# Hard Surface Detergency

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In a study of hard surface detergency using glyceryl trioleate, oleic acid, and octanoic acid soils with three types of anionic and three types of nonionic syndets, only potassium laurate showed maximum detergency at the CMC (critical micelle concentration), with the potassium laurate-octanoic acid system being an exception. In general glyceryl trioleate and oleic soil removal (180°F.) at the CMC was low, not over 40%; octanoic acid detergency at the CMC was substantially higher, 65 to 83%. Considerable differences in removal of the various soils by the same surfactants were found. A generalization was observed in the detergency of glyceryl trioleate soil—soil removal increased sharply on passing the CMC with increasing concentration until approximately 90% detergency was reached, at which point soil removal began to level off and approach 100% with a much smaller slope. Visual observations of the cleaning processes suggested a partial answer for the differences in soil removal. Removal of glyceryl trioleate soil by both anionic and nonionic syndets appeared to be due chiefly to a displacement action caused by preferential wetting of the basis metal. Removal of octanoic acid by the nonionic surfactants in a diffusing cloud of small particles seemed to be due to solubilization followed by emulsification and precipitation of the acid soil.

Several relationships were discovered in two series of analogs (polyethenoxyethers of nonyl phenol and tridecyl alcohol). It was found that the ratio of the HLB (hydrophile-lipophile balance) values of two analogs was approximately equal to the fifth root of the ratio of their CMC values. The correlation held for analogs varying by as much as 15 moles ethylene oxide. A linear relationship was also found between HLB value and the reciprocal of the ethylene oxide mole ratio for the polyethenoxyethers of nonyl phenol.

A SERIES OF PAPERS from this laboratory have reported numerical criteria and generalizations concerning the physico-chemical factors of the detergency mechanism (1–7). Recently some workers in the field have emphasized the importance of micellar solubilization and critical miselle concentration (CMC) in detergency (8–11); and have attached some significance to the correlation of maximum soft surface detergency (fabric substrata) with a critical washing concentration which is close to the CMC (12). In spite of the fact that detergency is the result of many factors, unsuccessful attempts have been made from time to time to correlate it with a single one, such as suspending power (18), carbon number (13), and maximum detergent ion concentration (12).

Most available detergency data, including the correlation of maximum detergency with CMC, are based on laundering tests with fabric surfaces. It seemed important therefore to study the variation of hard surface detergency (metal cleaning of the soak type) with surfactant concentration and type, using different classes of soils. This paper is an investigation of the hard surface (steel) detergency of various types of surfactants. In addition, micellar solubilization, suspending power, and interfacial tension were determined throughout the concentration range of each surfactant studied. This data would indicate the existence of any correlation with detergency as determined herein.

## Experimental

The experimental procedures for suspending power, micellar solubilization, and interfacial tension were essentially as previously described (1,5,6). Suspending power was determined at 180°F., with the tip of the 10-ml. pipette adjusted to 77 mm. below solution level in the 100-ml. settling cylinder at 180°F. The powder samples were 0.4000 g. chromic oxide, pigment "Imperial X-1134" of the Imperial Color, Chemical & Paper Corp., Glens Falls, N.Y. Initial suspension concentrations were 0.16%. The 10-ml. volumes of suspension withdrawn from the settling cylinders were diluted, as required, with surfactant solution of the same concentration as the suspending medium to fall within the calibration range of a Bausch & Lomb "Spectronic 20" spectrophotometer, calibrated in grams chromic oxide per 100 ml. suspension *versus* optical density at 425 m$\mu$. Micellar solubilization was measured at 180°F., using Orange OT (1-0-tolylazo-2-naphthol) and repeating the initial agitation of the dyestuff and surfactant solution at 8 and 16 min. after the beginning of the interaction. Dilution of the solubilizate aliquots was with 1:1 acetone-water mixture, as required, prior to colorimetric analysis. Interfacial tension values with glyceryl trioleate as the organic liquid phase (soil) were obtained with a du Nouy interfacial tensiometer at 28 ± 0.5°C. The platinum ring was immersed in the surfactant solution for 1 hr. in the test vessel, following which glyceryl trioleate was poured into the vessel. Tensions were determined after a 6-min. age of the interface. The glyceryl trioleate has been described previously (6).

Detergency testing was conducted as follows:

*Preparation of Test Panels.* Test panels of WD-1020, 18–20 gauge, cold-rolled steel, 2½ x 2½ in. in size, with a ¼ in. diameter hole placed ⅛ in. from one corner, were used. Sharp edges were removed with a file. Both faces of the panels were polished with No. 1 coarse emery cloth, stroking in one direction only. Panels were then degreased with ACS grade acetone using cotton swabs, wiped with paper toweling, dipped in absolute ethyl alcohol, and wiped dry with paper.

*Application of Soil to Test Panels.* The soiling material used in the first series of tests was glyceryl trioleate. The cleaned panel, suspended on a S-shaped hook fashioned from a paper clip, was dipped into a 400-ml. beaker of the oil at a temperature of 28 ± 0.5° C., and allowed to drain at the same temperature for 15 min. The remaining drop of oil in the lower corner of the panel was then removed with cotton. The amount of glyceryl trioleate adhering per panel was approximately 0.13 g., the exact amount being determined periodically for use in computing percentage soil removal.

