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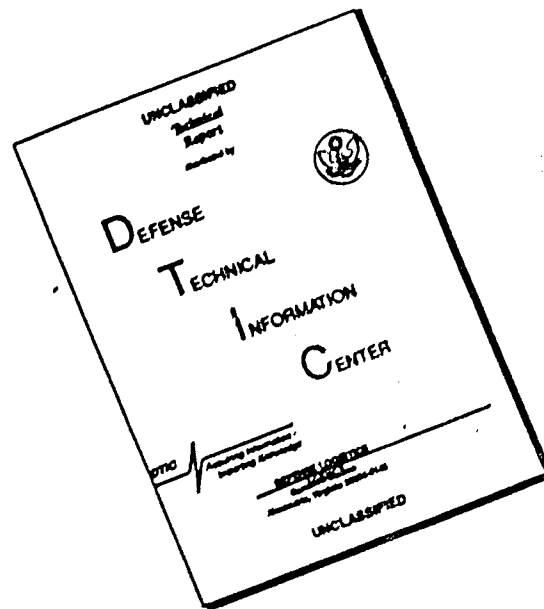
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DETERGENCY OF THE 12 TO 18 CARBON SATURATED
FATTY ACIDS

Report No. CCL # 123
OMS Code No. 5010.11.8420051
D. A. Project No 593-32-006
Author A. Mankowich
Date 14 June 1962

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By

A. Mankowich

14 June 1962

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Dept of the Army Project No.
593-32-006

Coating and Chemical Laboratory
Aberdeen Proving Ground
Maryland

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ABSTRACT

Systems of one surfactant (two anionic and three nonionic types were studied) with an homologous family of soils (the 12, 14, 16 and 18 carbon saturated fatty acids) were explored to determine the relationship of the detergencies of such systems to the physico-chemical nature (HLB, hydrophile-lipophile balance) of the soils. A series of systems of ethylene oxide homologs of nonyl phenol with the same soils was also investigated.

Neither surfactant HLB nor adsorptive energy of the surfactant polar group, alone, is responsible for the detergency of the 12 to 18 carbon fatty acids

Two semi-logarithmic relationships were derived for the nonyl phenol polyethenoxyether-fatty acid systems; namely, linearity of the R (ethylene oxide mole ratio)-log M/CMC and surfactant HLB-log M/CMC functions (M = surfactant concentration giving ca 100% removal of 16 and 18 carbon fatty acids, and CMC = critical micelle concentration).

Fatty acid soaps are poor detergents of the fatty acid soils. It is suggested that in such systems the chief action is van der Waals adsorption between hydrocarbon chains of the surfactant and soil, with adsorption increasing with increasing chain length of the former and concentration of the latter. Anionic sodium dodecyl benzene sulphonate is a good detergent of the fatty acids, soil removal being independent of soil chain length.

Polyoxyethylene (23) sorbitan monolaurate and the 12 and 15 ethylene oxide mole ratio adducts of tridecyl alcohol are poor detergents of the saturated fatty acids.

I. INTRODUCTION

Previous hard surface detergency studies at this Laboratory have shown that for several classes of soil (fatty acid, fatty alcohol, ester, and amine) a linear relationship exists between detergency and micellar solubilization beginning at about 90% soil removal, and that the constants of this function are connected to HLB (hydrophile-lipophile balance) of surfactant, soil dipole moment and/or soil boundary tension (1,2). These studies have covered systems consisting of several (four) surfactant homologs with one soil, and one surfactant with four classes of soil (2).

This paper explores systems consisting of one surfactant with a homologous family of soils, the 12, 14, 16 and 18 carbon saturated fatty acids.

II. DETAILS OF TEST

A. Method

Dynamic procedures were used in determining micellar (Orange OT) solubilization (3) and detergency. Some details of the detergency testing technique (preparation of test panels, cleaning procedure, and measurement of residual soil) have already been described (3). A slight change was made in the residual soil measurement by the substitution of ethyl alcohol for acetone as the degreasing solvent. Application of the fatty acid soils to the steel test panels was as follows: the molten acid was brushed on one face of the weighed panel with a small camel's hair brush. The panel was then hung vertically in a 105°C oven for a draining period depending upon the acid, as follows:

lauric acid	-----	1½ minutes
myristic acid	---	2 minutes
palmitic acid	---	3 minutes
stearic acid	----	3 minutes

The panel was then removed from the oven, cooled to room temperature, and reweighed. The weight of fatty acid per panel was 53 - 60 milligrams.

