Analyses of the component fatty acids were made by interesterification to form esters, which were separated into principally saturated and unsaturated fractions by low temperature crystallization. Each of these fractions was fractionated on a Todd column. The resulting fractions were examined spectrophotometrically and the percentage of each acid was calculated.

The oil of *Sebastiana lingustrina* contains an unusual fatty acid, probably 2,4-dodecadienoic acid.

REFERENCES

1. Brice, B. A., and Swain, M. L., J. Optical Soc. Am., *35*, 532 (1945) and personal communication.
2. Brown, J. B., Oil and Soap, *21*, 183-7 (1944).
3. Norris, F. A., and Terry, D. W., Oil and Soap, *21*, 193-6 (1944).
4. Potts, W. M., and Bolley, D. S., Oil and Soap, *23*, 316-18 (1946).
5. Shen, Tze-Hui, Chiso-Tung Univ. Research Institute, Ann. Report Bur. Chem., *3*, 17-36 (1936); Chem. Abst., *31*, 3309 (1937).
6. Small, J. K., "Manual of Southwestern Flora," Lane, Pa., Press of the Science Press Printing Co. (1933).

[Received September 8, 1950]

Properties of Some Newly Developed Nonionic Detergents

THOMAS H. VAUGHN, H. R. SUTER, LESTER G. LUNDSTED, and M. G. KRAMER, Research and Development Division, Wyandotte Chemicals Corporation, Wyandotte, Michigan

NONIONIC synthetic detergents are receiving increasingly wide recognition because of their versatility and excellent compatibility characteristics. Classification, general chemical and physical properties and applications have been adequately described (1, 2, 3).

Of particular interest has been the employment of nonionic detergents in the textile industry (4) and for the washing of synthetics, wool, and cotton. For the latter application, formulations containing nonionic compounds have been used successfully for both household and commercial laundering. This success has been attributed in part to the excellent suspending properties of the nonionics.

A New Series of Nonionics

Typical nonionic detergent molecules contain a hydrophobic unit usually derived from fatty acids, fatty alcohols, alkyl phenols, or mercaptans combined with a hydrophilic group which is, in most cases, a polyethylene glycol chain introduced into the structure by condensation of ethylene oxide with the hydrophobic base. These materials are not ionizable, and their characteristics are, to a considerable extent, dependent on the balance between hydrophobic and hydrophilic groups. A low complement of ethylene oxide to the hydrophobic base usually results in a liquid. Introduction of larger amounts of ethylene oxide into the molecule results in pasty or solid products, which generally have relatively poor detergency properties because of an overbalance in the direction of the hydrophilic portion of the molecule. Previous efforts to obtain a solid product of acceptable surface-active and detergency properties have failed in that the melting point was too low to permit flaking.

These laboratories have recently developed a series of nonionics ranging from liquids to hard solids by employing a hydrophobic unit not previously used in the manufacture of nonionics. As with other nonionics, variations in properties have been achieved by choice of the molecular weight of the hydrophobic unit and by adjustment of the hydrophilic-hydrophobic ratio. The physical, surface-active, and detergency properties of this series are such as to adapt the products to a wide variety of applications and, in fact, to permit true tailoring of formulations.

The properties of this new series of nonionic detergents have been described in detail (5). It is the purpose of this paper to present briefly the general properties and to discuss at greater length the detergency aspects of the new development. For ease of reference these products will be referred to by their trade name "Pluronic."[1] Each member is further designated by a letter and a two-digit number, the first digit of which designates the relative molecular weight of the hydrophobic unit and the second digit, the relative hydrophilic-hydrophobic ratio. "L" designates a liquid, "P" a paste, and "F" a solid of sufficiently high melting point to permit flaking. Pluronics L62, L64, and F68 comprise a series in which the molecular weight of the hydrophobic unit is constant while the hydrophilic component is increased. Pluronics L44 and L64 have the same hydrophilic-hydrophobic ratio, but Pluronic L64 contains a hydrophobic unit of higher molecular weight.

Four of these products will be surveyed to illustrate the variation of physical, surface-active, and detergency properties with chemical composition.

Physical Properties

The physical properties of this newly developed series of nonionic detergents, all of which contain 100% active agent, are given in part in Table I. The softening point of Pluronic L44 is slightly lower than that of Pluronic L64, as expected because of its lower molecular weight. Similarly the softening point increases from —32°C. for Pluronic L62 to 51-54°C. for Pluronic F68. The melting point of Pluronic F68 is such as to permit flaking to produce a free-flowing dustless product.

