Nonbuilt Heavy Duty Liquids: Detergency and Formulating Parameters

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ABSTRACT

The detergency of nonbuilt heavy duty liquids containing linear alkylate sulfonate and/or linear alcohol ethoxylate nonionic active is discussed. Single cycle detergency on a broad range of linear alkylate sulfonate-nonionic compositions was evaluated on cloths soiled in the laboratory with a mixture of synthetic sebum and dust and a commercially available soiled cloth, ACH #120A. The effects of multiple cycle wash testing also were covered. Formulating parameters to produce usable nonbuilt heavy duty liquids are discussed. The nonionic of choice for maximum detergency in nonbuilt heavy duty liquids should be derived from ca. a 14 carbon chain length alcohol with ca. 70% ethylene oxide. For optimum solubility, linear alkylate sulfonate should be the sodium salt derived from a linear alkylbenzene of ca. 235-240 mol wt, a product like that currently used in light duty liquids. The presence of linear alkylate sulfonate in nonbuilt heavy duty liquids helped reduce product clear point. Nonionics were found to give the best performance on cotton cloth. Linear alkylate sulfonates were most effective on synthetics. Multiple cycle testing with Spangler soil on nonbuilt heavy duty liquids was shown to be unnecessary. Mixed active systems gave the best overall product on the basis of performance and physical properties.

INTRODUCTION

In the past few years detergent manufacturers have been under increasing governmental pressure to produce zero phosphate heavy duty detergents. Indeed, millions of people now live in regions of our country with phosphate bans. Regardless of the arguments for and against the presence of sodium tripolyphosphate (STPP) in detergents, manufacturers have had to respond with nonphosphate detergent products to supply consumers in zero phosphate areas. In powdered products, this has taken the form of a modification in the surfactant system and replacement of STPP with sodium carbonate and/or sodium silicate.

Another type of detergent formulation that can be marketed in nonphosphate areas is a nonbuilt heavy duty liquid (NB-HDL). In these products, the phosphate builder has been removed and replaced with additional surfactant. NB-HDL offer the advantage of easy liquid handling. They give good detergency, are completely biodegradable, and can compete on a cost performance basis with conventional heavy duty powders. These characteristics have prompted marketing of NB-HDL outside zero phosphate regions to compete directly with conventional heavy duty powders and phosphate containing heavy duty liquids.

Very little has been published on performance properties of NB-HDL. Albin and coworkers (1) have reported on structural effects of alcohol derivatives on both oily soil and clay soil detergency. They found the optimum linear alcohol ethoxylate contained about 13.5 carbon atoms with ca. 65% ethylene oxide (9 moles). These optimums are similar to those reported by Matson (2) for use of nonionics in phosphate built heavy duty powders. The optimum alcohol ethoxysulfate reported by Albin (1) contained ca. 13.5 carbon atoms with ca. 40-55% ethylene oxide (3-6 moles).

The object this work was to define detergency optimums for different levels of linear alkylate sulfonate (LAS) and linear alcohol ethoxylates in NB-HDL, and then, with detergency data in hand, to define formulating limits to produce a liquid with acceptable physical properties.

EXPERIMENTAL PROCEDURES

Equipment

Detergency measurements were made in a conventional Terg-O-Tometer purchased from United States Testing Company, Inc. (Hobokin, NJ). Evaluations of cloth whiteness were measured on a Hunterlab Model D-25 Color Difference Meter using the L scale. Viscosities were measured on a Brookfield Model LVF viscometer using a #1 spindle at 60 rpm. Clear points were determined using a 30 ml sample size in a vacuum jacketed flask equipped with a mechanical mixing device. Samples were cooled to bring them to a cloudy condition, then warmed at 1-2 F/min to the clear point.

Materials

Reagents, unless otherwise specified, were purchased from commercial chemical suppliers and were of the best quality grade available. Nalkylene 500 alkylate® was a linear alkylbenzene (Conoco Chemicals, Houston, TX) with an average mol wt of 238. The Nalkylene 500-derived LAS used also was manufactured by Conoco Chemicals; it was designated C-550 slurry.

Alfonic 1218-60 nonionic® was typical of the commercial alcohol ethoxylates (Conoco Chemicals, Houston, TX). It was derived from a mixture of C_{12}, C_{14}, C_{16}, and C_{18} primary straight chain alcohols averaging ca. 13.7 carbon atoms. It had been ethoxylated to 60% by wt (~7 moles ethylene oxide [EO]).