B. Soils

The soils were reagent grade fatty acids with melting points as follows:

lauric acid	-----	42 - 43°C
myristic acid	---	52 - 53°C
palmitic acid	---	61 - 62°C
stearic acid	----	68 - 69.5°C

C. Surfactants

The surfactants included the following commercial ethylene oxide adducts of nonyl phenol:

Surfactant	Symbol	Ethylene Oxide Mole Ratio
nonyl phenyl pentadecaethylene glycol ether	NPPGE	15
nonyl phenyl eicosaethylene glycol ether	NPEGE	20
nonyl phenyl triacontaethylene glycol ether	NPTGE	30
nonyl phenyl tetracontaethylene glycol ether	NPTTGE	40
nonyl phenyl pentacontaethylene glycol ether	NP50E	50
nonyl phenyl decacontaethylene glycol ether	NP100E	100

Also studied were two polyethenoxyethers of tridecyl alcohol, a polyoxyethylene sorbitan monolaurate, an alkyl aryl sulphonate, and two soaps, as follows:

tridecyl dodecaethylene glycol ether -- ---- TODGE
tridecyl pentadecaethylene glycol ether ---- TDPGE
polyoxyethylene (23) sorbitan monolaurate ----- PSML
sodium dodecyl benzene sulphonate ----- SDBS
sodium oleate
potassium laurate

The CMC (critical micelle concentration) values of these surfactants are given in a previous paper (4).

III. RESULTS AND DISCUSSION

A. Fatty Acid Soaps

Tables XI and XII indicate that aqueous solutions of fatty acid soaps are poor detergents of solid fatty acid soils. The detergency isotherms of the 12, 14, 16, and 18 carbon acid soils with both soaps (excepting the potassium laurate - lauric acid system) attain a low maximum and then fall to "negative" detergency (residual soil) original soil). At the same soap concentration, detergency decreases with increasing number of carbons in the soil. A probable explanation of these results is the following, a theory previously advanced by other workers in the field: the binding energy of the fatty acid to the steel substrate consists of the adsorptive energy of its polar carboxyl groups to the steel plus the van der Waals cohesive forces between the hydrocarbon chains of its molecules. Thus the greater the chain length, the more strongly the fatty acid is adsorbed, and the more difficult it is to deterge. Since the polar groups of the soap detergents are also carboxyl, preferential adsorption of detergent ions on the substrate is minimized. The chief action is adsorption between the hydrocarbon chains of the acid soil and the fatty acid soap, and this increases with increasing chain length of the former and concentration of the latter.

B. Alkyl Aryl Sulphonate (SDBS) Detergency

Table X shows that sodium dodecyl benzene sulphonate is a good detergent of solid fatty acids. The detergency isotherms of all four acids approach 100% removal. Detergency is substantially independent of the length of the hydrocarbon chain of the acid. This indicates that the adsorptive energy of the polar sulphonate group is considerably higher than that of the carboxyl group, and that preferential wetting by the former occurs readily.

C. Polyethenoxyethers of Tridecyl Alcohol and Polyoxyethylene Sorbitan Monolaurate

Tables VII, VIII and IX indicate that the 12 and 15 ethylene oxide mole ratio adducts of tridecyl alcohol and polyoxyethylene (23) sorbitan monolaurate are poor detergents of the 12, 14, 16 and 18 carbon fatty acids.

The behavior noted in sections III-A, III-B and III-C indicates that removal of solid saturated fatty acid soils is related in part to the adsorptive energy (preferential adsorbability) of the detergent ions of anionic surfactants (or detergent molecules of nonionic agents). It is obviously an over-simplification to attribute detergency solely to the detergent ion or molecule. While the polar sulphonate group appears to be responsible for the excellent fatty acid detergency of sodium dodecyl benzene sulphonate, the same group is entirely ineffective as a soil remover in wetting agents like sodium isopropyl naphthalene sulphonate and in hydrotropes like sodium benzene sulphonate. These facts seem to point to a possible connection between detergency, surfactant HLB and soil HLB. But this investigation has shown that HLB cannot be the only factor involved in detergency. Table I reveals good fatty acid soil removal ability for the 100 ethylene oxide mole ratio adduct of nonyl phenol (HLB = 19.05). Sodium dodecyl benzene sulphonate, also an excellent detergent of the same soil, has an HLB value of 11.70.

