

of several of the **DM** oils. The author is also appreciative of the helpfulness and advice of Dr. W. I. Patnode, Dr. R. O. Sauer and Dr. D. W. Scott during the conduct of this investigation.

### Summary

The physical properties of a polymeric system arising from the equilibrium rearrangement of methylpolysiloxanes are a function not only of the average functionality of the system but also of the proportion of trifunctional units it contains. As the average functionality is increased toward the value of two, beyond which gelation occurs, the viscosity, density and viscosity temperature coefficients increase, and the proportion of volatile material decreases. As the proportion of branch units is increased, at constant average functionality, the viscosity and melting range decrease, the viscosity temperature coefficient and per cent. volatile increase, and the density and incipient gelation composition remain substantially unchanged.

The statistical theory of molecular size distribution based on the assumptions that only linear or branched molecules are present and that all reacting groups are equally reactive, has been adapted to the **TDM** polymers from the theories of

Stockmayer. Distillation analysis of these polymers reveals good agreement with the theory at low viscosities, whereas at higher viscosities considerable proportions of cyclic compounds are found. The viscosity *vs.* weight average molecular weight curve, calculated with the aid of statistical theory, serves to estimate the viscosity of mixtures of **DM** polymers, but does not accommodate the compounds  $M_2D_{x-2}$ . For this reason, the existence of a true relation between viscosity and weight average molecular weight in polysiloxanes is questioned.

Gelation occurs at average functionalities greater than two, rather than when  $m \leq 3l$  as predicted by the statistical theory, due to the perturbing effects of the presence of cyclic and polycyclic molecules. The increased proportion of cyclic and polycyclic structures that accompanies the increase in proportion of **T** units, together with the resultant increase in molecular complexity and the deviation from the theoretical size distribution, accounts for the changes in the physical properties that are observed as **T** units are introduced into **DM** polymers.

GENERAL ELECTRIC CO., THOMSON LABORATORY  
920 WESTERN AVE., WEST LYNN, MASS.

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## C-18 Alcohol Esters of Orthosilicic Acid

BY L. B. FALKENBURG,<sup>2</sup> H. M. TEETER AND J. C. COWAN

In connection with studies of new types of synthetic drying oils derived from the component fat acids of linseed and soybean oils, the orthosilicic acid esters of the alcohols corresponding to these fat acids were prepared. Since these esters would have a functionality<sup>3</sup> of four, it was anticipated that they would possess superior drying properties. Stearyl, oleyl and linoleyl orthosilicates were also prepared.

The drying times of thin films of refined linseed and soybean oils with and without driers have been compared with those of the orthosilicates of the corresponding alcohols. The drying times of the oils since they give soft tacky films were determined by the "finger" method which defines "set-to-touch time" as a period of drying after which oil will not adhere to the finger when the film is touched gently; those of the orthosilicates were determined with a Sanderson Drying Meter.<sup>4</sup> The driers were added as naphthenates. The results are given in the table.

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Present address: The Maytag Company, Newton, Iowa.

(3) Bradley, *Ind. Eng. Chem.*, **29**, 440 (1937).

(4) Sanderson, *Proc. Am. Soc. Testing Material*, **25**, Part II, 407 (1925); *ibid.*, **26**, Part II, 556 (1926).

TABLE I  
DRYING TIMES IN HOURS

Drier	Oils			Orthosilicates		
	None	0.5% Pb 0.05% Mn	0.1% Co	None	0.5% Pb 0.05% Mn	0.1% Co
Linseed	72	8	6	13	2.75	2
Soybean	144	16-24	12-14	96-120	4.5	3

The hard dry orthosilicate films developed after-tack rapidly at a rate roughly proportional to the original rate of drying, finally becoming soft and greasy or pasty. This effect may be caused by hydrolysis with atmospheric moisture possibly through catalysis by lower fatty acids resulting from oxidation. If the films were both dried and kept in a desiccator over phosphorus pentoxide, they retained their hardness indefinitely. Prolonged desiccation (six months) was found to inhibit materially the tendency to develop after-tack.

