at moisture contents above the critical value of 7%. The importance of the relationship presented in Figure 8 becomes evident in that it is applicable to all soybean oil meals irrespective of their history at moisture contents above 7%. The limitations on the relationship between relative humidity and moisture content shown in Figure 8 have been previously discussed. Below this moisture level the ratio rises sharply and the water-adsorbing capacity becomes temperature dependent. However the increase for the whey solubles starts at a higher moisture content, 12%, and the change appears to be more gradual. It is interesting to note that the sharp rise obtained by Makower (7) in the study of whole eggs and attributed by him to be due to the proteins involved does not occur until a moisture content of 5% is reached.

In general, the data obtained in this study corroborate visual observations that the materials increase in hygroscopicity in the following order: denatured meal, undenatured meal, water solubles, and whey solubles. It might be expected that a lyophilized product would give slightly different results from those of the spray-dried materials. Such a conclusion is improbable in view of the extreme heat treatment required to alter the adsorbing characteristics of the meal. Although proteins are known to be strongly hydrophilic, comparison of the data and observations from this investigation on soybean meals and fractions indicate that there is a component or components present in the complex system identified as the whey solubles which exerts considerable influence on the water-adsorbing capacity of these materials. The chemical nature of these materials, whether carbohydrates, phosphatides, or inorganic salts, is unknown at present, but visual observations following additional fractionation of the whey solubles indicate that the controlling substance or substances is present in the dialyzable portion. No material commonly defined as protein would occur in this fraction, and it must be concluded that the protein is not the component having the major influence on the hygroscopicity of the soybean oil meal and its fractions. The significance of this observation is the subject of another investigation.

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Tall Oil Studies. V. Detergency Evaluation of Some Nonionic Derivatives

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IN a previous publication (1) the condensation of tall oil with ethylene oxide to form nonionic detergents was described. For optimum detergency, approximately 13 moles of ethylene oxide was required per mole of tall oil. In such a molecule the hydrophobic radical consists of rosin and fatty acids containing unsaturated linkages, and the polyethenoxy radical possesses a hydroxyl group at the end of the hydrophilic chain.

$$R\text{-}(CH=CH)\text{—}COO\text{-}(CH_2\text{-}CH_2O)_{12}\text{-}CH_2\text{-}CH_2\text{-}OH$$

Both of these functional groups provide means of attaching other substituents, in the former case to the hydrophobic portion of the molecule, and in the latter to the hydrophilic group. The present study involves the preparation of derivatives such as the chloro-, bromo-, hydroxy-formoxy-, etc., of the hydrophobic unsaturated and various urethanes and esters of the hydrophilic hydroxyl group. In several additional experiments the hydrophilic chain was extended with ethylene oxide to 33, 43, and 57 moles of ethylene oxide. Detergency values of all the derivatives synthesized from the polyethenoxy tallate were determined on built mixtures.

Preparation of Derivatives

For these experiments a polyethenoxy tallate (I) was prepared by accurately condensing 13 moles of ethylene oxide with each mole of triple distilled Indusoil[1] (1, 2). The ethenoxy content of I was checked by a saponification equivalent.

The *chlorinated* (II) and *brominated* (III) derivatives were prepared by completely saturating the hydrophobic groups in one case with chlorine in carbon tetrachloride solution and in the other with bromine in ether. The *ozonide* (IV) was prepared by direct combination of 20 g. of I with 2 g. of ozone (4). The *hydroxy-formoxy* (V) and *hydroxy-acetoxy* (VI) derivatives were synthesized by the previously described (5) method by use of hydrogen peroxide and formic and acetic acids, respectively. The *maleic anhydride adduct* (VII) was prepared by maintaining 9.8 g. of maleic anhydride with 86.2 g. of I at 80°C. for two hours. An *excessively chlorinated* (VIII) polyethenoxy tallate was prepared by bubbling chlorine gas into 500 ml. of aqueous solution containing 86.2 g. of I for 16 hours. From the gain in weight it was noted that approximately 20% of chlorine had been introduced into the molecule; therefore it is quite possible that along with addition to the double bonds some chlorine may have been substituted along the hydrophilic chain. Sulfation with sulfur trioxide gas, using perchloroethylene as a solvent, followed by

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[1] West Virginia Paper and Pulp Company analyses indicate approximately 30 parts of rosin acid to 70 parts of fatty acids and approximately 1.7 unsaturated groups for each tall oil unit. See Ref. 3 for the proportions of different acids in tall oil.

neutralization likewise gave a product probably containing a sodium ester sulfate on the hydrophilic hydroxyl and a *sodium sulfonate* (IX) on the hydrophobic unsaturate. The *phenyl* (X) and *napthyl urethanes* (XI) as well as the benzoate (XII) and *3, 5 dinitrobenzoate* (XIII) derivatives were synthesized according to the procedures given in Shriner and Fuson (6). Additional ethenoxy units were added by further condensation of I with ethylene oxide gas in the presence of a small amount of potassium hydroxide catalyst until a total of *33* (XIV), *43* (XV), and *57* (XVI) moles of ethylene oxide had been introduced into the molecule.

