Non-Ionic Detergents From Wax

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NON-IONIC synthetic detergents possessing interesting detergency properties have been prepared by reacting the fatty acids obtained from paraffin wax oxidation with ethylene oxide. The paraffin used in this work was Ultax 20,* a low melting chemical grade wax having the physical properties shown in Table I.

TABLE I

Color	White
Melting Point	33.9°C.
Aniline Point	105.6°C.
Specific Gravity @ 80°C	0.7471
Refractive Index @ 80°C	1.4192
Iodine Number	0.3
Saybolt Viscosity @ 37.5°C	43.3 sec.
A.S.T.M.Distillation @ 10 mm.	
I.B.P	182°C.
10%	190°C.
50%	196.1°C.
90%	201.7°C.
Dry	204.4°C.
Molecular Weight	274

* Product of The Atlantic Refining Company.

The oxidations were carried out by bubbling air through the wax at the rate of 3.2 cc. per minute per gram of wax at a temperature of 150°C. for 16-24 hours. A promoting catalyst of 0.1% manganese naphthenate and 0.1% sodium carbonate was used to initiate the oxidation. Once through conversions of 45% were obtained with this conversion going to 98% by means of recycling.

The acids formed were separated from the unoxidized wax, aldehydes, and ketones by saponifying with 10% NaOH, separating, and then acidifying with HCl. Upon vacuum distillation of the separated naphtha soluble acids the products shown in Table II were obtained.

TABLE II

C_{10} acids	15.7%
C_{14} acids	8.4
C_{20} acids	24.2
C_{22} acids	13.7
C_{36} acids	11.8
Polyacids or Tar	26.2

No effort was made to determine the structure of the acids produced. The number of carbon atoms shown in Table II is an average value obtained by determining the acid value of the fraction tested. Each of the fractions shown in Table II was then reacted with ethylene oxide by contacting the gas with the fatty acid and a suitable catalyst at about 205°C. until the desired quantity of oxide as determined by the increase in weight was added. The minimum quantities of ethylene oxide required to give a completely water miscible product are shown in Table III.

It is also possible to make the ethylene oxide addition products without first removing the acids from the unoxidized wax. At the end of the oxidation cycle the temperature is raised to 205°C. and ethylene oxide bubbled into the mixture in the presence of suitable catalysts, such as sodium hydroxide. After the desired amount of ethylene oxide has been added, the reaction mass is diluted with several volumes of pentane and the ethylene oxide addition product settled out. This product appeared to be almost identical to the product derived from the composite C_{10}-C_{36} extracted acids. The wax acid non-ionics were in all cases amber to reddish colored liquids which possessed pleasant ester-like odors even though the original wax acids before reaction with the ethylene oxide possessed typical oxidized petroleum odors.

TABLE III

Acid Fraction	Equivalents of Ethylene Oxide to Give Water Solubility
C_{10}	17.6
C_{14}	7.0
C_{20}	5.4
C_{22}	6.9
C_{36}	7.6
Composite C_{10}-C_{36}	8.5

In evaluating the non-ionic detergents made, launderometer washing tests were run on both cotton and wool which were synthetically soiled. The soil solution in each case was the same, namely 3.1 g. of white mineral oil, 0.9 g. of hydrogenated cottonseed oil, and 1 g. of lampblack in 500 cc. of carbon-tetrachloride. The test swatches which measured 2″ x 4″ were soiled to a reflectance of 18 to 20 for cotton and 28 to 30 for wool and then used within 48 hours of their preparation. A Photovolt reflectometer was used to measure all the reflectances. The detergency tests were all run in an Atlas launderometer at 105°F. for wool and 120°F. for cotton. Philadelphia tap water which averages 85 p.p.m. of hardness was used in all tests.

In arriving at values for each detergent the following formula was used:

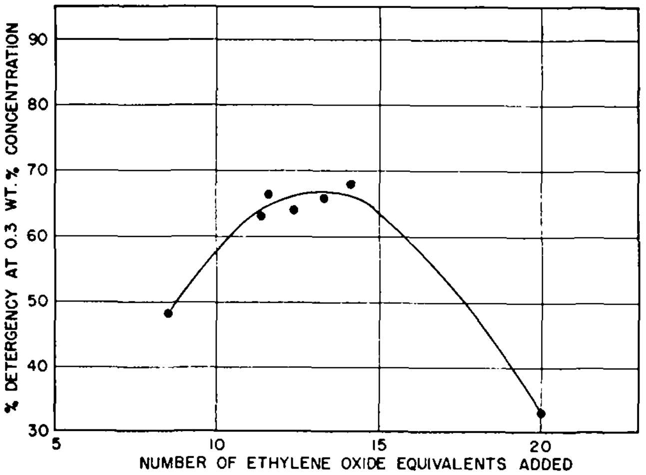

FIG. 1. Effect of varying ethylene oxide content in composite wax acid non-ionics $\left(\frac{40\text{ active}}{60\ \text{Na}_2\text{SO}_4}\right)$.