*Cleaning Procedure.* The "cleaned" and "soiled" test panel was then immersed for 2 min. by a copper hook through the ¼-in. hole, in 1,600 ml. of a distilled water solution of the surfactant contained in a 2-liter beaker and maintained at a temperature of 180° ± 1°F. Neither the test panel nor the solution was agitated. The panel was then removed from the cleaning solution and given two 6-sec. rinses in distilled water with no agitation, and with a 4-sec. drain between rinses. Each rinse consisted of 800 ml. distilled water at 28 ± 0.5°C. in a 1-liter beaker.

*Measurement of Residual Soil.* After rinsing the test panel was transferred to a tared Petri dish containing a small glass hook, dried for 60 min. at 50° ± 1°C., cooled in a desiccator, and reweighed. The test panel was then degreased with acetone, wiped with paper, rinsed in alcohol, wiped with paper, and weighed. Weight of residual soil and per cent soil removal (detergency) were then computed.

*Critical Micelle Concentrations.* Most of the CMC values were obtained from the literature as follows:

| Surfactant | | CMC (molarity) | Reference |
|---|---|---|---|
| Nonyl phenyl pentadecaethylene glycol ether | NPPGE | .000110 | 16 |
| Nonyl phenyl eicosa ethylene glycol ether | NPEGE | .000155 | 16 |
| Nonyl phenyl triaconta ethylene glycol ether | NPTGE | .000275 | 16 |
| Nonyl phenyl tetraconta ethylene glycol ether | NPTTGE | .000450 | This work |
| Tridecyldodecaethylene glycol ether | TDDGE | .000148 | 17 |
| Tridecylpentadecaethylene glycol ether | TDPGE | .000165 | 17 |
| Polyoxyethylene sorbitan monolaurate | PSML | .000106 | 17 |
| Sodium dodecyl benzene sulphonate | SDBS | .00150 | 15 |
| Sodium oleate | | .00110 | 14 |
| Potassium palmitate | | .00220 | 20 |
| Potassium laurate | | .0233 | 19 |

The CMC of nonyl phenyl tetracontaethylene glycol ether was determined graphically by plotting surface tension values obtained by the du Nouy interfacial tensiometer against logarithms of concentration. All nonionic surfactants and the SDBS were commercial preparations. The sodium oleate was a purified grade. The potassium soaps were prepared from technical grade fatty acids.

## Results and Discussion

1. *Detergency (Glyceryl Trioleate Soil) vs. Concentration.* Tables I and II indicate that only in the case of potassium laurate, of the surfactants studied, was there a coincidence of maximum hard surface detergency (glyceryl trioleate soil at 180°F.) and CMC. The difference between hard surface detergency and laundering tests was further pointed up by the fact that, with the exception of the two potassium soaps and the polyethenoxyethers of nonyl phenol containing 30 and 40 ethylene oxide mole ratios, hard surface detergency was low at the CMC, less than 40% glyceryl trioleate soil removal. In general the surfactants showed a sharp increase in detergency after passing the CMC. The sharp rise portions of the detergency-concentration curves started to level off at about 90% detergency for most of the surfactants. Figures 1 and 2 illustrate the latter phenomenon. The surfactant concentration corresponding to the 90% soil removal point was considered to be significant, and was designated as the CC-1 concentration.

