SURFACTANTS FROM ETHOXYLATED

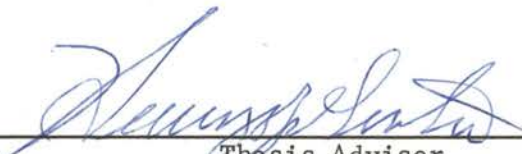HYDROXYLATED SPERM OIL

By

TED PAUL MATSON

Bachelor of Science
University of Oklahoma
Norman, Oklahoma
1949

Master of Education
University of Oklahoma
Norman, Oklahoma
1951

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of the Oklahoma State University
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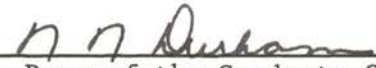
HYDROXYLATED SPERM OIL

Thesis Approved:

_____
Thesis Adviser

_____

_____

_____
Dean of the Graduate College

PREFACE

Sperm oil is an economical, readily available raw material which has historically been utilized in the detergent area. Soaps as well as natural fatty acids and alcohol derivatives have been partially replaced in the surfactant market by synthetically derived materials. The ethoxylated hydroxylated oils would have a relatively high molecular weight and thus could prove interesting in the utilization of these raw materials if they proved to have unusual detergent properties.

The purpose of this study is to cursorily explore the possibility of making surfactants with unusual properties by hydroxylation and ethoxylation of sperm oil, which includes the feasibility of sperm oil hydroxylation as well as the evaluation of resultant products.

Indebtedness is acknowledged to Dr. H. P. Johnston, Oklahoma State University, for his valuable guidance and patient understanding; and to D. R. Weimer, Continental Oil Company, for his advice and counsel; to Mrs. Doris Berry, Ponca City, Oklahoma, for help in preparation of the manuscript; and to Mrs. Ted P. Matson for her insistent nudging.

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INTRODUCTION

Sperm whale oil has been used in many applications. Before the discovery of petroleum it was used primarily as a lamp fuel. Today sperm oil is used in cutting oils, machinery lubricants, textiles, and leather processing. Sulfonated sperm oils are used in transmission lubricants. Alcohols and acids separated from the oil are being utilized in many industrial applications.

The purpose of this study was to evaluate some of the surfactant properties of ethoxylated hydroxylated sperm oil. The oil is a readily available, economical raw material which can be made susceptible to ethoxylation by hydroxylation across the double bonds. This gives active hydrogen sites for adding hydrophilicity and increased surface activity by ethoxylation. The feasibility and relative degree of these reactions are of prime concern in obtaining useful products for evaluation.

HISTORICAL

Sperm Oil

Sperm oil is a complex mixture of triglycerides and waxes, the esters being made up of both saturated and unsaturated alcohols and fatty acids. Many early investigators characterized the alcohols obtained from sperm oil (1,2,3,4). Ueno (5) reported the presence of several lower molecular weight alcohols. Tsujimoto (6) isolated the first unsaturated alcohol from sperm oil. Toyama and Akiyama (7) noted the occurrence of polyunsaturated alcohols in the blubber oil. Hofstadter (8) first detected glycerine in sperm oil indicating the presence of triglycerides. Other investigators made studies of the saturated and unsaturated fatty acid constituents (9,10,11). This cursory review of the early analytical background work done on sperm oil shows that it is a very complex mixture.

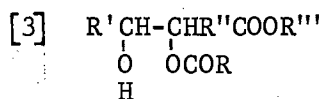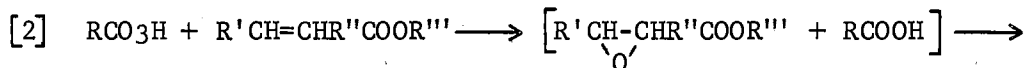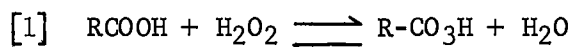The work in this study was done on raw 45° sperm oil. Owing to the complex nature of raw material the primary purpose was to see if the theoretically possible reactions will take place to a sufficient degree to result in surfactant materials of commercial interest.

Hydroxylation

Hydroxylation of fatty materials can be accomplished by the addition of hydrogen peroxide or peracids (12,13). The use of hydrogen

peroxide generally requires either large excesses of peroxide or additional reactants (14).

Swern et al. (15,16,17,18) have shown that by careful selection of the reaction conditions and the peracid the extent of glycol and epoxy derivatives can be controlled. Swern (19) reviews the subject of oxidation by peracids and has found that the use of 1% sulfuric acid with peracetic acid eliminates the formation of epoxy compounds and results in excellent yields of hydroxy-acetoxy compounds. Omission of the sulfuric acid results in good yields of the epoxy derivatives. If performic acid is used, quantitative yields of hydroxy-formoxy compounds are obtained without the use of sulfuric acid (15). The reactions involved are:

[1] $RCOOH + H_2O_2 \rightleftharpoons R\text{-}CO_3H + H_2O$

[2] $RCO_3H + R'CH=CHR''COOR''' \longrightarrow \left[R'\underset{\diagdown O \diagup}{CH\text{-}CH}R''COOR''' + RCOOH \right] \longrightarrow$

[3] $R'\underset{\underset{H}{O}\quad OCOR}{CH\text{-}CH}R''COOR'''$

In [1] above the peracid is formed. Though this is a reversible reaction it will go to completion if the peracid is allowed to react as formed in situ with the unsaturated compound. By using formic acid or by using 1% sulfuric acid with acetic acid the epoxy intermediate reacts to result in the hydroxylated compound in [3]. By heating for one hour at 100°C with an excess of 3N aqueous sodium hydroxide the glycol could be obtained as below (15):

$$R'\underset{\underset{H}{O}\quad OCOR}{CH\text{-}CH}R''COOR''' + H_2O \xrightarrow[NaOH]{\Delta} R'\underset{\underset{H}{O}\quad \underset{H}{O}}{CH\text{-}CH}R''COOR''' + RCOOH$$
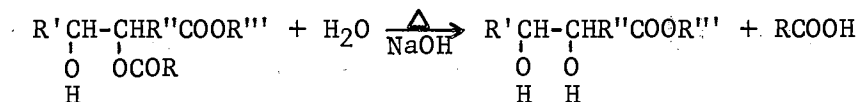
Swern et al. (15) have shown that this reaction using formic acid is so nearly complete that only 1.025 moles of H_2O_2 are required for each mole of unsaturation oxidized to the glycol. They have given analyses indicating degree of completion of the reaction applied to oleic acid, oleyl alcohol, and methyl ricinoleate.

The glycols of sperm oil were prepared by Severson and Johnston (20). This reaction was carried out by combining 176 grams of sperm oil, 648 ml glacial acetic acid, 6 grams of sulfuric acid and 88 grams of 30% hydrogen peroxide at a temperature of $40^{\circ}C$. The reaction was continued for 12 hours after which the crude product was washed and then saponified to the glycol. No attempt was made to stop at the hydroxy-acetoxy product, nor were any reactions carried out with performic acid.

