Consumer Testing Liquid Syndets. II. Biodegradable Formulations[1]

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Abstract

The results of experiments investigating the interrelated effects of biologically degradable nonionic and anionic synthetic detergents in a light duty liquid detergent are presented. The formulations studied explore the performance of various biodegradable nonionic candidates in the presence of a fatty based alkylolamide foam stabilizer and biologically "soft" alkyl aryl sulfonate at two levels of nonionic concentration. The nonionic detergents evaluated are all polyoxyalkylated, including products of natural and synthetic origin. Products based on unsaturated and secondary alcohols are included.

Consumer and laboratory test data show that biologically degradable detergents cannot be directly substituted in formulations without first testing their effect on the formulation itself. The data also show that small differences in molecular weight or in saturation of the materials being used can be reflected materially by technical differences in the finished product. These differences are manifested by analytical determination, by consumer panel evaluation using a duplicated balanced incomplete block design, and by standard dishwashing evaluation. The consumer panel data relate to dermatological properties, general performance and suds stability.

It is obvious that the big switch to biologically degradable surface active agents is not as smooth a changeover as had been hoped, this being especially true for smaller producers of chemical specialties who do not have extensive facilities for formulation testing. These data do, however, indicate that with a careful experimental approach and judicious experimentation that formulations having a performance superior to their nonbiodegradable counterparts can be prepared. It is also stressed that judiciously designed consumer panel evaluations can yield data that is just as precise and valid as can be obtained through some of the more sophisticated testing procedures that require investment in equipment and in training of test panels.

Introduction

During recent years increasing effort has been directed toward alleviating the problem of detergent residues in rivers, streams and potable water supplies (1). Much government concern and industrial effort has been directed toward providing synthetic detergents which are more susceptible to biological attack than are the materials currently being used. This topic has been the subject of many recent symposia.

It is apparent at this time that the switch to biologically degradable anionic synthetic detergents involves mainly the use of linear alkylate sulfonate (LAS) in place of the propylene tetramer alkylate sulfonate previously the work horse of the industry. When this fact became apparent it was decided to evaluate the performance of LAS in a standard formulation used as a light duty liquid synthetic detergent (2). This formulation using LAS was prepared and compared to an identical formulation containing sulfonates based on hard (ABS) detergents.

Laboratory personnel from Swift & Company's Research and Development Center participated in a home test of these two formulations. Participants in the testing program were instructed to use equal amounts of each sample to wash dinner dishes on two consecutive evenings. They then indicated the facial expression which best indicated their response from a standard 7-point hedonic scale as previously described (2). Separate opinions were requested for sudsing, general performance, and effect on hands. Twenty-three of the 40 questionnaires were returned in time to prepare the data on schedule. The results of this test are shown in Figure 1. As can be seen the difference in mean acceptance scores was not significant at the 0.05 level of probability. It was noted, however, that a general downward trend in performance had occurred, if indeed any trend was evident.

The precision of this evaluation could have been improved by sending out a larger number of samples, but the indication at this point was that direct substitution of LAS for ABS was not the answer to reformulation. It was, therefore, decided to investigate the simultaneous effect of substituting LAS for ABS and substituting biodegradable nonionic detergents representative of the materials being promoted by the industry as candidates for biologically degradable nonionic detergents for the biologically "hard" ethoxylated nonyl phenol currently being used in the reference formulation. This approach would then give a much more complete picture of the