The flaked product is relatively non-hygroscopic. By comparison with the data in Table I a typical commercial alkylarylsulfonate containing 40% active agent gained 6.2% in weight.

[1] ®, Wyandotte Chemicals Corporation, Wyandotte, Michigan.

TABLE I
Physical Properties of Pluronic Detergents

	Pluronic			
	L62	L64	F68	L44
Form	Liquid	Liquid	Flake	Liquid
Odor	Slight	Slight	Slight	Slight
Softening point, °C.	—32	—6	51-54[a]	—11
pH, 0.25% soln., at 25°C.	6.5-7.5	6.5-7.5	6.5-7.5	6.5-7.5
Moisture pickup, 7 days, 80% R.H., room temp., %	3.0	3.4	3.6	1.7
Solution rate, time to form a 2% solution at 25°C., minutes	11.5[b]	3.5	4.5	0.5
Solubility in water at 25°C., weight, %	0.5	∞	∞	∞

[a] Melting point by capillary tube method. [b] Determined at 22°C.

The rate of solution was determined by measuring the time required to effect complete solution of 4 grams of material in 200 ml. of water at 25°C. The mixture was stirred in a 600-ml. beaker using paddle wheels 1 x 3 in. in size, adjusted to clear the bottom of the beaker and operated at 100 rpm. The rate of solution of these nonionic detergents is reasonably rapid as compared with that of a flaked anionic detergent, which at the same concentration required seven minutes to effect solution. The solubility rate increases with increase in the hydrophilic portion of the molecule as shown by the increase in the rate of Pluronic L64 over that of Pluronic L62. Also Pluronic L44, being of lower molecular weight, dissolves more rapidly than Pluronic L64. The solution time for Pluronic F68, being greater than expected, indicates that physical form as well as molecular structure influences the solubility rate.

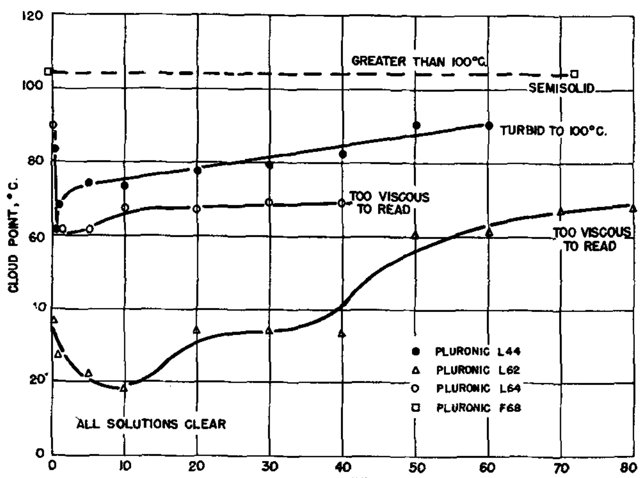

FIG. 1. Effect of concentration on cloud point of distilled water solutions of Pluronics.

Figure 1 shows the effect of concentration of the Pluronics on the cloud point which is defined as the temperature at and above which the solution becomes cloudy. Solid Pluronic F68 is miscible with water in all proportions giving liquid solutions containing 75% active agent at room temperature and solid solutions or gels at higher concentrations. Pluronics L64 and L44 are soluble in water in all proportions at temperatures up to 60°C. As measured by the cloud point, the solubility curves for the liquid Pluronics pass through a minimum critical solution temperature below which each Pluronic is miscible with water in all proportions. Flowable non-turbid solutions of Pluronic L62 are obtainable however in concentrations of 15% to about 75% at 25°C. With the exception of the decrease at the lower concentrations, the solubility of the liquid Pluronics increases with increase in temperature. With some exceptions other nonionic detergents have shown similar behavior.

When tested by the proposed ASTM Procedure (6), each of the Pluronics was found to be resistant to precipitation in the presence of the following metal ions: calcium, magnesium, copper, aluminum, ferrous iron, lead, zinc, and nickel.