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* Product of The Atlantic Refining Company.

$$\text{Per cent detergency} = \frac{\text{Laundered Reflectance} - \text{Soiled Reflectance}}{\text{Original Reflectance} - \text{Soiled Reflectance}} \times 100$$

In most non-ionic synthetic detergents there appears to be an optimum amount of ethylene oxide for maximum detergency. This relationship is shown in Fig. 1 for the composite wax acids. All the detergency data reported were obtained on the wax acid compounds containing near optimum amounts of ethylene oxide. Wool and cotton detergencies on the various molecular weight acid derivatives are shown in Figures 2A and 2B. They both indicate that the polyethylene glycol esters of the C_{10} acids are relatively poor detergents while the product derived from the composite acids is slightly superior to the best of the non-ionics derived from the individual acid fractions. On wool the C_{14} acid esters appear to have a quality edge with the detergency falling off as the molecular weight increases. On cotton all the materials from C_{14} to C_{36} acid esters appear to be too nearly alike to differentiate as to quality.

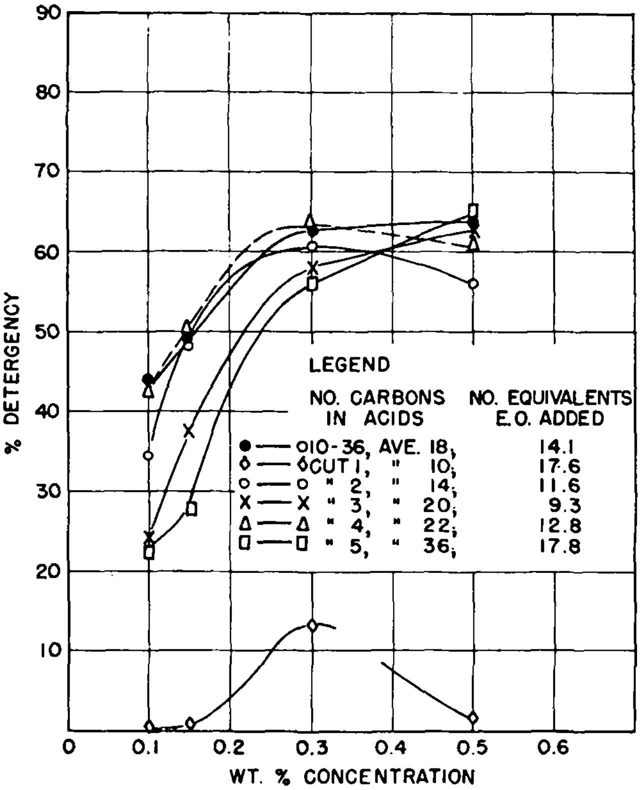

FIG. 2A. Variance in cotton detergency with non-ionics derived from wax acids of different carbon content $\left(\frac{40 \text{ active}}{60\ Na_2SO_4}\right)$.