D. Behavior of Ethylene Oxide Adducts of Nonyl Phenol

Tables I to VI, inclusive, give fatty acid soil removal data of ethylene oxide adducts of nonyl phenol. The following generalities are established:

(1) The 15R (15 mole ratio) adduct is a poor remover of 12 - 18 carbon saturated fatty acids, particularly at normal detergent concentrations (only ca 6% removal at 30.CMC or 0.29%). At 360.CMC, removal is 73 - 81%; and at 480.CMC (4.65%), lauric acid removal is 91%.

(2) The 20R adduct (NPEGE) is also a poor detergent of 12 - 18 carbon saturated fatty acids, 74% removal of stearic acid being the best value at concentrations up to 150.CMC or 2.57%. At 168.CMC, removal of palmitic and stearic acids becomes good, 92 - 95%.

(3) At normal detergent concentrations (to 24.CMC, or 1.02%), the 30R adduct is a poor detergent of saturated fatty acids. Good detergency of the 18, 16 and 14 carbon acids is obtained approximately at 48.CMC, 64.CMC, and 80.CMC, respectively.

(4) Detergency increases with increasing chain length of the 14, 16 and 18 carbon acid soils at the same concentration of 30, 40, 50 and 100 mole ratio nonyl phenol adducts. Removal of 12 carbon acid by the latter three adducts is considerably better than 14 carbon acid soil removal, and is substantially equivalent to the good detergency of stearic acid by these surfactants.

(5) Table XIII, a compilation of nonyl phenol adduct data at a practical detergency level (at concentrations providing ca 100% soil removal for most of the surfactants), emphasizes the following points: (a) the abnormally

high surfactant concentrations (2.7 - 3.8%) required to give good solid fatty acid soil removal; (b) the sharp decrease in the M/CMC ratio with increasing ethylene oxide mole ratio, R (where M = surfactant concentration giving ca 100%, 16 and 18 carbon fatty acid removal!); for values of R between 15 and 50, the R-log (M/CMC) function is linear (Figure 1); and the surfactant HLB-log (M/CMC) function is linear for values of R between 20 and 100 (Figure 1); the validity of these semi-logarithmic functions is confirmed because they indicate linearity between R and surfactant HLB, a relationship previously reported for ethylene oxide adducts of nonyl phenol (3); (c) poor detergency of the 15 mole ratio adduct.

IV. REFERENCES

1. Mankowich, A. "J. Am. Oil Chemists' Soc.", 39, 206 (1962)
2. Mankowich, A. Coating and Chemical Laboratory Report # CCL 119, 10 May 1962.
3. Mankowich, A. "J. Am. Oil Chemists' Soc.", 38, 589 (1961)
4. Mankowich, A. Coating and Chemical Laboratory Report # CCL 103, 17 March 1961.

APPENDIX A

Tables

TABLE I

NP100E DETERGENCY

Surfactant Molarity	% Soil Removal			
	Lauric Acid	Myristic Acid	Palmitic Acid	Stearic Acid
.00100 - CMC	98.8	40.0	24.1	62.8
.00200	98.5	----	31.3	89.3
.00300	----	37.1	49.2	96.4
.00600	----	80.8	99.3	99.6
.00800	----	99.4	----	----

TABLE II

NP50E DETERGENCY

Surfactant Molarity	% Soil Removal			
	Lauric Acid	Myristic Acid	Palmitic Acid	Stearic Acid
.000788 - CMC	45.0	14.2	25.5	44.6
.00158	94.0	----	----	----
.00217	99.3	----	----	----
.00236	----	----	----	63.5
.00315	----	42.2	----	----
.00433	98.3	----	28.9	89.5
.00630	----	----	53.0	ca 100.
.0126	----	72.6	99.5	ca 100.
.0189	----	99.8	----	----

TABLE III
NPTTGE DETERGENCY

Surfactant Molarity	% Soil Removal			
	Lauric Acid	Myristic Acid	Palmitic Acid	Stearic Acid
.000450 - CMC	----	10.6	----	17.4
.00264	----	17.4	----	----
.00528	62.4	33.3	27.2	43.3
.00792	90.9	----	43.4	65.4
.0106	95.7	29.3	57.5	94.9
.0158	93.2	49.2	99.4	ca 100.

