Amine Oxide/Alcohol Ethoxylate Blends: Zero-Phosphate, High-Performance, Hard-Surface Cleaners[1]

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ABSTRACT: Several instances of synergistic interaction have been identified between amine oxides and alcohol ethoxylates in various surfactant formulations. The purpose of this study was to examine whether these benefits could be observed within the framework of generic hard-surface cleaning formulations. Comparative evaluations were also carried out to determine the performance characteristics of low- and zero-phosphate systems in which alkyldimethylamine oxides and linear alcohol ethoxylates are used. Best cleaning was observed with 1:1 mixtures of the subject surfactants, but substantial improvements over alcohol ethoxylate alone also were noted with formulations that contained lower ratios of amine oxide. These systems displayed good cleaning performance when tested on vinyl floor tiles soiled with an oily/particulate soil.

JAOCS 72, 857–859 (1995).

KEY WORDS: Alcohol ethoxylates, alkyldimethylamine oxides, amine oxides, hard-surface cleaners, nonylphenolethoxylates, STPP, surfactants, synergy, tetradecyldimethylamine oxide, zero-phosphate.

The term "hard-surface cleaner" encompasses a wide variety of products in both consumer and industrial/institutional (I & I) markets (1). Consumer applications include bathroom cleaners (cleaners for tile, tub, shower, etc.), abrasives, cleaners intended for windows, glass, floors, or oven, dishwashing products, spray cleaners, plus all-purpose cleaners. Various automotive cleaning products also fall into this category. I & I applications are just as diverse, and the requirements are often more demanding than those just mentioned.

Amine oxides are a class of surfactants generally recognized as enhancing the performance of certain hard-surface cleaners. Low critical micelle concentration, good wetting, excellent soil emulsification, lime soap dispersion (2), and a mild effect on skin contribute to their use in a wide array of products. From testing of recent supermarket samples, it was determined that a premier supplier of consumer household surface cleaners utilizes alkyldimethylamine oxides throughout its product line. Some leading brands of dishwashing liquids were found to contain a substantial level of alkyldimethylamine oxide. Outside of the hard-surface cleaner field, amine oxides are present in a wide spectrum of products, ranging from personal-care products and laundry detergents (3) to drain cleaners and I & I applications.

Several instances of synergistic interaction (4) have been identified between amine oxides and alcohol ethoxylates in various surfactant fomulations (5). The purpose of this study was to examine whether these benefits could be observed within the framework of generic, hard-surface cleaning formulations. Comparative evaluations also were carried out to determine the performance characteristics of low- and zero-phosphate systems with alkyldimethylamine oxides and linear alcohol ethoxylates.

EXPERIMENTAL PROCEDURES

Glossary of terms. AE, linear alcohol ethoxylate [example: 1012-6 AE = blend of C_{10}–C_{12} linear alcohols, ethoxylated with an average of 6 moles ethylene oxide (EO)/mole alcohol]; NP-9, nonylphenol ethoxylate (9 moles EO); AX, amine oxide; STPP, sodium tripolyphosphate.

Procedures. American Society for Testing and Materials (ASTM) method ASTM D4488 (Section A5) was selected as the method to conduct this study (6). For practical purposes, a premixed particulate soil was obtained from U.S. Testing Company, Inc. (Hoboken, NJ) to use in place of the particulate soil component described in the ASTM method. The composition of this soil (Modified Sanders–Lambert Urban Soil; U.S. Testing Company, Inc.) is in wt%: hyperhumus, 38; Portland cement, 15, low-furnace carbon black, 1.5; synthetic red iron oxide, 0.3; powdered silica (200–300 mesh), 15; bandy black clay, 16.7; stearic acid, 1.5; oleic acid, 1.5; palm oil, 3; cholesterol, 1; vegetable oil, 1; N-octadecene (technical grade), 1; 1-octadecene (technical grade), 1; linoleic acid (technical grade), 2; and white mineral oil, 1.5. The oily blend component was mixed in-house according to the following recipe, heating as prescribed in the ASTM method (6): in wt%—kerosene, 30.7; mineral spirits (substituted for Stoddard solvent), 30.7; mineral oil (substituted for paraffin oil), 2.6; SAE 10 motor oil, 2.6; vegetable shortening, 2.6; olive oil, 7.7; linoleic acid, 7.7; squalene, 7.7; and 1618 α-olefin (Albemarle Corporation, Baton Rouge, LA) (substituted for octadecene-1), 7.7. In some instances, alternate ingredients

[1]Presented at the 85th AOCS Annual Meeting & Expo, May 10, 1994, Atlanta, Georgia.