Ethoxylation

Ethoxylation of active hydrogens by reaction with ethylene oxide has been known for some time and has been extensively done commercially for many years to obtain surface-active agents. The ethoxylation of alcohol was first reported in 1926 by I. G. Farbenindustrie (21), who condensed methanol, ethanol, and propanol in the presence of acidic and basic catalysts. Later, in 1934, Schoeller and Wittwer (22) successfully condensed octadecyl alcohol with ethylene oxide. In addition to alcohols, nonionic surfactants have also been made by the ethoxylation of alkylphenols, tall oils, fatty acids, amides, amines, and mercaptans (23).

Karabinos and co-workers (24,25) have outlined the procedure for this ethoxylation. Their ideas along with suggestions from companies

doing ethoxylation on a commercial scale (26,27) were utilized in lab-
oratory preparation in glass equipment for this study. This procedure
is given below.

A round-bottom, creased, Morton flask is fitted with a stirrer,
condenser, thermometer, and gas-dispersion thimble. The condenser is
connected through a safety bottle to a graduated cylinder containing
enough white oil to keep a hydrostatic head equivalent to 2.5 cm. Hg.
The gas-dispersion thimble is joined to a manifold connected to low
pressure nitrogen and a tank of ethylene oxide. The alcohol is charged
to the flask followed by 0.3 per cent powdered sodium hydroxide. The
flask and contents are then weighed. A slow stream of nitrogen is
started through the alcohol and the temperature raised to 150 to 160°C
by means of a glass-insulated heating mantle. Ethylene oxide gas is
admitted to the manifold and allowed to escape momentarily through a
three-way stopcock. The three-way stopcock is then turned to vent the
nitrogen to the atmosphere, and the ethylene oxide is simultaneously
introduced into the flask. This reaction should be carried out in a
well-ventilated hood and away from free flames.

Absorption takes place with a rise in temperature. The ethylene
oxide rate is increased to a point where an occasional bubble escapes
through the white oil. The temperature is permitted to rise to 180 to
220°C and is maintained within this range until the required amount of
ethylene oxide has been absorbed. The approximate extent of absorption
can be followed by keeping a weight balance on the ethylene oxide tank.
In shutting down, the ethylene oxide is vented to the air, and the
nitrogen is led into the flask and a slow stream bubbled through the
adduct until all of the ethylene oxide has been purged from the system.

The flask and contents are then weighed to determine the exact amount of ethylene oxide absorbed.

The free alkali is neutralized with either phosphoric or glacial acetic acid to a phenolphthalein end point (external indicator). A picture of the apparatus described above is given on the following page.

Basic catalysts generally used include sodium hydroxide, sodium ethoxide, sodium methoxide and potassium hydroxide. A study on catalyst effect (28) shows that the rate of addition of ethylene oxide is practically the same at 195-200°C for all of these catalysts.

The proposed mechanism for the polyethoxylation of alcohols has been given by Satkowski and Hsu (28) as:

1. $ROH + NaOH \rightleftharpoons RONa + HOH$

2. $RONa \rightleftharpoons RO^- + Na^+$

3. $RO^- + nCH_2\text{-}CH_2 \longrightarrow R(OCH_2CH_2)_nO^-$
   \O/
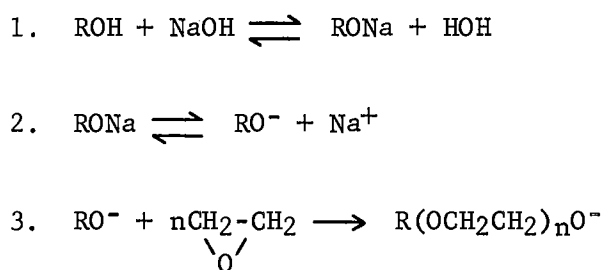
The product obtained from this reaction is a mixture of monoalkyl-poly(ethylene glycol) ethers containing various numbers of oxyethylene units. Karabinos & Quinn (29) have reported that the amount of the various ethers closely follows the Poisson distribution law. More recently investigators (30,31,32) have proven that the ethoxylation of alcohols, unlike phenols and acids, does not follow the Poisson distribution.

Potassium carbonate catalyst has been reported (23) for use when ethoxylating fatty acids. The most common acid catalyst used is boron
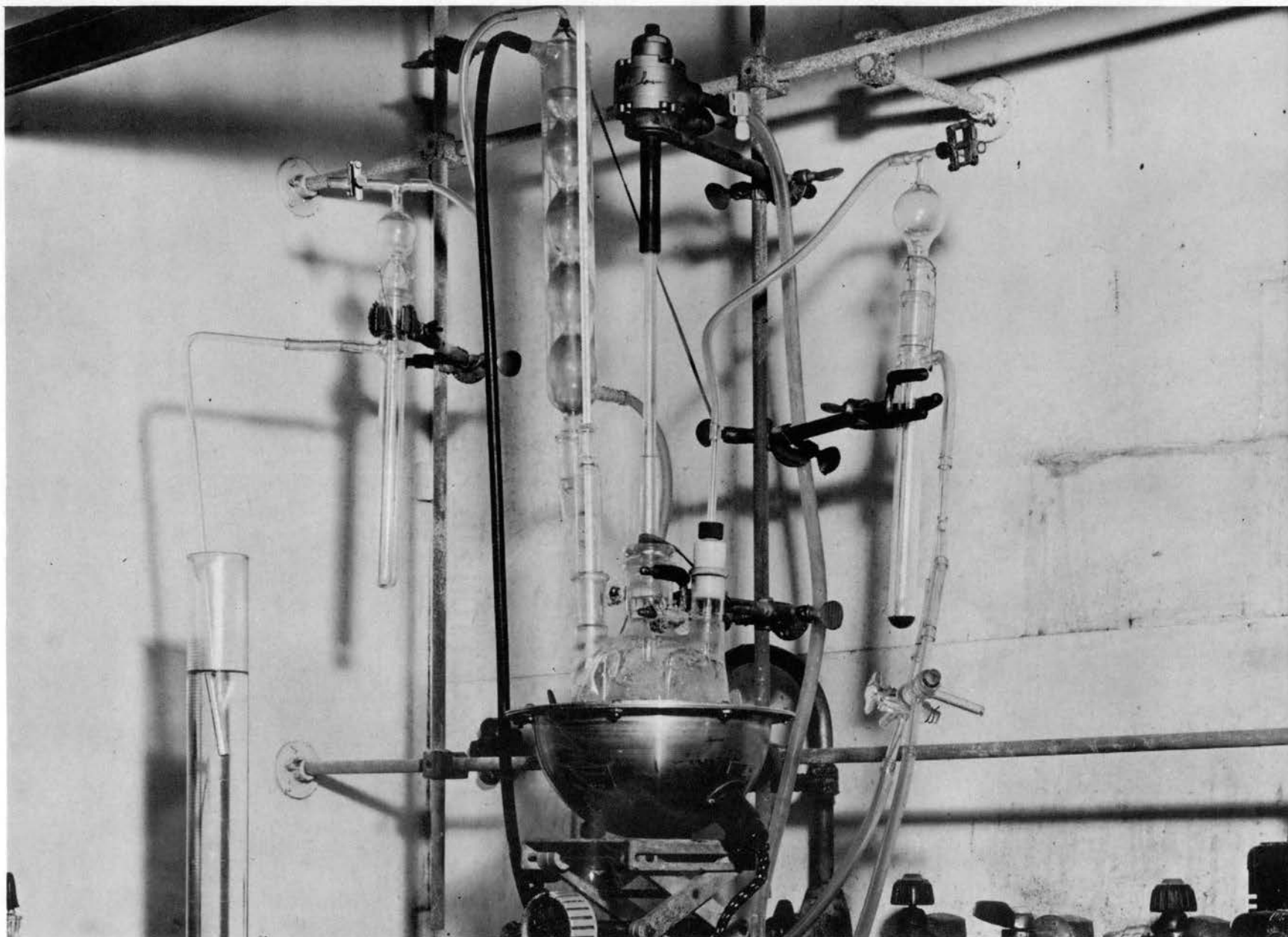
Figure 1. Laboratory Ethoxylation Apparatus