The individual alcohol homolog nonionics (Fig. 1) were prepared by ethoxylation of individual alcohol homologs to the desired levels of ethylene oxide. The individual homologs used were Alfol 10, Alfol 12, Alfol 14, and Alfol 16 alcohols® which were decanol, dodecanol, tetradecanol, and hexadecanol, respectively (Conoco Chemicals, Houston, TX).

For most detergency testing, cloths soiled with a synthetic sebum and dust mixture of the type described by Spangler (3) were prepared. Testfabrics®, S/419A cotton,

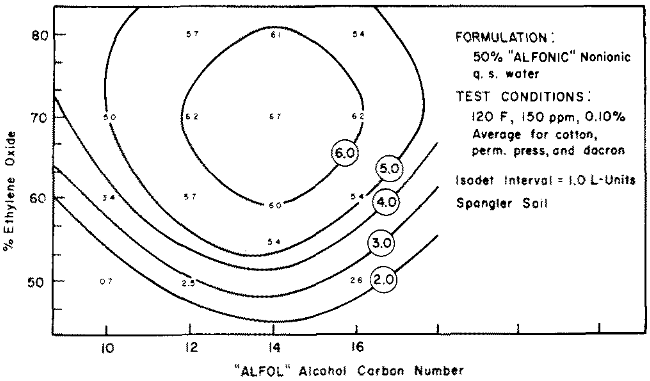

FIG. 1. Detergency for ethylene oxide level vs alcohol carbon number.

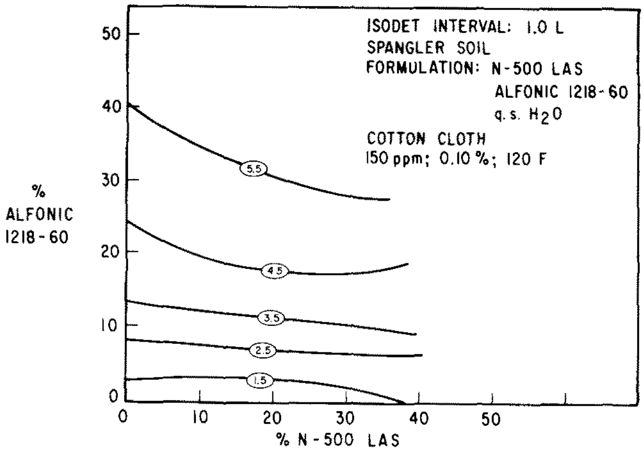

FIG. 2. Detergency for different linear alkylate sulfonate (LAS)-nonionic compositions, cotton cloth, spangler soil.

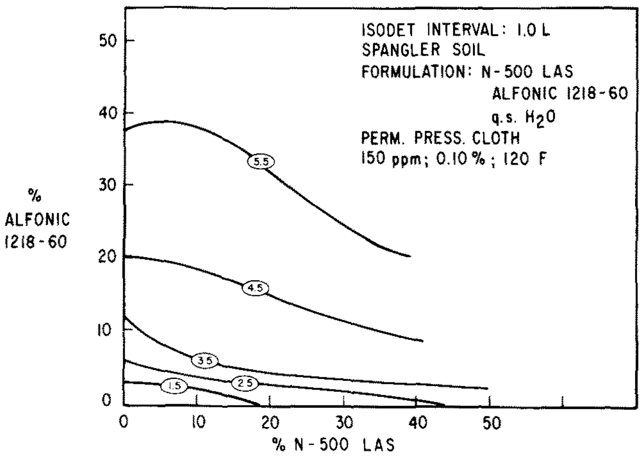

FIG. 3. Detergency for different linear alkylate sulfonate (LAS)-nonionic composition, permanent press cloth, spangler soil.

S/754 dacron, and S/7406WRL dacron/cotton blend with permanent press finish cloths were soiled by this procedure. In this mixture, the sebum consisted of fats, fatty acids, and waxes; the dust had been collected from the filters of office air conditioners and washed in alcohol. The synthetic sebum had the following composition: 10% palmitic acid, 5% stearic acid, 15% coconut oil, 10% paraffin, 15% spermaceti, 20% olive oil, 5% squalene, 5% cholesterol, 10% oleic acid, and 5% linoleic acid. Cloths typically read 70-75 L units reflectance after soiling. In the multiple cycle testing, the washed cloths were resoiled with the sebum and dust soil after washing, then dried and reused.