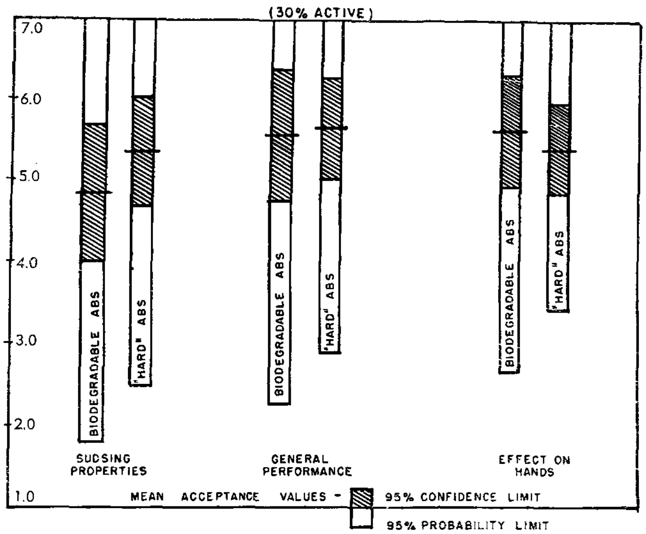

Fig. 1. Consumer panel evaluation of light-duty liquid detergents. Test of product formulated with biodegradable anionic versus nonbiodegradable (30% active).

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TABLE I
Characteristics of Test Nonionics

Test nonionic	Index of Refraction N_D^{25}	Hydroxyl value	Cloud Point @1%	Iodine value
Emulphogene TH-660 (Hydrogenated tallow Alcohol)	1.4558	81.9	164°F	1.1
Emulphogene TE-660 (Unsaturated Tallow Alcohol)	1.4584	89.2	160°F	17.3
Nonionic 2-JNR-69 (Ethoxylated Secondary Alcohol)	1.4542	110.1	93°F	
Alfonic 1214–6 (Ethoxylated ALFOL Alcohol.)	1.4545	110.0	146°F	
Alfonic 1218–6 (Ethoxylated ALFOL Alcohol.)	1.4552	102.1	157°F	
Alfonic 1618C-6 (Ethoxylated ALFOL Alcohol.)	1.4568	91.8	153°F	

reformulation requirements imposed by the industrial switch to "soft" detergents. Six biologically degradable nonionic detergents were evaluated at two levels of concentration in conjunction with LAS and an alkylolamide foam stabilizer. The evaluation of these twelve formulations used the balanced incomplete block design as described by Cochran and Cox (3). The evaluation included all possible paired comparisons using a nonexpert consumer panel chosen from the employees of Swift & Company's General Offices and Research and Development Center and each of the comparisons was made by two different individuals. Empirical laboratory performance tests and physical property determinations were also made on the materials.

The physical properties of the synthetic alcohol ethoxylates used in this experiment are shown in Table I. The Emulphogene TH-660 and TE-660 (Antara Div. General Aniline & Film Corp.) represent samples of ethoxylated hydrogenated tallow alcohol and ethoxylated unsaturated tallow alcohol, respectively. The ethoxylated Alfol alcohols (Continental Oil Co.) were representative of products prepared using Ziegler process petroleum chemistry. The ethoxylated secondary alcohols (Union Carbide Co.) completed the picture. Indices of refraction and hydroxyl values have been found to be useful analytical tools for rapid inexpensive identification of nonionic detergents (4) and are included in the chart for reference purposes.

The LAS used in the study was prepared by the action of sulphur trioxide on LAS alkylate. This produces acid of the high active variety. Solar CO (Swift & Company), a commercial alkylolamide foam stabilizer, was used as the foam booster and additional diethanolamine was added to neutralize the sulfonic acid for reasons previously described (2). The compositions of the test formulations are shown in Table II. The components other than the nonionic were held in the same relationship to one another while the

TABLE II
Formulae Used in Test Series

Component	Formula as used, %	Anhydrous Formula, %
Low level of nonionic:		
Test nonionic	7.20	24.0
Sulfonic acid	10.80	36.0
Solar CO	6.30	21.0
Diethanolamine	5.70	19.0
Water	70.00	......
High level of nonionic:		
Test nonionic	10.80	36.0
Sulfonic acid	9.00	30.0
Solar CO	5.40	18.0
Diethanolamine	4.80	16.0
Water	70.00	......

