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RELATIONSHIP OF SOIL REMOVAL TO HYDROPHILE-LIPOPHILE BALANCE

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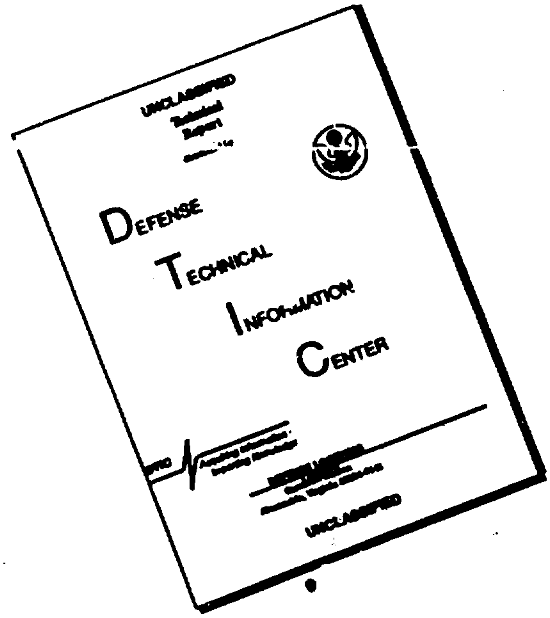

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RELATIONSHIP OF SOIL REMOVAL TO HYDROPHILE-LIPOPHILE BALANCE

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ABSTRACT

Concentration-detergency curves were developed for twenty-eight soil-surfactant systems. These systems consisted of three single-component soils and nonionic surfactants from two homologous series. An optimum surfactant concentration was shown to exist for each soil-surfactant system and was found to be related to the hydrophile-lipophile balance (HLB) of the surfactant. From data developed a relationship is apparent between the HLB of the soil and the HLB of the surfactant (of either homologous series) most effective for deterging this soil. The relationship points the way for optimization of surfactant type and concentration for a specific soil based on HLB calculations.

I. INTRODUCTION

The development of a theory for the mechanism of detergency has been the purpose of many investigations. As a result of these investigations three basic detergency mechanisms (1) for liquid soils have been recognized: emulsification, roll-back (formation of globules by oily soil in aqueous solution), and solubilization. These mechanisms operate in combinations or separately depending on the particular system.

The theory of detergency has not been developed to a state where detergency can usually be predicted for a given surfactant-soil system. The possibility of useful correlations existing between detergency and physicochemical factors believed to influence the above detergency mechanisms has been investigated by many. These physicochemical factors include micellar solubilization (2, 3), electrical forces such as zeta potential (4), critical micelle concentration (3, 5), hydrophile-lipophile balance of surfactant (6, 7), surface tension at critical micelle concentration (5), soil dipole moment (5), and soil viscosity (5). These references are examples only and are not intended to be complete. Correlations between the above physicochemical factors and detergency have been shown in some instances, but the application of these correlations to the selection of an efficient surfactant for a given soil is, at best, generally difficult. Indeed, the usual method of surfactant selection for a given, recurring soil is a time-consuming screening test or selection based on experience, without regard to close matching of soil and surfactant.

In the present study a relationship is indicated that would enable a close match between a known soil and surfactant without the usual screening test. For each of the soil-surfactant combinations studied, it is shown that there exists an optimum surfactant concentration, which relates to the hydrophile-lipophile balance (HLB) of the soil and the HLB of the most effective surfactant in a homologous series.

II. DETAILS OF TEST

The detergency test procedure and the temperature of the aqueous test solution (180°F.) were the same as earlier work at this laboratory (8).

The following three soils used in this investigation were from the group previously used at this laboratory: oleic acid, USP; lauryl alcohol, 98%, and 2, 6, 10, 14 tetramethylpentadecane, 98% +.

Two commercial-grade homologous series of nonionic surfactants were used. These were 100% active materials of the following classes.

1. Ethoxylates of tridecanol

$$C_{13}H_{27}(OCH_2CH_2)_nOH,$$

2. Ethoxylates of nonylphenol

C_9H_{19}  $(OCH_2CH_2)_nOH.$

These surfactants are further described in Table I.

III. DISCUSSION

Tables 2 thru 6 give the values of detergency (percent soil removal) for a range of concentrations from near zero through the practical range for this study. These values are plotted in Figures 1 thru 6. Portions of some of these curves were reported earlier (9) but were not sufficiently complete to permit some important comparisons between surfactant-soil systems. It can be seen from these curves that detergency increases approximately linearly with increases in concentration until a concentration is reached where there is a sharp change in slope. After this change in slope detergency may either increase at a lower rate or it may decrease. This concentration where the slope changes abruptly can be labeled "the optimum concentration" for the given surfactant-soil system since a further increase in concentration results in at best a small increase in detergency. This optimum concentration together with the corresponding value of detergency can be used for comparing the effectiveness of different surfactants for a given soil. As will be seen later, within a given homologous series, the surfactant having the lowest optimum concentration also shows maximum soil removal and is, therefore, the most efficient surfactant for the given soil.

Optimum concentration, as defined above, is plotted against surfactant HLB in Figures 7 thru 9. The values for these curves together with detergency values at optimum concentration are contained in Table 7. The HLB values were calculated from group numbers (Table 8) using the equation:

$$HLB = \sum \text{hydrophilic groups} - \sum \text{lipophilic groups} + 7.$$

These group numbers and the equation were developed for use in the selection of emulsifiers (10).

The first of these Figures, 7, shows the curve for both the tridecanol ethoxylates and the nonylphenol ethoxylates using oleic acid as soil. These two curves exhibit an "optimum concentration" minimum and thereby demonstrate that for this soil the surfactant HLB can be either too high or too low. For each curve a surfactant HLB of about 12 corresponds to the minimum optimum concentration. This HLB value of 12 is also the point at which maximum detergency occurs as can be seen when HLB is plotted against detergency at optimum concentration (Figure 10A). For oleic acid soil, then, the most effective surfactant from either class has an HLB of approximately 12 whether considering soil removal or surfactant concentration.

Figure 8 shows the relationship between surfactant HLB and optimum concentration for the two surfactant series using tetramethylpentadecane as soil. The curves have no minimum, but each one extrapolated towards the X-axis indicates that a surfactant having an HLB value of about 4 would have the lowest optimum concentration. This surfactant HLB of 4 corresponds to the value of maximum soil removal (Figure 10 B). These curves for Figures 7 and 8 show that for a given soil the HLB corresponding to the lowest optimum concentration does not change from one surfactant series to the other.

The third soil studied was lauryl alcohol. Since the first two soils showed each surfactant series to have the same "most effective HLB" for a given soil, it was considered redundant to evaluate both series with the third soil. Therefore, only the ethoxylated nonylphenol series was tested with lauryl alcohol. Figure 9 shows the relationship between surfactant HLB and optimum concentration for this soil. The minimum optimum concentration corresponds to an HLB of about 12, the same as for oleic acid soil. This HLB value of 12 is also in the range of maximum detergency for optimum concentrations (Figure 10 C).

The above Figures show that the most effective surfactant of a given homologous series for deterging a given soil varies with the type of soil. That is, a relationship is indicated between the molecular structure of the soil and the molecular structure of the most effective surfactant. Since the HLB of the most effective surfactant decreases in going from the polar soils (oleic acid and lauryl alcohol) to the non-polar soil (tetramethylpentadecane) it is suggested that the HLB of the most effective surfactant is related to the HLB of the soil.