trifluoride. Drew and Schaeffer (33) explain that industrially an
alkaline catalyst is preferred because it lessens the by-product
content. With BF_3 they found that the yield of the desired product
diminishes and that of the by-product increases with increasing ethyl-
ene oxide. Thus at 20 moles of ethylene oxide they reported that side
reactions eventually account for more than half of the total product.
In sodium hydroxide-catalyzed reactions water from all sources exactly
accounted for the amount of polyethylene glycol observed, but in boron
trifluoride reactions it accounted for only 7% of the polyethylene
glycol.

Ethoxylations of hydroxy and dihydroxystearic acids are reported
by Wrigley et al. (23) with good surface active properties.

Work has been done in this field (24,25) to determine the effect
of molecular weight and ethoxy chain length upon surfactant properties.
Matson (34) has shown that for different molecular weight alcohols the
optimum heavy duty detergency is obtained at about 60% ethylene oxide
content. He has also indicated (35) that at typical United States
washing conditions optimum detergency is obtained with an alkyl chain
length of C_{12} to C_{15} with 54 to 62 per cent ethylene oxide. At the
higher use temperatures of Europe, Matson (36) has shown that the op-
timum molecular weight increases to include carbon chain lengths up to
C_{17}.

EXPERIMENTAL

Sperm Oil

The 45° sperm oil used for this study had the following constants
as determined by Severson (20):

Saponification Value	141
Acid Number	2.6
Iodine Number	85.0
Per Cent Hydroxyl Groups	0.097

Hydroxylation

The procedure for the hydroxylation sperm oil is approximately
that which Swern et al. (15) used for hydroxyformylation of monounsat-
urated compounds including acids, alcohols, and esters. A compilation
of their experimentation indicated the use of 1.025 moles of hydrogen
peroxide per mole of unsaturation and approximately 23 moles of formic
acid, which is about thirty times the weight of hydrogen peroxide.

An example of early hydroxylations attempted in this study follows:
One hundred grams of sperm oil (0.335 mole of double bond) along with
350 grams of formic acid were added to a three-neck, creased, round-
bottom, one-liter flask. To this stirred mixture was added dropwise
39.4 grams of 29.6% hydrogen peroxide through a dropping funnel, the
temperature being maintained at 40°C by the use of a heating mantle

equipped with a Variac. One-gram samples were taken after 3, $3\frac{1}{2}$, 4,

$4\frac{1}{2}$, and 5 hours and tested with both potassium iodide-starch test paper

and "Clinistix" reagent strips for remaining peroxide. The samples

were later analyzed for remaining peroxide by the test method given in

Appendix B.

The final reaction mixture was poured into cold water and extract-

ed with ether. This process took many washings with a large excess of

water. Evaporation of the water-washed ether layer yielded the hydrox-

ylated product, which was labelled TM-1-4-13. If the structure of

whale oil for illustrative purposes is generalized as the ester shown

below, the reaction would be primarily as follows:

$$R'C=CR''C\overset{O}{\underset{OR'''}{\diagup}} + HC\overset{O}{\underset{OH}{\diagup}} + H_2O_2 \longrightarrow R'C-CR''C\overset{O}{\underset{OR'''}{\diagup}}$$
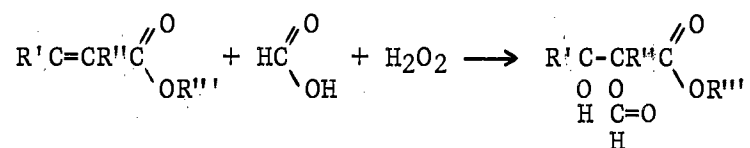
Per cent hydroxyl analyses were run on the reaction product as

well as on the original sperm oil by the method of Ogg et al. (37).

Iodine numbers were run on both the reaction product and the orig-

inal sperm oil by the standard method (38).

Large-scale hydroxylation was done by the same method. Sperm oil

(857.6 grams) was mixed with 3000 grams of formic acid in a five-liter

flask, and 320 grams of 30.0% hydrogen peroxide was added dropwise

with stirring at 40°C. The reaction was continued for eleven hours,

after which the reaction mixture was poured into cold water. Attempts

to extract with ether gave very bad emulsion problems. The extraction

mixture was divided into smaller portions and washed and re-washed many

times with large excesses of water. The water-washed ether layer was

evaporated to obtain sample No. TM-1-14. Only 772 grams of hydroxylated product was obtained.

Ethoxylation

Attempts at ethoxylation in glassware were made by the method given earlier in the Historical section of this paper. This procedure results in a pressure of about 0.48 psig. The dip tube on the vent line submerged in a cylinder of mineral oil creates a hydrostatic head not exceeding 2.5 cm of mercury. The reactions carried out in this manner were much too slow and therefore pressure apparatus was used.

A diagram of the pressure equipment is given in Figure 2.

The hydroxylated oil and catalyst were charged to the autoclave through the liquid charge line. Air was purged from the system with nitrogen. The autoclave was then evacuated to remove the nitrogen. The oil and catalyst were heated to reaction temperature and ethylene oxide addition was started. The addition of the ethylene oxide was controlled by pressure demand through a research control valve equipped with a Foxboro Controller which was set at the desired reaction pressure. When the required amount of ethylene oxide had been added, as measured by the weight loss of the ethylene oxide container suspended on a Baldwin strain cell, the addition was stopped. The digital read-out of the Baldwin strain cell gave readings to the nearest 2/1000 of a pound. The reactor contents were post-stirred until essentially all of the ethylene oxide had reacted. The end of the reaction was determined by a drop in pressure to a constant level. The autoclave and reaction product were then cooled by running cold water through the cooling coils. In most cases the autoclave was under vacuum after cooling.