Surface-Active Properties

Figures 2 and 3 show the surface tension of aqueous solutions of the Pluronics and their interfacial tension against Nujol as determined using the Du-

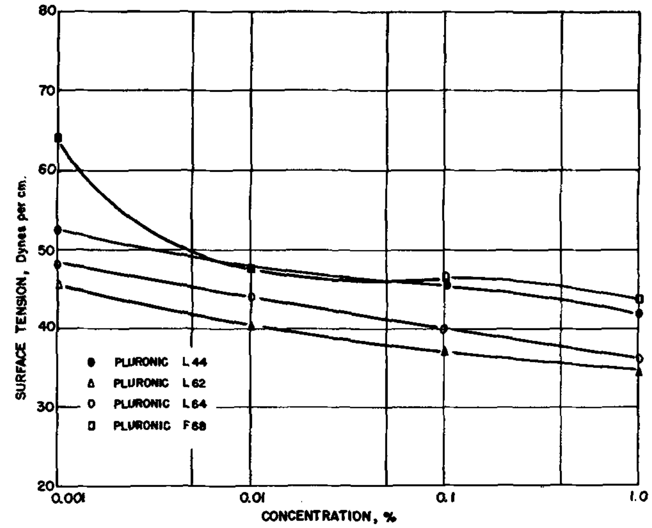

FIG. 2. Surface tension of aqueous solutions of Pluronics, temperature 25-30°C.

Nouy Tensiometer. It is evident that the surface and interfacial tension of these solutions is decreased as the weight of the hydrophilic group is decreased within the range under study. It is also indicated that an increase in molecular weight of the hydrophobic base has the same effect.

The wetting ability as determined by the Canvas Disk Method is shown in Figure 4. As measured by this procedure, all four of the Pluronics increase in wetting ability with increase in temperature when tested at 0.1% concentration. The opposite effect has been noted with certain, but not all, nonionics at present on the market. At temperatures below about 35°C. Pluronic L62 is the most efficient wetting agent, and the optimum temperature appears to increase with increase in hydrophilic content so that solid Pluronic F68 and Pluronic L44 continue to increase in wetting ability at temperatures beyond 90°C., at which temperature both are very efficient wetting agents.

Foaming properties, as measured by the Ross Miles Pour-Foam Method, are shown in Figure 5. When tested in distilled water at normal use concentrations, the products in this series increase in foaming ability

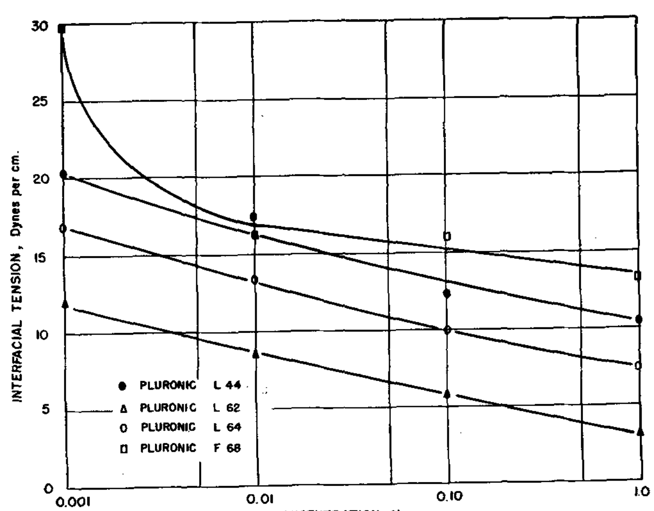

FIG. 3. Interfacial tension of aqueous solutions of Pluronics vs. Nujol — 30°C.

with increase in the percentage of hydrophilic group present. Although not shown in Figure 5, the foam from all four products is quite unstable, and although the initial foam height increases with increase in temperature, the instability also increases. Also in the presence of soil, oils, etc., these products foam very little and accordingly, for practical purposes, can be considered to be relatively non-foaming.

Detergency

The detergency properties of the Pluronics have been investigated with respect to the effect of temperature, concentration, water hardness, buildability with alkalies, and promotability with sodium carboxymethyl cellulose. The carbon soil removal and whiteness retention test procedures were essentially the same as described previously (7). The data are expressed on a relative basis, being referred to a standard alkylarylsulfonate reference detergent which has an arbitrarily assigned value of 100 for both carbon soil removal and whiteness retention when tested at 0.25% concentration in distilled water at 140°F. This reference detergent is different than that previously used. Also the soiled cloth for the carbon soil removal test was prepared by a continuous procedure instead of the batchwise process previously used and described (7). This type of soiled cloth which will be described in a subsequent publication has somewhat different tenacity characteristics with various detergents than the previous type. Consequently the relative values for carbon soil removal and whiteness retention reported here are not directly comparable with those reported in previous publications issuing from these laboratories.