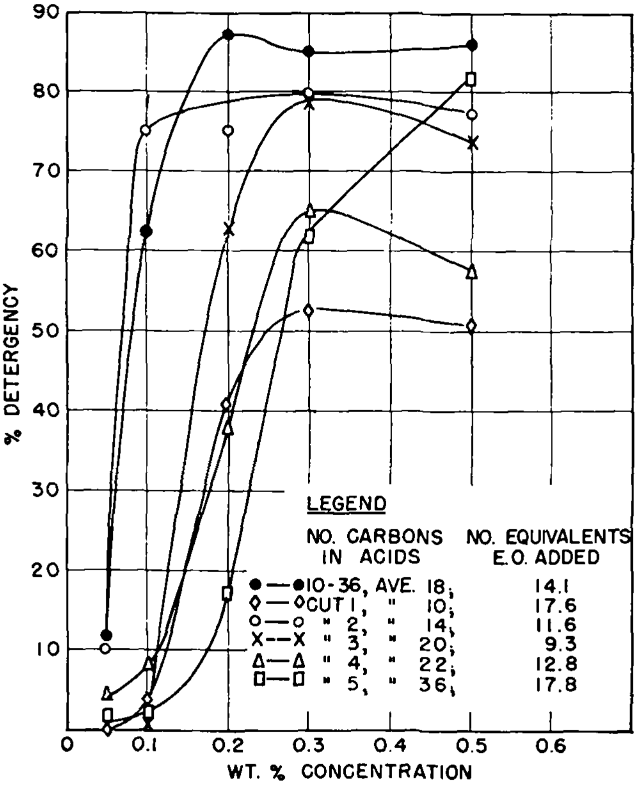

FIG. 2B. Variance in wool detergency with non-ionics derived from wax acids of different carbon content $\left(\frac{40 \text{ active}}{60\ Na_2SO_4}\right)$.

In Figures 3A and 3B the effects of diluting the non-ionic with sodium sulfate are shown. If the curves as shown are replotted on an active ingredient basis, it will be apparent that in the case of cotton detergency the sodium sulfate is merely a diluent while in the case of the wool detergency at the low concentrations (.05 to .15% active ingredient) the sodium sulfate shows synergistic properties.

In Figure 4 the effect of building with an alkali for improved cotton detergency is illustrated. Approximately 50% improvement in detergency is obtained by replacing up to one-third of the sulfate with tripoly-phosphate. No noticeable improvement in wool

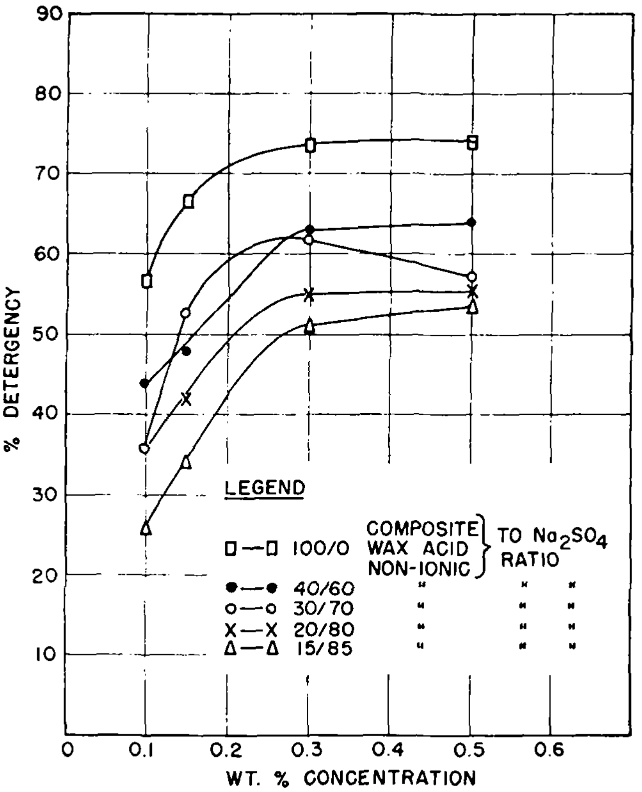

FIG. 3A. Cotton detergency with varying wax acid non-ionic to sodium sulfate ratios.

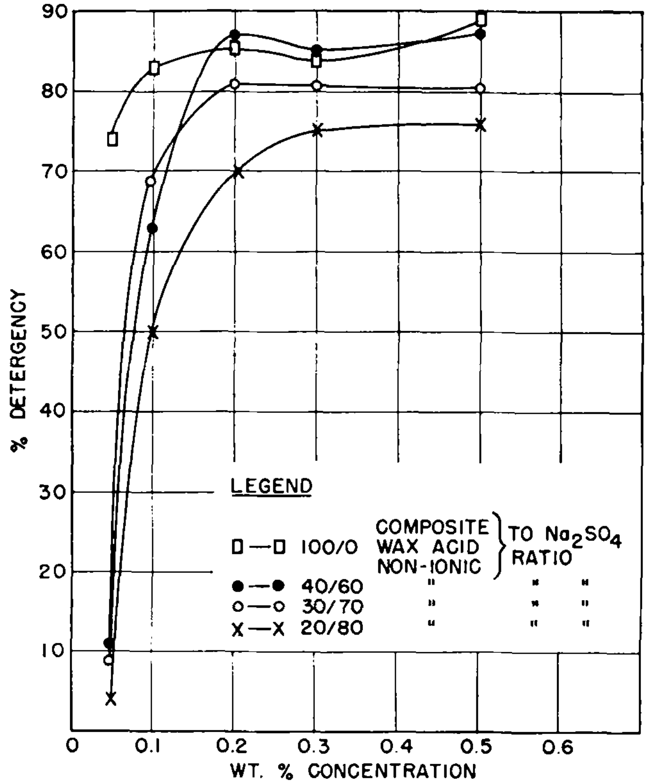

FIG. 3B. Wool detergency with varying wax acid non-ionic to sodium sulfate ratios.