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were used when the exact ingredients were not readily available; these are noted. The Gardner Abrasion Tester AG-8100 (Silver Springs, MD), cellulose sponges, and white vinyl floor tiles (Ampico VP11 Dry Back; American Biltrite, Sherbrooke, Quebec, Canada) were used in the cleaning tests.

Initial preparation of the unsoiled tiles included gentle washing with Comet® cleanser, thorough rinsing, and air-drying overnight. Initial reflectance readings (Lo) were then obtained as described below. A plastic template was used to mask a rectangular area (2.5 in. × 5 in.) on the tile. The particulate component (80 mg) was placed in the center of the masked area, eight drops of the oily blend were added to the particulate, and a paper towel was used to rub the mixture evenly onto the surface, as described in the ASTM method (6). Soiled tiles were prepared the afternoon before the cleaning step and allowed to air-dry at room temperature overnight in a laboratory hood. Reflectance readings on the soiled tiles (Ls) were taken. During the early stages of the experiment, soiled tiles whose reflectance varied significantly from the majority of the companion tiles ("outliers") were discarded. Ability to apply soil consistently improved with experience until all tiles could be used.

The cleaning step was conducted according to the ASTM method (6). All candidate solutions were evaluated at 0.2% surfactant concentration in deionized water. Each soiled tile was secured in the scrubbing apparatus, 20 mL of test solution was poured on the soiled area, and 50 mL of solution was poured onto a clean, damp sponge. Ten scrubbing cycles were run after a 1-min soak time. Tiles were immediately rinsed under a gentle stream of cool tap water, then set aside to air-dry overnight prior to final reflectance readings (Lc).

A HunterLab Colorimeter (Model D25-9; Fairfax, VA) was used for reflectance measurements. A thin circular plastic template (0.008 in. × 2.5 in. diameter) was utilized to keep the tile surface just off the colorimeter glass. Three readings per tile were taken: center, one inch to the left of center, and one inch to the right of center. These were then averaged. Cleaning efficiency, or percent soil removal, was calculated as follows:

$$\text{cleaning efficiency} = (Lc - Ls)/Lo - Ls) \times 100 \qquad [1]$$

Most of the cleaning solutions were tested in triplicate; in a few instances, only duplicates were run. Experimental error was less for the best-performing products (±2%) than for the poorest performers (±5%).

RESULTS AND DISCUSSION

A formulation, featuring two parts NP-9 plus one part STPP, was selected as the control formulation, based on the advice of a commercial supplier of hard-surface cleaning products. Results from this control formulation are included in all figures. Compared with results achieved with surfactant alone (Fig. 1), the beneficial effect of STPP used in combination with NP-9 surfactant is obvious. Comparing surfactants with no phosphate present, 1012-6 AE performed as well as NP-9; the cleaning efficiencies of the other three surfactants were much lower.

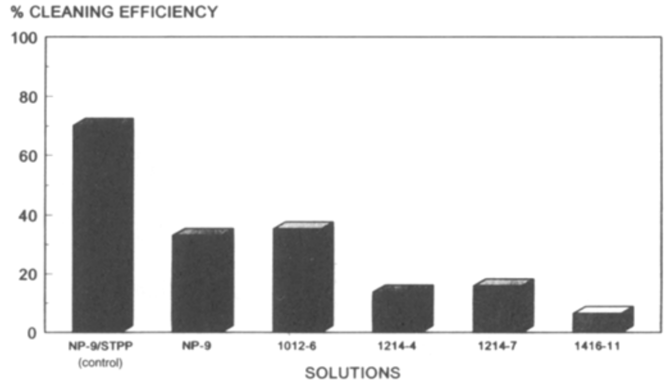

FIG. 1. Cleaning performance of selected alcohol ethoxylates. NP-9, nonylphenol ethoxylate (9 moles of ethylene oxide); STPP, sodium tripolyphosphate.

