ALKALINE METAL CLEANING COMPOSITIONS
AND PROCESS OF USING SAME

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No Drawing. Filed Apr. 19, 1960, Ser. No. 23,158

5 Claims. (Cl. 252—137)

This application is a continuation-in-part of our ap-
10 plication Serial No. 777,189, which was filed on Decem-
ber 1, 1958, and was issued as U.S. Patent No. 3,079,348
on February 26, 1963.

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

Broadly stated, the invention pertains to alkaline clean-
20 ing and, more particularly, to surfactants for use in alka-
line 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
25 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,
20 brass, and copper for plating, painting, enameling, rust
proofing, pickling, and other operations. Such prepara-
tion 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 preventative, lubricating greases, and
various forms of dirt. The alkaline cleaning solutions
may be used for soaking, spraying, or electrolytic types
30 of cleaning. Of these, the soaking or tank cleaning
35 technique is most important because of its widespread use
in industry.

In the soaking method of cleaning, the metal article
to be cleaned usually is dipped in or slowly transported
30 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 alkyl-
35 ary1 sulfonates and resin soaps. Usually, the concentra-
tion of the cleaning materials (alkali plus surfactant)
in the tank or bath is maintained between 2 and 10 per-
cent of the cleaning solution.

As oil, grease, and other soils are caused to be sepa-
40 rated from the part being cleaned in the tank, a scum-
like layer collects at the top of the bath. If the surfac-
tant employed is not thoroughly soluble in the hot alka-
iline solution, it also will tend to accumulate in this
surface layer. When the accumulation of scum in the
45 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 sur-
factant 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 ef-
fective cleaning agents in the bath to a point where the
operation of the bath becomes unsatisfactory much soon-
er than it otherwise would if such losses could be mini-
imized or eliminated. One obvious solution to this prob-
lem is to employ only surfactants that are soluble in hot
alkaline solutions.

There are available polyoxyalkylated tert. carbina-
50 mines 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. 652,648, now U.S. Patent

2,871,266, have a structure which may be generally re-
presented by the following formula:

\[
\begin{align*}
R_1 & \rightarrow \text{NH}(C_2H_5O)_{3}\cdot SO_4X^- \\
R_2 & \rightarrow \text{CO}_2H \\
R_3 & \rightarrow \text{SO}_3H
\end{align*}
\]

in which the values for \( R_1, R_2, \) and \( R_3 \) and \( m \) are the same as indicated above, and \( x \) is a monovalent cation such as an alkali metal or hydrogen.

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 de-
sired solubility could be overcome by completely (or essen-
tially so) sulfating the compound so as to obtain a
product having the following formula:

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

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in which \( R_1, R_2, \) and \( R_3 \) and \( m \) are alkyl groups whose total carbon atom content ranges from 7 to 23, and \( m \) is an integer of 6 to 101.
those otherwise excellent compositions. When less than 75 percent sulfated, the compositions are not compatible with strong alkali, such as a hot 5 percent sodium hydroxide solution. When more than 85 percent sulfated, the cleaning efficiency of the compositions is considerably diminished. Thus, it is essential, for maximum performance, that the polyoxyalkylated tert-carbinaminoes be sulfated between about 75 to 85 percent.

In actual practice, our preferred composition is an alkali metal salt, generally sodium salt, of the tert-carbinamine ethylene oxide$_{12-15}$-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 cleaning is prepared and used as disclosed herein.

Example 1 describes in detail the alkaline metal cleaning test which was employed to establish the utility of the present invention. Following Example 1, Table 1 lists a series of tert-carbinamine ethylene oxide compounds which have been sulfated in varying amounts from 0 to 100 percent. Also indicated for each of these compounds is the cleaning efficiency index as determined by the method described below. In this series, the ethylene oxide content has been maintained at 15.0 units, this being the amount present in one of the best of the completely sulfated compounds in accordance with the invention disclosed in our above-mentioned copending application. The actual conditions of test were made more severe than the ones which were employed in our other case in order to more sharply delineate the differences in cleaning effectiveness. This was done primarily by using less of the surfactant in the cleaning solution than the concentrations described in the examples in our other application.