TABLE IV
NPTGE DETERGENCY

Surfactant Molarity	% Soil Removal			
	Lauric Acid	Myristic Acid	Palmitic Acid	Stearic Acid
.000275 - CMC	10.5	6.5	----	18.9
.00110	----	10.5	----	----
.00440	----	16.6	----	----
.00660	64.1	20.8	----	48.9
.0132	89.7	29.5	81.8	98.4
.0176	69.3	68.2	99.7	ca 100.
.0220	----	98.2	----	----

TABLE V

NPEGE DETERGENCY

Surfactant Molarity	% Soil Removal			
	Lauric Acid	Myristic Acid	Palmitic Acid	Stearic Acid
.000155 - CMC	5.0	3.7	----	1.8
.00582	----	7.6	----	----
.0116	----	13.5	----	----
.0232	----	20.9	----	73.5
.0261	66.9	27.1	92.2	94.9
.0290	----	----	----	98.7
.0349	80.6	80.6	ca 100	98.9

TABLE VI

NPPGE DETERGENCY

Surfactant Molarity	% Soil Removal			
	Lauric Acid	Myristic Acid	Palmitic Acid	Stearic Acid
.000110 - CMC	3.0	4.2	----	1.8
.00110	----	6.5	----	9.2
.00330	----	5.7	----	----
.0132	----	11.2	----	22.7
.0264	47.7	19.2	29.2	35.6
.0396	78.1	73.4	77.0	81.1
.0528	91.0	----	----	----

TABLE VII

TDDGE DETERGENCY

Surfactant Molarity	% Soil Removal			
	Lauric Acid	Myristic Acid	Palmitic Acid	Stearic Acid
.000148 - CMC	----	4.1	17.3	Zero
.00711	3.6	residual soil > original soil	4.2	4.1
.0213	3.8	residual soil > original soil	8.3	12.4
.0426	13.7	8.2	----	9.4

TABLE VIII

TDPGE DETERGENCY

Surfactant Molarity	% Soil Removal			
	Lauric Acid	Myristic Acid	Palmitic Acid	Stearic Acid
.000165 - CMC	----	5.1	16.0	Zero
.00528	----	3.8	----	----
.0211	14.9	8.5	16.7	21.6
.0422	40.8	56.6	66.6	72.1

TABLE IX

PSML DETERGENCY

Surfactant Molarity	% Soil Removal			
	Lauric Acid	Myristic Acid	Palmitic Acid	Stearic Acid
.000106 - CMC	----	5.2	----	Zero
.00106	----	11.2	----	----
.0106	37.9	22.7	34.4	42.4
.0212	76.7	32.0	45.3	58.8
.0318	----	45.1	----	----

TABLE X

SDBS DETERGENCY

Surfactant Molarity	% Soil Removal			
	Lauric Acid	Myristic Acid	Palmitic Acid	Stearic Acid
.00150 - CMC	----	13.4	----	18.2
.00300	23.3	20.4	----	22.4
.00600	93.0	84.3	81.5	71.2
.00750	----	96.8	95.3	99.0
.00900	----	99.7	----	98.7
.0120	99.3	----	----	----

TABLE XI

SODIUM OLEATE DETERGENCY

Surfactant Molarity	% Soil Removal			
	Lauric Acid	Myristic Acid	Palmitic Acid	Stearic Acid
.00110 - CMC	----	10.4	16.9	10.4
.0132	15.4	22.2	----	----
.0264	55.0	58.4	48.5	Zero
.0792	78.0	49.5	residual soil > original soil	residual soil > original soil
.1056	42.0	3.7	----	residual soil > original soil

TABLE XII

POTASSIUM LAURATE DETERGENCY

Surfactant Molarity	% Soil Removal			
	Lauric Acid	Myristic Acid	Palmitic Acid	Stearic Acid
.0140	37.8	56.1	----	residual soil > original soil
.0233 - CMC	98.1	77.5	41.9	residual soil > original soil
.0466	98.3	58.6	residual soil > original soil	residual soil > original soil
.0932	----	residual soil > original soil	----	----

