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PROCESS OF CLEANING METAL SURFACES

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1 Claim. (Cl. 252—137)

This application is a continuation-in-part of our application Serial No. 777,186, which was filed on December 1, 1958, and was issued as U.S. Patent No. 3,079,416 on February 26, 1963.

This invention relates to improvements in the art of cleaning objects, particularly those made of metal, glass, etc.

Broadly stated, the invention pertains to alkaline cleaning and, more particularly, to surfactants for use in alkaline metal cleaning baths.

An object of the invention is to improve the cleaning efficiency of alkaline metal cleaners.

Other objects of the invention will in part be obvious and will in part be disclosed hereinafter.

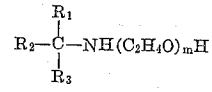
Alkaline cleaners are the most widely used means in industry for cleaning metal, glass, certain plastics, etc. They are primarily used to prepare metals such as steel, brass, and copper for plating, painting, enameling, rust proofing, pickling, and other operations. Such preparation includes the removal of various types of soil such as cutting oils, grinding, buffing, stamping, and drawing compounds used in various metal-forming operations, as well as rust preventatives, lubricating greases, and various forms of dirt. The alkaline cleaning solutions may be used for soaking, spraying, or electrolytic types of cleaning. Of these, the soaking or tank cleaning technique is most important because of its widespread use in industry.

In the soaking method of cleaning, the article to be cleaned usually is dipped in or slowly transported through a hot alkaline solution with little or no agitation present. The cleaning solutions employed generally are made of materials consisting of between about 88 to 99 percent by weight of various alkalies, such as caustic soda, sodium metasilicate, soda ash, trisodium phosphate, and tetrasodium pyrophosphate, and from about 1 to 12 percent by weight of a surfactant. Previously, the most widely used surfactants for this purpose have been alkylaryl sulfonates and rosin soaps. Usually, the concentration of the cleaning materials (alkali plus surfactant) in the tank or both is maintained between 2 and 10 percent of the cleaning solution.

As oil, grease, and other soils are caused to be separated from the part being cleaned in the tank, a scum-like layer collects at the top of the bath. If the surfactant employed is not thoroughly soluble in the hot alkaline solution, it also will tend to accumulate in this surface layer. When the accumulation of scum in the surface layer becomes so great that it tends to coat the otherwise clean part as it is withdrawn from the bath, it becomes necessary to skim the soil and undissolved surfactant from the top of the tank. Each time this is done, a considerable amount of the surfactant is removed and, of course, this tends to lower the concentration of the effective cleaning agents in the bath to a point where the operation of the bath becomes unsatisfactory much sooner than it otherwise would if such losses could be minimized

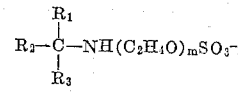
or eliminated. One obvious solution to this problem is to employ only surfactants that are soluble in hot alkaline solutions.

There are available polyoxyalkylated tert.-carbinamines which are known to have a detergent effect on metal surfaces and would appear to have other requisite characteristics for alkaline cleaning purposes. These compositions, which have been disclosed in copending U.S. application Serial No. 632,648, now U.S. Patent 2,871,266, have a structure which may be generally represented by the following formula:



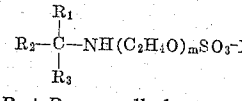
in which R_1, R_2, and R_3 are alkyl groups whose total carbon atom content ranges from 7 to 23, and m is an integer of 6 to 101.

The difficulty with compounds of the above-mentioned formulas is that they lack the requisite solubility property in hot alkaline solutions, such as, for example, 5 percent sodium hydroxide. It was thought that this lack of desired solubility could be overcome by completely (or essentially so) sulfating the compounds so as to obtain products having the following formula:



in which the values for R_1, R_2, R_3, and m are the same as indicated above, and X is a monovalent cation such as an alkali metal or hydrogen. However, when a number of these compounds were sulfated, they were found to have a materially decreased cleaning efficiency notwithstanding the fact that the product was quite soluble in hot alkaline solutions. This effect appeared difficult to explain or otherwise account for, and so efforts were made to determine the mechanism of this change in cleaning performance.

