PROPERTIES OF FISH AND VEGETABLE OIL MIXTURES

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In consequence of the increasing interest in the utilization of various fish oils for the most diverse commercial operations, their substitution where possible for the more valuable vegetable oils, and the lack of intimate and complete knowledge of their physical and chemical properties, it has seemed desirable to continue and extend the work which was carried out recently by one of us,[a] on fish oils of known origin. The uncertainty of the various tests which have been applied to any oil to detect possible adulteration by another of inferior value has been due rather to the want of a full conception of the behavior of fish oils under all circumstances than any inherent difficulty connected with the problem. A careful study of mixtures of fish oils with each other and with vegetable oils should yield results of value to both analyst and manufacturer.

In this article there are presented the results of the analysis of dogfish liver (*Mustelus canis*), soya-bean, linseed, China-wood oils, and mixtures of these with each other. The fish oil was extracted from livers by steam pressure by the method previously described by one of us. Mixtures were made up by weight. The viscosity, density, index of refraction, saponification number, acid number, and iodine number were then measured according to the following description.

VISCOSITY AND FLUIDITY.

It has been shown that the fluidites of fish-oil mixtures are additive, and it should be expected that the same condition would obtain with all oils except in those cases where there is association, decomposition, or some other exceptionally disturbing factor. As the viscosity of an oil is of particular interest to the paint manufacturer, and fish oils are used largely for outside paints or to adulterate oils for other purposes, this property has therefore been especially considered in our study of these oils.

[a] White, G. F.: A study of the viscosity of fish oils. The fluidity of fish oil mixtures as an additive property. Journal of Industrial and Engineering Chemistry, vol. 4, p. 106–110, and p. 267–270, 1912. Easton, Pa.

A viscosimeter capable of very accurate measurement gave satisfactory service in our previous work[a] and a new one was made and calibrated according to the method already given. Following are the constants obtained for this instrument:

Length of capillary (approximate)	1. 6 cm.
Volume of left limb	2. 1310 c. c.
Volume of right limb	2. 0748 c. c.
Pressure correction (30°), left limb	−0. 30 cm.
Pressure correction (30°), right limb	− . 30 cm.
Ratio of r^4 to l	. 00005835
	. 00005822
	. 00005837

The formula used for the calculation of the viscosity was

$$n = \frac{\pi r^4 p t}{8 v l} - \frac{v d}{8 \pi t l}$$

where n is the viscosity, r the radius, and l the length of the capillary, v the volume of liquid passing through the capillary, d the density of the liquid, p the pressure, and t the time of flow. As has been stated, the method of calibration and manipulation has been fully described in previous papers.

In the following tables are presented the results of the viscosity measurements, which were taken at 30°, 50°, 70°, and 90°, for the right and left limbs, the average of the two, and the reciprocal of the latter value, which is the fluidity. The China-wood oil was measured at 35° and the value at 30° extrapolated from the curve, as the oil was so viscous at the lower temperature that the time necessary for a determination was very long. The pure oils were cooled after measurement at 90° and the viscosity redetermined at 30° to note any possible change due to chemical decomposition.

TABLE I.—DOGFISH-LIVER OIL.

Temperature.	Viscosity.			Fluidity.
	Right limb.	Left limb.	Average.	
Degrees.				
30	0. 4143	0. 4140	0. 4142	2. 414
50	. 2113	. 2110	. 2112	4. 735
70	. 1247	. 1247	. 1247	8. 020
90	. 08046	. 08063	. 08055	12. 41
30	. 4142	. 4142	. 4142	2. 414

TABLE II.—LINSEED OIL.

Temperature.	Viscosity.			Fluidity.
	Right limb.	Left limb.	Average.	
Degrees.				
30	0. 3312	0. 3311	0. 3312	3. 019
50	. 1757	. 1757	. 1757	5. 692
70	. 1071	. 1069	. 1070	9. 346
90	. 07103	. 07119	. 07111	14. 06
30	. 3312	. 3316	. 3314	3. 016

[a] White, G. F., op. cit.