ACH #120A cotton cloth, a commercial pre-soiled cloth, was purchased from ACH Fibre (Boston, MA).

Test Methods

Terg-O-Tometer test conditions were: temperature, 120 F; wash time, 10 min; rinse time, 5 min; concentration, 0.10%; hardness, 150 ppm (as $CaCO_3$); agitation rate, 100 rpm; cloth load, a) Spangler, 3 soiled cloths of each type/pot, and b) ACH, 6 soiled/pot; and cloth swatch size, 3½ in. x 4¼ in.

The Terg-O-Tometer procedure was as follows. The soiled cloths first were sorted into stacks having 1 L unit range from darkest to whitest cloth. Each cloth in a particular stack then was assigned an L value equal to the median value of that stack; cloths within a particular stack then were used interchangeably. For a particular test, cloths from only one stack were employed.

To begin washing, a calculated amount of $CaCl_2/MgCl_2$

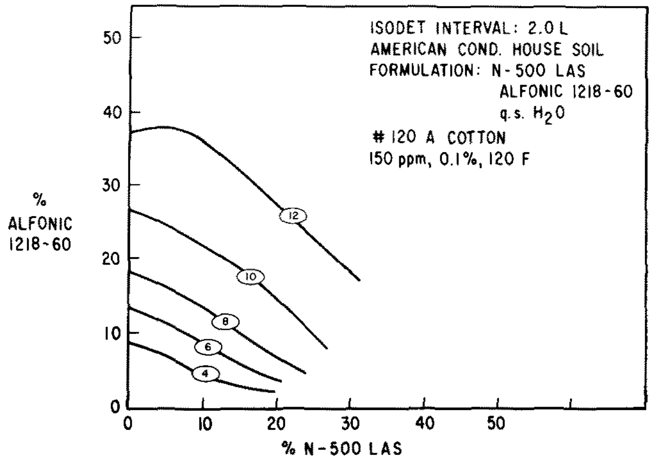

FIG. 4. Detergency for different linear alkylate sulfonate (LAS)-nonionic compositions, American conditioning house #120A cotton.

hardness concentrate was placed in each Terg-O-Tometer pot to bring the water to the test hardness. Distilled water at 120 F was added. Each component of the test formulation was added from 2% stock solutions by syringe. The agitators were turned on for 3 min before the soiled cloths were added. These were washed, rinsed, passed through a padder, and dried in a print drier. Next, each cloth was measured for whiteness using the L scale of the reflectometer. The L value of the washed cloth was used in evaluating performance. All tests were run in duplicate so a statistical evaluation of results could be made. A computer program has been written to allow convenient use of the statistical method of Hartley (4,5). Error mean squares on the order of .04-1.0 typically were obtained.

In all single cycle washing, isodet graphs were constructed. In these graphs, lines of equal detergency were drawn at some L unit interval. For the convenience of dealing with smaller numbers, the L value of the washed cloths minus a constant was used. In Figures 2-4, each isodet was drawn using 32 data points, with each data point run in duplicate.

RESULTS AND DISCUSSION

Nonionic Selection

An evaluation was made of optimum alcohol carbon chain length and optimum ethylene oxide content. Nonionic optimization was done in an all-nonionic formulation containing 50% nonionic. Average detergency values for cotton, permanent press, and dacron are presented in Figure 1. Each individual cloth type gave similar results.

The results in Figure 1 show that the best detergency using Spangler sebum and dust soil was obtained with a nonionic having ca. 14 carbon atoms and containing ca. 70% ethylene oxide by wt. Alfonic 1218-60 nonionic was selected as the nonionic of choice for all subsequent work, because it was one of the commercial products closest to the determined optimum.

LAS Selection

For formulating reasons, the LAS should be chosen to give maximum solubility. This suggests a low mol wt starting alkylate. A starting alkylate of 238 mol wt designated Nalkylene 500 alkylate was chosen. This linear alkylbenzene has an average side chain length of ca. 11.4 carbon atoms. It yields a sodium LAS of ca. 340 equivalent wt.