In the course of the investigation which ensued, it was discovered that not all of the polyoxyalkylated tert.-carbinamines would function efficiently as metal cleaners after they had been sulfated. Specifically, the sulfated amines which proved to be useful were those having the following formula:



in which $R_1+R_2+R_3$ are alkyl groups whose total carbon atom content ranges from 11 to 14, m is an integer of from 6 to 101, and X is a monovalent cation such as an alkali metal or hydrogen.

A further discovery was that, of these sulfated amines which had been demonstrated to possess utility as metal cleaners, only those having a certain narrow range of ethylene oxide units, namely, between 12.5 and 17.5, gave metal cleaning results which are substantially as good as the results obtained with the non-sulfated compositions. At the same time, these compounds containing the indicated narrow range of ethylene oxide units also had the added advantage of complete solubility in the hot alkaline solution and thereby eliminated the objection described above, namely, the excessive losses caused when

the surface of the cleaning baths had to be skimmed to remove the scum-like layer.

In actual practice, the preferred composition is an alkali metal salt, generally the sodium salt, of the tert.-carbinamine - ethyleneoxide-$_{12.5-17.5}$ sulfate. Such compounds are completely soluble in 5 percent sodium hydroxide at temperatures of 0°–100° C. They are also soluble in concentrations such as 10 percent caustic, although not throughout this entire temperature range.

Of course, it should be understood that the sulfated amines defined above need not be present in the pure secondary amine form as indicated. For example, it is quite possible that mixtures of such secondary amines and even some tertiary amines will be present, possibly as a by-product of the method of preparing the secondary amines. The presence of the tertiary amines will in no way interfere with the effectiveness of the single or mixed secondary amines as alkaline cleaning agents when the cleaner is prepared and used as disclosed herein.

The following examples describe in detail the alkaline metal cleaning test method which was employed to establish the principal utility of the present invention. Following Example 1, Table I lists a series of sulfated tert.-carbinamine-ethylene oxide compounds and indicates the cleaning efficiency of each of those compounds as tested by the method described below. In this series, the ethylene oxide content was stepped up several units at a time from a value of 5.0 to 30.0 so as to demonstrate the effect previously mentioned whereby a certain narrow range of the sulfated product performs excellently in metal cleaning baths, whereas products above and below that range perform unsatisfactorily.

EXAMPLE 1

The following test method was used for evaluating the comparative efficiencies of various alkaline metal cleaners. The method was adapted from a procedure used throughout the industry and which is described by S. Spring, H. Forman, and L. Peale in "Method of Evaluating Metal Cleaners," Ind. and Eng. Chem., Analytical Edition, vol. 18, No. 3, pp. 201–204 (1946). Briefly, the test consists of carefully cleaning thin SAE 1010 steel panels (3" x 3") and uniformly coating them with a thin film of "brightstock" mineral oil (Saybolt viscosity 150 sec. at 210° F.) which is drained for one hour at 35° C. The coated panel is then rotated for 5 minutes at 30 r.p.m. in a 1000-ml. beaker of the solution being tested. That solution, which is maintained at a temperature of 82°±2° C. in an oil bath, consists of 5 percent of the detergent being tested. The detergent consists of 3 percent active surfactant, 31 percent sodium hydroxide, 31 percent sodium carbonate, and 35 percent sodium metasilicate pentahydrate. (The actual concentration of the surfactant in the cleaning bath was 0.15 percent.)

Following this period of alkaline cleansing, the panel is rinsed in an overflowing beaker of warm water which is approximately 40° C., allowed to drain in air for 20 seconds, and then subjected to a light spray of deionized water for approximately 10 seconds on each side. Any area on the panel which is still coated with residual oil will exhibit readily visible droplets which are termed "water breaks." On clean areas, a continuous water film will be observed. By means of a transparent plastic sheet which is the size of the test panel, and which has been ruled off into 100 squares of uniform dimensions, it is possible to determine the percentage of surface area which does not show any water breaks. This value represents an index of the cleaning efficiency of the alkaline cleaner which has been used. Three such panels are run, readings taken for each side of each panel, and the average of the six sides is considered to represent the cleaning efficiency index for the particular cleaner composition being tested. For the particular oil and the concentration of surfactant used, etc., the limit of acceptability has arbitrarily been set at 80 percent or above, these being values that have been found to represent levels of cleaning efficiency which are acceptable in a representative number of typical industrial applications.