TABLE III.—SOYA-BEAN OIL.

Temperature.	Viscosity.			Fluidity.
	Right limb.	Left limb.	Average.	
Degrees.				
30	0.4067	0.4058	0.4063	2.461
50	.2060	.2065	.2063	4.847
70	.1207	.1209	.1208	8.278
90	.07807	.07836	.07822	12.79
30	.4069	.4067	.4068	2.458

TABLE IV.—CHINA-WOOD OIL.

Temperature.	Viscosity.			Fluidity.
	Right limb.	Left limb.	Average.	
Degrees.				
30	....	....	1.859	0.5379
35	1.591	1.587	1.589	.6293
50	.7796	.7805	.7801	1.282
70	.3699	.3717	.3708	2.697
90	.2126	.2128	.2127	4.702
35	1.933	1.957	1.946	.5139

TABLE V.—DOGFISH-LIVER AND LINSEED OIL MIXTURES.

25 PER CENT LINSEED.

Temperature.	Viscosity.			Fluidity.
	Right limb.	Left limb.	Average.	
Degrees.				
30	0.3954	0.3943	0.3949	2.533
50	.2027	.2018	.2023	4.943
70	.1204	.1201	.1203	8.313
90	.07784	.07798	.07791	12.84

50 PER CENT LINSEED.

30	0.3712	0.3712	0.3712	2.694
50	.1930	.1925	.1928	4.694
70	.1150	.1152	.1151	8.688
90	.07554	.07561	.07558	13.23

75 PER CENT LINSEED.

30	0.3555	0.3556	0.3556	2.812
50	.1866	.1866	.1866	5.354
70	.1123	.1124	.1124	8.897
90	.07425	.07427	.07426	13.47

TABLE VI.—DOGFISH-LIVER AND SOYA-BEAN OIL MIXTURES.

25 PER CENT SOYA BEAN.

Temperature.	Viscosity.			Fluidity.
	Right limb.	Left limb.	Average.	
Degrees.				
30	0.4121	0.4125	0.4123	2.425
50	.2121	.2094	.2108	4.744
70	.1234	.1227	.1231	8.123
90	.07952	.07934	.07941	12.59

50 PER CENT SOYA BEAN.

30	0.4099	0.4130	0.4115	2.430
50	.2074	.2082	.2078	4.813
70	.1215	.1227	.1221	8.190
90	.07930	.07954	.07942	12.59

75 PER CENT SOYA BEAN.

30	0.4074	0.4071	0.4073	2.455
50	.2072	.2075	.2074	4.822
70	.1210	.1214	.1212	8.251
90	.07852	.07865	.07859	12.72

TABLE VII.—DOGFISH-LIVER AND CHINA-WOOD OIL MIXTURES.

50 PER CENT CHINA WOOD.

Temperature.	Viscosity.			Fluidity.
	Right limb.	Left limb.	Average.	
Degrees.				
30	....	....	0.7950	1.258
35	0.6926	0.6942	.6934	1.442
50	.3895	.3875	.3885	2.574
70	.2085	.2080	.2083	4.801
90	.1258	.1259	.1259	7.943

The viscosity and fluidity are pictured graphically in figures 1 to 3. According to Bingham's fluidity hypothesis,[a] the fluidities of liquid mixtures should be additive when there is no association or action between the components. This is true when the fluidity-temperature curve is linear. It may be seen from figure 2 that the fluidities of dogfish, linseed, and soya-bean oils are nearly linear functions of the temperature and their curves have the same slope.

Figure 3 shows that mixtures of these oils have fluidities which are linear functions of the composition. On the other hand, China-wood oil behaves differently. Its

[a] Bingham, E. C. and Harrison, J. P.: Viskosität und fluidität. Zeitschrift für physikalische Chemie, bd. 66, p. 1-32, 1909. Leipzig.