detergency is observed with phosphate building. In Figures 5A and 5B the comparative detergencies of wax acid non-ionics and non-ionics in which the lyophobic part of the molecule was varied are shown. On wool the wax acids appear to behave as do the more

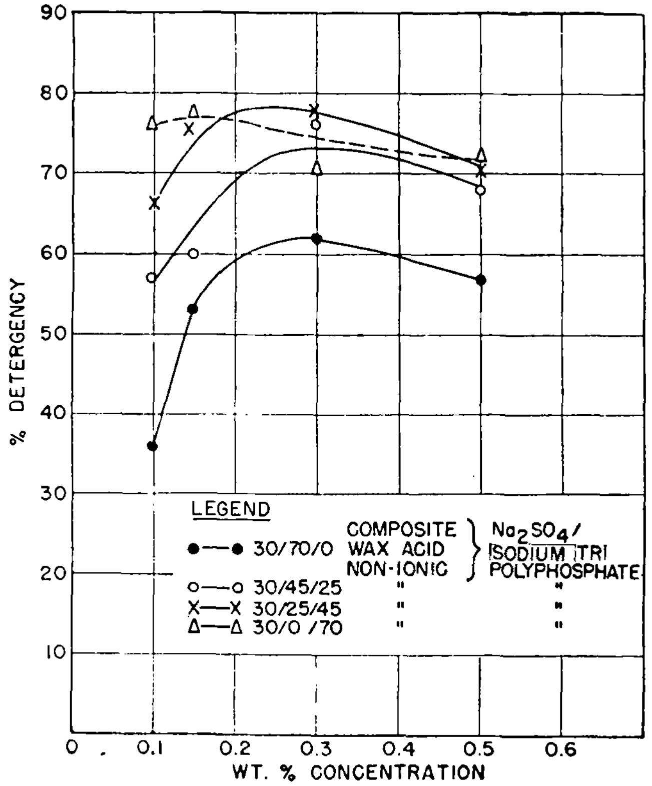

FIG. 4. Effect of building cotton detergency with an alkali (sodium tri polyphosphate).

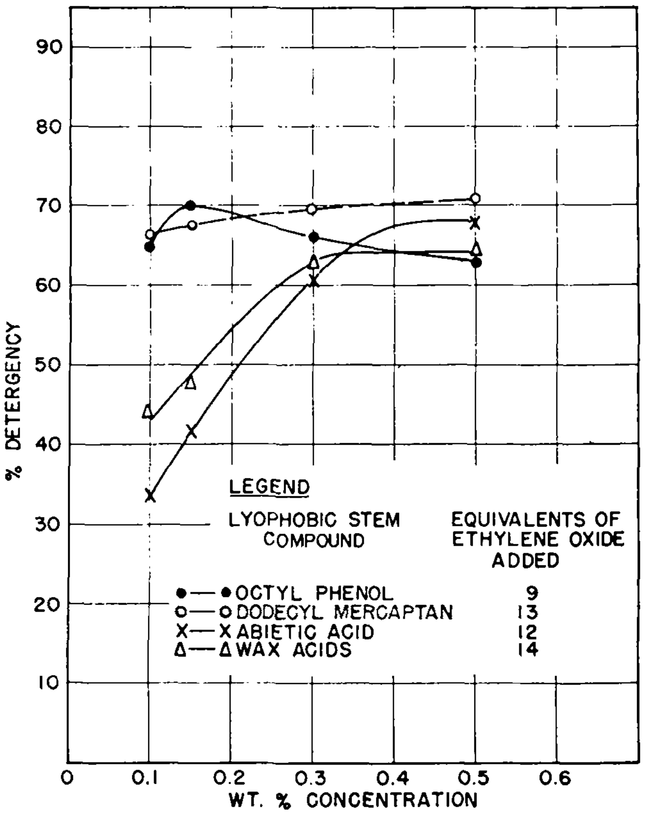

FIG. 5A. Cotton detergency of various type non-ionics $\left(\frac{40\text{ active}}{60\ Na_2SO_4}\right)$.