DIGITAL READ-OUT

FOXBORO CONTROLLER

TO VACUUM OR NITROGEN

STIRRER MOTOR

CONTROL VALVE

ASHCROFT TRANSMITTER

H₂O IN

BALDWIN STRAIN CELL

T.C.

H₂O OUT

LIQUID CHARGE LINE

PRESSURE CONTROLLED RESEARCH CONTROL VALVE

120 PSIG N₂

N₂

EO

THERMOCOUPLE

COOLING COIL

EO CHARGE LINE

ETHYLENE OXIDE STORAGE CYLINDER

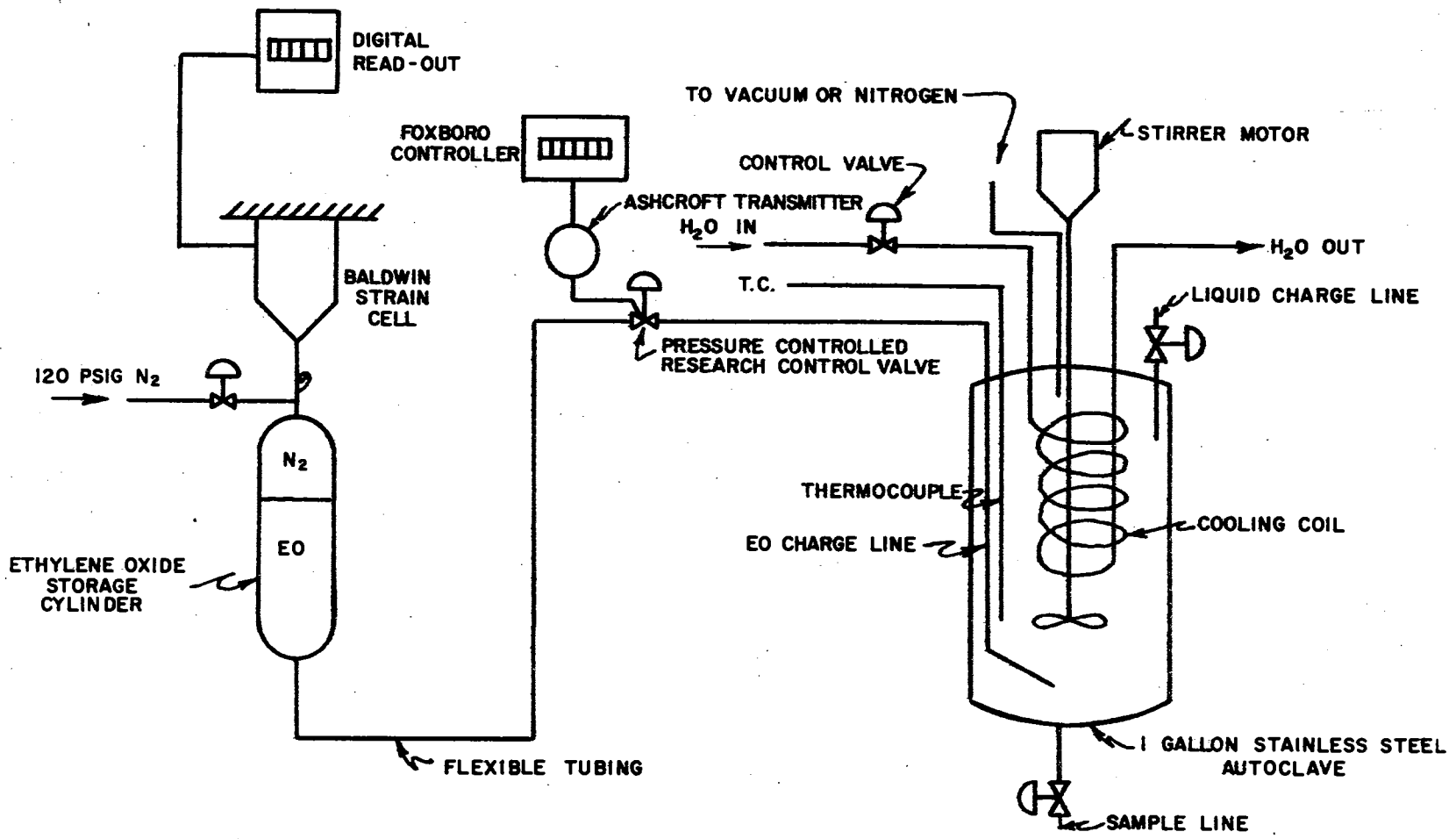1 GALLON STAINLESS STEEL AUTOCLAVE

FLEXIBLE TUBING

SAMPLE LINE

FIGURE 2 ETHOXYLATION PRESSURE EQUIPMENT

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The product was removed from the autoclave through the bottom sample line and weighed as a secondary check on the weight of ethylene oxide added.

The first ethoxylation was a one-shot attempt to make a 60% ethylene oxide adduct. This reaction was carried out at 180-200°C using 0.15% NaOH catalyst at pressures of 10 to 20 psig. Only 50% ethylene oxide addition was reached. This 50% adduct was labelled TM-1-9 and its surface active properties evaluated. Wetting tests, Krafft point, and detergency tests were run on TM-1-9.

Owing to the lack of complete reaction with a basic catalyst, another attempt at ethoxylation was made using an acid catalyst. For this reaction 0.3% BF_3 was used as the catalyst. The procedure is as shown above with the reaction carried out on a charge of 500 grams of TM-1-14 hydroxylated product at 180-210°C and pressures of 12 to 42 psig. Table I on the following page gives a sample run sheet of this particular reaction and shows the actual progress of the ethoxylation. Approximately 50-gram samples were to be taken at 5% ethylene oxide intervals between 20% and 80% inclusively. The first three samples were obtained in forty minutes total reaction time. The fourth portion took 2½ hours to react and the fifth took over 3½ hours. Therefore the reaction was stopped after obtaining samples only containing up to 40% ethylene oxide. Table II shows the finished calculated weight of the five samples obtained.

Special Ethoxylation

During the conduct of this study after only fifty per cent adduction was obtained on the NaOH-catalyzed ethoxylation of the hydroxylated

TABLE I

ETHOXYLATION OF SAMPLE NO. TM-1-14

charge   500 grams

catalyst 1.5 grams BF_3

Time	Temp., °C	Pressure psig	Balance Reading	Comments	Sample No.	Weight
9:38 A.M.	194	12	3197	start E.O.*		
9:43	206	21	3150			
9:49	200	26	3072	stop E.O.	1	50.2
9:53	210	14	3072	start E.O.		
10:01	203	27	3033	stop E.O.	2	50.0
10:10	199	14	3033	start E.O.		
10:18	196	30	2993	stop E.O.	3	51.0
10:44	190	16	2993	start E.O.		
10:47	190	42	2950	stop E.O.		
11:35	200	26	2950			
12:48 P.M.	190	14	2950		4	53.0
12:51	180	14	2950	start E.O.		
2:00	200	32	2905	stop E.O.		
4:00	200	22	2905			
8:00	90	14	2905		5	612.7

* E.O. = ethylene oxide

TABLE II

ETHYLENE OXIDE CONTENTS OF BF_3-CATALYZED
ETHOXYLATION PRODUCTS

Sample No.	Proposed E.O.* Content	Actual E.O. Content
TM-1-19-1	20%	20.0%
TM-1-19-2	25%	25.1%
TM-1-19-3	30%	30.1%
TM-1-19-4	35%	35.1%
TM-1-19-5	40%	40.0%

* E.O. = ethylene oxide

product it was decided to try a "one-shot" combination saponification and ethoxylation of the sperm oil itself. This was to be attempted by adding a stoichiometric amount of sodium hydroxide to effect de-esterification and immediately ethoxylating to 60% ethylene oxide.