TABLE I

Physico-Chemical Data and Triolein Detergency

| Surfactant molarity | % removal, glyceryl trioleate at 180°F. | Suspending power, mg. $Cr_2O_3$ per 100 ml. suspension, 180°F. | Micellar solubilization, mg. orange OT per 100 ml. solution, 180°F. | Interfacial tension *vs.* glyceryl trioleate, ergs/per sq. cm., 28°C. |
|---|---|---|---|---|
| Nonylphenylpentadecaethylene glycol ether: | | | | |
| .000110 CMC | 31.5 | 148 | 0.1 | 3.1 |
| .000220 | 40.9 | 140 | .... | 2.3 |
| .000440 | 63.8 | 136 | 1.4 | 1.2 |
| .000830 | 92.9 | 130 | 2.6 | 0.6 |
| .00125 | ...... | ...... | 3.8 | .... |
| .00165 | 99.0 | 123 | 4.5 | 0.5 |
| Sodium oleate: | | | | |
| .00110 CMC | 15.0 | 190 | 0.1 | 4.3 |
| .00214 | 22.0 | 205 | 0.5 | 0.9 |
| .00263 | 75.6 | 209 | 0.8 | 0.7 |
| .00329 | 92.9 | 205 | 1.7 | 0.3 |
| .00494 | 95.3 | 205 | 3.1 | 0.2 |
| .00592 | 96.9 | 213 | 4.1 | 0.1 |
| Polyoxyethylene sorbitan monolaurate: | | | | |
| .000106 CMC | 1.6 | 155 | 0.4 | 5.2 |
| .000212 | 2.8 | 160 | 0.7 | 2.4 |
| .000425 | 12.9 | 138 | 1.0 | 1.4 |
| .000850 | 40.2 | 138 | 1.9 | 1.0 |
| .00170 | 86.8 | 140 | 4.5 | 0.6 |
| .00255 | 92.6 | 140 | 6.8 | .... |
| .00383 | ...... | ...... | 9.3 | .... |
| .00510 | 97.4 | 140 | 12.1 | 0.2 |
| Sodium dodecyl benzene sulphonate: | | | | |
| .00150 CMC | 12.4 | 125 | 0.2 | 2.7 |
| .00760 | 83.6 | 164 | 1.7 | 0.2 |
| .0152 | 90.0 | 108 | 4.6 | 0.2 |
| .0230 | ...... | ...... | 7.0 | .... |
| .0304 | 92.3 | 9 | 10.3 | 0.2 |
| Nonyl phenyl triacontaethylene glycol ether: | | | | |
| .000275 CMC | 61.7 | 133 | 0.4 | 1.8 |
| .000550 | 78.7 | 140 | 1.2 | 1.8 |
| .000750 | 71.7 | 135 | 1.7 | 1.8 |
| .00110 | 76.3 | ...... | 2.6 | 1.8 |
| .00220 | 84.0 | 130 | 5.3 | 1.6 |
| .00325 | ...... | ...... | 7.3 | .... |
| .00440 | 84.1 | 130 | 9.3 | 1.6 |
| Nonyl phenyl eicosaethylene glycol ether: | | | | |
| .000155 CMC | 16.1 | 140 | 0.4 | 1.5 |
| .000310 | 25.6 | 140 | 0.8 | 0.7 |
| .000620 | 46.5 | 140 | 1.9 | 0.3 |
| .00124 | 89.6 | 125 | 3.7 | 0.3 |
| .00187 | ...... | ...... | 5.1 | .... |
| .00248 | 96.6 | 120 | 6.4 | 0.2 |
| Tridecyldodecaethylene glycol ether: | | | | |
| .000148 CMC | 3.1 | 140 | 0.4 | 4.5 |
| .000594 | 16.5 | 140 | 1.3 | 1.4 |
| .00237 | 81.2 | 120 | 4.7 | 0.2 |
| .00340 | 92.4 | 115 | 6.2 | 0.2 |
| .00510 | ...... | ...... | 8.2 | .... |
| .00680 | 98.8 | 125 | 10.2 | 0.2 |
| Tridecylpentadecaethylene glycol ether: | | | | |
| .000160 CMC | 6.7 | 140 | 0.5 | 2.7 |
| .000660 | 28.9 | 125 | 1.5 | 0.6 |
| .00264 | 77.7 | 125 | 4.9 | 0.2 |
| .00320 | 91.3 | 115 | 5.2 | 0.2 |
| .00480 | ...... | ...... | 7.5 | .... |
| .00640 | 96.0 | 115 | 9.3 | 0.2 |
| Nonyl phenyl tetracontaethylene glycol ether: | | | | |
| .000450 CMC | 79.5 | 125 | 0.8 | 1.4 |
| .000480 | 87.3 | 115 | 0.9 | 1.3 |
| .000662 | 91.5 | 103 | 1.4 | 1.3 |
| .00132 | 94.1 | 103 | 3.0 | 1.2 |
| Potassium laurate: | | | | |
| .0140 | 88.6 | 185 | 0.2 | 2.1 |
| .0150 | 95.0 | 183 | 0.2 | 1.9 |
| .0175 | 97.8 | 205 | 0.5 | 1.8 |
| .0233 CMC | 98.9 | 188 | 0.8 | 1.3 |
| .0280 | 99.2 | 109 | 1.1 | 0.8 |

TABLE II

Potassium Palmitate

| Surfactant molarity | % Removal glyceryl trioleate, at 180°F. |
|---|---|
| .00220 CMC | 77.7 |
| .00270 | 90.2 |
| .00306 | 96.7 |
| .00340 | 98.0 |
| .00540 | 98.1 |

2. *The CC-1 Point and (CC-1/CMC) Ratio–Glyceryl Trioleate Soil.* The surfactants represented in Figs. 1 and 2 as illustrating the leveling off of detergency at approximately 90% soil removal include an unsaturated fatty acid soap, a polyoxyethylene sorbitan monolaurate, two polyethenoxyethers of nonyl phenol (15 and 20 ethylene oxide mole ratios) and