**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 No. 1010 steel panels (3" x 3") and uniformly coating them with a thin film of "bright-stock" mineral oil, 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°–82.2° C. in an oil bath, contains 0.07 percent active surfactant and 5 percent of a heavy duty alkaline cleaner consisting of 30 parts caustic soda, 35 parts soda ash and 30 parts sodium metasilicate penta-hydrate.

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 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 commercial product of the surfactant used, etc., the minimum limit of acceptability has arbitrarily been set at 70 percent, this being a level of cleaning efficiency which has been found to represent a minimum of acceptability in a number of typical industrial applications.

Employing tests as such as described above for each of the cleaning compositions, which differed from one another only by the degree of sulfation of the amine surfactant which was included, results obtained were as indicated in Table 1 which follows:

**Table 1**

<table>
<thead>
<tr>
<th>t-Alkyl Amino (EO)$_n$</th>
<th>Cleaning Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Insoluble in 5% NaOH</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>100%</td>
</tr>
<tr>
<td>20</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

1. Norm.—The surfactants employed were sulfated, polyoxyalkylated t-alkylamines, the amines being a commercially available mixture in the ratios t-C$_3$H$_7$-NH$_2$·t-C$_3$H$_7$-NH$_2$·t-C$_3$H$_7$-NH$_2$·t-C$_3$H$_7$-NH$_2$. The surfactants were all in the sodium form and the number of ethylene oxide units was 15. Their formulas, therefore, were t-C$_3$H$_7$-NH$_2$·(OCH$_2$CH$_2$O)$_{15}$H$_2$Na.

Similar data is obtained with compounds which are the same except that, instead of using the mixture of amines, the amine which is polyoxyethylated and sulfated is one in the range of t-C$_3$H$_7$-NH$_2$ to t-C$_3$H$_7$-H$_2$N$_2$H$_2$NH$_2$.

It is readily apparent from the data in the table that the polyoxyalkylated t-carbinamines which, prior to sulfation, have excellent metal cleaning abilities when used in combination with strong alkalis are: (1) not compatible with strong alkali (and therefore unsatisfactory products) when sulfated below 75 percent, because their incompatibility with the alkali causes surface "loading" and resultant excessive losses of the cleaner; (2) satisfactory cleaners (in combination with strong alkali) when sulfated between 75 and 85 percent; and (3) unsatisfactory cleaners (with strong alkali) when sulfated over 85 percent and only a relatively small percentage of the surfactant is employed. A further indication of the comparative effectiveness of the present invention may be had from the fact that a commercially available alkyl aryl sulfonate, which heretofore had been considered to be among the finest surfactants known for alkaline metal cleaning applications, only rated a 13 percent cleaning efficiency index under identical test conditions.

The various amines described above can be prepared by procedures similar to that disclosed in 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 2 and 3 are described preparations of two amines by a suitable process (the latter being the polyoxyethylene adduct of the amine produced in the former example). In Examples 4 and 5 are described typical preparations of a sulfated amine in accordance with the present invention.

**EXAMPLE 2**

In a suitable reaction vessel, there were combined 500 g. (2.54 molcs.) t-dodecylamine, 45.8 g. (2.54 molcs.) water and 160 g. methanol. This mixture was heated to 80° C. and 139 g. (3.05 molcs.) of ethylene oxide was 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 3**

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. ethylene oxide 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-ethyleneoxide₁₂₃₄₅) had a neutral equivalent of 855.5 which was equivalent to t-dodecylamine combined with 15 mols. of ethylene oxide.