Employing tests such as described above for each of the cleaning compositions, which differed from one another only by the nature of amine surfactant which was included, results obtained were as indicated in Table I which follows:

Table I

t-Alkyl Amine $(EO)_xSO_4$ Surfactant [1]	Cleaning Efficiency (Percent)
5	75
10.0	77
12.5	92
15	93
17.5	83
20	35
30	55

[1] NOTE.—The surfactants employed were sulfated, polyethoxylated t-alkyl amines, the amines being a commercially available mixture in the ranges t-$C_{12-15}H_{25-31}NH_2$. The surfactants were all in the sodium form. The formula for the sulfated amines may be represented as t-$C_{12-15}H_{25-31}NH(C_2H_4O)_mSO_3Na$ in which m=the number of units per unit of amine shown in the first column above.

EXAMPLE 2

Following the procedure of Example 1, a comparable cleaning composition is obtainable by employing

t-$C_{12}H_{25}NH_2$

instead of the mixture of amines. This amine also is sulfated and the ethylene oxide content of the polyethoxylated product is between 12.5 and 17.5 units per unit of amine.

EXAMPLE 3

Following the procedure of Example 1, a comparable cleaning composition is obtainable by employing

t-$C_{15}H_{31}NH_2$

instead of the mixture of amines. This amine also is sulfated and the ethylene oxide content of the polyethoxylated product is between 12.5 and 17.5 units per unit of amine.

EXAMPLE 4

The procedure of Example 1 is repeated except that, instead of the "brightstock" mineral oil, there is used SAE 40 motor oil. A cleaning result close to that set forth in Example 1 is obtained; i.e., the same relative performance is obtained with respect to the various contents of ethylene oxide in the different surfactants.

EXAMPLE 5

The procedure of Example 1 is repeated except that, instead of employing panels of SAE 1010 steel, copper panels are employed. A cleaning result close to that set forth in Example 1 is obtained.

EXAMPLE 6

The procedure of Example 1 is repeated except that, instead of employing panels of SAE 1010 steel, stainless steel panels are employed. A cleaning result close to that set forth in Example 1 is obtained.

It is readily apparent from the foregoing examples, and particularly the data in Table I, that the amine surfactants having from 12.5 to 17.5 units of ethylene oxide are above the level of acceptability (minimum of 80 percent) indicated previously with regard to their comparative cleaning efficiencies. The compounds having less or more than those amounts are, by the same token, not acceptable. A further indication of the comparative effectiveness of the present invention may be had from the fact that a commerically available alkylaryl sulfonate, which heretofore had been considered to be among the finest surfactants known for alkaline metal cleaning applications, only rated a 31 percent cleaning efficiency index under identical test conditions.

The various amines described above can be prepared by procedures similar to that disclosed in copending U.S. application Serial No. 632,648 and may be sulfated by any of several well-known methods, using sulfuric acid, sulfur trioxide, chlorosulfonic acid, or other suitable sulfating agents. In EXAMPLES 7 and 8 are described preparations for two amines by a suitable process (the latter being the polyoxyethylene adduct of the amine produced in the former example). In Examples 9 and 10 are described typical preparations of a sulfated amine in accordance with the present invention.

EXAMPLE 7

In a suitable reaction vessel there were combined 500 g. (2.54 mols) t-dodecylamine, 45.8 g. (2.54 mols) water, and 160 g. methanol. This mixture was heated to 80° C. and 139 g. (3.05 mols) of ethylene oxide were added at 80°–85° C. over a period of 2 to 8 hours. At the end of this time, the product was isolated by distillation to remove the methanol and water. The yield of product [N-(t-dodecyl)ethanol amine] amounted to 618.2 g. and had a neutral equivalent of 246.8. This was equivalent to N-(t-dodecyl)amine combined with 1.18 mols of ethylene oxide. This neutral equivalent indicated that the product contained a small amount of the diethanol amine.