The cleaning characteristics of C_{14} AX are demonstrated in the figures. With no phosphate, C_{14} AX outperformed the NP-9/STPP control (Fig. 2). Performance of a 1:1 amine oxide/NP-9 blend was about midway between straight AX and the control. In combining these two surfactants, the NP-9 appeared to act as an extender for the AX rather than as a synergist (i.e., the 1:1 blend performed better than the value obtained by averaging the results of the two individual components, but not better than the result for AX alone).

Figure 3 features C_{14} AX blended with 1012-6 AE at various levels. This cleaning system demonstrated actual synergy in that a 1:1 blend outperformed the straight AX, and a 1:4 blend gave equivalent results to AX alone. These surfactant systems, with no phosphate, outperformed the NP-9/STPP control.

Some alternate builders were evaluated in combination with NP-9 surfactant as possible replacements for STPP (Fig. 4). Sodium citrate performed better under these conditions than sodium carbonate or sodium silicate, and almost as

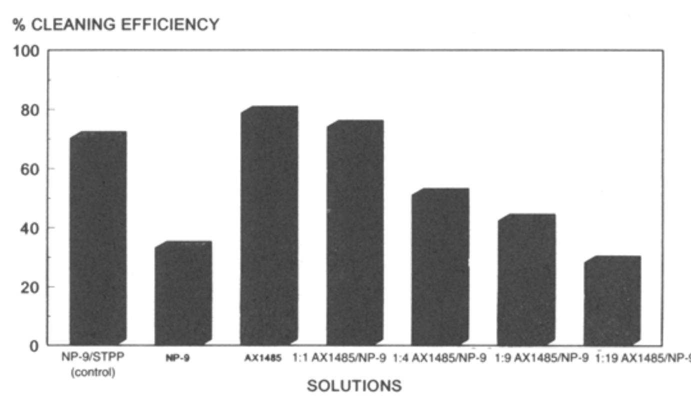

FIG. 2. Cleaning performance of nonylphenol ethoxylate/amine oxide (AX) blends. Abbreviations as in Figure 1. AX1485, ADMOX® SC-1485 AX (tetradimethylamine oxide dihydrate) (Albemarle Corporation, Baton, Rouge, LA).

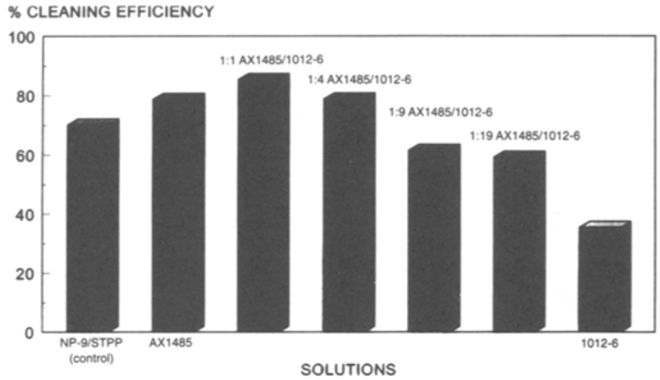

FIG. 3. Cleaning performance of 1012-6 alcohol ethoxylate/amine oxide blends. Abbreviations as in Figures 1 and 2.

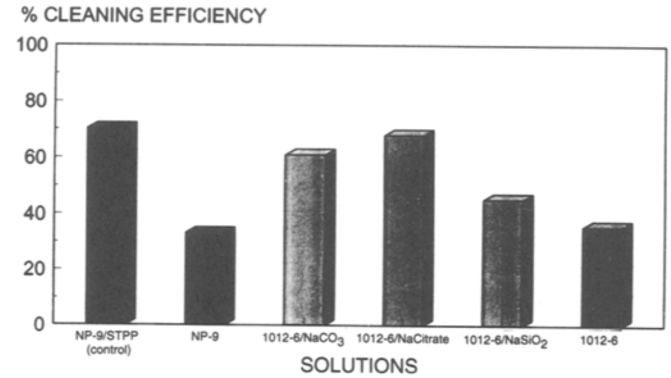

FIG. 5. Influence of builder type on cleaning performance of 1012-6 alcohol ethoxylate. Surfactant/builder ratio, 2:1. Abbreviations as in Figure 1.