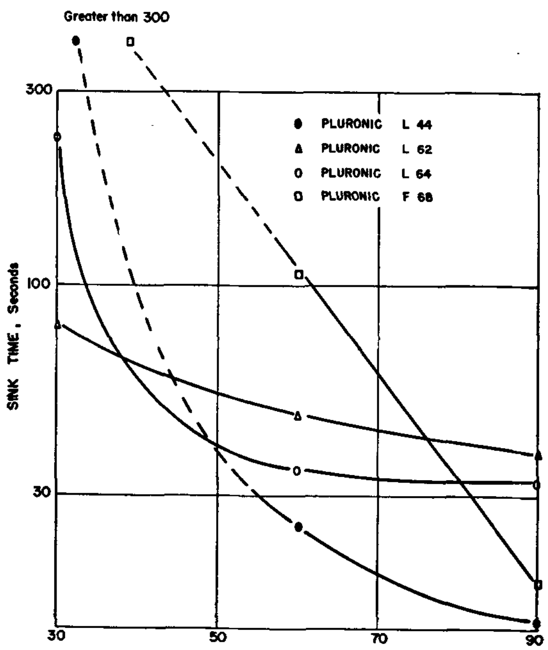

FIG. 4. Variation of sink time with temperature (Canvas Disk Test), 0.1% concentration.

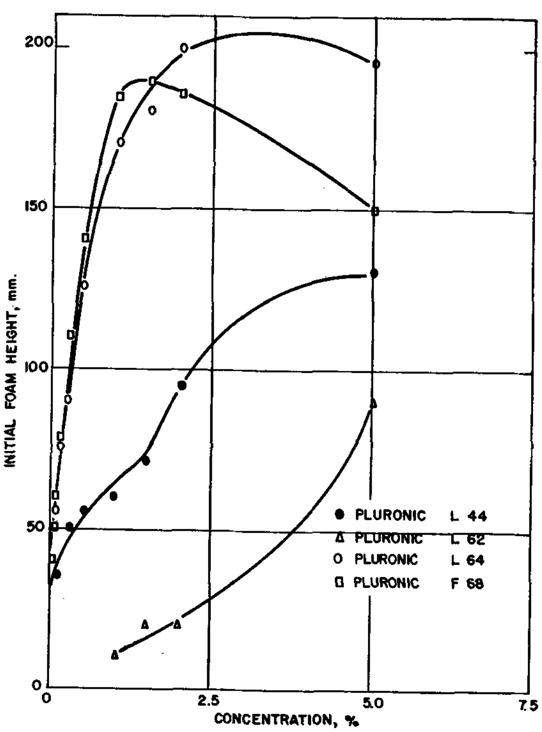

FIG. 5. Foaming properties of Pluronic in distilled water at 110°F. (Ross-Miles Pour-Foam Method).

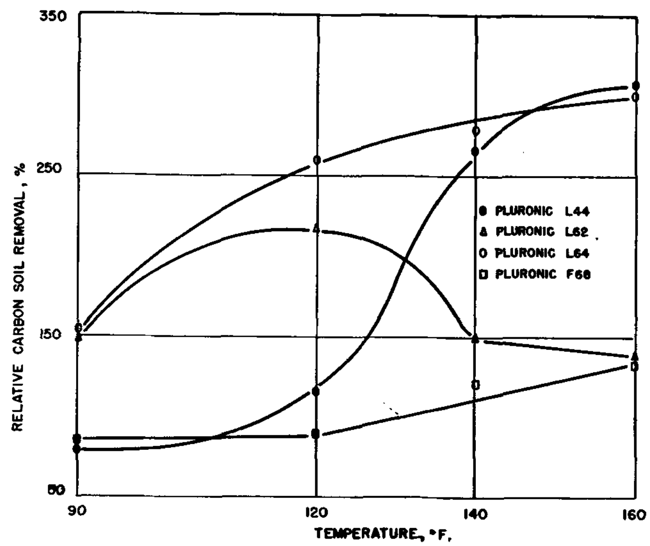

FIG. 6. Effect of temperature on carbon soil removal properties of Pluronics. 0.1% concentration in distilled water.

The effect of temperature on the carbon soil removal properties of the Pluronics is shown in Figure 6. The carbon soil removal properties of Pluronic L62 increase with increase in temperature to a maximum at 120°F. and then decrease with further increase in temperature. The other Pluronics increase with increase in temperature over the range studied with Pluronic F68 being affected least by temperature change. At temperatures below about 130°F. Pluronics L44 and F68 have the lowest values. At 160°F. Pluronic L44 reaches the same high level as Pluronic L64. Above 130°F. all four Pluronics at 0.1% concentration in distilled water are superior to the standard alkylarylsulfonate (100% by definition as the reference standard) at 0.25% concentration and 140°F. It will be noted that at any temperature over the range studied a Pluronic having carbon soil removal values 1.5 times that of alkylarylsulfonate is available and that values as great as three times that of alkylarylsulfonate are obtained at the higher test temperatures.

