labeled "Stripped" gave results which fell with good regularity on a straight line, as shown in Fig. 5. The position of the line, however, was some 25° below that for soybean oil or tristearin which did not seem reasonable in view of the structure of the castor oil molecule. Assuming that the sample used had received some unknown treatment either by the refiner or in stripping, several other samples were tried. A commercial grade of refined oil (Baker Castor Oil Co.) having acetyl values of 146.5 and 146.3 before and after distillation, respectively, gave very erratic results which extended over an abnormal temperature range, as can be seen from the plot in Fig. 5. After treatment in the tensimeter, the acetyl value was found to be 143 ± 2%, the uncertainty being due to errors introduced because of the small sample available for analysis. The degree of dehydration, however, seemed small to account for the large disparity in the data. Other undesirable reactions must occur, although the fact that the greatest variations are at the lower temperatures makes it difficult to offer an explanation on the basis of thermal effects. The examination of two other samples of castor oil, one a U.S.P. product and the other a refined grade, yielded similar results.

It was not possible to get data when using corn oil because of the tendency of the pendulum to stick to the orifice. Apparently the corn oil polymerized too rapidly to be successfully handled in the tensimeter and that oil which reached the orifice was sufficiently tacky to cause the diaphragm of the pendulum to stick. The orifice heater aggravated this condition perhaps by even further overheating the oil. After several attempts to collect data with fresh samples of corn oil, these measurements were abandoned.

The constants for Dühring's rule[12] for the triglycerides have been determined and are listed in the last column of Table I. The constants were computed from the absolute temperatures at the 2 pressures, 50 μ and 1 μ for contiguous members of the series in the order listed in Table I. The constant as determined is the ratio of the absolute temperature difference for one triglyceride at 2 pressures to that for the other triglyceride at the same 2 pressure values. Expressed more precisely, the relationship has the following form: $T'_A - T_A/T'_B - T_B$ = constant, where $(T'_A - T_A)$ equals the absolute temperature of one triglyceride at 50 and 1 μ, respectively, and $(T'_B - T_B)$ equals the corresponding temperatures for the other triglycerides. The Dühring constant is calculated from the temperature data of the indicated material with that of the material next lower in the list. For example, the value 0.920 is the ratio of the difference of the two temperatures for tributyrin to that for tricaproin. The constancy of this quantity is good over the entire series investigated, as can be noted from the computed values in Table I.

Summary

The vapor pressure–temperature relationships for 9 simple triglycerides, 10 mixed triglycerides and 4 natural fats have been determined by the pendulum-tensimeter method. In most every instance a straight-line relationship between temperature and pressure was obtained. Abnormal behavior with 2 unsaturated synthetic triglycerides and 2 natural fats was encountered. Latent heats of vaporizations for each material are calculated, and constants for Dühring's rule are also computed.

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(12) Roehl, *Ind. Eng. Chem.*, **30**, 1320 (1938).

ROCHESTER 13, NEW YORK RECEIVED FEBRUARY 24, 1949

[CONTRIBUTION FROM THE LABORATORIES OF DISTILLATION PRODUCTS, INC.]

Vapor Pressures of Phlegmatic Liquids. II. High Molecular Weight Esters and Silicone Oils[1]

BY E. S. PERRY AND W. H. WEBER

The vapor pressures of a number of simple and mixed triglycerides have been reported in a previous paper.[2] At the time of these measurements there was available in this Laboratory a number of molecularly distilled phthalate and sebacate esters whose pressure–temperature relationships could be determined by the pendulum–tensimeter method.[3] A knowledge of the vapor pressures of this class of materials is of importance in certain aspects of their use as plasticizers and vacuum pump fluids. Therefore, the determination of their vapor pressures seemed advisable and worthy of publication.

The pressure–temperature curves for a few of these esters, particularly dibutyl phthalate, di-2-ethylhexyl phthalate, and di-2-ethylhexyl sebacate, have been obtained by others[3] [4,5,5a] using both

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(1) Communication No. 152 from Laboratories of Distillation Products, Inc.

(2) Perry, Weber and Daubert, THIS JOURNAL, **71**, 3720 (1949).