The HLB value for these soils can be calculated from the empirical group numbers used for surfactants. Figure 11 shows the relationship between soil HLB and the HLB of the most effective surfactant. Data for this Figure are given in Table 9. This Figure indicates that the HLB for the most effective surfactant is constant for higher HLB soils. But for lower HLB soils the HLB for the most effective surfactant decreases with a decrease in soil HLB. This relationship for lower HLB soils is especially significant since the liquid soils most difficult to remove are in the lower HLB range. In general agreement with the present study, Arai (11) found that for anionic surfactants the most effective surfactant HLB decreases with a decrease in the polarity of the soil.

Further investigations are needed to firmly establish the above relationships of soil HLB to surfactant HLB and to extend the soil HLB range. Also, an investigation is needed to determine whether for a given soil the optimum HLB is the same for anionic and nonionic surfactants.

V. CONCLUSION

The weight-percent concentration of surfactant at which a sharp change in slope occurs in the detergency-concentration plot can be taken as the "optimum surfactant concentration" for the given surfactant-soil system. This optimum concentration can in turn be used to indicate the most effective surfactant in a nonionic homologous series for deterging a given soil. Using this approach it was shown that for a given soil the most effective surfactant from each of the two homologous series studied had the same HLB value.

The data further indicated that within a nonionic homologous series the HLB of the most effective surfactant for deterging a given soil generally decreases as the hydrophobic properties of the soil increases, that is, as the HLB value of the soil decreases.

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APPENDIX A

TABLE 1

DESCRIPTION OF SURFACTANTS

	Ethylene Oxide Units Per Molecule (n)	Molecular Weight
Tridecanol Ethoxylates	12	728
	15	860
	20	1080
	30	1520
	40	1960
Nonylphenol Ethoxylates	15	880
	20	1100
	30	1540
	40	1980
	50	2420
	100	4620

TABLE 2

DETERGENCY OF TRIDECANOL ETHYOXYLATES USING OLEIC ACID SOIL

Ethylene Oxide Units Per Molecule (n)	Surfactant Concentration - Weight Percent	Detergency - % Soil Removal
12	0.020	2.7
	0.063	5.2
	0.358	40.2
	0.574	58.8
	0.726	74.7
	0.901	82.4
	1.068	75.9
	1.268	65.1
	1.862	53.6
15	0.058	5.3
	0.087	24.6
	0.171	41.0
	0.263	56.6
	0.374	64.0
	0.520	74.8
	0.633	71.4
	0.848	61.7
	1.168	51.6
	1.574	39.4
20	0.029	11.3
	0.105	57.9
	0.175	90.4
	0.287	96.3
	0.485	97.1
	0.777	94.5
	1.149	93.0
	1.553	90.5
30	0.003	4.4
	0.031	54.3
	0.049	84.1
	0.064	86.2
	0.125	94.8
	0.312	95.4
	0.385	96.2
	0.633	94.9
	1.064	93.9
	1.519	97.0
	1.930	97.3

TABLE 2 (CONTINUED)

DETERGENCY OF TRIDECANOL ETHYOXYLATES USING OLEIC ACID SOIL

Ethylene Oxide Units Per Molecule (n)	Surfactant Concentration - Weight Percent	Detergency - % Soil Removal
40	0.031	22.0
	0.072	92.2
	0.127	91.2
	0.207	95.2
	0.422	97.5
	0.771	97.1
	1.125	97.2
	1.601	97.3
	2.141	97.6
	2.621	97.8

TABLE 3

DETERGENCY OF NONYLPHENOL ETHOXYLATES USING OLEIC ACID AS SOIL

Ethylene Oxide Units Per Molecule (n)	Surfactant Concentration - Weight Percent	Detergency - % Soil Removal
15	0.009	3.9
	0.062	8.7
	0.132	12.8
	0.220	25.2
	0.308	40.3
	0.440	68.3
	0.528	83.0
	0.563	85.7
	0.704	85.8
	0.880	80.0
	1.232	64.9
	1.584	49.7
	1.760	44.2

TABLE 3 (CONTINUED)

DETERGENCY OF NONYLPHENOL ETHOXYLATES USING OLEIC ACID AS SOIL

Ethylene Oxide Units Per Molecule (n)	Surfactant Concentration - Weight Percent	Detergency - % Soil Removal
20	0.055	13.3
	0.136	39.1
	0.220	61.0
	0.274	72.6
	0.330	78.7
	0.440	87.2
	0.495	87.4
	0.605	88.4
	0.660	84.1
	0.770	79.9
	0.880	71.7
	0.990	67.7
	1.100	62.1
30	0.008	10.8
	0.012	17.8
	0.015	42.7
	0.023	60.5
	0.027	77.5
	0.034	85.4
	0.046	92.8
	0.054	93.3
	0.077	96.1
	0.069	94.2
	0.108	97.2
	0.131	98.3
	0.154	97.8
40	0.005	6.8
	0.010	12.7
	0.022	66.1
	0.026	80.2
	0.032	85.4
	0.050	92.8
	0.099	97.6
	0.158	98.2
	0.238	98.6

TABLE 3 (CONTINUED)

DETERGENCY OF NONYLPHENOL ETHOXYLATES USING OLEIC ACID AS SOIL

Ethylene Oxide Units Per Molecule (n)	Surfactant Concentration - Weight Percent	Detergency - % Soil Removal
50	0.012	12.2
	0.017	28.9
	0.024	50.6
	0.036	74.6
	0.048	82.2
	0.053	86.8
	0.058	88.7
	0.073	88.5
	0.097	90.4
	0.131	94.2
	0.145	96.1
	0.182	95.8
100	0.116	21.4
	0.231	36.5
	0.462	48.9
	0.693	62.5
	0.924	79.8
	1.155	88.3
	1.386	93.1
	1.617	96.9
	1.848	98.7
	2.310	99.3
	2.772	99.4
	3.234	99.4

TABLE 4

DETERGENCY OF TRIDECANOL ETHOXYLATES USING TETRAMETHYLPENTADECANE AS SOIL

Ethylene Oxide Units Per Molecule (n)	Surfactant Concentration - Weight Percent	Detergency - % Soil Removal
12	0.006	52.0
	0.016	50.9
	0.028	57.4
	0.030	64.3
	0.039	70.0
	0.055	74.0
	0.108	84.0
	0.223	89.3
	0.295	88.6
	0.397	90.6
	0.591	92.0
15	0.011	60.3
	0.026	62.8
	0.052	67.2
	0.067	72.3
	0.094	75.8
	0.133	80.3
	0.168	81.1
	0.250	83.7
	0.349	85.1
	0.419	89.1
20	0.027	56.0
	0.053	60.9
	0.119	73.1
	0.173	78.3
	0.227	79.7
	0.272	82.3
	0.346	84.0
	0.443	86.0
	0.540	89.1
30	0.015	41.7
	0.075	47.1
	0.152	53.1
	0.227	58.0
	0.326	59.7
	0.525	63.1
	0.757	67.7

TABLE 4 (CONTINUED)

DETERGENCY OF TRIDECANOL ETHOXYLATES USING TETRAMETHYLPENTADECANE AS SOIL

Ethylene Oxide Units Per Molecule (n)	Surfactant Concentration - Weight Percent	Detergency - % Soil Removal
40	0.099	34.6
	0.204	39.1
	0.303	48.6
	0.393	53.7
	0.494	54.6
	0.651	55.1
	0.811	54.9
	0.940	58.9