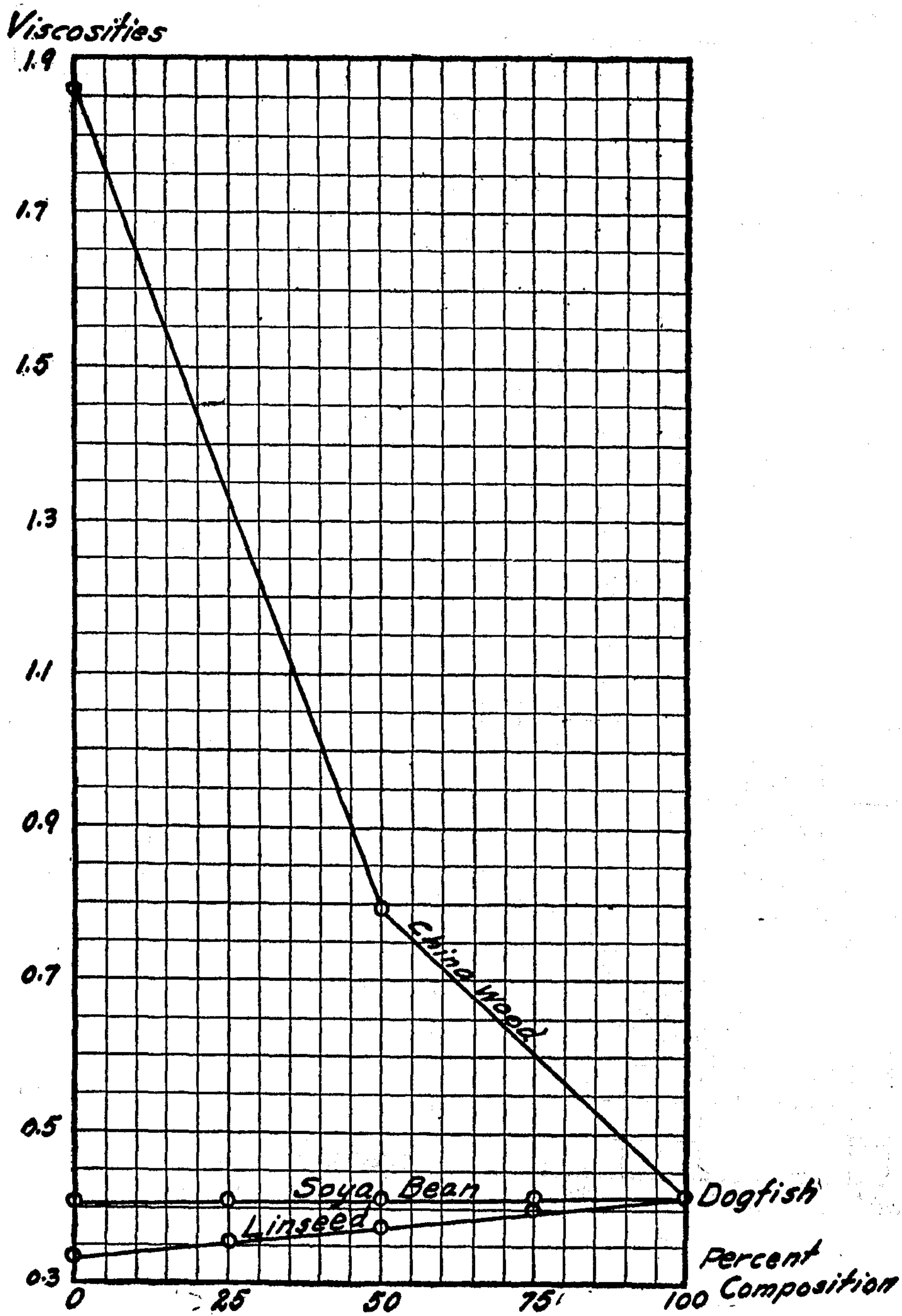

FIG. 1.—Viscosity Curves, 30°.