(3) Hickman, Hecker and Embree, *Ind. Eng. Chem.*, **9**, 264 (1937).

(4) Verhoek and Marshall, THIS JOURNAL, **61**, 2737 (1939).

(5) Kapff and Jacobs, *Rev. Sci. Instruments*, **18**, 581 (1947).

(5a) A recent publication on this subject by Small, Small and Cowley, *Trans. Faraday Soc.* (London), **44**, 810 (1948), has come to the authors' attention since the original manuscript of this paper was submitted for publication. Their dynamic method gave results which are in closer agreement than previously published results (from dynamic methods) to those of the present paper.

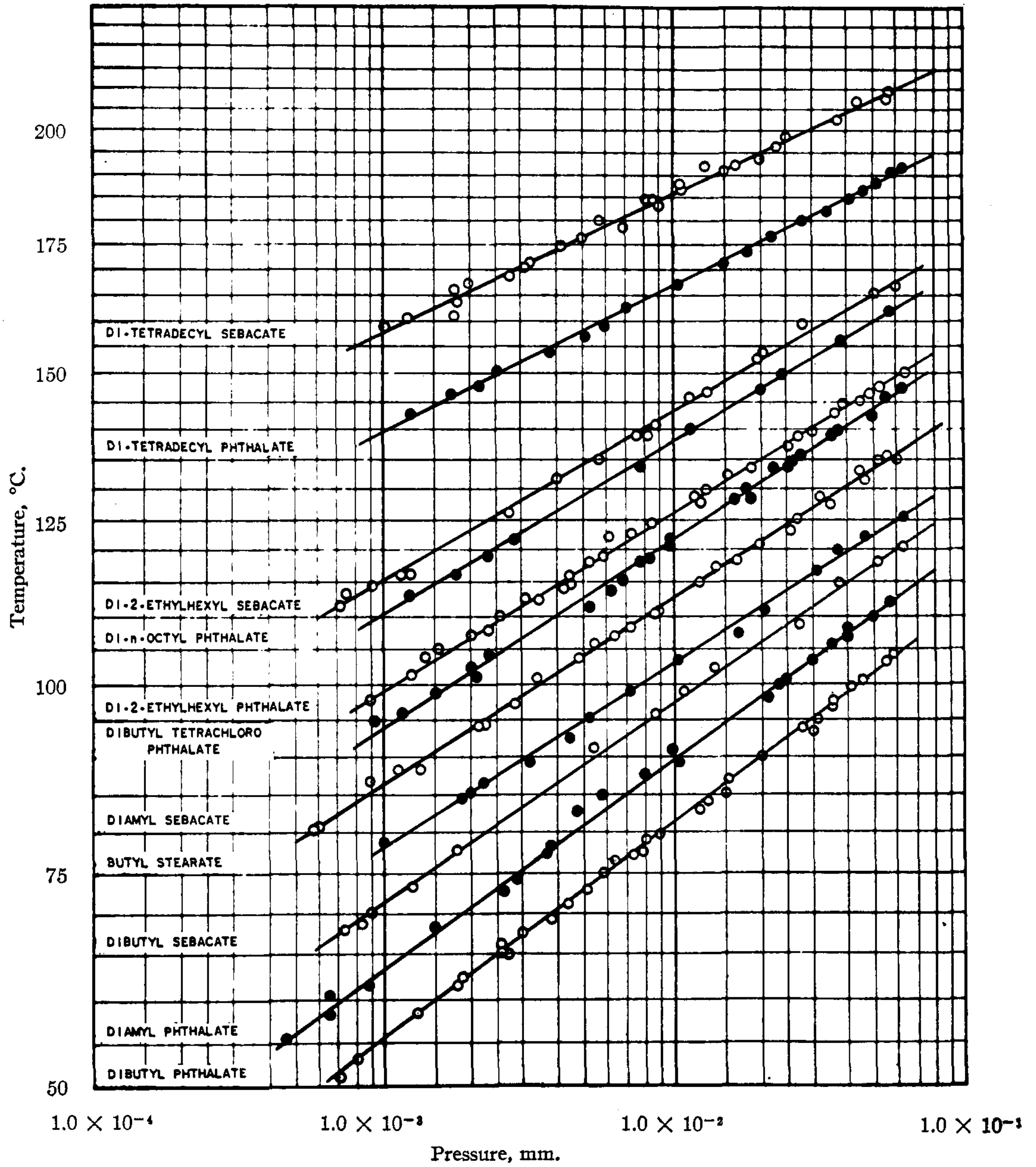

Fig. 1.—Experimental vapor pressure data.