TABLE 5

DETERGENCY OF NONYLPHENOL ETHOXYLATES USING TETRAMETHYLPENTADECANE AS SOIL

Ethylene Oxide Units Per Molecule (n)	Surfactant Concentration - Weight Percent	Detergency - % Soil Removal
15	0.035	49.4
	0.053	64.9
	0.070	66.8
	0.088	82.8
	0.220	84.0
	0.352	85.8
	0.572	89.4
	0.704	90.6
	0.792	92.7
	0.880	94.3
	1.012	95.8
20	0.094	47.1
	0.127	55.3
	0.188	71.0
	0.252	75.5
	0.332	77.6
	0.502	80.1
	0.685	80.7
	0.898	82.8
	1.106	83.4
	1.345	84.9
	1.925	89.1

TABLE 5 (CONTINUED)

DETERGENCY OF NONYLPHENOL ETHOXYLATES USING TETRAMETHYLPENTADECANE AS SOIL

Ethylene Oxide Units Per Molecule (n)	Surfactant Concentration - Weight Percent	Detergency - % Soil Removal
30	0.200	50.5
	0.308	56.2
	0.385	60.7
	0.539	65.6
	0.616	65.9
	0.924	68.0
	1.386	68.9
	1.848	70.1
	2.310	73.1
40	0.198	32.9
	0.317	38.7
	0.495	46.2
	0.594	52.0
	0.875	53.2
	1.564	57.1
	2.534	62.2
	3.172	66.5
50	0.605	45.0
	0.726	47.4
	0.968	53.5
	1.089	55.3
	1.379	63.4
	2.178	65.9
	2.904	67.0
	3.267	68.0
	3.630	68.6
100	0.438	36.3
	0.938	44.1
	1.438	50.8
	2.374	63.7
	2.507	66.8
	3.750	67.1

TABLE 6

DETERGENCY OF NONYLPHENOL ETHOXYLATES USING LAURYL ALCOHOL AS SOIL

Ethylene Oxide Units Per Molecule (n)	Surfactant Concentration - Weight Percent	Detergency - % Soil Removal
15	0.004	34.3
	0.009	34.3
	0.022	46.8
	0.035	59.1
	0.053	71.0
	0.070	84.8
	0.079	87.1
	0.097	91.2
	0.106	94.5
	0.123	96.4
	0.150	97.9
20	0.006	27.0
	0.011	39.7
	0.017	50.1
	0.028	62.2
	0.033	82.4
	0.039	84.7
	0.044	92.6
	0.066	94.9
	0.088	95.2
	0.110	99.1
	0.138	97.9
	0.165	98.9
30	0.002	48.6
	0.003	62.7
	0.005	81.2
	0.008	89.1
	0.010	98.5
	0.015	98.1
	0.062	99.8
	0.108	100.0
	0.154	99.5

TABLE 6 (CONTINUED)

DETERGENCY OF NONYLPHENOL ETHOXYLATES USING LAURYL ALCOHOL AS SOIL

Ethylene Oxide Units Per Molecule (n)	Surfactant Concentration - Weight Percent	Detergency - % Soil Removal
40	0.001	34.1
	0.004	54.5
	0.007	75.1
	0.010	77.1
	0.019	96.0
	0.030	94.4
	0.079	97.4
	0.089	98.9
	0.119	99.5
	0.166	99.5
50	0.002	32.5
	0.004	36.4
	0.005	47.3
	0.012	71.8
	0.019	88.9
	0.022	90.9
	0.024	95.2
	0.028	97.3
	0.031	98.7
	0.036	98.8
	0.049	98.8
	0.064	100.0
	0.082	99.0
100	0.002	33.0
	0.006	47.7
	0.013	60.7
	0.022	71.6
	0.033	81.2
	0.044	92.5
	0.063	93.4
	0.092	96.5
	0.125	96.1
	0.157	97.4
	0.185	99.0

TABLE 7

OPTIMUM PERCENT CONCENTRATIONS WITH CORRESPONDING DETERGENCY VALUES

Surfactant		Oleic Acid		Tetramethyl-pentadecane		Lauryl Alcohol	
Ethylene Oxide Units Per Molecule (n)	HLB	Optimum % Concentration	% Soil Removal	Optimum % Concentration	% Soil Removal	Optimum % Concentration	% Soil Removal
Nonylphenol Ethoxylates							
15	6.73	0.64	88	0.09	83	0.074	88
20	8.38	0.52	88	0.30	77	0.045	94
30	11.68	0.035	88	0.48	66	0.010	99
40	14.98	0.035	88	0.60	52	0.013	95
50	18.28	0.048	82	1.40	64	0.024	95
100	34.78	1.40	94	2.50	67	0.038	94
Tridecanol Ethoxylates							
12	6.[illegible]9	0.84	87	0.08	84		
15	7.68	0.45	77	0.11	80		
20	9.33	0.19	96	0.16	78		
30	12.63	0.070	95	0.23	58		
40	15.93	0.075	92	0.39	54		

TABLE 8

EMPIRICAL GROUP NUMBERS USED FOR CALCULATING HLB

	Group Number
Hydrophilic Groups	
-OH	1.9
$-(OCH_2CH_2)-$	0.33
-COOH	2.1
Lipophilic Groups	
$-CH-$, $-CH_2-$, $-CH_3$, $= CH-$	0.475

TABLE 9

HLB OF MOST EFFECTIVE SURFACTANT COMPARED TO HLB OF SOIL

Soil HLB		HLB of Most Effective Surfactant
Lauryl Alcohol	3.2	12
Oleic Acid	1.0	12
Tetramethylpentadecane	-2	4