To carry out this experiment 45 grams of sperm oil was charged to a small ethoxylation cell along with 4.54 grams of sodium hydroxide, and 82.5 grams of ethylene oxide was added slowly at 177 to 216°C in order to result in an adduct containing 62.5% ethylene oxide. Table III is a reproduction of the run sheet for this reaction.

The sample was labelled TM-1-7 and was evaluated for detergency properties. Before further tests and evaluations recent Japanese work (39) along the same lines was discovered and this line of promising work was regretfully abandoned.

Surfactant Evaluations

For most commercial detergent uses the main properties considered in evaluating surfactant raw materials are wetting ability, detergency, and foaming properties (23,34,35,36). Jay Harris gives an excellent review of contemporary screening tests and evaluation techniques in his book, "Detergency Evaluation and Testing" (40). Surface tension and emulsification are sometimes included but the former has little concrete relation to detergent performance and emulsification ability is of prime use when evaluating emulsifiers for a specific system.

As stated earlier, sample TM-1-9 was evaluated for wetting properties, Krafft point, and detergency.

Wetting was evaluated by the Draves-Clarkson (41) skein test. A revised procedure by which these evaluations were run is given in

TABLE III

SIMULTANEOUS SAPONIFICATION AND ETHOXYLATION

Charge: 45 grams sperm oil
           4.54 grams NaOH
           82.5 grams ethylene oxide (E.O.)

Time	Temp., °C	Pressure, psig	Comments
10:15	177	negative	on temp.
10:30	175	negative	start E.O.
10:35	180	25	
10:40	191	25	
10:45	210	0	
10:50	216	10	reaction extremely hot - hard to control
10:55	200	10	
11:00	140	10	over-cooled trying to control
11:03	219	10	
11:06	199	5	
11:09	204	12	
11:12	182	5	
11:14	166	20	E.O. in
11:25	199	20	
11:35	207	20	shut down

Appendix A. This procedure basically calls for measurement of the time necessary for a cotton skein to become wetted by a solution causing the skein to sink. Replicate runs are made and normally sinking time in seconds is plotted versus concentration of wetting agent in order to determine the concentration necessary to effect a certain wetting time. The following results were obtained with TM-1-9:

TABLE IV

WETTING PROPERTIES OF TM-1-9

| Concentration | Wetting Time (in sec.) | |
	24°C	60°C
0.05%	indeterminate	-
0.10%	indeterminate	-
0.20%	indeterminate	-
0.50%	indeterminate	125
0.55%	indeterminate	106
0.60%	indeterminate	98
1.00%	180	41

The Krafft point (42) is a useful tool in measuring the relative solubility of nonionic surfactants. Adducts which contain more than five moles of ethylene oxide are usually water-soluble at a one per cent concentration. Krafft point may be defined as the temperature at which a one per cent solution of an ethoxylate clouds when heated. The nonionic ethoxylates are more soluble in cold water than in hot and thus show decreasing solubility as the solution is heated, finally forming a cloud at the point of insolubility.

The actual test is a modification which gives more reproducible results. It is run by adding one milliliter of the adduct to 100 ml of distilled water at room temperature. This solution is placed in a jacketed test tube and heated in an oil bath until a heavy cloud is produced. The tube is removed from the bath and stirred with a thermometer until the solution clears sufficiently that the mercury thread of the thermometer may be seen through the solution. This point is recorded as the Krafft point; it was found to be $60^{\circ}C$ for TM-1-9.

The method for evaluating cotton detergency is given in Appendix A. This test is run in the Terg-O-Tometer, which in essence is a bench-scale washing machine consisting of a bank of four small agitator washers in 2-liter beakers. The speed of rotation of the agitators is adjustable. A water bath with built in heater allows for temperature control.

The reflectances of standard soiled cloths are measured before washing. After putting the cloths through washing, rinsing, drying and ironing operations the reflectances of the washed cloths are read. The difference in reflectance between the washed and unwashed cloths is a measure of the detergency of the test solutions. Three swatches each of three different soiled cloths are evaluated in each pot. This gives a more realistic evaluation of the true detergent properties since each cloth is sensitive to different types of surfactants.

Detergency tests were run comparing sample TM-1-9 with a commercially available nonionic, ALFONIC® 1218-6 nonionic, from Continental Oil Company. These two nonionics were evaluated by the Terg-O-Tometer detergency method at $49^{\circ}C$, 100 rpm, and at 50 and 300 ppm hardness. The detergent formulation contained 20% active TM-1-9, 35% sodium

tripolyphosphate, 5% sodium metasilicate, 30% sodium sulfate and 1%
sodium carboxymethylcellulose with the total detergent concentration
being 0.2%. The results are found in Table V with the least signifi-
cant difference (LSD) given for each cloth.

Sample TM-1-7, obtained from the simultaneous de-esterification
and ethoxylation of sperm oil, was evaluated for detergency compared
with ALFONIC® 1218-6 nonionic by the Terg-O-Tometer test at 49°C in a
formulation containing 10% nonionic surfactant, 50% sodium tripolyphos-
phate, 5% sodium metasilicate, 15% sodium sulfate and 10% water. The
results of this evaluation are given in Table VI.

Analytical Methods

Hydroxyl analyses were run by the method of Ogg, Porter, and
Willits (37). The procedure involves treating with excess acetic an-
hydride in the presence of p-toluenesulfonic acid. The excess acetic
anhydride is hydrolyzed, and the acetic acid is titrated with standard
sodium hydroxide. A blank is determined by hydrolyzing and titrating
an equivalent amount of acetylating reagent. The hydroxyl content is
calculated from the difference between the two titrations and expressed
as per cent hydroxyl.

Iodine number was done by the Wijs method (38). The sample is
weighed into carbon tetrachloride, Wijs solution is added and the flask
allowed to stand in the dark. Potassium iodide is added and the solu-
tion is titrated with sodium thiosulfate to a starch end point. The
iodine number is expressed in terms of the number of centigrams of
iodine absorbed per gram of sample.