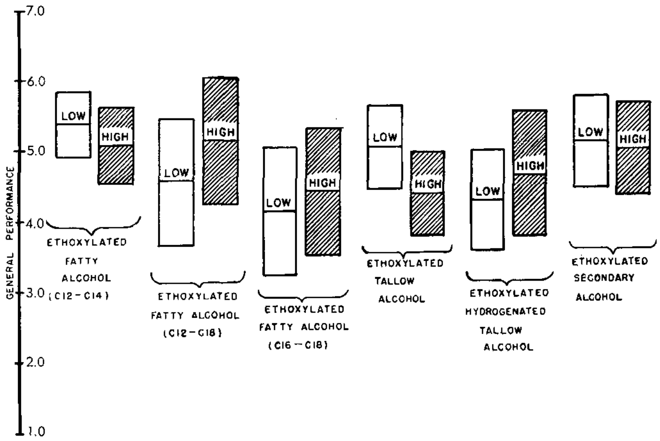

FIG. 2. General performance. Means and 95% confidence intervals.

concentration of the finished salt of the alkyl aryl sulfonate and the concentration of the nonionic detergent were varied.

The balanced incomplete block design used to estimate the consumer response required that each evaluator be provided with a pair of samples and a questionnaire. Each of the samples was assigned a 3 digit random number for identification purposes.

Pour foam data as originally suggested by Ross and Miles was determined according to the official method of the American Society for Testing Materials (5,6). Surface tension data as proposed by DuNoüy was also determined in accordance with the ASTM (7–9). Wetting time for cotton skeins as defined by the AATCC (10) was determined using a 3.000-g hook. The physical and chemical properties of the finished products were determined.

The samples were also subjected to a modified version of the CSMA hand dishwashing test. This test was conducted in the Customer Service Laboratories of the Continental Oil Company (11).

Results

Statistical analysis of the data and interpretive techniques previously elucidated were used (2,3). Differences in general performance were not significant at the 0.05 probability level; however, there appeared to be some interesting trends as evidenced in Figure 2 showing the mean ratings and their 95% confidence intervals. Increasing the average molecular weight of the ethoxylated straight chain synthe-

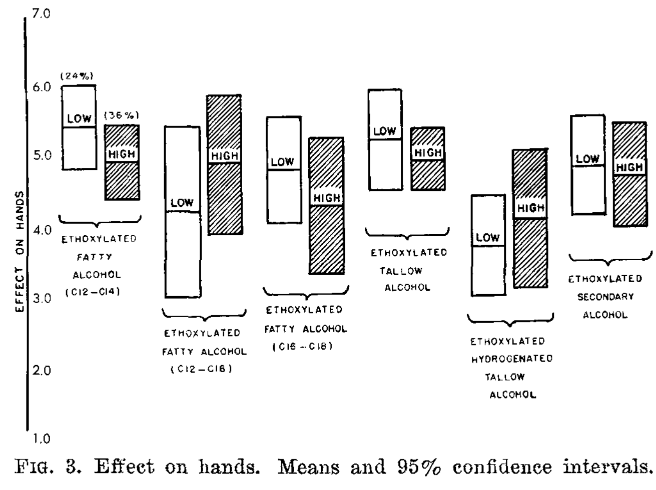

FIG. 3. Effect on hands. Means and 95% confidence intervals.

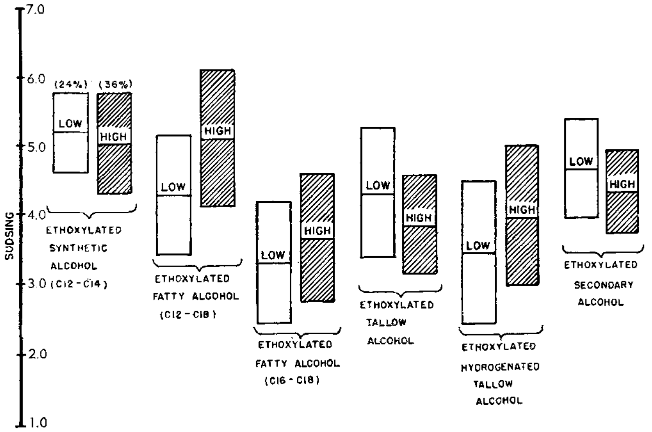

FIG. 4. Sudsing. Means and 95% confidence levels.