the static pendulum-tensimeter method and dynamic methods. The agreement, however, between the methods of Verhoek and Marshall[4] and the pendulum tensimeter has been much better than that between the pendulum tensimeter and the dew-point method of Kapff and Jacobs.[5] The present results substantiate this point and definitely indicate that the dew-point method yields higher values.

In the present paper are reported the vapor pressure curves for fourteen esters, including new data for the three esters mentioned above, and for two commercial silicone fluids.

Experimental

The apparatus and procedure were identical to that described in the first paper.[2] One variation in the procedure was made in an attempt to increase the accuracy of the readings. Since these esters are fluids at room temperature, the return of the condensate to the boiler causes no difficulties. Consequently, a longer time for the establishment of equilibrium at each temperature was permissible. In spite of the additional time, the readings showed no better consistency over the methods used with the triglycerides.

The phthalates and sebacates of di-*n*-butyl, di-*n*-amyl and di-2-ethylhexyl alcohols were obtained from vacuum pump fluid stocks of Distillation Products, Inc. Di-*n*-octyl phthalate, di-*n*-tetradecyl phthalate and di-*n*-tetradecyl sebacate were synthesized in this Laboratory.

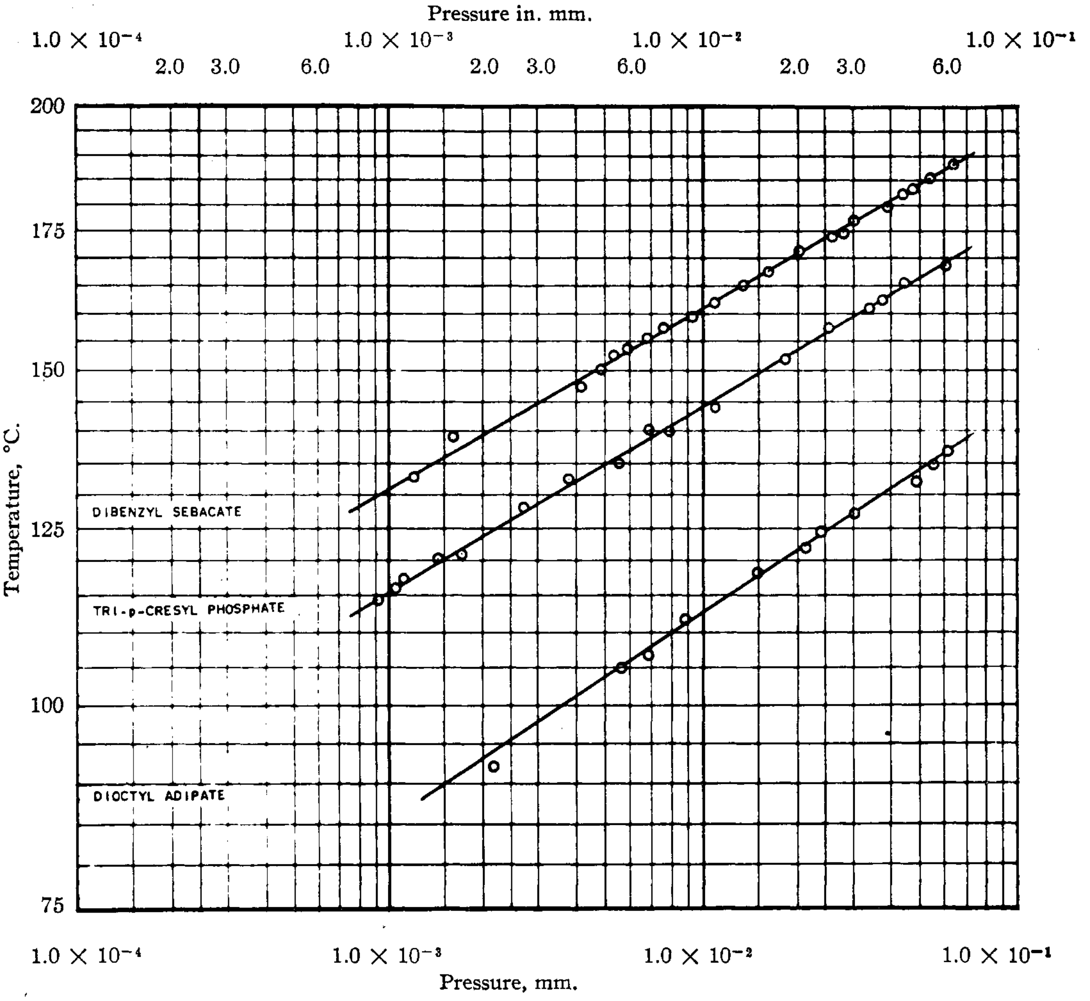

Fig. 2.—Experimental vapor pressure data.

The esterification was carried out in xylene using *p*-toluenesulfonic acid as catalyst. The tri-*p*-cresyl phosphate was a white-label quality product purchased from Eastman Kodak Company. The dibenzyl sebacate was obtained from Resinous Products and Chemical Company. The butyl stearate was a commercial-grade plasticizer sold by Commercial Solvents Corporation. The dibutyl tetrachlorophthalate was an experimental ester furnished by Commercial Solvents Corporation to whom we are grateful for the sample and permission to publish the results. The authors are indebted to the Pigments Department of E. I. du Pont de Nemours and Company, Inc., for supplying the samples of dioctyl adipate used in the measurements.