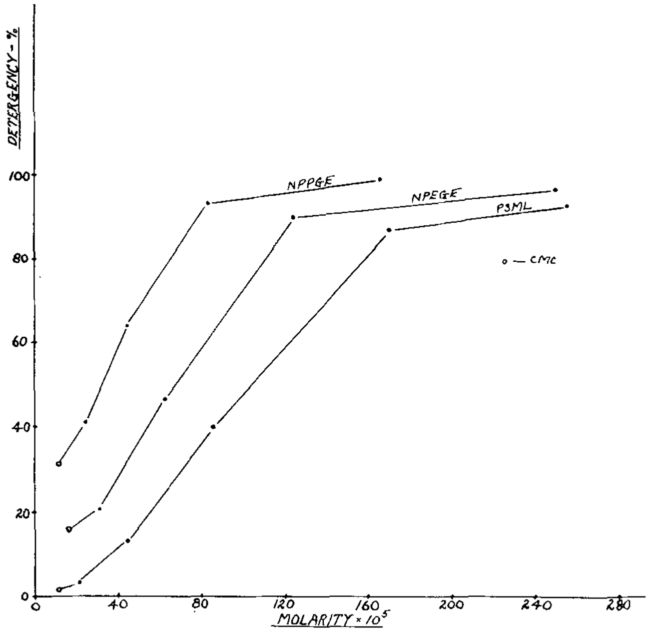

FIG. 1. Detergency-concentration curves, glyceryl trioleate soil.

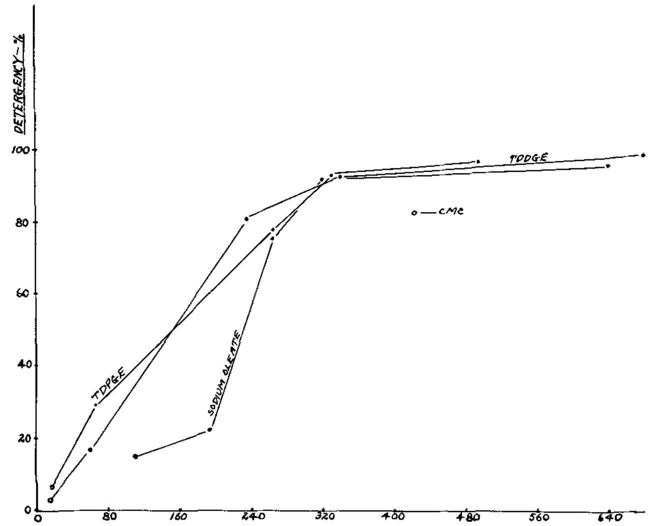

FIG. 2. Detergency-concentration curves, glyceryl trioleate soil.

two polyethenoxyethers of tridecyl alcohol (12 and 15 ethylene oxide mole ratios). Of the surfactants not shown in Figs. 1 and 2, an alkylaryl sulphonate (SDBS) and two additional analogs of the polyethenoxyethers of nonyl phenol (30 and 40 ethylene oxide mole ratios) exhibit similar leveling off of detergency at approximately 90% soil removal (glyceryl trioleate soil).

It seems therefore that the CC-1 point should play an important and practical role in the hard surface detergency testing and evaluation of syndets. In the past it has been customary to resort to questionable expedients in order to compare the intrinsic hard surface detersive abilities of syndets. Unrealistic solution temperatures, cleaning times, and solution concentrations, entirely unrelated to plant practice, have been utilized in test procedures designed to give detergencies considerably below the maxima of the syndets. Such practices have been necessary because a) quantitative cleanliness evaluation at or close to 100% detergency is a laborious and time-consuming operation; b) at or close to 100% detergency, cleanliness evaluation is not sensitive enough to changes in the operating parameters; c) it is difficult to differentiate between detersive efficiencies close to 100%. Thus while it has been necessary to compare syndets under conditions leading to considerably less than perfect cleaning, there should be a limit below which the test results are open to the criticism that they deviate too much from plant practice. Comparison of syndets at the CC-1 point appears to be the solution to this problem. At the 90% glyceryl trioleate soil removal point, detergency has begun to level off, and is no longer rising sharply with increase in concentration. Also, while 90% soil removal is an appreciable detergency, cleanliness evaluation at this level can be performed by the simple gravimetric method, as in this study. Realistic temperatures and cleaning times can be used; in addition there is a still more important advantage. If the CC-1 concentration of a surfactant is divided by its CMC, a multiple of the CMC is obtained. The value of this multiple or ratio (CC-1/CMC), appears to vary with surfactant type (for glyceryl trioleate soil). Table III shows that for glyceryl trioleate soil, the (CC-1/CMC) ratio is dependent on type of surfactant, and that analogs have approximately the same ratio.

TABLE III
CC-1/CMC Ratios

| Surfactant | CC-1/CMC |
|---|---|
| Nonyl phenyl pentadecaethylene glycol ether | 7.6 |
| Nonyl phenyl eicosaethylene glycol ether | 8.0 |
| Nonyl phenyl triacontaethylene glycol ether | 8.0 |
| Tridecyldodecaethylene glycol ether | 21.6 |
| Tridecylpentadecaethylene glycol ether | 19.4 |
| Polyoxyethylene sorbitan monolaurate | 20.3 |
| Sodium dodecyl benzene sulphonate | 10.1 |
| Sodium oleate | 2.9 |
| Potassium palmitate | 1.2 |
| Potassium laurate | 0.6 |

3. *Correlation of Detergency (Glyceryl Trioleate Soil) and Solubilization.* To determine the degree of correlation between detergency and micellar solubilization, these data were plotted for some of the surfactants investigated. Solubilizations corresponding to 95% detergency were read off the plots. The results are given in Table IV and indicate no correlation between hard surface detergency (glyceryl trioleate soil) and solubilization at 180°F. (Orange OT dye solubilization).