**EXAMPLE 4**

In a suitable reaction vessel, there were combined 213.5 g. (0.25 mol.) t-alkylaminopolyoxyethylene (from Example 3 above) with 62.5 g. (0.625 mol.) 98% sulfuric acid, at a temperature of 60°–65°C over a two-hour period. At the end of this time, there was mixed with this reaction mixture 51 g. (1.27 mol.) NaOH dissolved in 600 cc. of water. After separation of the excess sodium sulfate the product (237 g. of t-alkylamino-poloxoyethylene sulfate) was isolated as a pale amber, viscous liquid (viscosity 5,120 cps.). Analysis of this product gave results indicating that the material was 77.0% sulfated. This product was soluble in boiling 5% sodium hydroxide and soluble up to 62° in 7% sodium hydroxide.

**EXAMPLE 5**

This preparation was carried out exactly as in Example 4 using 449.6 g. t-alkylamino-poloxoyethylene (0.5 mols.) 138 g. (1.375 mols.) 97.6% H₂SO₄ and 90 g. (2.25 mols.) NaOH dissolved in 475 g. water. The yield of the product (t-alkylamino-poloxoyethylene sulfate), a pale amber viscous liquid, was 475 g. (viscosity 5,860 cps.). Analysis of this product indicated that it was 85% sulfated.

This product was soluble in boiling 5% NaOH and soluble up to 75° C. in 7% aqueous NaOH.

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, any of the sulfated poloxoyalkylated tert.-carbinamines described in our previously mentioned copending application will certainly be suitable. Further, 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 0.07 percent, respectively, that were employed by way of illustration in the examples. The surfactant which is the subject of the present invention is readily soluble in lower or higher concentrations of alkali and will, within the stipulated ranges of ethylene oxide content and degree of sulfation, 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 claims.

The following claims:

**We claim:**

1. A cleaning composition consisting essentially of about 88–99% by weight of a mixture of a salt from the class consisting of alkali metal hydroxides, silicates, carbonates, and phosphates, the alkali metal being selected from the group consisting of sodium and potassium, and about 1 to 12 percent by weight of a mixture of at least one each of sulfated and unsulfated t-carbinamine polyoxyethylene compounds, the alkyl groups in each of the amino compounds having a total of about 11 to 14 carbon atoms, the number of oxyethylene units per amine unit present being in the range of from 12.5 to 17.5, and the proportion of sulfated to unsulfated compounds being from about 75 to 85 percent of the former to about 25 to 15 percent of the latter.

2. The composition of claim 1 in which the sulfated t-carbinamine polyoxyethylene compound has a monovalent cation selected from the group consisting of hydrogen and the alkali metals.

3. The composition of claim 1 in which the sulfated t-carbinamine polyoxyethylene compound is a mixture selected from the group consisting of compounds in the range of

\[ t\text{C}_8\text{H}_{17}\text{NH}[(\text{C}_2\text{H}_4\text{O})_{m}\text{SO}_3]^+ \]

and the unsulfated t-carbinamine polyoxyethylene compound is a mixture selected from the group consisting of compounds in the range of

\[ t\text{C}_8\text{H}_{17}\text{NH}[(\text{C}_2\text{H}_4\text{O})_{m}\text{H}] \]

the values for \( m \) in all four formulas being about 12.5 to 17.5, and \( X \) in the first two formulas being a monovalent cation which is a member of the class consisting of \( H \) and the alkali metals.

4. A cleaning solution consisting essentially of water and from about 2 to about 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 group consisting of sodium and potassium, and about 1 to 12 percent by weight of a mixture of at least one each of sulfated and unsulfated t-carbinamine polyoxyethylene compounds, the alkyl groups in each of the amino compounds having a total of about 11 to 14 carbon atoms, the number of oxyethylene units per amine unit present being in the range of from 12.5 to 17.5 and the proportion of sulfated to unsulfated compounds being from about 75 to 85 percent of the former to about 25 to 15 percent of the latter.

5. In the process of cleaning metal surfaces involving the removal of soils therefrom by treatment with a hot aqueous alkaline cleaning composition, the improvement which consists of carrying out the metal cleaning operation essentially by means of the solution of claim 4 maintained at hot temperatures up to about 100°C.

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