APPENDIX B

FIGURE 1. DETERGENCY OF TRIDECANOL ETHOXYLATES USING OLEIC ACID SOIL

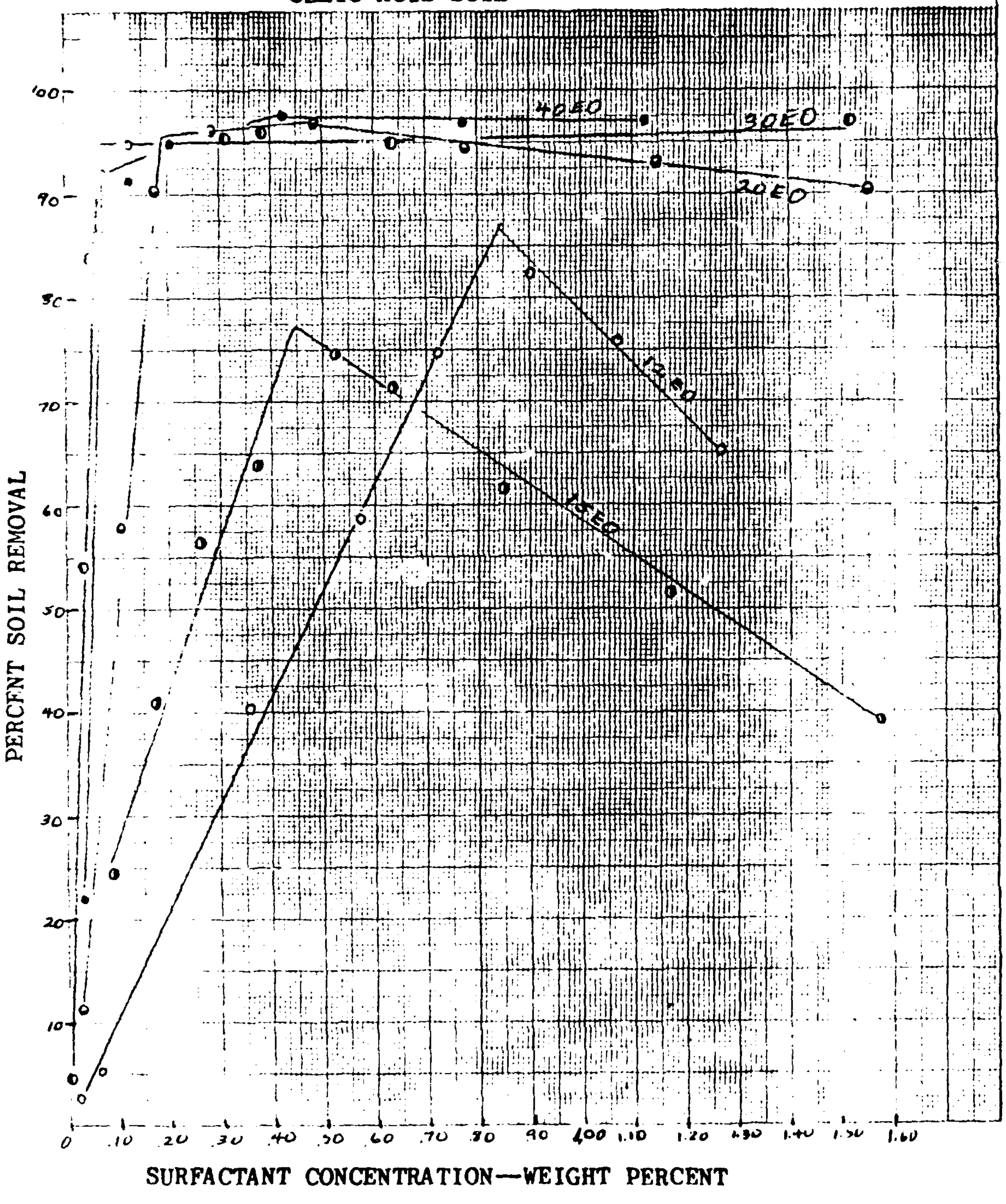

FIGURE 2. DETERGENCY OF NONYLPHENOL ETHOXYLATES USING OLEIC ACID AS SOIL

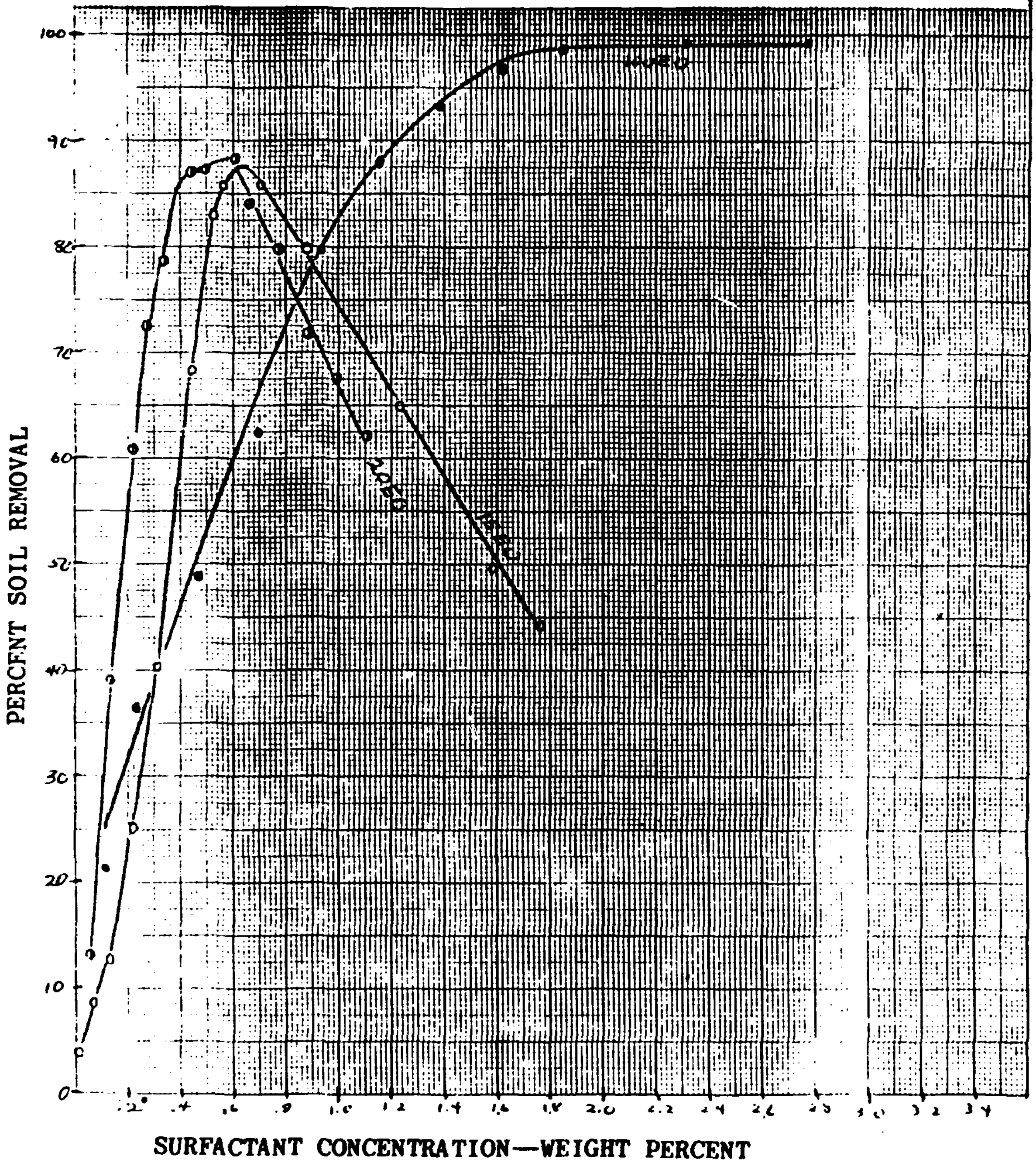

FIGURE 3. DETERGENCY OF NONYLPHENOL ETHOXYLATES USING OLEIC ACID SOIL