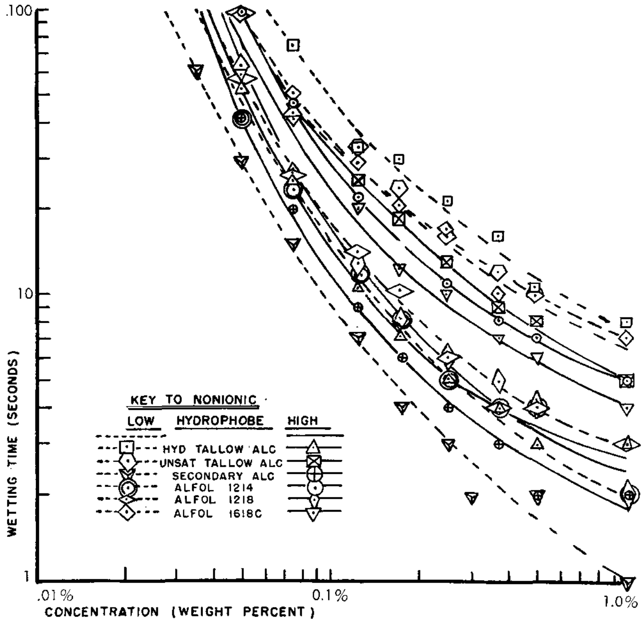

FIG. 5. Wetting time.

tic alcohols decreased the acceptability of the formulation. This effect was more pronounced at the low level of nonionic than at the high level. Ethoxylated hydrogenated tallow alcohol had approximately the same characteristics as the ethoxylated synthetic alcohol having approximately the same molecular weight. It is of interest to note that the ethoxylated secondary alcohol and ethoxylated primary alcohol, having approximately the same molecular weight, appear to be comparable from a performance standpoint. It was also apparent that the ethoxylated unsaturated tallow alcohol provided a more acceptable product at the low level of nonionic than did the completely hydrogenated analog. The differences at the high level of nonionic did not, however, reflect this same trend.

The effect of these variations in formulation on the hands is illustrated in Figure 3. Trends similar to those experienced in general performance were indicated, with little difference noted between the secondary and primary alcohols or between the natural and synthetic alcohols in the 16–18 carbon range with the possible exception of the low level of nonionic. The unsaturated tallow alcohol ethoxylates proved to be significantly superior to the ethoxylated saturated materials and were comparable in performance to the materials based on 12 to 14 carbon alcohols.

Figure 4 shows the tendency of the materials to produce copious suds and retain them throughout the washing cycle. Here again the same trends were evident. The acceptability of the product decreased with increasing molecular weight, particularly at the low concentration, and the high level of nonionic became more acceptable as the molecular weight was increased. It appears from these and other data that the effect of unsaturation in tallow alcohol is simply to increase its acceptability or to render its performance more like that of the lower molecular weight materials.

Wetting time measurements were made at concentration increments from 1.000% to 0.035%. These measurements generated the wetting time curves shown in Figure 5. Examination of these data revealed that the relationship of wetting time to concentration was an exponential function. The AATCC method recommends that these data be plotted on log paper to form a straight line, implying that the relationship is a log log function. They did, in fact, form a family of curves having only slight curvature, but obviously not straight lines. Another way of looking at these data is to record the concentrations required to wet the skein in a given time. Values were determined for 15-second periods and 20-second periods. These values provided data for which analy-