Figure 7 shows the effect of temperature on the whiteness retention properties of the Pluronics. All of the products have excellent whiteness retention which is typical of nonionics as a class. With increase in temperature the whiteness retention properties decrease in essentially a linear manner. The whiteness retention values are higher with Pluronic L64 than with Pluronic L62 or F68, indicating that under these test conditions there is an optimum hydrophilic-hydrophobic ratio.

The effect of concentration in distilled water at 140°F. on the carbon soil removal properties of the Pluronics is shown in Figure 8. The carbon soil removal properties for each of the Pluronics increase

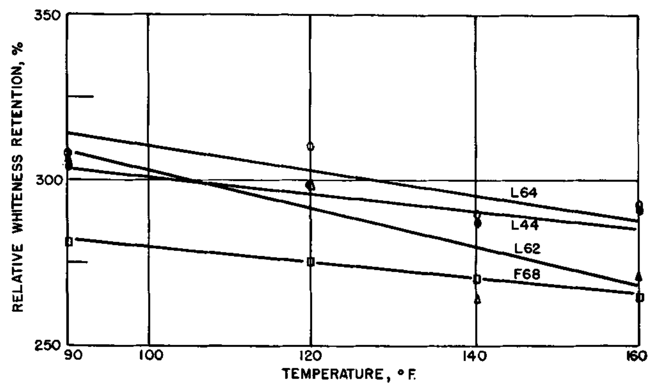

FIG. 7. Effect of temperature on whiteness retention properties of Pluronics. 0.1% concentration in distilled water.

with increase in concentration and at about 0.05% concentration are superior to the alkylarylsulfonate reference detergent tested under the same conditions at 0.25% concentration. There is a wide variation in effectiveness of the series wherein the hydrophilic-hydrophobic ratio was varied. Pluronic L64, which has the intermediate hydrophilic-hydrophobic ratio,

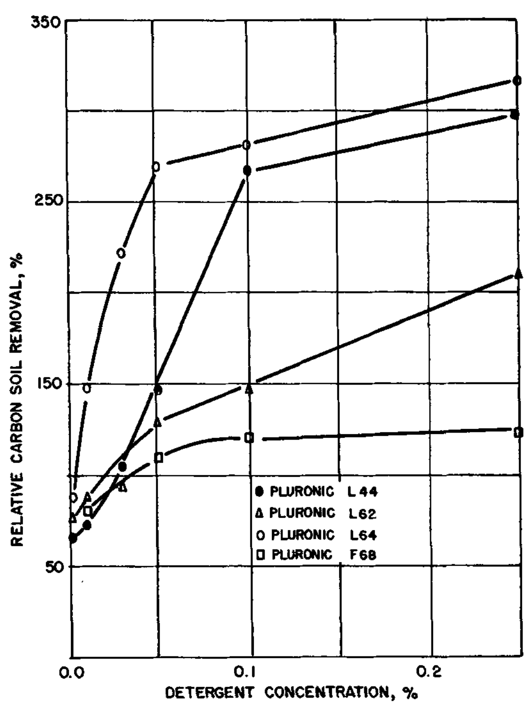

FIG. 8. Effect of concentration on carbon soil removal properties of Pluronics. Distilled water at 140°F.

has an outstandingly high ability to remove soil particularly at low concentrations (0.01-0.05%). The other Pluronics in the series have lower carbon soil removal values than Pluronic L64. This agrees with the indication previously noted for whiteness retention effects and the observations of other workers (8) that there is an optimum hydrophilic-hydrophobic ratio for maximum detergency.

As shown in Figure 9, whiteness retention properties of the Pluronics increase with increases in concentration to a level of more than 260% of alkylarylsulfonate at 0.05% concentration, beyond which only relatively small changes occur.

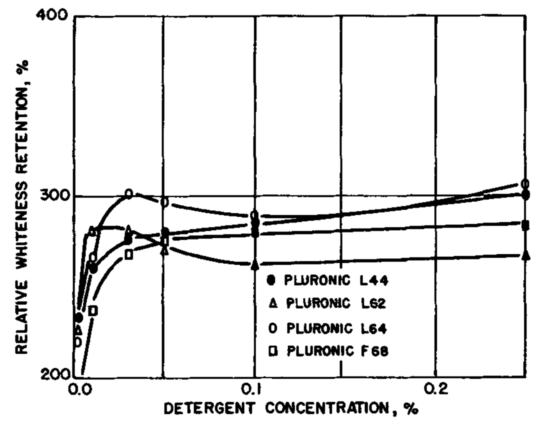

FIG. 9. Effect of concentration on whiteness retention properties of Pluronics. Distilled water at 140°F.