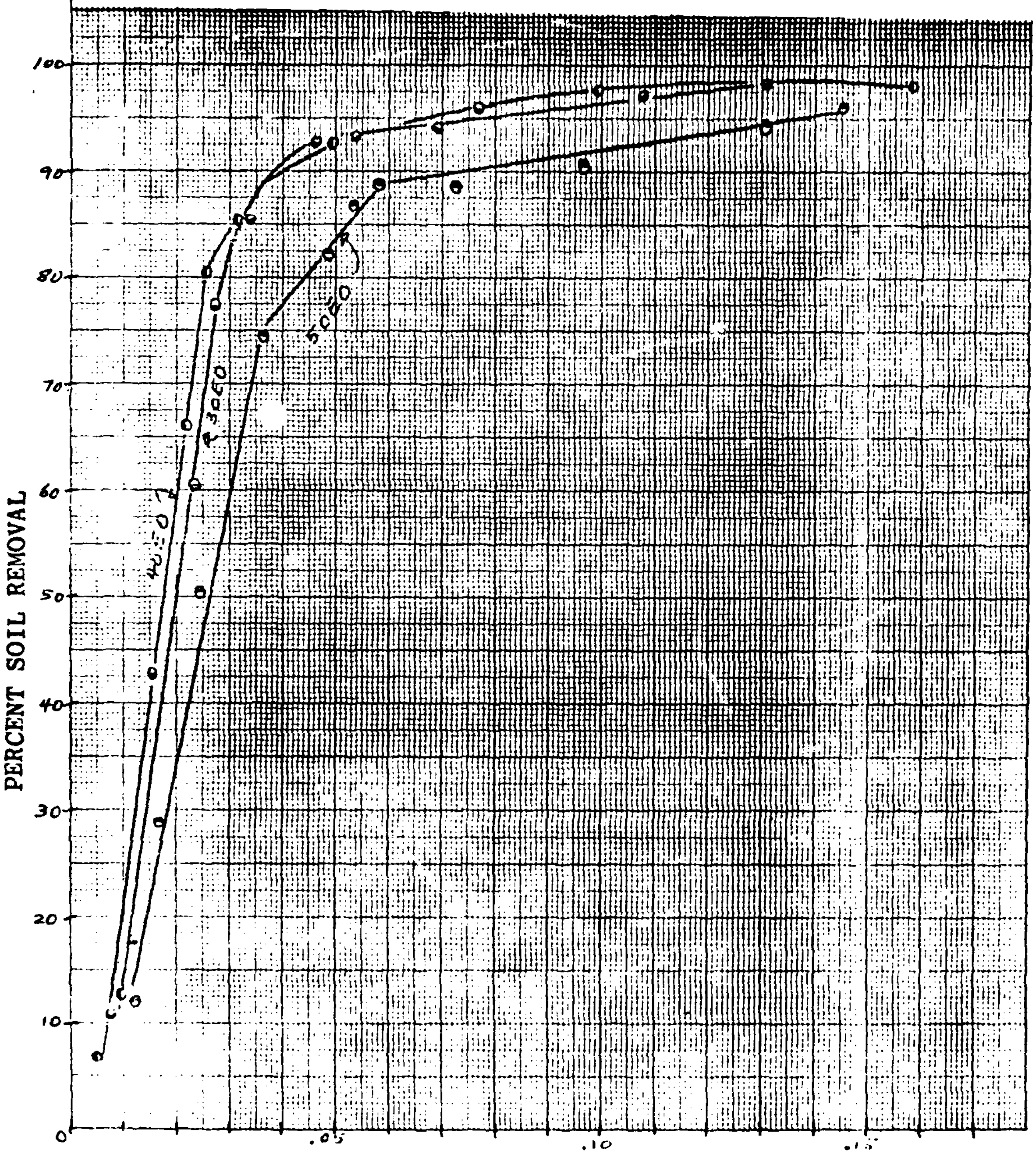

FIGURE 4. DETERGENCY OF TRIDECANOL ETHOXYLATES USING TETRAMETHYLPENTADECANE AS SOIL

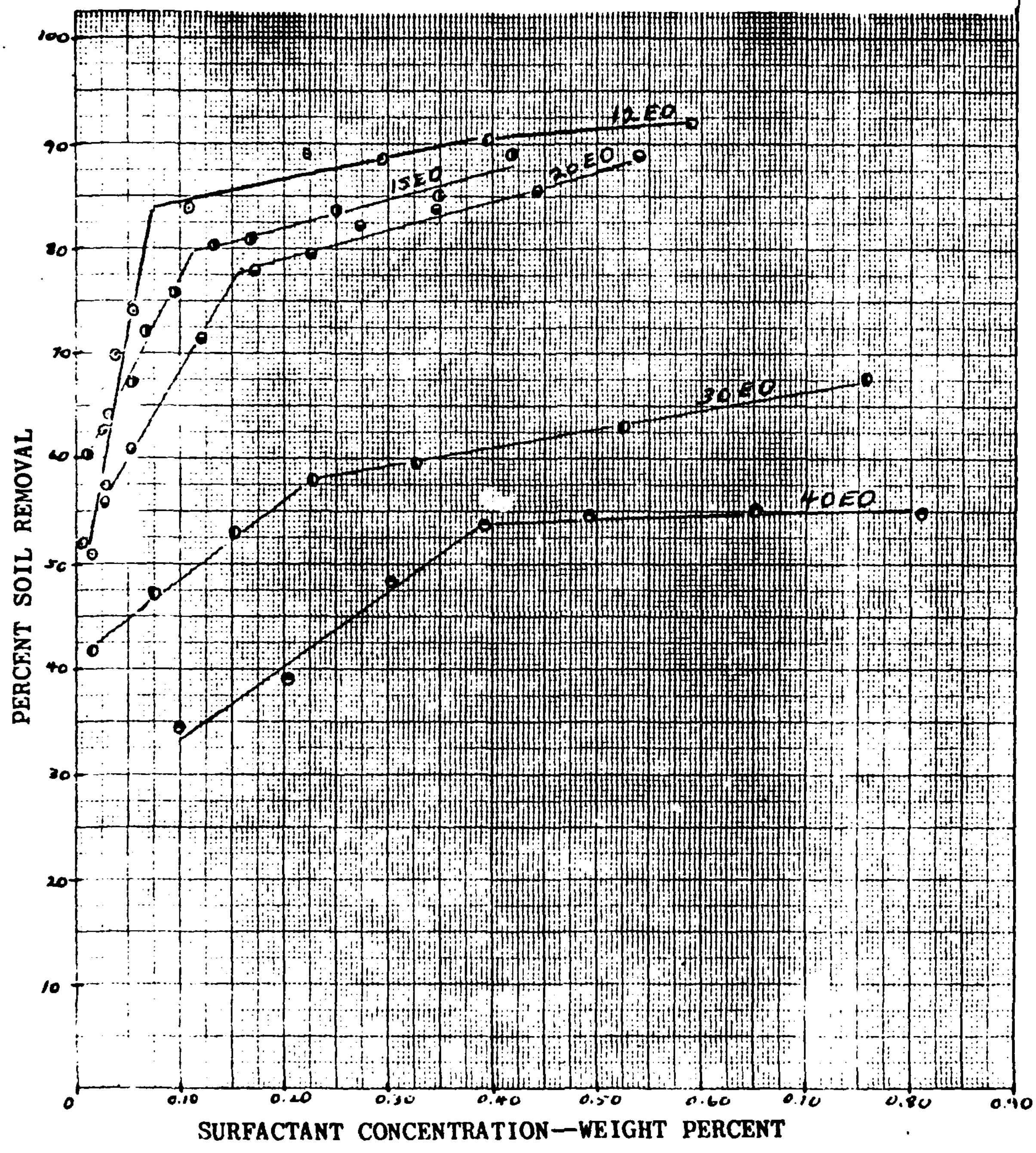

FIGURE 5. DETERGENCY OF NONYLPHENOL ETHOXYLATES USING TETRAMETHYLPENTADECANE SOIL