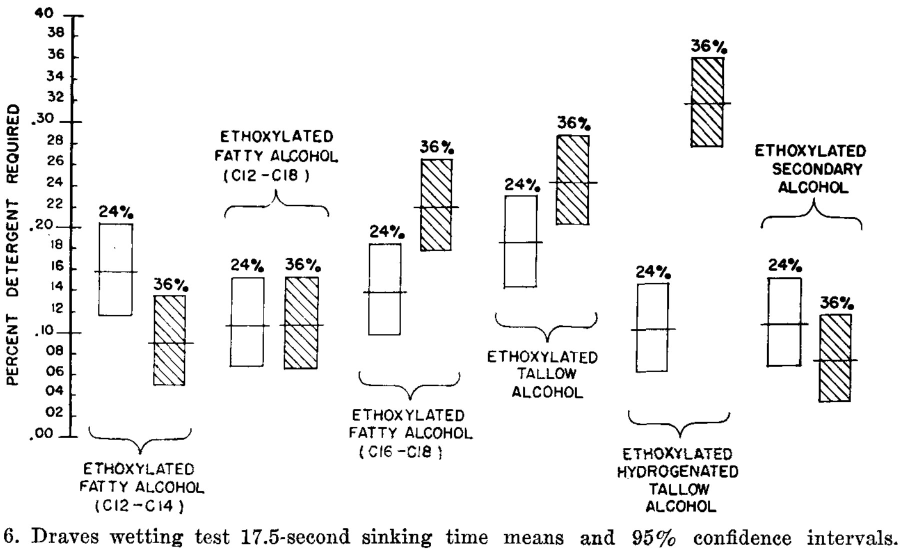

FIG. 6. Draves wetting test 17.5-second sinking time means and 95% confidence intervals.

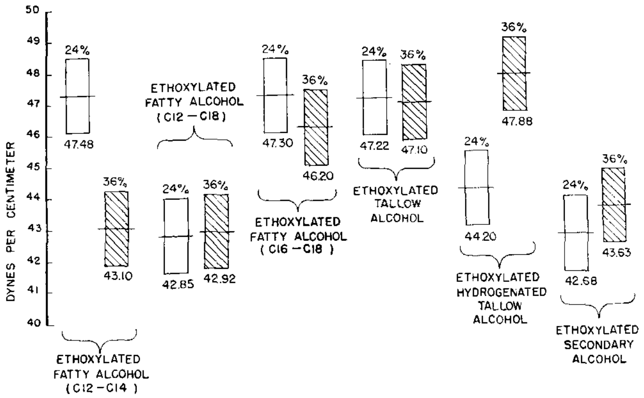

FIG. 7. Average surface tension means and 95% confidence intervals.

sis of variance was appropriate. The analysis of variance revealed a highly significant nonionic by concentration interaction which was averaged for 20- and 15-second data and is illustrated in Figure 6. It can be seen that the high molecular weight nonionics required significantly less detergent to produce the required wetting time at the 24% concentration than they did at the 36% concentration, indicating that in the biodegradable formulations lower nonionic contents of this type give better wetting times.

Surface tension determinations also revealed the same highly significant interaction which was independent of the concentration permitting the surface tension readings of the detergent at 10^{-4}, 10^{-3}, 10^{-2} and $10^{-1\%}$ to be averaged. Figure 7 reveals that the higher molecular weight alcohol derivatives had significantly higher surface tensions than did the lower derivatives. It was also shown with the 12 to 14 carbon straight chain derivatives that the 36% concentration of nonionic produced solutions having a lower surface tension than did the 24% concentration nonionic. The situation was reversed for the ethoxylated hydrogenated tallow alcohol derivatives. An overall interpretation of the curves themselves was not practical.

Ross Miles foam height gave differences mostly at the higher concentrations. The 12 to 14 carbon straight chain alcohol derivatives gave higher foam values than did the 12 to 18 carbon alcohol derivatives. These differences were essentially independent of the concentration of the nonionic. The unsaturated tallow alcohol nonionics produced lower foam than the 12 to 14 carbon normal synthetic alcohol and with both of these the 36% concentration gave lower foam than the 24% concentration, a difference which was evident to a much lesser extent with the ethoxylated secondary alcohol derivatives. These differences are shown in Figure 8, where the means averaged over the detergent concentrations and their 95% confidence intervals are plotted.

TABLE III
Laboratory Dishwashing Evaluations
Hardness: 50 ppm Concentration: 0.05%

Test nonionic base	Performance No. of plates washed: Low nonionic formula	High nonionic formula
C_{12}-C_{14} Fatty alcohol	16.0	17.0
C_{12}-C_{18} Fatty alcohol	14.5	15.0
C_{16}-C_{18} Fatty alcohol	9.3	10.0
Unsaturated tallow alcohol	10.0	10.0
Hydrogenated tallow alcohol	8.0	10.0
Ethoxylated secondary alcohol	18.0	18.0
Reference standard formulation	17.25	