Figures 10 and 11 show that both carbon soil removal and whiteness retention properties of the Pluronics are depressed by hard water.[2] With respect to carbon soil removal properties, the products are for these test conditions in the same general order in water of varying hardness as in distilled water except that solid Pluronic F68 is affected less than the other Pluronics. With regard to whiteness retention for the series having varying hydrophilic-hydrophobic ratios, Pluronic L64, which has the highest level in distilled water, is depreciated by hard water considerably more than Pluronic L62 and F68. In water of low to average hardness the solid nonionic has excellent whiteness retention properties.

An investigation was also made of the ability of sodium carboxymethyl cellulose[3] to promote the detergency properties of the Pluronics, the effect of builders on carbon soil removal and whiteness retention of these nonionic detergents and the detergency characteristics of ternary systems of nonionic-sodium carboxymethyl cellulose-builder systems. In this series of tests, carbon soil removal and whiteness retention properties were determined at 140°F. in both distilled water and water of 15 grains per gallon hardness. Test solutions consisted of 0.1% of the Pluronic, 0.1% Pluronic plus 0.15% builder, 0.1% Pluronic plus 0.025% Carbose D, and the ternary system consisting of 0.1% of Pluronic plus 0.025% Carbose D plus 0.15% builder. Builders studied in this series consisted of soda ash, modified soda,[4] sodium tripolyphosphate and sodium metasilicate.

[2] Prepared by dissolving the proper quantities of calcium chloride and magnesium chloride in distilled water to give mol ratio of Ca:Mg of 2:1 and 15 grains per gallon hardness expressed as $CaCO_2$ equivalent.
[3] Carbose D, ®, Wyandotte Chemicals Corporation.
[4] Yellow Hoop, ®, Wyandotte Chemicals Corporation.

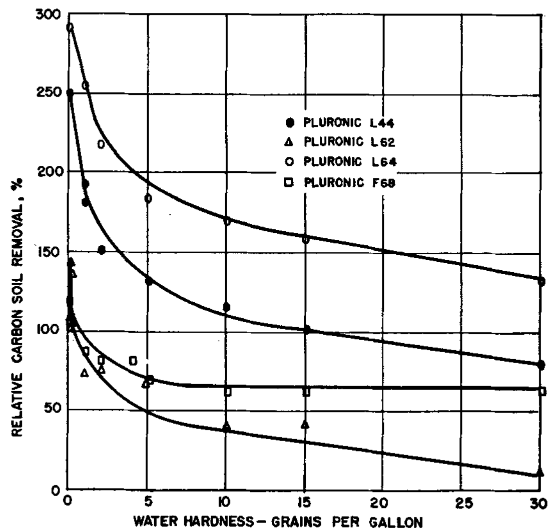

FIG. 10. Effect of water hardness on carbon soil removal properties of Pluronics. 0.1% concentration at 140°F.

The carbon soil removal and whiteness retention properties of these systems are shown in Table II. In distilled water Pluronic L62 is the only nonionic detergent in this series whose carbon soil removal properties are improved by the addition of Carbose D. However in hard water the carbon soil removal properties of all four Pluronics under study are improved by its addition. The increase is very slight with Pluronic L62 and progressively greater with increase in hydrophilic-hydrophobic ratio. With Pluronic L44 a very substantial increase in carbon soil removal properties is obtained by the addition of Carbose as compared with that of Pluronic L64, which has a higher molecular weight. It is apparent that with the exception of Pluronic L62, the addition of Carbose D serves in large part to off-set the depreciating effect of water hardness on the carbon soil removal properties of the Pluronics.

When tested in distilled water, the addition of builders decreases the carbon soil removal properties of all the Pluronics except in the case of Pluronic L62, with which soda ash has essentially no effect and sodium tripolyphosphate causes an increase. With this Pluronic also the depreciating effect due to modified soda and sodium metasilicate is considerably less than noted with the other Pluronics. In 15-grain water the addition of builders to the Pluronics results in an increase in carbon soil removal properties. With Pluronic F68 this increase is negligible, when using soda ash and modified soda, and generally is less than obtained with the other Pluronics when using sodium tripolyphosphate and sodium metasilicate.