4. *Analog Correlation.* While no correlation was found between detergency and micellar solubiliza-

TABLE IV
Correlation of Detergency

| Surfactant | Micellar solubilization, mg. orange OT per 100 ml. solution, at 95% detergency |
|---|---|
| Nonyl phenyl pentadecaethylene glycol ether | 3.2 |
| Nonyl phenyl eicosaethylene glycol ether | 5.8 |
| Nonyl phenyl tetracontaethylene glycol ether | 3.7 |
| Tridecyldodecaethylene glycol ether | 7.7 |
| Tridecylpentadecaethylene glycol ether | 8.5 |
| Polyoxyethylene sorbitan monolaurate | 8.4 |
| Sodium oleate | 2.9 |
| Potassium laurate | 0.4 |

tion, several relationships were discovered in two series of analogs, the polyethenoxyethers of nonyl phenol and tridecyl alcohol. It was found that the ratio of the HLB (hydrophile-lipophile balance) values (21) of two analogs was equal approximately to the fifth root of the ratio of their CMC values. The correlation held with analogs varying by as much as 15 moles ethylene oxide (see Table V). It is interesting, but probably fortuitous, that a fifth root is involved in this relationship, because HLB values of nonionic surfactants of the two types being considered are computed by dividing their oxyethylene weight percentages by 5. A linear relationship was also found between HLB value and the reciprocal of the ethylene oxide mole ratio, R, (Figure 3), for the polyethenoxyethers of nonyl phenol. It is obvious that HLB would increase with increasing $C_2H_4O$ content, and therefore decrease with the reciprocal of increasing ethenoxy content. The equation for the nonyl phenols was computed to be:

$$\text{HLB} = 19.45 - \frac{66.8}{\text{R}}$$

TABLE V

Analog Correlation

| Surfactant | Ethylene oxide mole ratio | CMC molarity | HLB | HLB ratio | Fifth root CMC ratio |
|---|---|---|---|---|---|
| Polyethenoxyethers of tridecyl alcohol: | | | | | |
| TDDGE | 12 | .000148 | 14.5 | ...... | ...... |
| TDPGE | 15 | .000165 | 16.0 | 1.10 | 1.02 |
| Polyethenoxyethers of nonyl phenol: | | | | | |
| NPPGE | 15 | .000110 | 15.0 | ...... | ...... |
| NPEGE | 20 | .000155 | 16.0 | 1.07 | 1.07 |
| NPTGE | 30 | .000275 | 17.2 | 1.15 | 1.20 |
| NPTTGE | 40 | .000450 | 17.78 | 1.19 | 1.33 |

Notes:

(1) Ratio values are for example, in the second horizontal column for the second surfactant over the first; and in the third horizontal column for the third surfactant over the first.

(2) In following, representing the surfactants by subscripts indicating their ethylene oxide mole ratios:

$$\frac{\text{HLB}_{30}}{\text{HLB}_{20}} = 1.08 \text{ and } \left(\frac{\text{CMC}_{30}}{\text{CMC}_{20}}\right)^{1/5} = 1.12$$

$$\frac{\text{HLB}_{40}}{\text{HLB}_{30}} = 1.03 \text{ and } \left(\frac{\text{CMC}_{40}}{\text{CMC}_{30}}\right)^{1/5} = 1.10$$

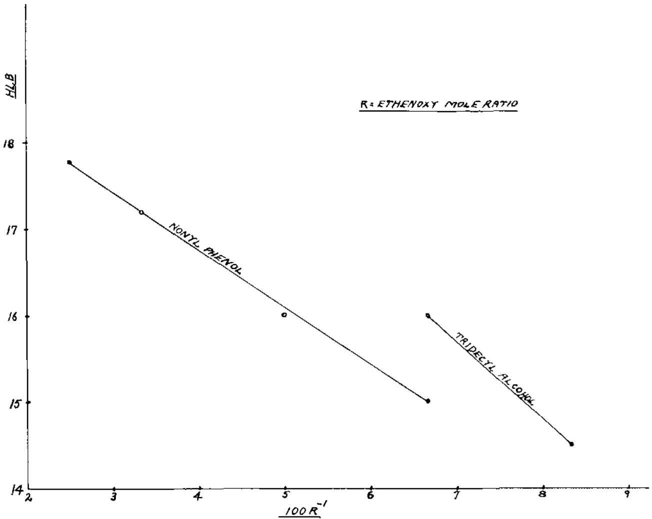

FIG. 3. HLB-Ethenoxy mole ratio function.

A further correlation can be obtained by combining the above equation with the equation of Hsiao *et al.* (16), between CMC and R for nonyl phenol analogs:

In (CMC) = 0.056 R + 3.87 (Hsiao *et al.*), if (CMC) is expressed in micromolar units.