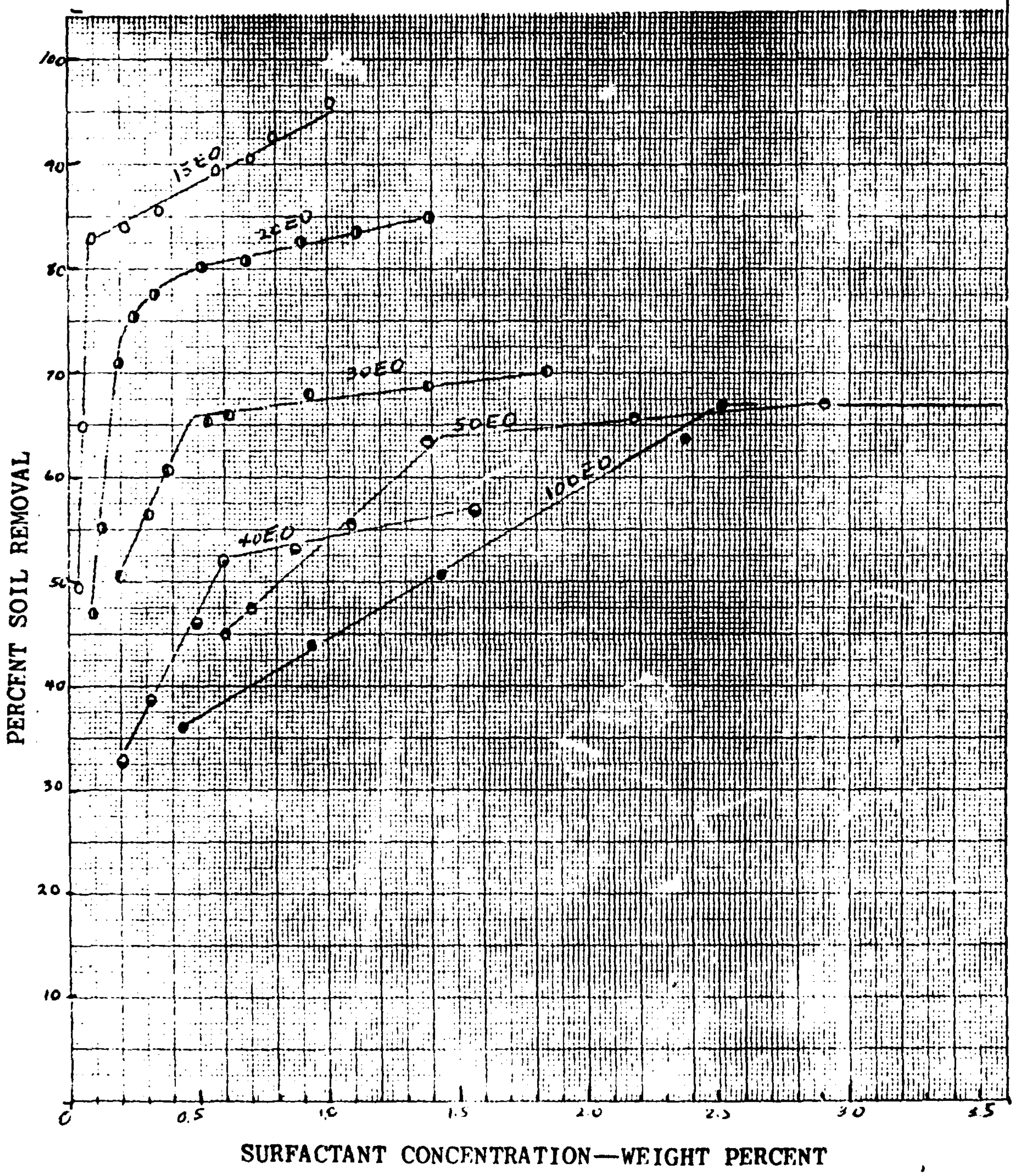

FIGURE 6. DETERGENCY OF NONYLPHENOL ETHOXYLATES USING LAURYL ALCOHOL SOIL

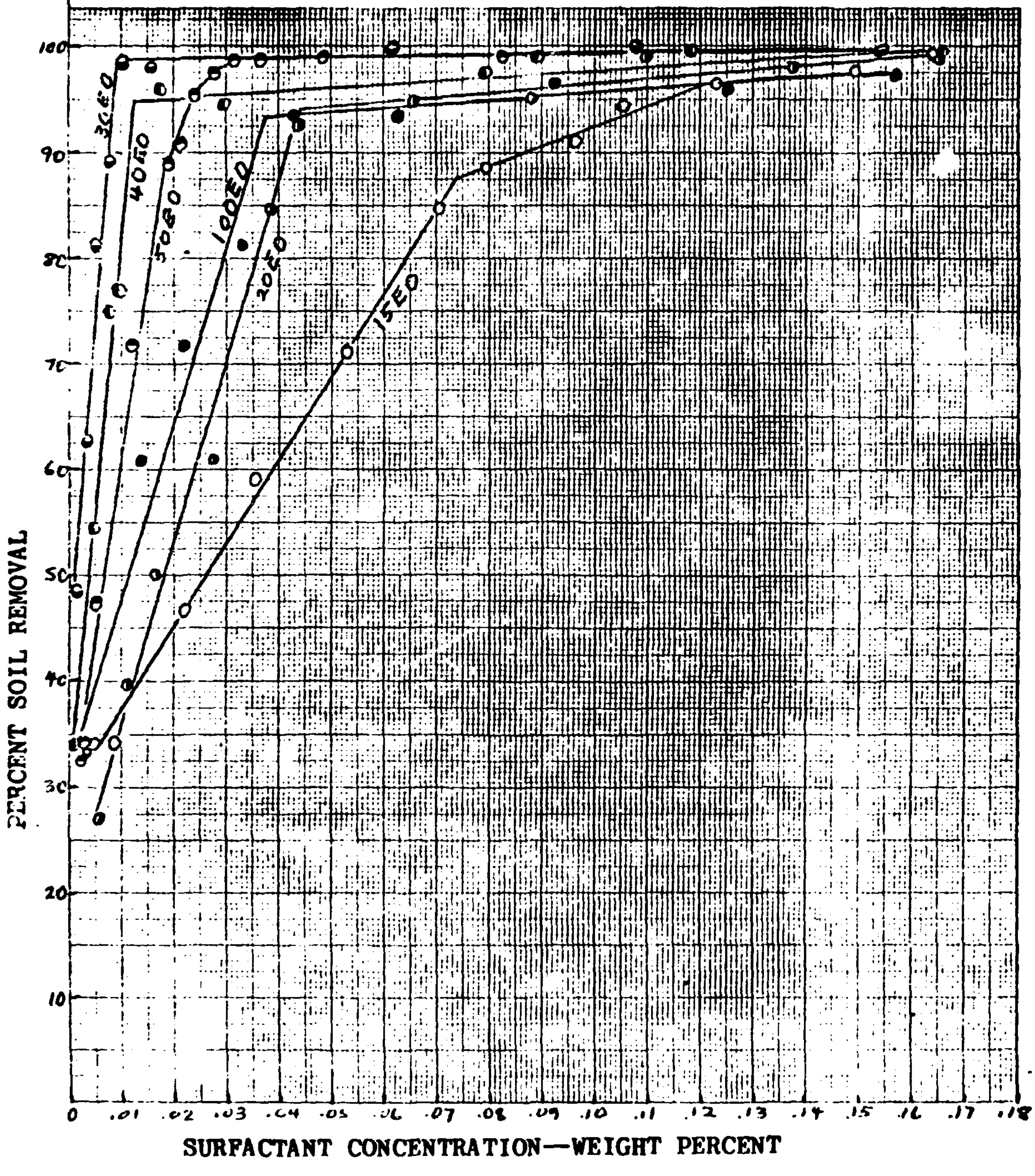

FIGURE 7. OPTIMUM CONCENTRATIONS FOR OLEIC ACID SOIL

o NONYLPHENOL ETHOXYLATES

+ TRIDECANOL ETHOXYLATES