Regardless of the source or purity of these materials, each one was distilled in the cyclic molecular still before being used for the vapor pressure determinations. This consisted of removing 3 strip cuts which totaled 25% of the original charge. The 2 succeeding 25% fractions were used for the measurements. Dibenzyl sebacate, however, was first fractionated in a laboratory column equivalent to 6 theoretical plates. The distillate was then redistilled in the molecular still, as described above, to ensure complete removal of volatile constituents, if any, which could have been formed during the fractionation at the higher pressures. All of the esters were water-white with the exception of the dibutyl tetrachlorophthalate. Its amber color persisted even after treatment with a contact bleaching agent.

The silicone oils are commercial vacuum pump fluids made by the Dow Corning Corporation. These were used *per se* without the additional purification because distillation would alter their vapor pressure characteristics by removing the lower-boiling constituents. The exact nature of these fluids is not known, of course, but they are perhaps methyl and phenyl substituted polysiloxanes.

Results and Discussion

The experimental results of pressures and temperatures are plotted in Figs. 1, 2 and 3. The derived constants A and B for the Clausius–Clapeyron equation, $\log P = -A/T + B$, where $A = L/2.3R$, and the latent heats of vaporization L have been computed for each ester and are given in Table I. In all cases the experimental pressure–temperature values fall on a straight line with good regularity over the temperature range studied. There appears to be a rough linear relationship between decreasing vapor pressure and increasing molecular weights for all aliphatic esters with the exception of the chlorinated dibutyl phthalate. A plot of latent heats of vaporization as a function of the total number of carbon atoms in the alcohol side-chains for each