It is interesting to note that, with few exceptions, the carbon soil removal properties of the ternary nonionic-sodium carboxymethyl cellulose-builder systems are greater than those of either the binary nonionic-builder or the nonionic-sodium carrboxymethyl cellulose system. This effect is obtained in both distilled and in hard water and generally is greater with sodium tripolyphosphate than with any of the other builders. Further evidence of the synergistic effect which is obtained in these ternary systems is that with the solid Pluronic F68 in distilled water, and generally for all four Pluronics in 15-grain water, the carbon soil removal properties of the ternary system are greater than those of either the nonionic alone or of the binary systems noted above. In addition to overcoming the depreciative effect of hard water on carbon soil removal properties by the addition of sodium carboxymethyl cellulose, the formulation into a ternary system affords a means of preparing a product which in many cases has carbon soil removal properties in hard water which are as good and, indeed in several cases, particularly with Pluronic L44, better in 15-grain water than can be obtained in any primary, binary, or ternary system in distilled water.

In distilled water the addition of sodium carboxymethyl cellulose has essentially no effect on the whiteness retention properties of the four Pluronics. In hard water however the addition of sodium carboxymethyl cellulose effects a very pronounced increase in whiteness retention properties. This effect is so pronounced as entirely to overcome for practical purposes the depreciative effect of water hardness on the whiteness retention properties.

In every case, when tested in distilled water, the addition of builders to the Pluronics results in a decrease in whiteness retention. In hard water sodium tripolyphosphate additions cause an increase in the whiteness retention properties of each of the four Pluronics and sodium metasilicate effects an increase in the case of all but Pluronic L62. Pluronic L64 is affected favorably by each of the four builders under investigation. In the case of each builder however the whiteness retention properties of this binary system are less than those of the nonionic-sodium carboxymethyl cellulose system. In the nonionic-sodium carboxymethyl cellulose-builder systems, whiteness retention properties are increased considerably above those of the binary nonionic-builder system but never, except in the case of Pluronic L62 and F68 with sodium tripolyphosphate, reach the level obtained with a nonionic-sodium carboxymethyl cellulose combination. It will be noted that the addition of Carbose or Carbose-builder results in a level of whiteness retention in hard water which very closely approaches the level obtained with any of the systems studied in distilled water.

Under all conditions studied sodium tripolyphosphate appears to be the most effective builder for

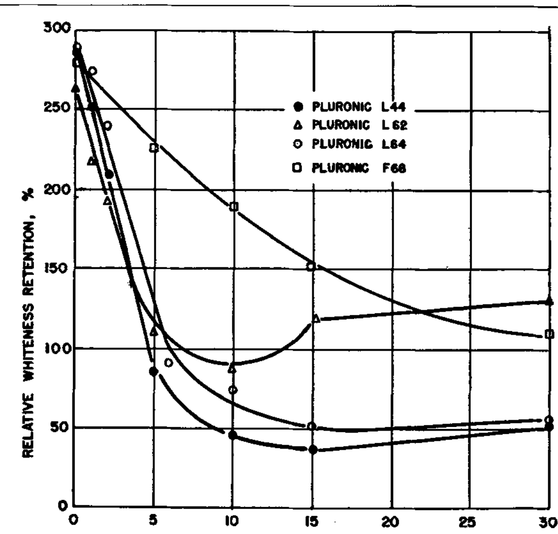

FIG. 11. Effect of water hardness on whiteness retention properties of Pluronics. 0.1% concentration at 140°F.

TABLE II

Effect of Carbose and Builders on Carbon Soil Removal and Whiteness Retention Properties of Pluronics
0.1% Concentration, 140°F.

Type of Water	Carbon Soil Removal								Whiteness Retention							
	L44		L62		L64		F68		L44		L62		L64		F68	
	D[a]	H[b]	D	H	D	H	D	H	D	H	D	H	D	H	D	H
0.1% Pluronic	266	104	147	41	279	161	122	64	286	37	263	120	288	52	284	148
0.1% Pluronic + .15% soda ash	171	181	150	116	197	220	105	64	97	29	243	83	134	90	192	141
0.1% Pluronic + .15% modified soda	186	178	138	116	199	202	77	71	121	26	215	88	146	57	207	143
0.1% Pluronic + .15% sodium tripolyphosphate	177	187	180	164	223	224	118	106	177	101	204	166	151	131	211	181
0.1% Pluronic + .15% sodium metasilicate	142	187	139	56	205	220	96	92	179	41	224	110	152	58	233	153
0.1% Pluronic + .01% Carbose	214	171	181	159	252	200	105	104	282	126	268	152	287	231	281	232
0.1% Pluronic + .025% Carbose	215	190	195	45	245	199	116	110	284	272	270	240	286	284	278	240
0.1% Pluronic + .025% Carbose + .15% soda ash	252	279	165	106	258	244	178	135	244	228	286	232	260	238	264	195
0.1% Pluronic + .025% Carbose + .15% modified soda	248	262	159	89	250	240	151	138	251	225	279	196	267	270	269	216
0.1% Pluronic + .025% Carbose + .15% sodium tripolyphosphate	256	309	218	219	275	259	182	170	264	261	281	263	270	254	263	254
0.1% Pluronic + .025% Carbose + .15% sodium metasilicate	233	229	191	90	245	199	153	107	256	225	279	181	264	262	253	209