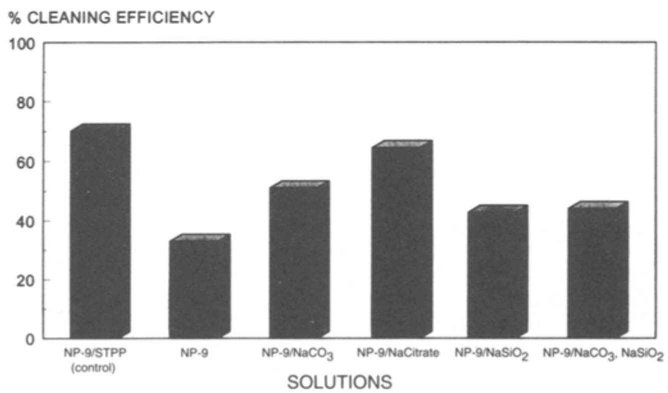

FIG. 4. Influence of builder type on cleaning performance of nonylphenol ethoxylate. Surfactant/builder ratio, 2:1. Abbreviations as in Figure 1.

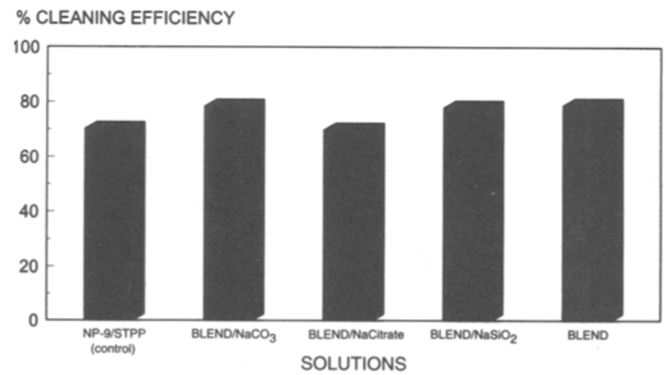

FIG. 6. Influence of builder type on cleaning performance of an amine oxide/alcohol ethoxylate blend. (C_{14} alkyldimethylamine oxide/1012-6 alcohol ethoxylate, 1:4), surfactant/builder ratio, 2:1. Abbreviations as in Figure 1.

well as the control formulation featuring STPP. A 1:1 builder blend of sodium carbonate/sodium silicate displayed no synergy. Figure 5 shows that with 1012-6 AE as the surfactant, sodium citrate again outperformed the other two alternates (STPP was not included in the variants). When sodium citrate was used, NP-9 and 1012-6 AE surfactants exhibited comparable cleaning.

Figure 6 indicates that the performance of a 1:4 AX/1012-6 AE blend was not enhanced by the use of any of the three alternate builders. The blend, plus either sodium carbonate or sodium silicate, performed equivalent to the surfactant blend alone. Surprisingly, sodium citrate did not perform quite as well as the other builders with this blend (STPP was not included in the variants).

The results of this hard-surface cleaning study are exciting with regard to the benefits that can be obtained with AXs (particularly tetradecyldimethylamine oxide) in conjunction with linear alcohol ethoxylates. The most significant observations include the inherent ability to remove oily/particulate soil without the use of phosphates and the synergy observed when tetradecyldimethylamine oxide is blended with 1012-6 AE. One can achieve performance equivalent or superior to a phosphate/alcohol ethoxylate blend by using a nonphosphate/alcohol ethoxyolate/AX blend. Supplemental work in this area, suggested by these results, might include testing of systems that feature lower-carbon number alcohol ethoxylates (e.g., 610-3 AE) plus AX.

ACKNOWLEDGMENTS

The authors wish to thank Albermarle Corporation for support of the work featured in this study, and also personnel at U.S. Testing Inc. and Zep Inc. (Atlanta, GA) for technical advice.

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[Received September 29, 1994; accepted April 3, 1995]