid alkanolamide of the formula:

$$R_2-\overset{O}{\overset{\|}{C}}-\overset{N}{\overset{|}{N}}-R_3O-(C_2H_4O)_n-H$$

wherein R_2 represents the residue of a higher fatty acid containing an average of from about eight to about 18 carbon atoms, R_3 represents an alkylene group containing from two to about five carbon atoms, n represents a positive number having an average value of from about 2 to about 10, and X is either hydrogen or the radical $-R_3O(C_2H_4O)_n-H$; and (C) from about 0.15 to about 1.0 part by weight, per part by weight of the aforesaid alkaryl sulfonic acid or salt, of an alkali metal salt of a sulfonated higher fatty acid containing from about 12 to about 20 carbon atoms. Typically the foaming assistant additive also contains sufficient water to at least form a solution of the aforesaid ingredients (A), (B), and (C). This combination of materials forming the present foam assistant is found to be highly effective in foam generation and foam stability when added to an industrial cleaning composition having a highly alkaline or highly acid character.

Another aspect of the present invention is a foamable industrial cleaning composition containing a small but effective amount of the aforesaid foam assistant composition, which amounts usually range from about 0.01 to about 0.20 parts by weight per part by weight of the primary active cleaning materials usually highly acidic or basic, in the industrial cleaning solution.

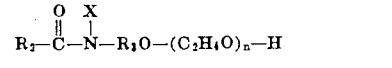
In another embodiment, the present invention provides a method for assisting the generation of copious and stable foams using industrial cleaning compositions containing highly alkaline or highly acid materials.

The present foam assistant contains as an essential ingredient an alkarylsulfonic acid or sulfonate the primary purpose of which is to induce foam in the industrial cleaning solution to which the foam assistant is added. These sulfonic acids or salts are most readily represented by the general formula:

$$R_1—Ar—SO_3.Y$$

wherein R_1 represents a higher alkyl group containing from about eight to about 20 carbon atoms; Ar represents an aryl group, and Y represents hydrogen or an alkali metal cation. Preferably R_1 contains from about 12 to about 16 carbon atoms and thus represents, for example, a dodecyl, tridecyl, or hexadecyl group or the like. The aryl nucleus represented by Ar can be benzyl, phenyl, napthyl, or other like aryl radical. Most preferably Ar is a benzyl radical. While sulfonic acids of the above general formula (when Y is hydrogen) are suitable, it is generally preferred to use alkali metal sulfonates wherein Y is sodium, potassium or the like. Other sulfonate salts; that is, the amine salts such as those wherein Y in the above formula represents, for example, diethyl amino ($Et_2N—$) or the like; and the ammonium salts; are suitable for use with substantially more neutral solutions of industrial cleaning compositions. It has been found that the foaming assistants of this invention must utilize either the sulfonic acid or the alkali metal sulfonate. The preferred alkarylsulfonate is the sodium salt of either dodecyl benzene sulfonic acid or tridecyl benzene sulfonic acid, which when used in the foaming assistant produced the greatest volume of stable copious foam per unit of weight when added to either a highly acidic or highly basic industrial cleaning composition.

A second essential ingredient of the present foaming assistant is an ethoxylated fatty acid alkanolamide which serves primarily as a foam stabilizer. This particular foam stabilizer, in contrast to more standard types of foam stabilizers, serves to stabilize foams produced using solutions including those which are either highly alkaline or highly acid. This ingredient is most conveniently represented by the general formula:



wherein R_2, R_3, n and X are as previously described. Most preferably R_2 is the residue of a higher fatty acid containing on the average from about 12 to about 18 carbon atoms, (for example, the residue of mixed fatty acids derived from coconut oil); X is hydrogen; R_3 is lower alkylene such as ethylene or propylene and n is a number having an average value of from about 4 to about 10 most preferably about 5. Typical examples of such materials include the commercially available ethoxylated coconut fatty acid monoethanolamides containing 2, 5 or 10 moles, on the average, of condensed ethylene oxide, for example those containing an average of about 5 ethoxy groups $—(C_2H_4O)—$.

The alkarylsulfonic acids or alkali metal salts thereof used in the preferred compositions of this invention are characterized by low solubility in concentrated highly alkaline or highly acid solution. The foaming assistants of the invention therefore include sufficient amounts of an alkali metal salt of sulfonated higher fatty acid to solubilize the alkarylsulfonate in either highly alkaline or highly acid solutions. The sulfonated higher fatty acid may contain from about 12 to about 20 carbon atoms on the average. The alkali metal salt of the chose sulfonated acid may be the sodium, potassium, lithium or other like salt. The presently preferred solubilizer is the sodium salt of sulfonated oleic acid. The amount normally ranges between 0.15 and about 1.0 parts by weight for each part by weight of the alkaryl sulfonic acid or alkali metal salt thereof.