Also for maximum solubility and compatibility, sodium salt of the sulfonate was chosen over potassium salt. Table I clearly illustrates the better solubility of the sodium salt. Potassium LAS historically has been used in built HDL, but

TABLE I

Solubility of Sodium vs Potassium Linear Alkylate Sulfonate[a]

Active (%)	Clear Point (F) Na+ salt	K+ salt
15	-	48
20	43	65
25	48	84
30	55	104
35	72	-
40	101	-

[a]Derived from Nakylene 500 alkylate by SO_3 sulfonation.

this was because of the superior solubilities of potassium salts of phosphate builders, not because of potassium LAS solubility. Also for maximum solubility, sulfur trioxide was used for sulfonation rather than oleum. This reduced the inorganic salt level which significantly improved water solubility.

The LAS of choice then was the sodium salt derived from sulfur trioxide sulfonation of Nalkylene 500 alkylate. This commercial product used was Conoco C-550 slurry.

Single Cycle Detergency for NB-HDL Containing LAS and/or Nonionic

Figures 2-4 present detergency evaluations of various NB-HDL compositions containing 0-40% nonionic and 0-40% LAS. Some of these compositions could not be formulated into clear liquid products. However, because detergency evaluations were made using 2% stock surfactant solutions, the detergency of such systems was measured.

Using Spangler sebum and dust soil (Figures 2 and 3), there was a broad optimum in detergency on both cotton and permanent press cloth. This optimum was generally in the region bounded by the coordinates (% nonionic, % LAS) of (25,0) (20,40), (30,40), and (40,0). At any point within this region, very little difference in performance occurred.

The nearly horizontal nature of the isodet lines in Figure 2 suggested that with the oily Spangler soil, a nonionic was more effective in detergency than LAS. In going to permanent press cloth (Fig. 3), the isodet line slopes increased, suggesting that the LAS in an LAS plus nonionic formulation was more effective on permanent press than on cotton. This effect of LAS was even more pronounced on dacron.

On the less oily ACH #120A cotton cloth (Fig. 4) the line slopes were greater yet. These data suggest that with a less oily, more particulate soil, LAS was more effective in NB-HDL.

Multiple Cycle Detergency for NB-HDL Containing LAS and/or Nonionic

In multiple cycle detergency tests of NB-HDL with Spangler sebum and dust soil, a nearly linear response of detergency to cycle number was obtained through 5 wash cycles (Figure 5). Detergency data are presented for the average of cotton, permanent press, and dacron cloth performance. Very similar results were obtained for all 3 cloth types except that the more highly nonionic formulations did better on cotton cloth, while an improvement in synthetic fiber detergency was noted with LAS present. The detergency test results (Fig. 5) showed that Formulations B and C gave nearly equal performance with both being better than A.

It was interesting to note that in multiple cycle washing of NB-HDL with Spangler soil the formulation with the highest single cycle detergency had the lowest slope, while that with the poorest single cycle detergency had the steepest slope. This meant there should never be any inversion of product performance with increasing wash cycles. Multiple cycle detergency testing of these types of products on Spangler soil, therefore, was not necessary; the product ranking found after one cycle also was found after 5 cycles.

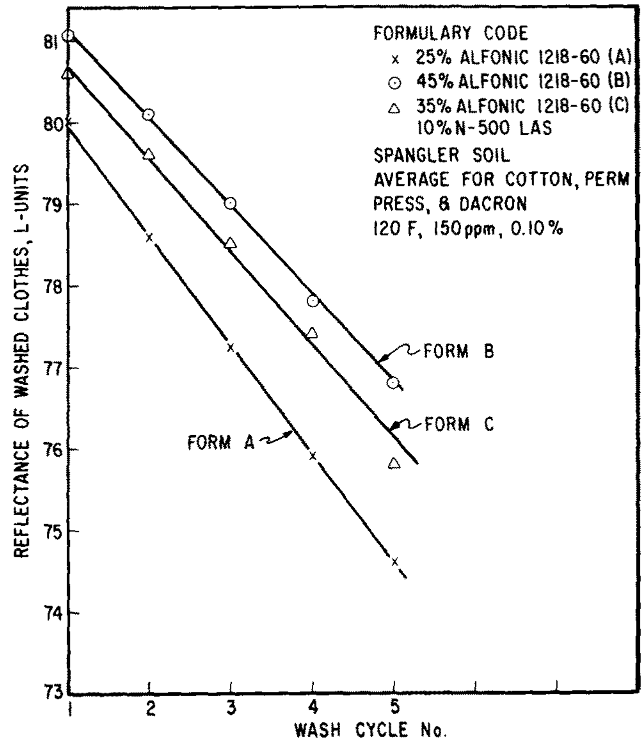

FIG. 5. Multiple cycle detergency of nonbuilt-heavy duty liquids. Form A = 25% Alfonic 1218-60 nonionic; Form B = 45% Alfonic 1218-60 nonionic; Form C = 35% Alfonic 1218-60 nonionic, 10% N-500 linear alkylate sulfonate.