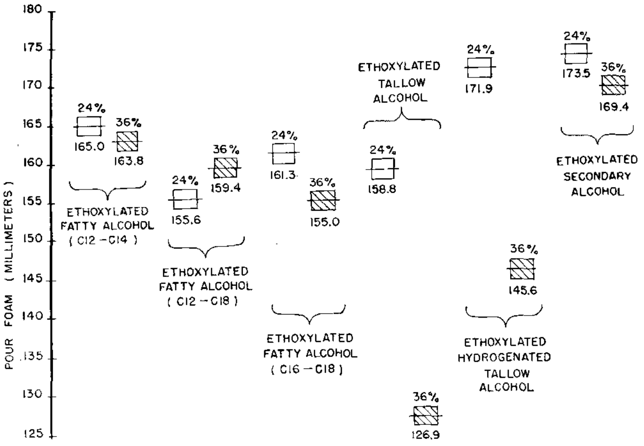

FIG. 8. Pour foam means and 95% confidence intervals.

Viscosity measurements are shown in Figure 9 with confidence intervals from an assumed 5% coefficient of variation that has been suggested from previous experience (4). A variety of significant differences are evident, however, the ultimate meaning of these differences is not known. It is interesting to note the wide divergence of the saturated tallow alcohol derivative from the synthetic derivative having approximately the same composition.

Table III gives the results of the modified CSMA laboratory dishwashing evaluation at a concentration of 0.05% and 50 ppm hardness. Here it can be seen that at the low level of nonionic the lower molecular weight alcohol ethoxylates and the unsaturated tallow alcohol derivatives had the higher performance. At the high level of nonionic the low molecular weight secondary alcohol and the low molecular weight primary alcohol derivatives stood alone in their superior performance. This is in agreement with the consumer evaluation panel. The difference between the primary and secondary alcohol derivatives was further examined at a level of 0.10%. Here the differences in performance, though extremely small, remained in the same direction as they were in the consumer panel test with the indication being that lower molecular weight alcohol ethoxylates would give superior performance.

A further experimental product was prepared using the low level of nonionic and Alfonic 1012–6 (a C_{10}-C_{12} fatty alcohol ethoxylate) as the nonionic component, this giving a lower molecular weight

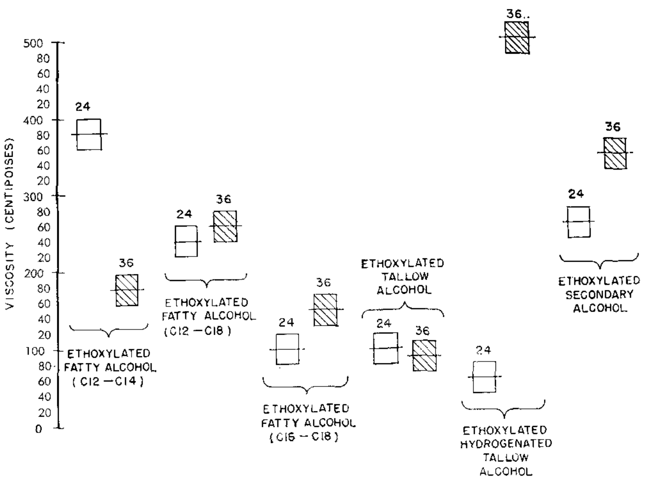

FIG. 9. Viscosity as a function of composition.

TABLE IV
Laboratory Dishwashing Formulations

Formulation	Performance (No. plates washed)			
	50 ppm hardness		300 ppm hardness	
	0.05%	0.10%	0.05%	0.10%
Reference standard	17.25	24.50	16.50	23.00
C_{10}-C_{12} Primary—lo-nonionic	22.0	30.5	21.0	30.0
C_{12}-C_{14} Primary—lo-nonionic	17.0	......	16.5	......
C_{11}-C_{15} Secondary—hi-nonionic	18.0	27.0	16.0	24.0

alcohol than had previously been tested. The values are shown in Table IV, compared to a standard acceptable commercial product used as a reference standard. As can be seen this yielded a product of very acceptable performance characteristics.

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