Excellent foaming of highly alkaline cleaning compositions is achieved by including per part by weight of active strongly alkaline cleaning ingredient, from about 0.004 to about 0.04 parts by weight, of (A) an alkali metal salt of a sulfonated higher fatty acid, in combination with about 0.004 to about 0.04 part by weight of (B) an alkyl aryl sulfonate and about 0.002 to about 0.02 part by weight of (C) an ethoxylated higher fatty acid alkanol amide. Excellent foaming of highly acidic cleaning compositions is similarly achieved by including, per part by weight of active strongly acidic cleaning ingredient, about 0.06 to about 0.08 parts by weight of (A) an alkali metal salt of a sulfonated higher fatty acid, in combination with about 0.06 to about 0.08 parts by weight of (B) an alkyl aryl sulfonate and about 0.03 to about 0.04 parts by weight of (C) an ethoxylated higher fatty acid alkanolamide. The excellent foaming ability is believed to be due to a synergistic effect resulting in part, from the increased solubility of the alkyl aryl sulfonate in highly alkaline, or solutions imparted by the alkali metal salt of a sulfonated high fatty acid.

In those cases where the foaming assistant is to be sold as the separate item of commerce, it is usually preferred that the composition contain water in amounts at least sufficient to form a solution of the three essential ingredients. The amount of the water required will vary with varying proportions of the three ingredients and the water solubility thereof. Large amounts of water may be used if desired but are usually avoided for economic packaging or related reasons. It will be understood that the foaming assistant may be added as a preblended mixture or solution, or that the composition may be formed in situ, by adding to an industrial cleaning composition amounts of the individual ingredients which will produce effective results.

A complete dry mix formulation may be prepared, including the industrial cleaning ingredients and the foaming assistant of this invention. The complete formulation may be dissolved in water at a use location to a concentration of about 0.05 to about 1.5 pounds per 8.33 pounds of water (1 gallon at standard conditions), and stable copious foams produced therefrom.

A foaming assistant of this invention has the following composition:

Ingredient	Parts by Weight
Sodium salt of dodecyl or tridecyl benzene sulfonic acid	1.0
Sodium salt of sulfonated oleic acid	0.15 to 1.0
Ethoxylated coconut fatty acid monoethanolamide (containing average of 5 moles ethylene oxide per mole of amide)	0.15 to 1.0

An embodiment foaming assistant of this invention is a concentrated aqueous solution of the above materials further containing about 30 to about 32 weight percent sodium salt of dodecyl benzene sulfonic acid; about 30 to about 32 weight percent sodium salt of sulfonated oleic acid; about 15 weight percent ethoxylated coconut fatty acid monoethanolamide having an average of 5 ethoxy groups $—(C_2H_4O)—$ per mole; and about 18 to about 22 weight percent water. This concentrated solution has a pH of about 12.0. It is eminently suitable as an assistant for producing stable, copious foams from an industrial cleaning solution containing, for example, caustic soda in concentrations of up to 10 or 15 percent by weight.

By way of reference, it will be understood that a highly acidic industrial cleaning solution is one having a pH up to about pH_4 whereas a highly basic industrial cleaning solution is one having a pH from about pH_9 to about pH_{14}.

The present foaming assistant is typically used in amounts ranging from about 0.01 to about 0.20 parts by weight of assistant per part by weight of the primary active cleaning material either acidic or basic in the industrial cleaning solution. Higher relative proportions of foaming assistant provide dryer foams when all other foaming conditions are substantially unchanged. For example, good, relatively dry, stable, copious foams are produced by adding to alkaline-type industrial cleaning solutions about 0.01 to about 0.10 part; and preferably about 0.025 to about 0.040 part by weight foaming assistant per part by weight of active alkaline cleaning materi-

al. Higher relative concentrations of foaming assistant are used with acidic industrial cleaning solutions, e.g., those based upon sulfamic acid as the primary active cleaning material. In the latter instance about 0.15 to about 0.20 part by weight foaming assistant per part by weight of acidic cleaning material are used to produce relatively dry, stable, copious foam.

The following formulation is presented as an example of a dry composition capable of producing stable, copious, foam when put into solution at a concentration of about 0.05 to about 1 part by weight per 8.33 parts by weight of water (i.e., 1 gallon of water at standard conditions). All parts are parts by weight unless otherwise indicated.

Ingredient	Parts Range	Parts Preferred
Inorganic alkaline cleaning compounds*	78.5 to 88.5	83.5
Sodium dodecyl benzene sulfonate	4 to 8	6.0
Sodium salt of sulfonated oleic acid (43.5% active basis)	3.5 to 7.5	5.5
Ethoxylated coconut fatty acid monoethanolamide (average of 5 ethoxy groups)	0.8 to 4.8	3.0
Calcium silicate	1.0 to 3.0	2.0
Total	100	100

*The inorganic alkaline salts may be entirely caustic soda, or blends of caustic soda with soda ash, complex phosphates (tetrasodium pyrophosphate, sodium tripolyphosphate, trisodium phosphate or sodium hexametaphosphate) and/or sodium metasilicate; with or without appropriate sources of chlorine, such as chlorinated trisodium phosphate or alkali metal chloroisocyanurates.)

The calcium silicate serves as a moisture absorbent and anticaking agent.