The CMC-HLB function for the nonyl phenols then becomes:

$$\log \text{CMC} = \frac{1.68\ (20.42 - \text{HLB})}{19.45 - \text{HLB}}$$

5. *Detergency vs. Interfacial Tension and Suspending Power.* While the hard surface detergencies of most of the surfactants studied were rising sharply as the CMC values were passed, with maximum glyceryl trioleate soil removal still to be attained, the interfacial tension values were dropping rapidly. The latter had already attained a minimum in most cases on passing their 90% detergency points. Micellar solubilizations continued their sharp increase with increasing concentration in the 90 to 100% detergency range. Variation in suspendibility with increasing surfactant concentration, starting with the CMC in each case, was not considerable. However, all three types of nonionics investigated dropped slightly in suspending power from a maximum at the CMC. Sodium oleate solutions rose slightly in suspending power; and an alkylaryl sulphonate increased appreciably after passing the CMC, but fell off sharply at the CC-1 point. Sodium oleate solutions had the best suspending power values, about 1.5 times larger than the nonionics. It is of interest to note that the $Cr_2O_3$ powder used herein obviously possesses a lesser degree of hydrophilicity and/or a greater degree of specific adsorbability for nonionic molecules than the $MnO_2$ powder used in some of the classic suspending power investigations (22). Work at this laboratory has indicated that nonionic surfactants of the type studied herein do not suspend a hydrophilic powder like $MnO_2$ but are excellent suspenders of oleophilic powders.

6. *Hard Surface Detergency–Acid Soils.* Figures 4, 5, 6, and 8 show graphically the results of similar hard surface detergency tests using octanoic acid and oleic acid soils. Octanoic acid has been described previously (6), and the oleic acid was USP grade. As with the

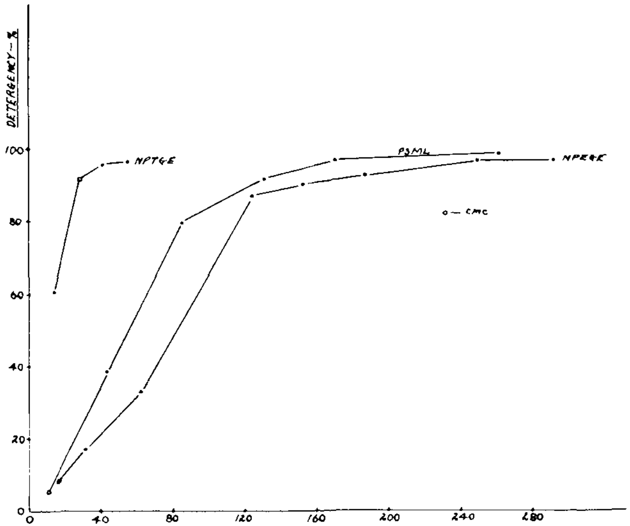

FIG. 4. Detergency curves, oleic acid soil.

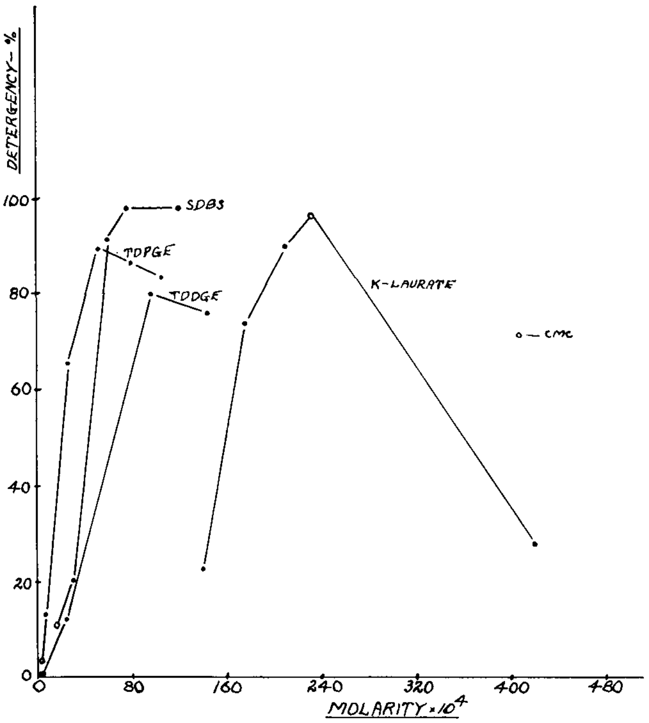

FIG. 5. Detergency curves, oleic acid soil.

glyceryl trioleate soil, a preponderance of evidence was obtained that CMC does not coincide with maximum hard surface detergency using oleic acid or octanoic acid soils. The reverse was true only with the potassium laurate-oleic acid system (as in the case of the potassium laurate-glyceryl trioleate system). Harris (23) and others (24,25) have also found that maximum hard surface detergency is attained at concentrations considerably greater than the CMC.