When baked three and one-half to five hours at 120°, films of the orthosilicate of soybean alcohols (containing 0.5% lead and 0.05% manganese) showed no change after thirty days. Films were almost water-white and had a hardness of 10 as measured with a Sward hardness rocker. They

TABLE II  
 C-18 ALCOHOL ESTERS OF ORTHOSILICIC ACID

Alcohol	Yield, %	$n_D^{20}$	I. V.	Analyses, %						Molecular weight	
				Carbon		Hydrogen		Silicon		Calcd.	Found <sup>a</sup>
				Calcd.	Found	Calcd.	Found	Calcd.	Found		
Stearyl	84 <sup>b</sup>	...	...	78.3	78.4	13.4	13.5	2.54	2.59	1106	<sup>c</sup>
Oleyl	78 <sup>d</sup>	1.4622	89.0 <sup>e</sup>	78.8	78.8	12.8	12.7	2.55	2.92	1098	1183
Linoleyl	69	1.4721	184.5 <sup>f</sup>	79.4	79.2	12.1	12.2	2.57	2.80	1090	1058
Soybean	82	1.4682	142.7	..	79.0	..	12.2	..	2.68	..	1100
Linseed	76	1.4711	164.7	..	..	..	..	..	2.77	..	1070

<sup>a</sup> Determined cryoscopically in benzene. <sup>b</sup> Yield of crude silicate. <sup>c</sup> Insol. benzene at its freezing point. <sup>d</sup> M. p. ca. -25°. <sup>e</sup> Calcd. 92.8. <sup>f</sup> Calcd. 186.6.

were unaffected by exposure for ninety hours to cold water. Exposure for ten minutes to boiling water resulted in very soft films which recovered in one hour to tacky films. After twenty hours the films were only slightly softer than the original. Cold 0.1 *N* sodium hydroxide softened the films after three hours, and after eighteen hours they were almost completely destroyed. The films showed no tendency to yellow during these tests. However, after prolonged exposure in a laboratory office, the baked films gradually deteriorated. They were soft at sixty days and greasy and pasty after ninety days of exposure.

### Experimental

**Materials.**—Stearyl alcohol, obtained from the Eastman Kodak Company, was recrystallized twice from a mixture of equal volumes of ligroin and ethanol; m. p. 59°. Oleyl alcohol, obtained from the Eastman Regional Research Laboratory, was used without further purification; I. V. 91.5 (calculated, 94.6);  $n_D^{20}$  1.4568. Linoleyl alcohol, and alcohols of soybean and linseed oils were prepared by reduction of the ethyl or methyl esters of the corresponding fat acids with sodium and alcohol.<sup>5</sup> Linoleyl alcohol: I. V. (iodine value) 189.1 (calcd. 190.7),  $n_D^{20}$  1.4658. Soybean alcohols: I. V. 147.9,  $n_D^{20}$  1.4630. Linseed alcohols, I. V. 180.1,  $n_D^{20}$  1.4662. Ethyl orthosilicate, obtained from the Carbide and Carbon Chemicals Corporation, was used without further purification.

**Procedure.**—The preparation of stearyl orthosilicate will be given as typical. A mixture of 50 g. (0.185 mole) of stearyl alcohol, 9.2 g. (0.045 mole) of ethyl orthosilicate and 0.2 g. (0.0038 mole) of sodium methoxide was heated at 205–210° for six hours, in a 200-ml. round-bottom flask fitted with an inlet tube for carbon dioxide, a thermometer and a 6-inch unpacked distilling column with head, the ethanol formed being collected in a trap chilled with acetone-Dry Ice mixture. Approximately 96% of the theoretical amount of ethanol was recovered. Any residual ethanol and unreacted ethyl orthosilicate was then re-

moved under 15-mm. pressure. The residue was cooled, dissolved in 1 liter of ether, filtered and chilled at 0° for twenty-four hours. The white precipitate weighed 42 g. (84.4%), m. p. 55.5–56.0°. Further purification was accomplished by boiling for ten minutes with 250 ml. of methanol and by recrystallization of the residue in 125 ml. of ligroin. The yield was 29 g. of a white microcrystalline powder, m. p. 55.8–56.2°. The analysis is given in Table I.

Orthosilicates of oleyl, linoleyl, soybean and linseed alcohols were prepared by a similar procedure. Since the products were liquids, purification was accomplished by repeated extraction with warm methanol followed by removal of dissolved methanol by warming *in vacuo*. Yields, analyses, and other data are given in Table II. The carbon and hydrogen contents were obtained by standard microanalysis and the silicon contents were determined by ashing with dilute nitric acid and assuming that the residue was silicon dioxide. Melting points are uncorrected. Iodine values were determined by the half-hour Wijs method.

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### Summary

1. Orthosilicic acid esters of stearyl, oleyl and linoleyl alcohols and of the alcohols derived by reduction of the fat acids of soybean and linseed oils have been prepared.

2. Films of the orthosilicates of linseed and soybean alcohols dried to films which upon exposure gradually became tacky and disintegrated.

3. After baking, films of the orthosilicate of soybean alcohols were hard, and had excellent resistance to cold water, hot water and cold dilute alkali. The tendency to deteriorate upon exposure was reduced but not eliminated in these films.

(5) Kass and Burr, *This Journal*, **62**, 1796 (1940).