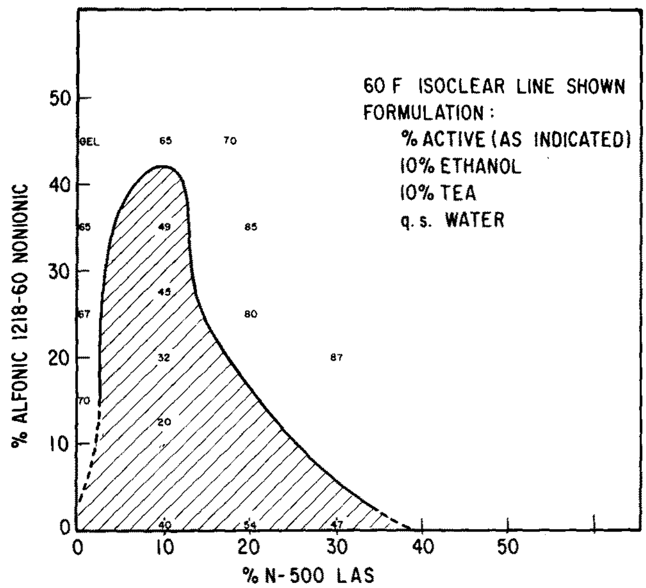

FIG. 6. Clear points for different compositions of linear alkylate sulfonate (LAS)-nonionic containing nonbuilt heavy duty liquids.

Physical Properties of Formulated NB-HDL

Figures 6 and 7 present clear point and viscosity data, respectively, on formulated NB-HDL. Product clear point was important because it was a measure of solubility and related to the temperature at which a liquid product had to be maintained if it was to remain clear. A clear point should be as low as possible for maximum solubility. A clear point

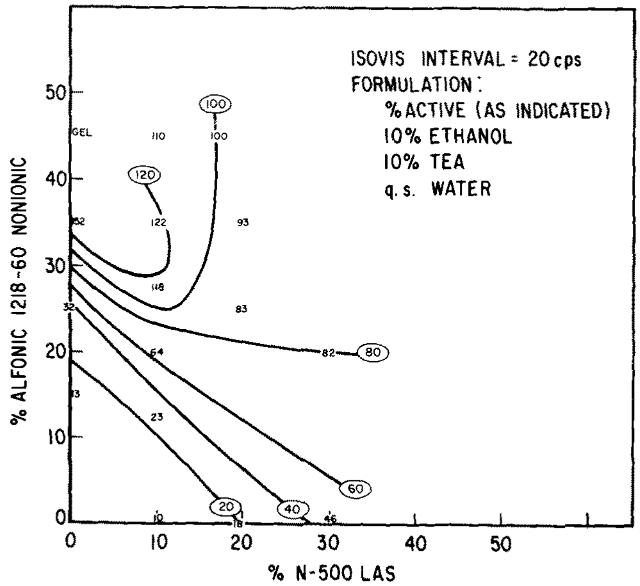

FIG. 7. Viscosities for different compositions of linear alkylate sulfonate (LAS)-nonionic containing nonbuilt heavy duty liquids.

of 55-60 F was considered acceptable for most liquid detergent products.

In Figure 6, an isoclear line was drawn for products having a 60 F clear point. Individual numbers are discreet data points. All LAS plus nonionic compositions within the shaded area of the graph in Figure 6 had a clear point of ≤60 F. It is apparent from Figure 6 that NB-HDL containing only nonionic surfactant had clear points which were too high. The addition of some LAS had the beneficial effect of reducing formulation clear point.

Product viscosity in NB-HDL was important only in that a product should be of low viscosity (100-120 cps or less) that excessive hangup would not occur in the container used to measure and dispense the product. Figure 7 shows the viscosities expected from NB-HDL containing various levels of nonionic and/or LAS. Points of equal viscosity have been joined together with isovis lines at a 20 centipoise interval.

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[Received October 7, 1976]

A Guide for Authors is Located in JAOCS 52(January):56A(1975)