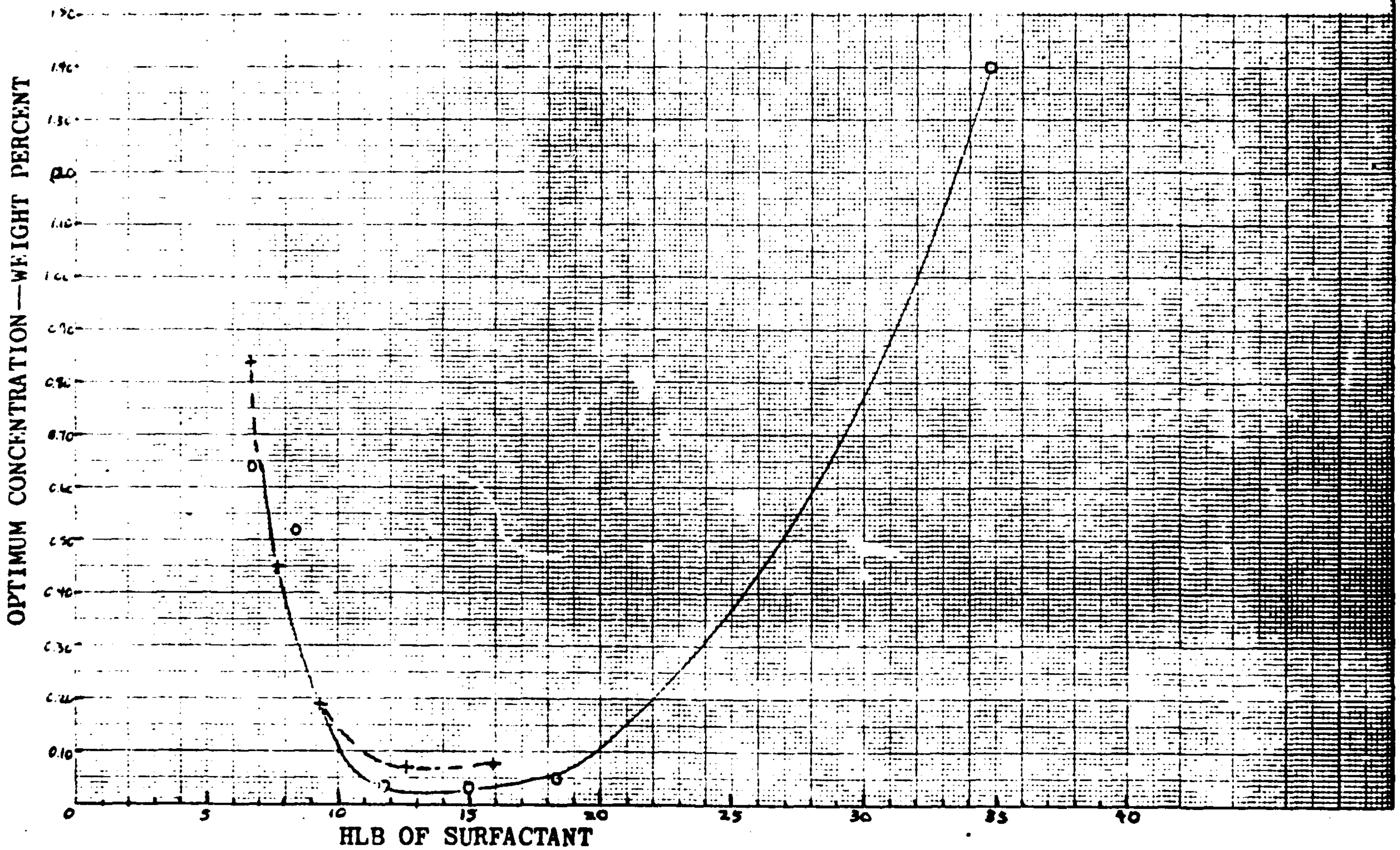

FIGURE 8. OPTIMUM CONCENTRATIONS FOR TETRAMETHYLPENTADECANE SOIL

o NONYLPHENOL ETHOXYLATES

+ TRIDECANOL ETHOXYLATES

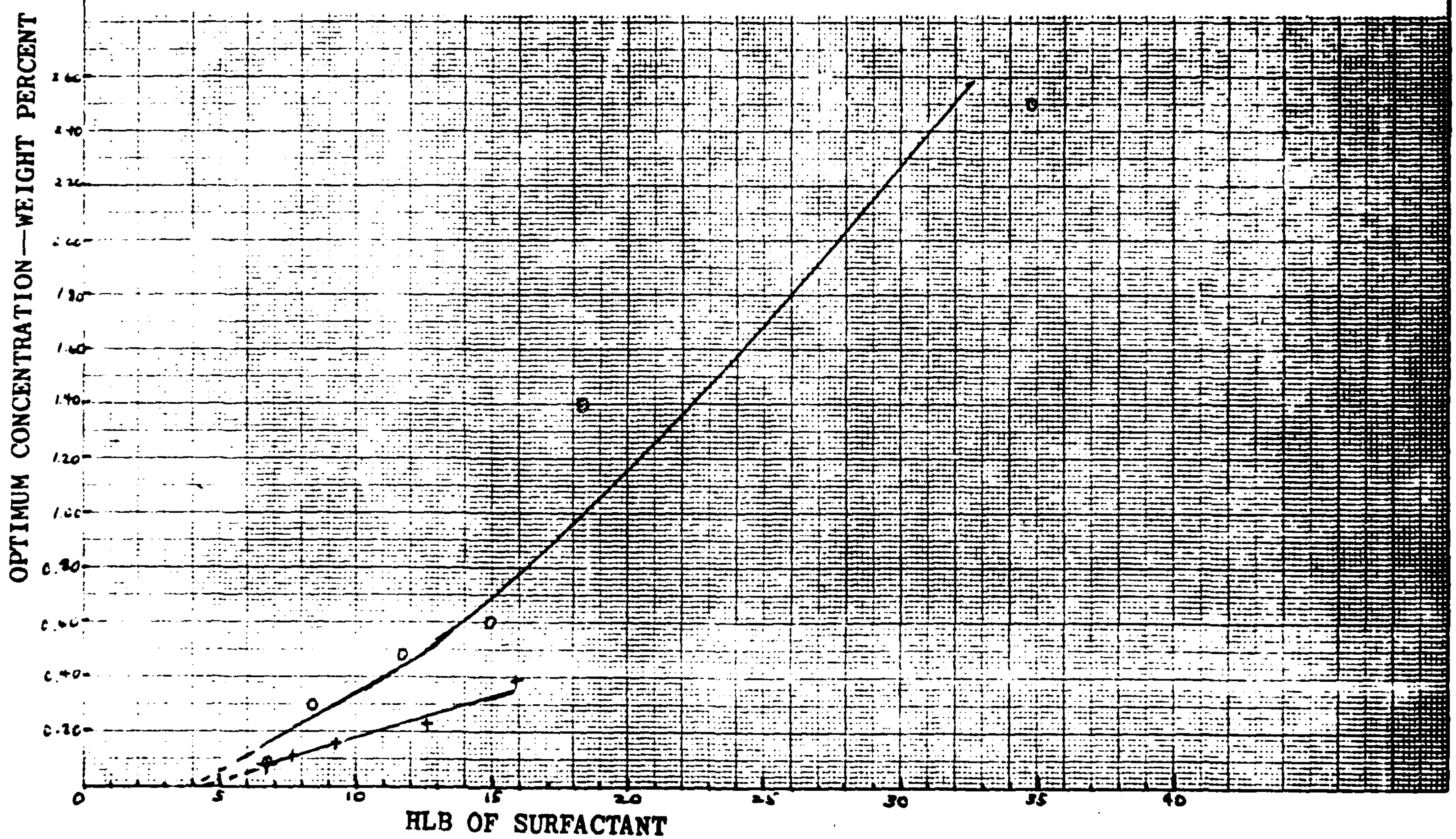

FIGURE 9. OPTIMUM CONCENTRATIONS FOR LAURYL ALCOHOL SOIL USING NONYLPHENOL ETHOXYLATES