TABLE V

DETERGENCY OF TM-1-9

Active	Total Raw Reflectance Readings					
	50 ppm hardness			300 ppm hardness		
	Cloth I	Cloth II	Cloth III	Cloth I	Cloth II	Cloth III
TM-1-9	241.0	514.0	355.5	217.5	419.5	351.5
ALFONIC® 1218-6	261.0	520.0	409.5	246.5	495.5	399.0
LSD	9.0	20.0	15.0	9.0	20.0	15.0

TABLE VI

DETERGENCY OF TM-1-7

| Nonionic | Total Raw Reflectance Readings | | | | | |
| | 50 ppm hardness | | | 300 ppm hardness | | |
	Cloth I	Cloth II	Cloth III	Cloth I	Cloth II	Cloth III
TM-1-7	206.0	514.0	384.5	188.0	426.5	370.5
ALFONIC® 1218-6	209.0	522.0	413.0	200.0	487.0	405.5
LSD	9.0	20.0	15.0	9.0	20.0	15.0

Peroxide analysis was run in a similar method as that of Wheeler
(43) with some changes. The method used is given in Appendix B. In
general, this analysis involves refluxing the sample with sodium iodide,
isopropyl alcohol, and acetic acid. Any peroxides present will oxidize
iodide to iodine, which is titrated with standard thiosulfate solution.
The end point is indicated by a dead-stop electrometric titration
apparatus (44).

Polyethylene glycol was determined by the method given in Appen-
dix B (45). By this procedure the nonionic surfactant and the glycol
are separated by partitioning between ethyl acetate and 30% sodium
chloride solution. The sodium chloride solution containing the glycols
is then extracted with chloroform and the glycols recovered by evapora-
tion and weighed.

DISCUSSION

Hydroxylation

During hydroxylation the use of both potassium iodide starch test paper and "Clinistix" reagent strips proved successful as an indication of remaining peroxide; however, the best procedure is to run the reaction longer than absolutely necessary in order to use up all of the peroxide. One-gram samples taken during the reaction of sample TM-1-4-13 were analyzed for peroxide with the following results:

TABLE VII

PEROXIDE ANALYSIS OF SAMPLES FROM
HYDROXYLATION RUN NO. TM-1-4

Sample	Time of Reaction	Meq. Peroxide/1000 Liters
TM-1-4-A	3 hrs.	3.0
TM-1-4-B	3½ hrs.	2.0
TM-1-4-C	4 hrs.	2.0
TM-1-4-D	4½ hrs.	1.0
TM-1-4-E	5 hrs.	2.1
TM-1-4-F	13 hrs.	2.0

These results indicate that the samples contained less than 1 ppm peroxide. Samples A thru E gave a positive test for peroxide

immediately after sampling on potassium iodide starch test paper and yet the same samples after 13 hours gave a negative test as did TM-1-4-F. This would indicate that the remaining small quantity of peroxide reacted in the remaining time at room temperature and was used up. This also would indicate that the peroxide contents of samples A thru E would have been considerably higher if the samples had been analyzed immediately.

The proper time of reaction was not ascertained but most certainly is less than thirteen hours. It was more convenient to start reactions in the late afternoon. Then several hours could be taken to adjust temperatures after the reaction had reached stability. This could be followed by overnight reaction at constant conditions, making it possible to take off the completed reaction product the next morning. Therefore, this procedure was followed on subsequent hydroxylations.

Hydroxyl numbers run on TM-1-4-13 gave a percent hydroxyl of 1.70%. A simultaneous analysis of the parent sperm oil gave 0.13%, which compares to the previous analysis (20) of 0.10%. Hydroxyl analysis of products of subsequent hydroxylations gave comparable numbers (1.65%, 1.81%).

Iodine numbers run on TM-1-4-13 gave an average of 2.6 compared with 80.2 for the parent oil. These figures would indicate that unsaturation had been reduced from 0.3 mole per 100 grams down to 0.01 moles of unsaturation per 100 grams. This would also indicate that the hydroxylation reaction was fairly complete but that a considerable portion of the product was epoxide. It might also be pointed out that though Swern et al. (15) obtained "near quantitative" yields of hydroxy-formoxy compounds with pure compounds, when they worked with commercial

oleic acid (red oil) they obtained only 60% yield based on the oleic
acid content of the starting material. Red oil usually consists of 65
to 75% oleic and 25 to 35% saturated and polyunsaturated acids.

Sperm oil is an even more complicated mixture and it was therefore
felt better to obtain a cursory evaluation of surfactants from the in-
completely hydroxylated material than to spend all of the available
time on the hydroxylation procedure and characterization.

Ethoxylates

Attempts to ethoxylate hydroxylated sperm oil in the low-pressure
glass apparatus proved to be much too slow even with increased catalyst
level. Therefore, all test ethoxylations were run in the pressure
equipment.

It might have been assumed that using sodium hydroxide catalyst in
an ester ethoxylation would cause trouble, but in reality this method
worked better than using the acid catalyst. Though only 50% ethylene
oxide was reached this appears to be a fair accomplishment considering
the nature of the material to be ethoxylated. This becomes more inter-
esting in light of the fact that only 40% ethylene oxide adduction was
reached with BF_3, when the acid catalyst was expected to solve all
problems.

The BF_3-catalyzed 40% adduct, sample TM-1-14, was analyzed by the
method in Appendix B for polyethylene glycol and found to contain
12.7%. This, in part, accounted for its limited reaction in addition
to the limited available hydroxyl with which to react. Let us examine
the effect of polyethylene glycol formation.

One of the greatest limitations in ethoxylating even pure com-
pounds is in knowing how much ethylene oxide has reacted with the com-
pound to give the desired products. The easy way out is to specify
that the finished product contain a certain percentage of ethylene
oxide units. In this case one only has to add enough ethylene oxide
to meet that qualification with no mention of where the ethylene oxide
went. Many different impurities can react with the ethylene oxide to
result in quantities of product other than the desired ethoxylate. One
of the greatest offenders is water. Water reacts with the oxide to
form polyglycols. Therefore one of the prime concerns is to keep water
out of the reactant. Ethoxylation of typical alcohols results in poly-
glycol contents of two to five percent in commercial products. Drew
(33) says that with NaOH catalyst, water from all sources (including
that from the reaction of NaOH with the alcohol) exactly accounts for
the amount of polyethylene glycol. However, in boron trifluoride
reactions, water only accounted for 7% of the polyethylene glycol.
Acid-catalyzed, water-producing side reactions are responsible for the
large amount actually found.

Now it can be seen why only 40% adduction was obtained with BF_3.
A combination of the following effects would seriously limit reaction:
(a) large molecules with limited hydroxyl content, (b) interference of
reactive and non-reactive side-reaction products, and (c) excessive
water production, which in itself would be more reactive to ethylene
oxide than the difficult-to-approach, high molecular weight hydroxyl
compounds. In examining Table I it can be seen that the reaction took
more than eleven hours to obtain a 40% adduct when ordinarily a 60 or
70% ethoxylation can be run in 3 or 4 hours.