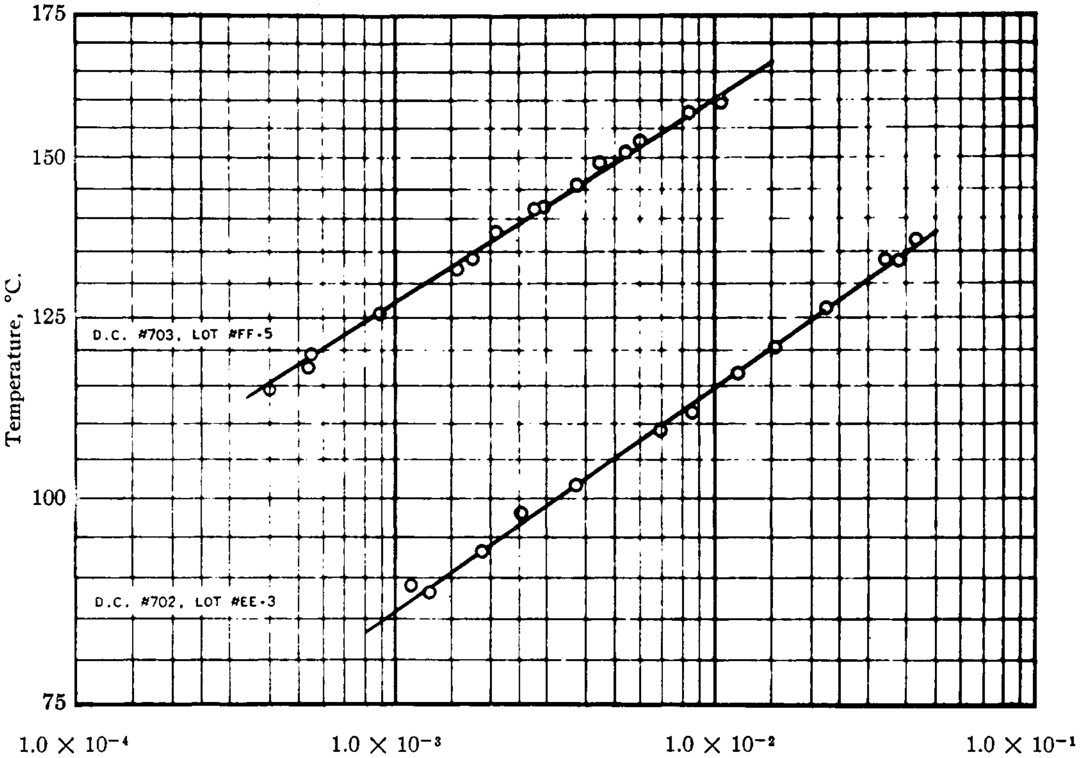

Fig. 3.—Experimental vapor pressure data.

of the phthalate and sebacate series also follows a nearly linear course, as shown in Fig. 4. The hollow circles are the points for the phthalate ester series and the solid dots represent the values for the sebacate esters. The number at each point is the order of listing of the esters in Table I. The depression of the vapor pressure by the aromatic nucleus in dibenzyl sebacate is clearly indicated in the figure. Likewise, the effect of the heavy chlorine atoms in lowering the vapor pressure of dibutyl tetrachlorophthalate over that of the parent dibutyl phthalate is evident. The lower vapor pressure of the normal octyl phthalate as compared to that for the isoöctyl phthalate is manifested in the disparity of the computed latent heats for these two isomeric esters. This is in agreement with the general behavior of aliphatic compounds in that the boiling point decreases with increased branching.

The constants for Dühring's rule, calculated as described in the previous paper,[2] are listed in Table II for each pair of adjacent members for both the phthalate and sebacate esters, excluding dibenzyl sebacate and dibutyl tetrachlorophthalate. The values of Table II are in good agreement with the theory for Dühring's rule.

The values of latent heats previously published for some of the esters are listed in Table I for comparison purposes. In every case the present values are lower than those published. Agreement is best between the values of this work and those of Hickman, Hecker and Embree[3] also using the pendulum tensimeter. Although somewhat higher, the values reported by Verhoek and Marshall[4,5a] are in consistent agreement with those of this report. The results of the dew-point method,[5] however, are considerably higher than those obtained by either of the other two methods. The results are not consistent over the range of esters studied and the values obtained for repeated determinations on the same material are at variance. For example, 2 values reported for

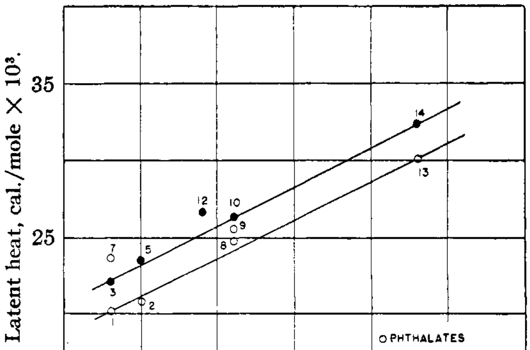

Fig. 4.—Relationship between molecular weights and latent heats.