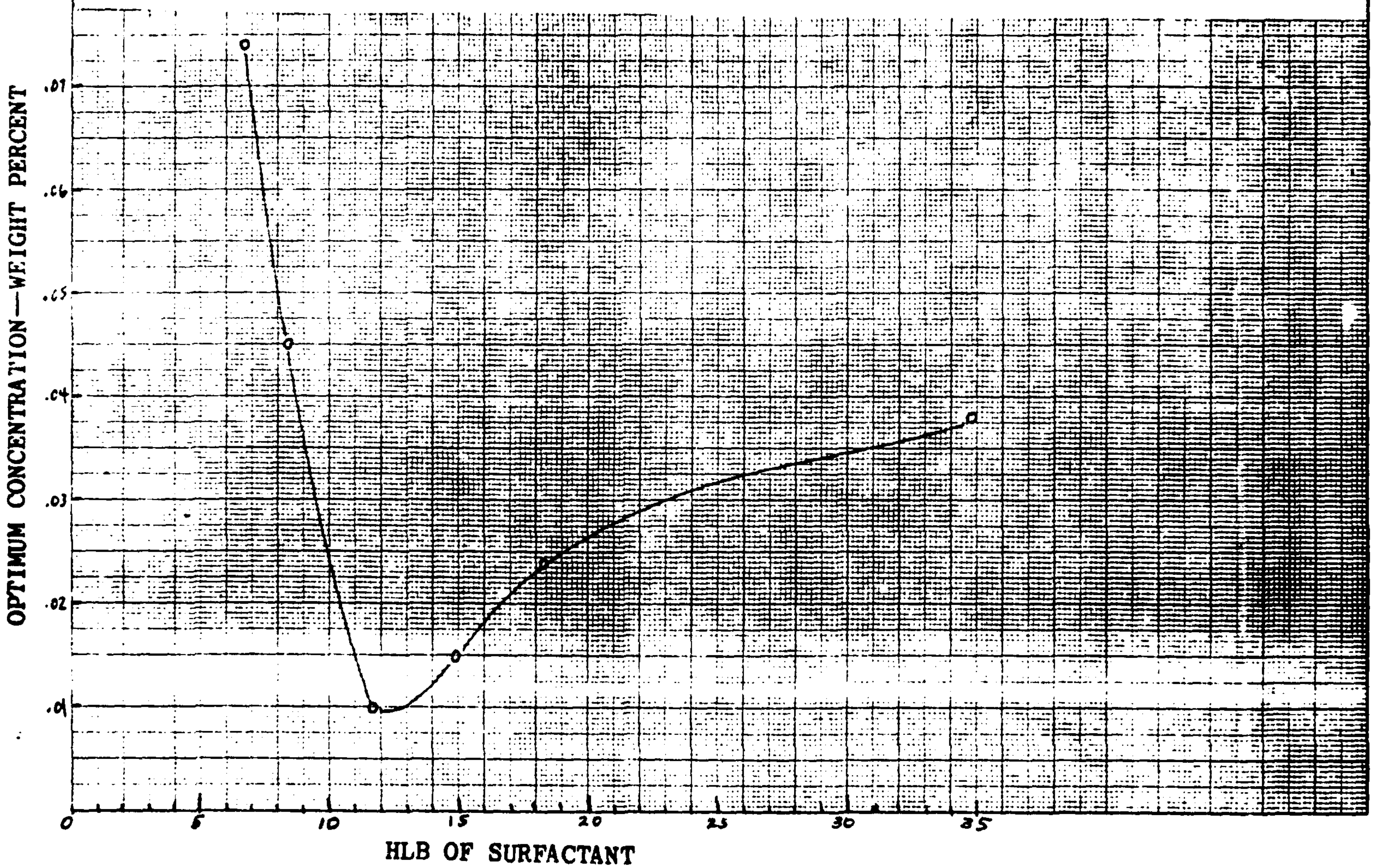

FIGURE 10. PERCENT SOIL REMOVAL AT OPTIMUM CONCENTRATION

+ NONYLPHENOL ETHOXYLATES

⊙ TRIDECANOL ETHOXYLATES

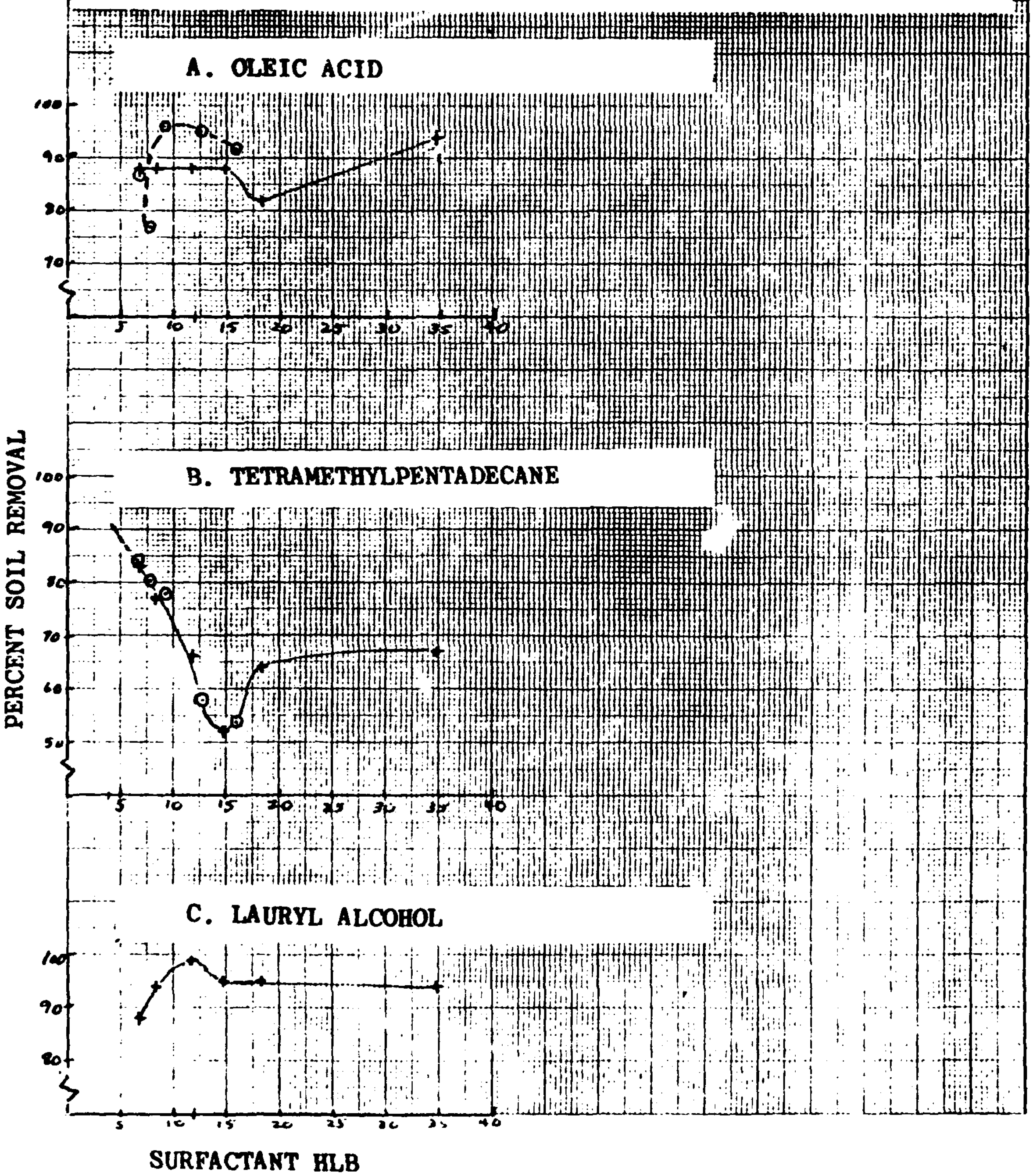

FIGURE 11. VARIATION OF MOST-EFFECTIVE SURFACTANT HLB WITH HLB OF SOIL