The detergency tests on all of these substances were carried out according to the method of Vaughn and Suter (7), using a launderometer. In each case a test mixture was prepared, using 20% by weight of the derivative, 20% tetrasodium pyrophosphate, 20% sodium tripolyphosphate, 39% soda ash, and 1% carboxymethylcellulose. All results were compared to an arbitrary standard, taken as 100% and consisting of the above alkaline builders and 20% of the starting material I. Detergency tests were carried out on 0.25 g. of each test mixture in 100 ml. of water. The results of these tests carried out at 140°F. are shown in Table I.

Effect of Various Substituents on Detergency

From the results in Table I it would seem that, in general, the introduction of substituents either to the hydrophobic or hydrophilic portion of the molecule reduces the effectiveness of the product from the detergency standpoint. The chlorinated derivative (II) and the 3,5 dinitrobenzoate (XIII), on the other hand, seemingly possess slightly higher activity than the parent polyethenoxy tallate (I). Very marked lowering in detergency was noted with those products VIII and IX where the substituents groups had presumably entered into both ends of the molecule.

In particular, the introduction of anionic groups into a nonionic detergent is deleterious. Ozonolysis of the hydrophobic groups with probable rupture of the molecule likewise produces an undesirable effect.

TABLE I

Detergency Values of Built Nonionic Tall Oil Derivatives

Derivatives of Polyethenoxy Tallate (13)		Detergency Values			
		Whiteness Retention		Soil Removal	
		Hard Water[a]	Soft Water	Hard Water[a]	Soft Water
I. Polyethenoxy Tallate (13)	A	100	100	100	100
II. Chlorinated	A	103	104	100	100
III. Brominated	A	94	103	100	99
IV. Ozonide	A	75	74	86	90
V. Hydroxy-Formoxy	A	97	110	95	97
VI. Hydroxy-Acetoxy	A	91	104	96	96
VII. Maleic Anhydride Adduct	A	85	100	94	97
VIII. Excessively Chlorinated	A-B	57	66	63	76
IX. Sodium Sulfonate	A-B	65	64	77	97
X. Phenyl Urethane	B	98	106	96	95
XI. Napthyl Urethane	B	98	107	76	85
XII. Benzoate	B	91	99	92	94
XIII. 3,5 Dinitrobenzoate	B	112	103	98	99
XIV. Polyethenoxy Tallate (33)	B	106	101	99	100
XV. Polyethenoxy Tallate (43)	B	105	101	97	98
XVI. Polyethenoxy Tallate (57)	B	103	100	95	96

[a] 252 p.p.m. hardness.
A. Derivative of the hydrophobic double bond
B. Derivative of the hydrophilic hydroxyl group
A-B. Probable derivative of both groups

Extension of the polyethenoxy chain to 57 ethenoxy units decreased soil removal values of the products slightly but did not adversely affect the whiteness retention. This is not in accord with previous results on the short chain acids (2), which showed a marked drop in detergency with increasing ethenoxy chain. It should be emphasized that the experimental error in the detergency tests may be as high as ± 3% so that, *e. g.*, detergency values of 98 or 102% should in all probability be considered equivalent to the standard.

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Densities and Viscosities of Trichloroethylene Miscellas of Cottonseed Oil, Fish Oil, and Beef Tallow

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THE densities and viscosities of soybean oil miscellas for three solvents, hexane, trichloroethylene, and ethylene dichloride, for three temperatures have been reported by Johnstone, Spoor, and Goss (4). The densities of trichloroethylene miscellas of wheat germ oil, cottonseed oil, and milkweed seed oil (2) and of methylene chloride-soybean oil miscellas at 25°C. (1) have been reported previously from this laboratory. The present paper reports data on the densities and viscosities of trichloroethylene miscellas of cottonseed oil, fish oil, and beef tallow for four temperatures.

Experimental Methods

The cottonseed oil was the crude oil produced by the extraction of prime cottonseed by trichloroethylene and had a density of 0.932 g. per cc. at 25°C., an iodine number of 112, and a free fatty acid content of 1.10%. The fish oil was produced by the trichloroethylene extraction of a mixed fish scrap from California[1] and had a density of 0.951 at 25°C. The concentrated miscella direct from the extraction proc- miscellas used were produced directly by dilution of

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[1] Courtesy of Stanley Hiller, San Francisco.