TABLE I

EXPERIMENTAL DATA AND CALCULATED CONSTANTS OF THE ESTERS

	Material	Temp. (P_1 = 50μ) °C.	Temp. (P_1 = 50μ) °K.	Temp. (P_2 = 1μ) °C.	Temp. (P_2 = 1μ) °K.	A	B	L	L published	No. carbons in alcohol chains
				Esters						
1	Di-*n*-butyl phthalate	102	375	55	328	4450	13.58	20,300	21,400[3] 23,440[4] 25,500[5]	8
2	Di-*n*-amyl phthalate (Amoil)	111	384	63	336	4560	13.57	20,900	29,300[5]	10
3	Di-*n*-butyl sebacate	118	391	71	344	4850	14.10	22,200	....	8
4	*n*-Butyl stearate	123	396	78	351	5220	14.88	23,900	....	..
5	Di-*n*-amyl sebacate (Amoil-S)	134	407	86	359	5180	14.42	23,700	29,300[5]	10
6	Di-isoöctyl adipate	135	408	85	358	4960	13.85	22,700	....	..
7	Di-*n*-butyl tetrachlorophthalate	144	417	94	367	5210	14.20	23,800	....	8
8	Di-2-ethylhexyl phthalate (Octoil)	148	421	99	372	5440	14.62	24,900	25,600[3] 28,500[5]	16
9	Di-*n*-octyl phthalate	160	433	110	383	5620	14.68	25,700	....	16
10	Di-2-ethylhexyl sebacate (Octoil-S)	165	438	115	388	5780	14.90	26,400	29,800[5]	16
11	Tri-*p*-cresyl phosphate	168	441	115	388	5480	14.12	25,100	27,110[4]	..
12	Dibenzyl sebacate	185	458	131	404	5860	14.50	26,800	28,910[4]	14
13	Di-*n*-tetradecyl phthalate	188	461	139	412	6580	15.97	30,100	....	28
14	Di-*n*-tetradecyl sebacate	208	481	158	431	7080	16.42	32,400	....	28
				Silicones						
15	DC-702, Lot EE-3	138	411	86	359	4820	13.42	22,000	14,200[6]	..
16	DC-703, Lot FF-5	187	460	127	400	5210	13.02	23,800	14,780[6]	..

TABLE II

DÜHRING'S RULE CONSTANTS

	Material	Dühring's rule constant
	Phthalates	
1	Di-*n*-butyl phthalate	
		0.979
2	Di-*n*-amyl phthalate	
		.980
8	Di-2-ethylhexyl phthalate	
		.980
9	Di-*n*-octyl phthalate	
		1.040
12	Di-*n*-tetradecyl phthalate	
	Sebacates	
3	Di-*n*-butyl sebacate	
		0.979
5	Di-*n*-amyl sebacate	
		0.962
10	Di-2-ethylhexyl sebacate	
		1.000
14	Di-*n*-tetradecyl sebacate	

Amoil are 29,300 and 31,700, while 2 determinations on Amoil-S gave 29,300 and 28,700.

The latent heats of vaporization for the silicone fluids DC-702 and DC-703 are found to be much higher when calculated from present data than those reported in the commercial literature[6] of the manufacturer. Both sets of values are given in Table I. Boiling points at 10^{-2} mm. mercury for the 2 fluids taken from Fig. 3 are 115° for DC-702 and 160° for DC-703 as compared to 160 and 200°, respectively, reported in reference 6. A complete study of the vapor pressures of pure cyclic and linear methylpolysiloxanes has been made by Wilcock[7] but a comparison of his results with the present ones was not feasible because of the uncertainty of the structure of the commercial oils used in the present investigation.

Summary

The vapor pressure–temperature relationships for five phthalate, five sebacate, 1 stearate, 1 adipate and 1 phosphate esters have been determined. Also 2 commercial silicone fluids have been examined. The latent heats of vaporization for each of these materials are computed and compared with previously published values. Constants for Dühring's rule are computed for each of the phthalate and sebacate series.

ROCHESTER 13, NEW YORK RECEIVED FEBRUARY 24, 1949

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(6) Dow Corning Silicone Notebook Fluid Series No. 2 issued July, 1946.

(7) Wilcock, THIS JOURNAL, **68**, 691 (1946).