Practice of the present invention is illustrated by the following nonlimiting specific examples. In each example, the foam assistant appears as a concentrated aqueous solution containing, in parts by weight, about 21 parts water, about 31 parts of the sodium salt of dodecyl benzene sulfonic acid, about 33 parts of the sodium salt of sulfonated oleic acid, and about 15 parts of an ethylene oxide condensate of coconut fatty acid monoethanolamide containing an average of about 5 ethoxy groups —(C_2H_4O)— per mole. Each of the three individual essential ingredients forming foam assistant is commercially available. The foaming assistant was added, in varying proportions, to a variety of typical industrial cleaning solutions and foams were produced using a pneumatic foaming device. In all of the examples, summarized in the following table I, a copious, stable, relatively dry foam was produced.

TABLE I

	Industrial cleaner	Concentration [a]	Amount [b]
Example:			
1	A [1]	1.0	2.0
2	A	0.5	1.0
3	A	0.375	0.75
4	A	0.25	0.5
5	A	0.125	0.25
6	B [2]	1.0	2.0
7	B	0.5	1.0
8	C [3]	0.5	0.5
9	C	0.375	0.375
10	C	0.25	0.25
11	C	0.125	0.25
12	D [4]	0.5	5.0
13	D	0.25	2.5
14	D	0.125	1.25

[a] (Pounds per gallon) of cleanner in solution to be foamed.
[b] Gallons of concentrated (about 80 weight percent) solution of Foaming Assistant added to 50 gallon drum of solution to be foamed.

Industrial cleaner A is a commercially available material containing as primary cleaning ingredients, by weight, about 70 parts caustic soda, 14 parts sodium metasilicate, 5 parts sodium tripolyphosphate, 5 parts tetra sodium pyrophosphate and 4 parts soda ash.

Industrial cleaner B is a commercially available material containing as primary cleaning ingredients, by weight, about 70 parts caustic soda and about 28 parts soda ash.

Industrial cleaner C is a commercially available material containing as primary cleaning ingredients, by weight, about 60 parts chlorinated trisodium phosphate, 23 parts soda ash, and 17 parts sodium tripolyphosphate.

Industrial cleaner D is a commercially available material containing as the primary cleaning ingredient about 90 percent by weight sulfamic acid.

EXAMPLES 15–16

In a like manner, dry, stable copious foams were prepared from industrial cleaning solutions containing about 7 percent by weight and about 3.5 percent by weight phosphoric acid by adding to 50 gallon drums of these solutions 1.0 gallon and 0.5 gallon, respectively, of the same concentrated (about 80 weight percent) solution of foaming assistant used in examples 1–14.

Similar results have been accomplished with industrial cleaning solutions including alkali metal bisulfates or on citric acid as primary cleaning agents.

Wet foams having good stability may be prepared in the same manner as that described in examples 1–16 by reducing the proportion of foaming assistant to about one-half the amount used for making the dry foams of those examples.

Of particular note with respect to examples 8 through 11 was the observation that the foaming assistant of this invention does not interfere with the chlorine stability of solutions of chlorinated alkaline cleaning materials.

What is claimed is:

1. An industrial cleaning solution which consists essentially of:

I. a foaming assistant composition consisting essentially of:

A. 1.0 part by weight of sodium salt of dodecyl or tridecyl benzene sulfonic acid;

B. 0.15 to 1.0 part by weight of sodium salt of sulfonated oleic acid;

C. 0.15 to 1.0 part by weight of ethoxylated coconut fatty acid monoethanolamide having an average of about 5 ethoxy —(C_2H_4O) — groups per mole; and

II. a solution of 0.05 to about 1.5 parts by weight per 8.33 parts water of a primary active cleaning ingredient selected from the group consisting of:

A. alkaline cleaners selected from the group consisting of alkali metal hydroxide, chlorinated trisodium phosphate, alkali metal phosphates, alkali metal silicates, alkali metal carbonates and mixtures thereof; and

B. acid cleaners selected from the group consisting of alkali metal bisulfates, citric acid, phosphoric acid, sulfamic acid and mixtures thereof;

wherein said primary active cleaning solution includes from about 0.01 to about 0.20 part by weight of said foaming assistant composition per part by weight primary active cleaning ingredient, and wherein at least about 0.5 part by weight of chlorinated trisodium phosphate per part by weight of said primary active cleaning ingredient is included.

2. The solution of claim 1 wherein the foaming assistant composition is present in an amount from about 0.01 to about 0.10 part by weight of foaming assistant composition per part by weight of primary active cleaning ingredient.

3. The solution of claim 2 wherein the foaming assistant composition is present in an amount from about 0.025 to about 0.040 part by weight of foaming assistant composition per part by weight of primary active cleaning ingredient.

4. The solution of claim 1 wherein the primary active cleaning ingredient is at least about 0.6 part by weight of sodium hydroxide.

5. The solution of claim 1 wherein the primary active cleaning ingredient is at least about 0.85 part by weight of sulfamic acid and the primary active cleaning solution includes from about 0.15 to about 0.20 part by weight of foaming assistant composition.

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