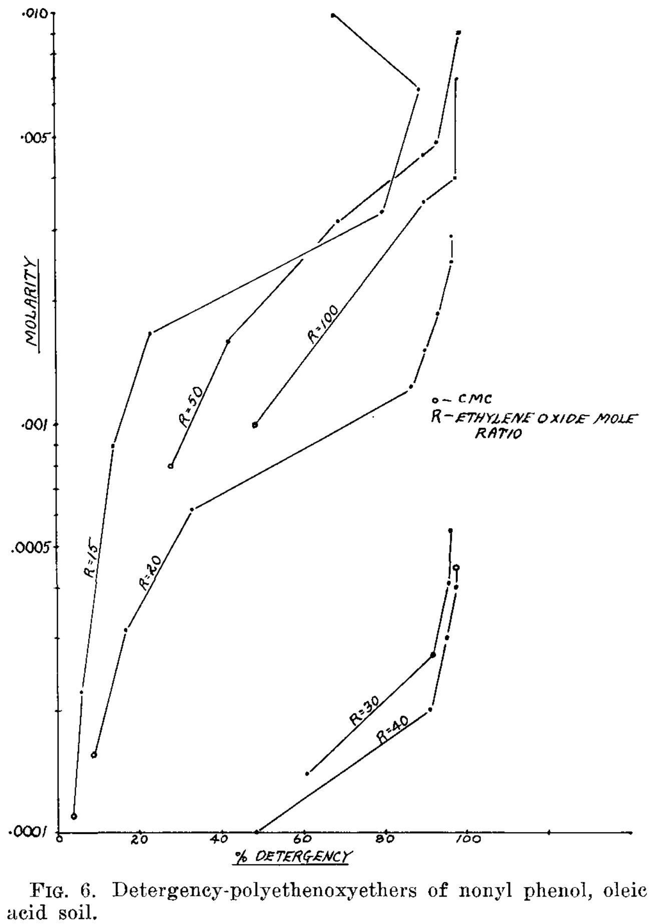

FIG. 6. Detergency-polyethenoxyethers of nonyl phenol, oleic acid soil.

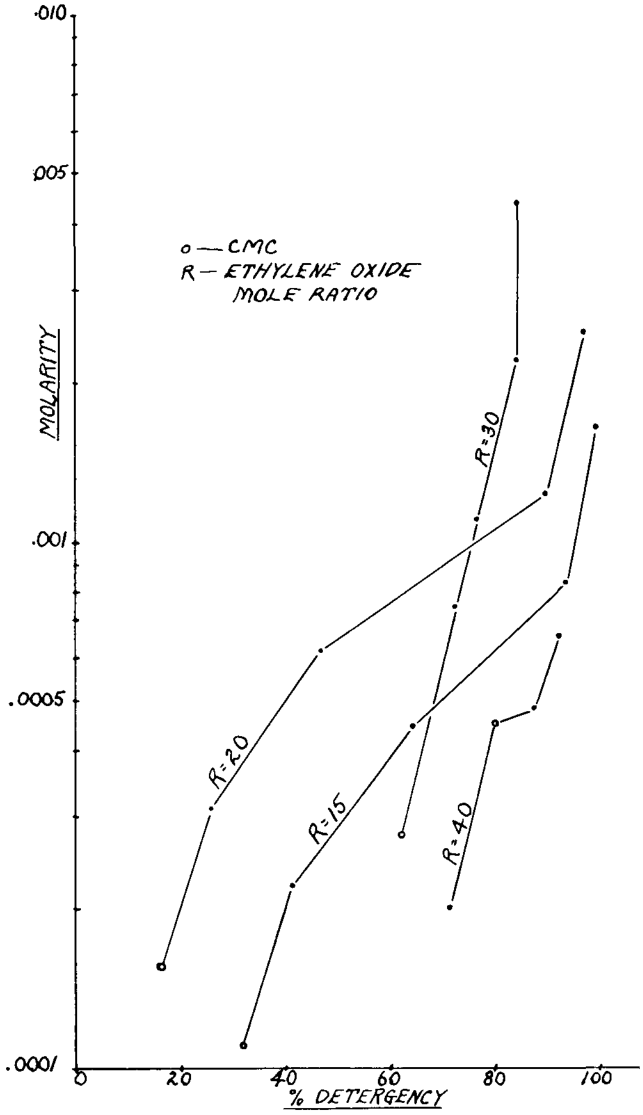

FIG. 7. Detergency-polyethenoxyethers of nonyl plenol, glyceryl trioleate soil.