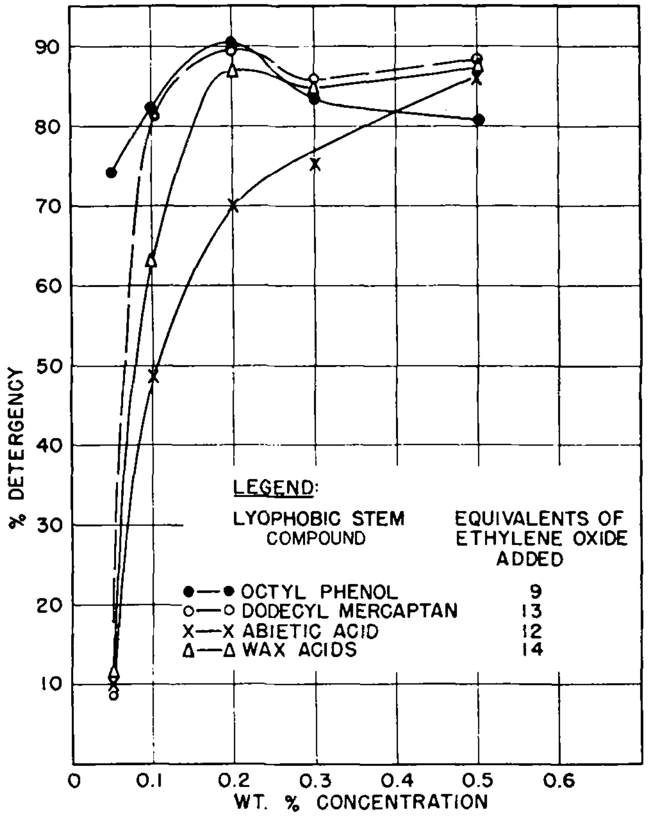

FIG. 5B. Wool detergency of various type non-ionics $\left(\frac{40\text{ active}}{60\ Na_2SO_4}\right)$.

common type non-ionics while on cotton the efficiency seems to be poorer at the lower concentrations but at use concentrations again to be comparable with other type non-ionics.

The sudsing characteristics of the wax acid non-ionics were observed in launderometer tests as well as in many of the empirical shaking tests. In most instances the amount of suds formed was small and not too lasting.

Conclusion

Non-ionic synthetic detergents having detergent properties similar to those of alkyl phenol polyethylene glycol ethers and alkyl mercapto polyethylene glycol ethers can be prepared by reacting the optimum quantity of ethylene oxide with the composite crude fatty acids made by the air oxidation of low melting chemical grade paraffin wax.

Testing of Drying Oils. II. Evaluation of Natural and Synthetic Oils*

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IN a previous paper Bolley and Gallagher (1) have described in detail a method for the preliminary examination of drying oils. This method has been used by the National Lead Company's Research Laboratory for the evaluation of a large number of oils. It is the purpose of this paper to present some of the data obtained during the evaluation program.

Since this is a preliminary evaluation which is to be completed in a relatively short time, the scheme does not include exposure tests. The object is to characterize the oils to determine their probable application; final evaluation must await exposure tests. Accelerated exposure tests were not included since these have been found to be unreliable in many cases.

One test has been added to the evaluation program as previously described. This is the determination of flash point according to the standard A.S.T.M. Method D92-33 and was included when it was noticed that some synthetic oils had relatively low flash points. A comparison of the data presented in this paper with the previously published method will disclose that not all of the tests have been reported. Although all the tests were actually run on the oils, it seemed desirable to eliminate the results of lesser interest and significance in order to keep the already lengthy tables of data to a minimum.

The following oils, referred to in the abreviated form used in the tables, were tested:

G Bodied Linseed—An alkali refined, bleached, and refrigerated linseed oil heat bodied to a G viscosity.

Conjugated Linseed—A refined linseed oil catalytically treated to contain 8.1% conjugated linoleic isomer and 0.5% conjugated linolenic isomer.

Linseed Penta.—Technical pentaerythritol esterified with nearly equivalent amounts of linseed oil fatty acids.

Dehydrated Castor—Regular commercial unbodied dehydrated castor oil.