[a] Distilled water. [b] Hard water, 15 grains per gallon.

these nonionics, which might be expected because of its sequestering properties. Among the other builders there appears to be no definite relationship between alkalinity and building effect.

Summary

The general properties of a new series of nonionic surface active agents, including a flaked product, have been presented briefly with evidence of their relationship to molecular weight and hydrophilic hydrophobic ratio.

A study of the effect of temperature and concentration on the detergency properties of the Pluronics has shown the existence of an optimum hydrophilic-hydrophobic ratio for maximum detergency. Both carbon soil removal and whiteness retention properties are impaired by an increase in water hardness. This depreciative effect of hard water may be almost entirely overcome by the addition of sodium carboxymethyl cellulose to the Pluronics.

The building effect of soda ash, modified soda, sodium tripolyphosphate, and sodium metasilicate on these nonionic detergents has been investigated. In general, these builders reduce carbon soil removal and whiteness retention properties in distilled water. However in hard water these detergency properties are improved.

It has also been found, with several exceptions, that the carbon soil removal properties of ternary Pluronic-sodium carboxymethyl cellulose-builder systems are greater than either binary combination with the nonionic detergent, regardless of water hardness. This synergistic effect is further evidenced by the fact that in hard water the carbon soil removal properties of the ternary systems are greater than those of the nonionic detergent alone or in either binary combination. Formulation into the ternary system improves the whiteness retention properties over those of nonionic-builder systems, but, with several exceptions, does not provide the level obtained with Pluronic-sodium carboxymethyl cellulose combinations.

Among the builders studied sodium tripolyphosphate is the most effective builder for these nonionics.

REFERENCES

1. Schwartz and Perry, "Surface Active Agents," Interscience Publishers Inc., 1949.
2. McCutcheon, John W., Soap and Sanitary Chemicals, *25*, No. 8, 35-45; No. 9, 43-53; No. 10, 41-52 (1949).
3. Cross, J. M., Presented at the Chemical Specialties Manufacturers Association Meeting of June 13, 1950, Chicago, Ill.
4. Sisley, J. P., American Dyestuff Reporter, *38*, 513-521 (1949).
5. Pacifico, Carl R., Lundsted, Lester G., and Vaughn, Thomas H., Soap and Sanitary Chemicals, *26*, No. 10, 40-43, 73, 90 (1950).
6. ASTM Bulletin No. *141*, August 1946.
7. Vaughn, Thomas H., and Suter, H. R., J. Am. Oil Chem. Soc. *27*, 249-257 (1950).
8. Griesinger, W. K., Nevison, J. A., and Gallagher, G. A., J. Am. Oil Chem. Soc., *26*, 241-244 (1949).

[Received October 5, 1950]

Drying Oils From Xylitol[1]

H. M. TEETER, E. W. BELL, and J. C. COWAN, Northern Regional Research Laboratory, Peoria, Illinois[2]

THE preparation of drying oils by esterification of sorbitol and manitol with unsaturated fatty acids is well known (1). However no similar use of xylitol appears to have been reported. Lazarev (5), Kiselev and Lubman (4) have employed xylitol in the preparation of modified alkyd resins, and Carson and Maclay (2) have described several saturated fatty acid esters of xylitol.

This paper reports a brief investigation of the direct esterification of xylitol with linseed and soybean fat acids. The objects of this investigation were to determine the extent to which esterification could be carried and to determine the drying properties of the esters.

Esterifications of xylitol with soybean and linseed fat acids were conducted without a catalyst and also in the presence of a calcium-barium acetate catalyst (1). A 5:1 molar ratio of fat acid to xylitol was used in each esterification.

In all cases an average of approximately four hydroxyl groups per molecule of xylitol were esterified. Kiselev and Lubman (4) report similar results in the preparation of xylitol palmitate and oleate by direct

[1] Presented at the 118th National Meeting of the American Chemical Society, Sept. 3-8, 1950, in Chicago, and at the American Oil Chemists' Society Meeting, Sept. 26-28, 1950, in San Francisco.

[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.