Appreciable differences in hard surface detergency were obtained with the glyceryl trioleate and oleic acid soils when using the two polyethenoxyethers of tridecyl alcohol and sodium oleate soap. The detergency-concentration function of the tridecyl alcohol analogs with glyceryl trioleate soil increased sharply to about 90% soil removal and then leveled off while approaching 100%. With oleic acid soil the function of the homolog with an ethylene oxide mole ratio of 15 rose sharply to a maximum of about 90% detergency and then dropped sharply; the function of the homolog with the 12 ethylene oxide mole ratio rose sharply to about 80% soil removal and then decreased sharply. The detergency-concentration function for sodium oleate with glyceryl trioleate soil also conformed to the pattern of sharp rise to about 90% detergency followed by a leveling off approaching

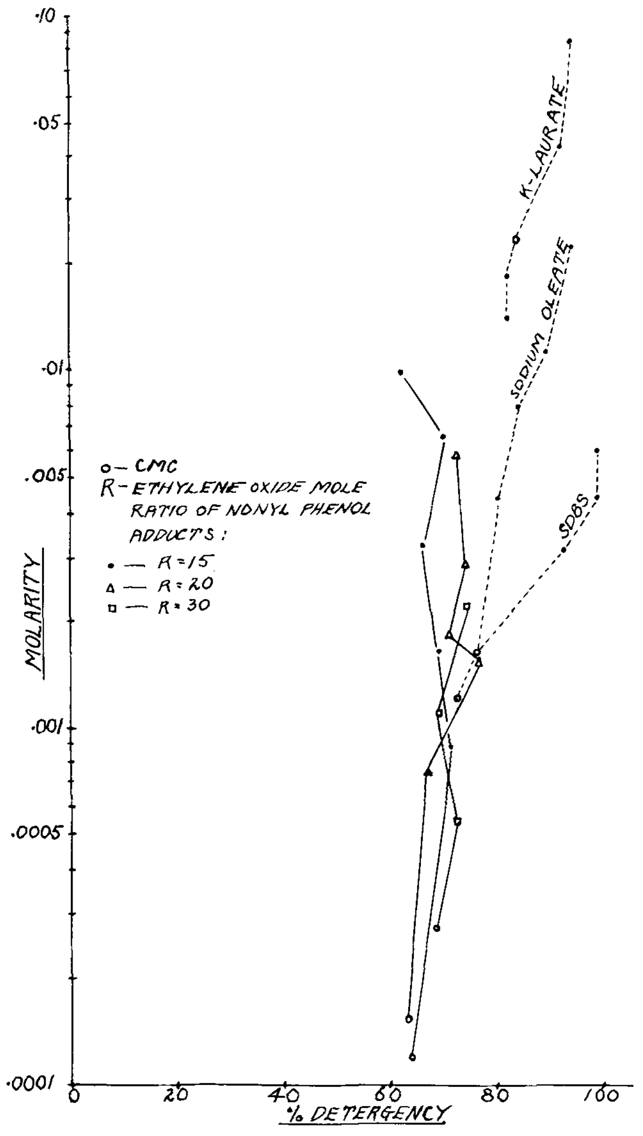

FIG. 8. Detergency, octanoic acid soil.

100% soil removal. However, no detergency-concentration function was obtained for the sodium oleate-oleic acid system. Zero soil removal was obtained at the CMC, with as much as 20% more residual soil found at higher concentrations (0.046M) than was on the test panels originally.

Hard surface detergencies of octanoic acid systems showed appreciable differences from oleic acid systems (Figure 8). Detergencies of the polyethenoxyethers of nonyl phenol (15, 20 and 30 ethylene oxide mole ratios) using octanoic acid soil did not exceed 75%, while removal of oleic acid attained 90 to 100%. The detergency-concentration function for the sodium oleate-octanoic acid system reached about 94%, while that of the sodium oleate-oleic acid system was negative (more residual soil than original weight on test panels). In the potassium laurate-octanoic acid system, maximum detergency did not occur at the CMC, and detergency did not decrease after reaching the CMC as with oleic acid soil.

Visual observation of the hard surface cleaning of the various surfactant-soil systems has suggested a partial answer for the differences in soil removal obtained. Removal of glyceryl trioleate soil by both the anionic and nonionic syndets appeared to be due principally to a displacement action through preferential wetting of the steel basis metal, the soil film being progressively divided into smaller and smaller areas until the latter became small droplets that detached themselves from the test panel and rose to the surface of the cleaning solution. The removal of octanoic acid soil by the nonionic surfactants was obviously by a different action. A few moments after the immersion of an octanoic acid-soil test panel in a cleaning solution, clouds of very small, milky particles could be observed diffusing away from the test panel. It is suggested that the detergent mechanism in such cases was primarily a micellar solubilization of the acid soil followed by emulsification, and finally by precipitation of the acid in the form of discrete particles (8).

7. *CMC and Physicochemical Factors.* No significant changes in micellar solubilization or interfacial tension were observed at the CMC. On passing the CMC with increasing concentration, solubilization increased sharply and interfacial tension dropped rapidly. Detergency leveled off at about the 90% soil removal point (glyceryl trioleate soil), but solubilization continued to rise sharply. While three types of nonionic surfactants showed maximum suspendibility at the CMC, decreasing thereafter in this factor with increasing concentration, these decreases as well as the increases occurring with two types of anionic surfactants were not considered substantial enough to permit the conclusion that an outstanding change in suspending power had occurred at the CMC. It could be stated that suspending power had attained a minimum for most of the nonionic surfactants at the 90% soil removal point (glyceryl trioleate soil).

## Acknowledgment

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