Fatty Tall Oil—Tall oil processed to remove a large amount of the rosin acids and the fatty acid concentrate esterified with technical pentaerythritol.

G Bodied Soybean—Refined soybean oil heat bodied to a G viscosity.

Conjugated Soybean—A refined soybean oil catalytically treated to contain 10.1% conjugated linoleic isomer and 1.2% conjugated linolenic isomer.

Soybean Penta.—Technical pentaerythritol esterified with nearly equivalent amounts of soybean oil fatty acids.

Soybean Mannitol—One mol. of mannitol esterified with four mols. of soybean oil fatty acids.

Soybean Sorbitol—One mol. of sorbitol esterified with four mols. of soybean oil fatty acids.

Q Bodied Linseed—An alkali refined, bleached, and refrigerated linseed oil heat bodied to a Q viscosity.

Linseed Polypenta.—Technical polypentaerythritol esterified with nearly equivalent amounts of linseed oil fatty acids.

Linseed Mannitol—One mol. of mannitol esterified with four mols. of linseed oil fatty acids.

Linseed Sorbitol—One mol. of sorbitol esterified with four mols. of linseed oil fatty acids.

TABLE I

Chemical Constants

	Visc.	Color	Appearance	Odor	Acid Value	Sap. Value	Acetyl Value	Iodine Value	% Unsap.	% Ash	Ref. Index	Specific Gravity
G Bodied Linseed	G	6	Clear	Normal	2.1	189.0	5.4	165.0	1.43	0.000	1.4841	0.9430
Conjugated Linseed	F	7	Clear	Bodied Oil	3.3	190.7	7.4	154.7	1.20	0.000	1.4838	0.9431
Linseed Penta	I—	12—	Clear	Bodied Oil	4.0	180.9	28.4	155.6	1.99	0.000	1.4850	0.9524
Dehydrated Castor	H+	6	Clear	Normal	8.5	198.3	1.6	137.3	0.96	0.000	1.4820	0.9377
Fatty Tall Oil	J—	10	Clear	Fatty	6.7	170.8	3.6	133.1	4.80	0.055	1.4861	0.9490
G Bodied Soybean	F	5+	Clear	Normal	2.2	189.6	5.0	119.0	1.15	0.000	1.4765	0.9358
Conjugated Soybean	G	6	Clear	Normal	3.2	192.3	3.4	118.5	0.92	0.000	1.4771	0.9356
Soybean Penta	H+	12	Clear	Normal	3.3	185.9	52.2	125.1	1.00	0.000	1.4796	0.9475
Soybean Mannitol	G	7—	Clear	Normal	29.5	183.2	3.1	112.1	0.71	0.000	1.4774	0.9402
Soybean Sorbitol	F	6	Clear	Normal	16.5	185.1	7.8	119.6	0.80	0.020	1.4775	0.9463
Q Bodied Linseed	U	5	Clear	Bodied Oil	5.9	192.2	6.9	141.4	1.06	0.000	1.4858	0.9585
Linseed Polypenta	Q	11+	Clear	Bodied Oil	1.6	181.2	45.3	154.3	1.54	0.006	1.4852	0.9592
Linseed Mannitol	T	10	Clear	Normal	31.3	179.7	7.3	131.8	2.05	0.000	1.4862	0.9654
Linseed Sorbitol	P	9	Clear	Bodied Oil	18.2	185.0	8.0	146.8	1.63	0.018	1.4857	0.9606
Soybean Polypenta	P	10	Clear	Bodied Oil	1.2	177.0	37.4	129.8	0.89	0.013	1.4819	0.9553
Soybean Maleic Glyc	Q	8	Clear	Normal	6.3	212.6	37.5	120.1	0.14	0.000	1.4800	0.9592
Soybean Maleic Penta	S—	9	Clear	Normal	14.5	221.0	24.1	120.5	1.63	0.005	1.4806	0.9614
Z2 Bodied Linseed	Z2	6	Clear	Bodied Oil	6.6	194.0	4.8	123.8	1.54	0.000	1.4890	0.9664
Linseed Maleic Glyc	Z1+	7—	Clear	Acrid	7.9	211.8	23.4	138.0	1.05	0.014	1.4879	0.9763
Linseed Maleic Penta	Z2+	7	Clear	Acrid	11.8	212.8	24.8	155.5	0.98	0.000	1.4872	0.9731

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* Presented at 22nd annual fall meeting, American Oil Chemists' Society, Nov. 15-17, 1948, New York City.