Table II is an illustration of the accuracy of the equipment. Calculations of amount of charge and amount of ethylene oxide to add were made based on withdrawal of 50-gram samples at 5% ethylene oxide levels. The actual ethylene oxide contents were within 0.1% of the proposed percentages in each case.

Surfactant Evaluations

The NaOH-catalyzed ethoxylate TM-1-9 was evaluated for wetting properties as shown in Table IV. These data indicate that this ethoxylate has very poor wetting properties at 24°C. High temperatures and high concentrations are necessary to obtain reasonable wetting times. The 100-second wetting concentration (41) at 60°C is almost 0.6% where good wetting agents would have 25 second wetting concentrations in the range of 0.03%.

The Krafft point for TM-1-9 was 60°C. Normally 50% ethylene oxide adducts of most nonionic surfactants would give a one per cent cloud point at less than 38°C. The high figure for TM-1-9 is probably due to the nature of the ethoxylation. If only one-third of the molecules had been ethoxylated then those molecules would be 75% ethylene oxide ethoxylates and the other two-thirds would be unreacted. This would tend to make the actual nonionic concentration lower and the cloud point of that material much higher, which would also help explain the poor wetting.

Cotton detergency tests on TM-1-9 are given in Table V. These tests indicate that compared with a commercial nonionic detergent in a heavy duty formulation the sperm oil ethoxylate is significantly poorer on all cloths at 300 ppm hardness and poorer on two of three

cloths at low hardness. On Cloth II the two nonionics are not significantly different.

In a realistic evaluation of the nonionic agent itself these results are not completely discouraging. First, the ethylene oxide content is considerably below the optimum, which for this molecular weight should be at least 65 to 70% ethylene oxide or higher (35). Secondly, the incomplete hydroxylation probably results in approximately one-third of the concentration of actual nonionic agent, and thirdly, the remaining unethoxylated material being fatty in nature detracts from the detergency ability of the amount of surfactant that is there. In the face of these odds the sample did a presentable job of cleaning.

The evaluation of sample TM-1-7 in cotton detergency is shown in Table VI. These results indicate that at 50 ppm hardness the commercial is better than the sperm oil-based surfactant only on cloth III. The detergency abilities are not significantly different at 50 ppm on cloths I and II. The sperm oil surfactant is significantly poorer in detergency on all three cloths at high hardness. This is probably due to the soaplike nature of a large portion of this product.

At high temperatures and at 50 ppm hardness it is not at all inconceivable that the sperm oil product would be better than the commercial product. Not only will the higher molecular weight (ALFONIC®️ 1218 nonionic has an average chain length of C_{14}) of the oil adduct cause it to perform better (36) but the undoubtedly present soap portion would give added performance at high temperatures. This type of product could have application in Europe where high washing temperatures are used. In these applications low foam in desired. The soap/nonionic detergent mixture might in itself give the required low foam,

particularly since the nonionic is in the molecular weight range for

lower foam.

CONCLUSIONS AND RECOMMENDATIONS

The reaction conditions used for hydroxylation are evidently not satisfactory. Further study of the reaction could possibly result in introduction of more hydroxyls which in turn would result in more complete ethoxylation. Glycols could be tested but do not have as much chance for success in household detergent applications as do the monohydroxy compounds.

Glycols of hydroxylated sperm oil could have excellent demulsification properties for oil field use. These glycols could be further combined with ethylene oxide and/or esterified with fatty and dimer acids.

Poor ethoxylate quality was due to the nature of the material ethoxylated rather than the ethoxylation procedure. Caustic catalyst can be used and would probably be best for future work. No work should be done with acid catalyst. A cursory look at potassium carbonate catalyst could be taken. All ethoxylations should be carried out in pressure equipment.

The detergent properties of the subject products were relatively poor; however, considering the difficulties encountered and the nature of products there are still potentially good prospects for further investigations. Future investigations should include higher-temperature evaluations. If detergency properties are good, foam properties should also be tested.

Detergency properties of simultaneous de-esterification and ethoxylation products looked very interesting. A study of the reaction itself in addition to a study to ascertain optimum ethylene oxide concentrations could prove fruitful. This type of ethoxylation requires considerable care and caution to keep the reaction under control. The equipment should have adequate quick cooling available for this purpose.

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APPENDIX A - SURFACTANT EVALUATION PROCEDURES

Terg-O-Tometer Detergency Test

Scope:

This test method is used to evaluate cotton detergency of experimental surfactant and builder combinations. The procedure is designed to duplicate the use of detergent products in an agitator washer.

Summary of Method:

The Terg-O-Tometer, a laboratory-scale multiple washing machine, is used to simulate the action of an agitator-type home washer. The desired amounts of formulation components are added to one liter of water at a controlled temperature and hardness. Following the washing and rinsing of standard soiled cloths, the degree of detergency is determined by comparing reflectance readings of the cloths before and after the detergency test. The least significant difference method of statistical analysis is used to determine if a real difference exists between experimental samples.

Apparatus and Materials:

1. Terg-O-Tometer, manufactured by U. S. Testing Co.
2. Photoelectric Reflection Meter Node 610, manufactured by Photovolt Corp.

3. Three types of standard soiled cloths:

    (1) Testfabrics, Inc. cotton soil test cloth

    (2) American Conditioning House standard soil

        cloth, ACH No. 115.

    (3) U. S. Testing Company cotton standard soil cloth.

4. Maytag home clothes dryer.

5. Sunbeam iron.

Procedure:

One-liter solutions of the detergent are prepared with distilled water of sufficient temperature to be a few degrees higher than the required temperature. The solution is poured into the washing receptacle and stirred a minute or two in order to equalize its temperature with that of the bath.

The 3 x 4 inch cloths of known reflectance are then placed in the beaker. The test is started and operation of the machine is continued for 10 minutes at a speed of 100 RPM.

Upon completion of the washing cycle, the machine is shut off. The agitator is removed from the beaker, which is then removed from the bath. The solution is poured out, and the fabric is squeezed out by hand. The empty beaker is rinsed and replaced in the bath. One liter of rinse water of the proper temperature and hardness is poured in, the agitator and cloth are replaced, and the machine is operated for five minutes.

After rinsing, the fabric swatches are dried in a home dryer and ironed, and the change in reflectance determined.

The reflectometer is operated according to the manufacturer's recommendation, using a green tristimulus filter. A panel having known reflectance serves as a standard for calibration of the instrument.

Standard test conditions are as follows:

1. Temperature - 49°C

2. Time - 10 minute wash and 5 minute rinse

3. Agitator speed - 100 RPM

4. Water hardness - 50 and 300 ppm

5. Detergent concentration - 0.2%

6. Formulation - 20% active

        50% tripolyphosphate

        5% silicate

        15% sodium sulfate

        0.8% CMC

Duplicate runs are made and the "least significant difference" (LSD) calculated by the following method:

$$LSD = t \sqrt{(EMS) (4)}$$

where:

EMS = error mean square, or the sum of squares (s.s.) divided by the number of test samples within a run (n).

t = the value of t from a statistical table of student "t" values for the number of degrees of freedom (numerically equal to n) of the EMS.

$$s.s. = \frac{\sum\limits_{1}^{n}\left(\sum R_1 - \sum R_2\right)^2}{2}$$

where:

R_1 = total of reflectance values for each

sample in run #1.

