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.

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Drying Oils From Xylitol[1]

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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

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esterification. No remaining hydroxyl was found when the products were analyzed, indicating that the unesterified hydroxyl had been lost by dehydration.

The drying times of the two soybean fat acid esters were determined after addition of 5% of oil drier. The ester prepared without a catalyst (Ester I) set to touch in six hours and still showed considerable tack after six days. The ester prepared with use of the calcium-barium acetate catalyst (Ester II) set to touch in 4.5 hours and had only a light tack after six days.

Paints were made from both esters with basic carbonate white lead as the pigment. The paint from Ester I was thick and thixotropic, buttery under the brush; the film showed brush marks. The paint from Ester II had a normal viscosity. Both paints showed very objectionable crawling on the glass plates used for the drying tests. The paint from Ester I dried to the "brush-off-sand" point on the Sanderson drying machine (6) in 2¾ hours. There was moderate tack after 17 hours, and the film was flat. The paint from Ester II dried to the "brush-off-sand" point in 4¾ hours. There was no tack after 17 hours, and the film was glossy. Similar paints containing only soybean oil as the vehicle dried to the "brush-off-sand" point in 14 hours and were not tack-free in 72 hours. The difference in gloss between the two paint films was surprising. However an investigation of this point was beyond the scope of this study. The drying time of both paints and, in particular, their ability to lose residual tack rapidly after the initial set-to-touch are thus superior to the corresponding properties of similar paints containing only soybean oil as the vehicle. However the causes of the tendency toward thixotropy and crawling must be identified and removed before the soybean esters can be considered favorably for use as paint oils.

Of the linseed esters, only the one prepared in the presence of the calcium-barium acetate catalyst was used in surface coatings. After addition of 5% of oil drier, films of this ester set to touch in 3.5 hours. A paint made from this ester with basic carbonate white lead as the pigment set to touch in four hours. It gave a highly glossy film, which had moderate tack after 72 hours. This paint was not thixotropic and did not show crawling.

Materials

Xylitol was prepared by catalytic reduction of xylose (7). Soybean fat acids were obtained by saponification of soybean oil. They had an acid value of 198 and an iodine value of 142. The linseed fat acids were a commercial preparation having an acid number of 195 and an iodine value of 194.

Preparation of Esters

Soybean Fat Acid Esters. 1. Soybean fat acids and xylitol in a molar ratio of 5:1 were heated under an inert atmosphere for 12 hours at 235° C. The product had a color of 15-16, viscosity of C, and an acid value of 42.8, which corresponds to 1.3 unesterified hydroxyl groups per molecule. Determination of the percentage of hydroxyl indicated that no hydroxyl was present.

2. Soybean fat acids and xylitol in a molar ratio of 5:1 were heated at 160° for 12 hours in the presence of 0.5% of a catalyst consisting of three parts by weight of calcium acetate and one part of barium acetate. The reaction mixture was then heated to 260° over a 6-hour period, cooled, and filtered. The product had a color of 16-17, a viscosity of B, and an acid value of 32.2 which corresponds to 1.01 unesterified hydroxyl per molecule. Analysis showed that no hydroxyl was present.

Both esters were deacidified by the Wesson method (3) prior to evaluation in surface coatings. After refining Ester I had a color of 14, a viscosity of C, and an acid value of 0.8. Ester II had a color of 15, a viscosity of C, and an acid value of 0.8.

Linseed fat acid esters. 1. Linseed fat acids and xylitol in a molar ratio of 5:1 were heated under an inert atmosphere for 12 hours at 235° C. The product had a color of 16-17 (Gardner), a viscosity of D (Gardner), and an acid number of 43.6. This acid number indicates that about 1.3 hydroxyl groups were not esterified. Additional fat acid and 1% of *p*-toluene sulfonic acid were added, and the reaction was continued for six hours. No further esterification was observed. The product was highlypolymerized (viscosity Z_3-Z_4).

2. Linseed fat acids and xylitol in a molar ratio of 5:1 were heated at 160-170° for 11 hours in the presence of 0.5% of a catalyst consisting of three parts by weight of calcium acetate and one part of barium acetate. The product had a color of 13-14, a viscosity of I, and an acid value of 31.1, which corresponds to 1.0 unesterified hydroxyl per molecule. Analysis indicated that no hydroxyl was present. After deacidification by the Wesson method, the acid value was 2.4.

Preparation of Surface Coatings

Oil films. The xylitol ester was mixed with 5% by volume of an oil drier (meeting Federal Specification No. TT-D-651a, Type I, and containing 2.3% lead, 0.79% manganese, and 0.11% calcium), flowed on glass plates, and examined at intervals.

Paints. The xylitol ester (1 oz.) was thoroughly mixed with 2¼ oz. basic carbonate white lead, 10 cc. of mineral spirits and 5% by volume (based on oil) of oil drier. The paint was then brushed onto glass plates for testing in the Sanderson drying machine.

Summary

Esters of xylitol with linseed and soybean fat acids were prepared. An average of four of the five hydroxyl groups in xylitol could be esterified, one group being lost by dehydration. These esters were evaluated in paints. Although thixotropy and crawling were objectionable in the soybean ester paints, the speed of drying and loss of residual tack were superior in comparison to the corresponding properties of paints containing only soybean oil as the vehicle.

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