EXAMPLE 8

In an appropriate reaction vessel, there were combined 402.3 g. N-(t-dodecyl)ethanol amine (from above), having a neutral equivalent of 246.8, with 989.7 g. ethyleneoxide in the presence of 1.6 g. powdered potassium hydroxide at 140°–180° C. When the reaction was complete, the catalyst was neutralized by the addition of a strong acid. The isolated product amounted to 1392.2 g. of a light yellow liquid which tended to solidify on standing at room temperature. This product (t-dodecylamine-ethyleneoxide$_{15}$) had a neutral equivalent of 855.5 which was equivalent to t-dodecylamine combined with 15 mols of ethylene oxide.

EXAMPLE 9

To a 1-liter, three-necked flask containing 17.6 g. (0.2 mol) dioxane and 150 cc. carbontetrachloride, cooled to 0°–10°, was added dropwise, with good agitation, a cooled solution (5° C.) of 17.6 g. (0.22 mol) liquid SO_3 dissolved in 150 cc. carbontetrachloride. When this addition was complete, a second solution, containing 171.1 g. t-dodecylamine-ethyleneoxide$_{15}$ (0.2 mol) dissolved in 300 cc. carbontetrachloride, was added dropwise over a 1-hour period at 0°–20° C. This solution was stirred for an additional 30 minutes at 0°–20° C. after completion of the addition. This reaction mixture was then neutralized by the careful addition of 9.6 g. (0.24 mol) sodium hydroxide dissolved in 400 cc. water. The resulting thick emulsion was allowed to stand in a separatory funnel until separation of the carbontetrachloride was complete. Stripping of the aqueous layer gave 180.2 g. of a light amber viscous oil. (Viscosity =33,400 cps.)

Analysis of the product (t-alkylamino-polyoxyethylene sulfate) gave the following results:

Analysis.—Calculated: N, 1.47; S, 3.36; sulfated ash, 7.52. Found: N, 1.48; S, 3.27; sulfated ash, 5.81.

This product was found to be soluble in boiling 5 percent and 7 percent NaOH.

EXAMPLE 10

In a suitable reaction vessel, there were combined 213.5 g. (0.25 mol) t-alkylaminopolyoxyethylene with 100.0 g. (1.0 mol) 98 percent sulfuric acid, at a temperature of 60°–65° C. over a 2-hour period. At the end of this time, there was mixed with this reaction mixture 81 g. (2.03 mols) NaOH dissolved in 800 cc. of water. After separation of the excess sodium sulfate, the product (239 g. of t-alkylamino-polyoxyethylene sulfate) was isolated as a pale amber, viscous liquid (viscosity, 33,000 cps.).

It will be apparent to anyone skilled in the alkaline cleaner art that certain variations from the compositions and methods set forth above by way of illustration are readily feasible without departing from the scope of the present invention. For example, although the specific examples described a typical alkaline cleaning composition made with sodium hydroxide, other alkalies of high pH may be employed. Nor must the percentages of the alkali and surfactant be limited to the 5 percent and 0.15 percent, respectively, that were employed by way of illustration in the examples. Nor must the surfactants be made by the particular methods herein described. The surfactants which are the subject of the present invention are readily soluble in lower or higher concentrations of alkali and will, within the stipulated ranges of ethylene oxide content, perform with comparable efficiency in the cleaning of metal and other surfaces. Moreover, the amounts of surfactant may be varied with a proportionate effect on cleaning efficiency. Still other modifications are possible, all obviously within the scope of the following claim.

We claim:

A process of cleaning metal surfaces involving the removal of soils therefrom which comprises treating such surfaces with a hot aqueous cleaning solution that consists essentially of water and from about 2 to 10 percent of a mixture of alkali and surface active materials, said mixture consisting of about 88–99 percent by weight of a salt from the class consisting of alkali metal hydroxides, silicates, carbonates, and phosphates, the alkali metal being selected from the class consisting of sodium and potassium, and about 1 to 12 percent by weight of a t-carbinamine polyoxyethylene sulfate, the alkyl groups in said amino compound having a total of about 11 to 14 carbon atoms, and the number of oxyethylene units per amine unit present being in the range of from 12.5 to 17.5.

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