R_2 = total of reflectance values for each

sample in run #2.

This means that in comparing two samples from within a test group, if their totals differ by the LSD or more the samples are significantly different at the 95% confidence level. This calculation is made for each of the three soiled cloths.

APPENDIX B - ANALYTICAL PROCEDURES

Determination of Peroxide Number

Scope:

This method is used to determine the peroxide number of olefins or unsaturated oils. The peroxide number measures the degree of oxidation that an olefin has undergone. The method is not recommended for use on samples containing conjugated diolefins.

Outline of Method:

The sample is refluxed with sodium iodide, isopropyl alcohol, and acetic acid. Any peroxides present will oxidize iodide to iodine, which is titrated with standard thiosulfate solution. The end point is indicated by a dead-stop electrometric titration apparatus. Peroxide number is the milliequivalents of constituents per 1000 g of sample that will oxidize sodium iodide.

Apparatus:

Isopropyl alcohol, 99%, reagent grade

Acetic acid, glacial

Sodium iodide, saturated solution in isopropyl alcohol.

    Add 25 g of sodium iodide (NaI) to 100 ml of isopropyl

    alcohol and reflux for 10 minutes; cool to room temperature.

Sodium thiosulfate, N/20 standard solution. Dissolve

    12.5 g of sodium thiosulfate ($Na_2S_2O_3$ - $5H_2O$)

    crystals in freshly boiled and cooled water and

    dilute to one liter. Standardize by any accepted

    procedure.

Procedure:

Weigh 5-10 g of the sample into a 250-ml standard-taper Erlenmeyer flask. Add 40 ml of isopropyl alcohol and 2 ml of glacial acetic acid. Connect the flask to a reflux condenser, heat to reflux, and add 10 ml of the saturated solution of sodium iodide.

Reflux 5 minutes, cool, and transfer the contents of the flask into a 150-ml beaker, washing the flask with 5 ml of water and adding the washing to the beaker.

Before running a sample, make a blank determination, following the above procedure except for the addition of the sample. Set the sensitivity control of the titration apparatus about one-quarter turn from its extreme counterclockwise position and adjust the electric eye so that it is just closed when the blank becomes colorless by addition of the 0.05N thiosulfate (Note 1).

With the controls set as described above, slowly titrate the sample with 0.05N thiosulfate until the eye closes.

Calculation:

$$\text{Peroxide number} = \frac{(A - B) \times N \times 1000}{W}$$

where:

A = ml of thiosulfate solution to titrate sample

B = ml of thiosulfate solution to titrate blank

N = normality of thiosulfate solution

W = sample weight in grams

Note

The settings of the controls are those to be used with the circuit described by Kieselbach in Analytical Chemistry 21, 1578 (1949). Other settings may be needed when using a different circuit.

Determination of Glycols in Nonionic Detergents by Extraction

Scope:

This method may be used to determine the glycol content of ethylene oxide condensates. The method effectively separates both simple glycols and polyglycols of high molecular weight from the nonionic detergent. If desired, the glycol-free nonionic detergent may be recovered.

Outline of Method:

The nonionic detergent is separated from the glycols by partitioning between ethyl acetate and 30% sodium chloride solution. The sodium chloride solution containing the glycols is then extracted with chloroform and the glycols recovered by evaporation of the chloroform.

Apparatus:

Separatory funnels

Steam bath and source of dry, oil-free air

Vacuum oven and vacuum source (20-25 in Hg)

Reagents:

Ethyl acetate, reagent grade

Chloroform, reagent grade

Sodium chloride solution, 30%. Dissolve 300 g of reagent
    grade sodium chloride (NaCl) in water, and dilute to
    one liter.

Procedure:

Weigh about 10-12 g of sample into a 250-500 ml separatory funnel. Add 50 ml of ethyl acetate and 50 ml of 30% sodium chloride solution. Shake for two minutes, then allow to stand at least 15 minutes for phase separation. Draw the lower aqueous sodium chloride layer into a second clean separatory funnel. Repeat the extraction of the ethyl acetate solution contained in the first funnel with an additional 50 ml of sodium chloride solution. After phase separation, combine the sodium chloride extracts in the second funnel. Counterextract once with 50 ml of fresh ethyl acetate. After separation, transfer the sodium chloride solution into a clean separatory funnel and discard the ethyl acetate solutions.

Remove the glycols from the sodium chloride solution by two separate 50-ml extractions with chloroform. Allow at least 15 minutes between extractions for a clear separation. Collect the chloroform extracts in a tared 150-ml beaker, and evaporate the chloroform on a steam bath using a gentle stream of dry, oil-free air directed at the surface of the liquid to aid in the evaporation. Dry the sample in a vacuum oven (20-25 in Hg) for one hour at 50°C. Allow the sample to cool in a desiccator and weigh. Check the dried material for the presence of sodium chloride and make any necessary correction (Note 1).

Calculation:

$$\text{Per cent glycols} = \frac{G}{W}\ 100$$

where:

G = grams of dry, salt-free glycols

W = sample weight in grams

Notes

1. When this procedure is carefully practiced, no sodium chloride should be present in the beaker with the dried glycols. If observation of this material indicates the presence of chloride, it must be corrected for.

VITA

Ted Paul Matson

Candidate for the Degree of

Master of Science

Thesis: SURFACTANTS FROM ETHOXYLATED HYDROXYLATED SPERM OIL

Major Field: Chemistry

Biographical:

Personal Data: Born in Ponca City, Oklahoma, January 5, 1929,
the son of Paul T. and Lola Matson.

Education: Attended grade schools in Altus, Oklahoma City, and
Enid, Oklahoma and junior high schools in Oklahoma City and
Clinton, Oklahoma; graduated from Clinton High School in
1945; received the Bachelor of Science degree from the
University of Oklahoma, with a major in Geology, in August,
1949; received the Master of Education degree from the
University of Oklahoma, with a major in School Administration,
in June, 1951; completed requirements for the Master of
Science degree in July, 1967.

Professional Experience: Taught and coached in the Binger, Okla-
homa, public schools in 1949-50 and in the Ponca City Public
Schools, Ponca City, Oklahoma, 1951 thru 1956; joined
Continental Oil Co. in 1957 and served as a research chemist
in the fields of oil field chemicals and household deter-
gents and is now Product Development Coordinator for Oil
Field Chemicals; in 1964-5 served as technical advisor in
surfactants to the Managing Director of Condea Petrochemie
Gesellschaft; has done extensive research in the field of
surfactants and was a lecturer for the American Oil Chemists'
Society Short Course on Advances in Soaps and Detergents at
Princeton in 1963; has been active in the AOCS and served on
the National Program and Planning Committee; has authored
numerous papers and patents in the detergent field.