TABLE XIII

PRACTICAL DETERGENCY OF NONYL PHENOL ADDUCTS

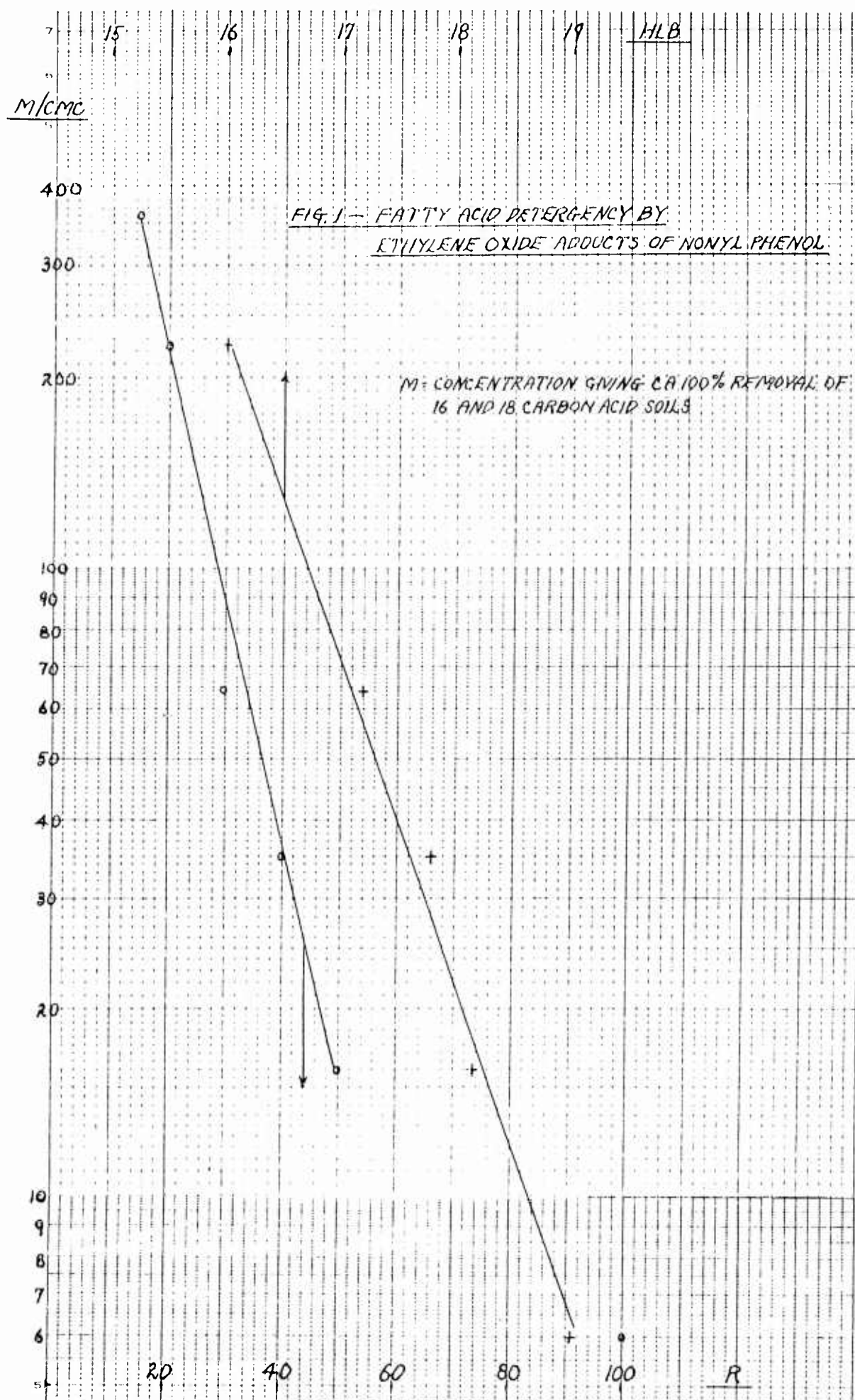
Surfactant	Mole Ratio R	HLB	Concentration		% Soil Removal ***			
			M *	M, CMC	12C	14C	16C	18C
NPPGE	15	15.00	.0396	360	78.1	73.4	77.0	81.1
NPEGE	20	16.00	.0349	225	80.6	80.6	ca 100	98.9
NPTGE	30	17.20	.0176	64	69.3	68.2	99.7	ca 100
NPTTGE	40	17.78	.0158	35	93.2	49.2	99.4	ca 100
NP50E	50	18.18	.0126	16	----	72.6	99.5	ca 100
NP100E	100	19.05	.00600	6	----	80.8	99.3	99.6

* - molarity giving ca 100% removal of 16 and 18 carbon saturated acids

*** - soil = saturated fatty acids.

APPENDIX B

Figure



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