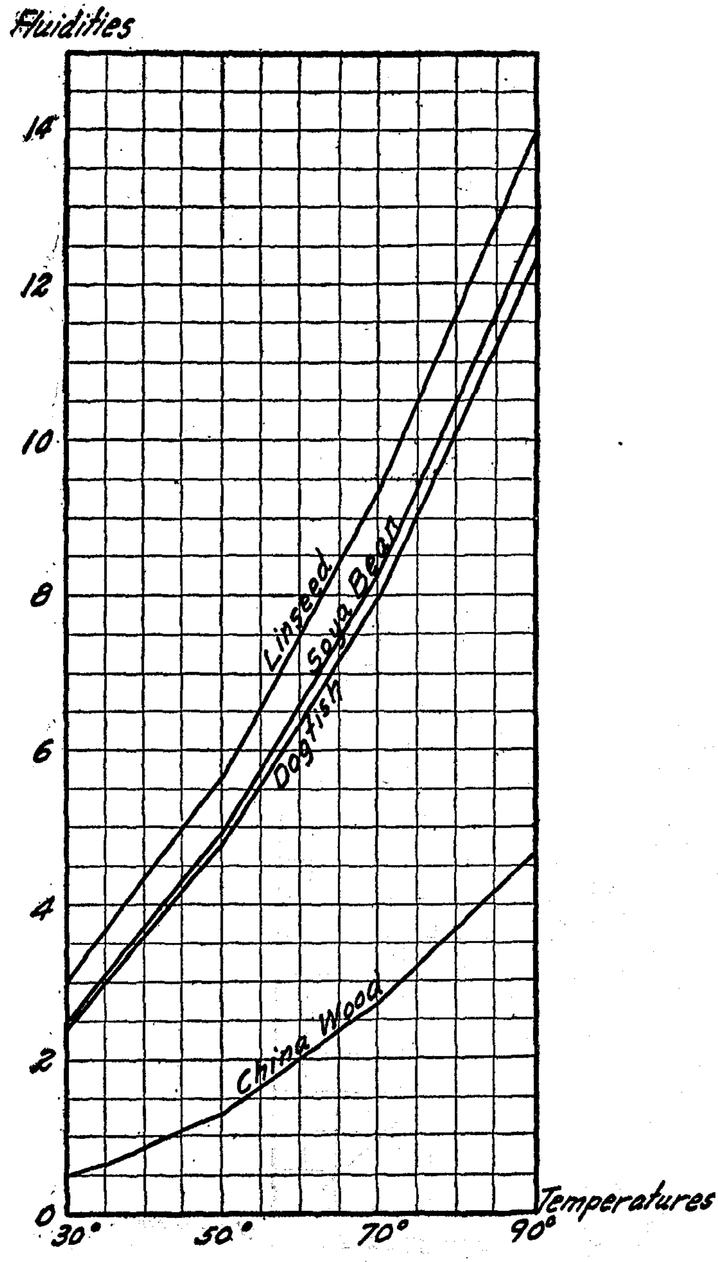

FIG. 2.—Fluidity curves, 30°–90°.

fluidity curve does not have the same slope as those of the other oils, and also its fish-oil mixtures do not give additive fluidities. The data in table IV show that it changes in composition on being heated to 90° since its viscosity at 35° changes from 1.589 to 1.946. The values for the other oils remain constant.

It is interesting to note how much more viscous is the China-wood oil than the other three oils, this property being a good test of its purity, since a little adulteration by other oils of viscosity approximating the others would lower the viscosity of the China-wood oil markedly.

The viscosity curves of the mixtures are given for 30° in figure 1. As has been shown before, the linear curves obtained for soya-bean oil and linseed oil mixtures were to be expected, since the viscosities of the components are nearly identical. Neither the viscosity nor the fluidity curves for the China-wood oil mixtures are linear.

DENSITY.

There is little to be said in regard to the data furnished by specific gravity determinations. These were made by use of the Ostwald pycnometer. The results are given in table VIII and shown by graphs in figures 4 and 5. Figure 4 shows that the densities

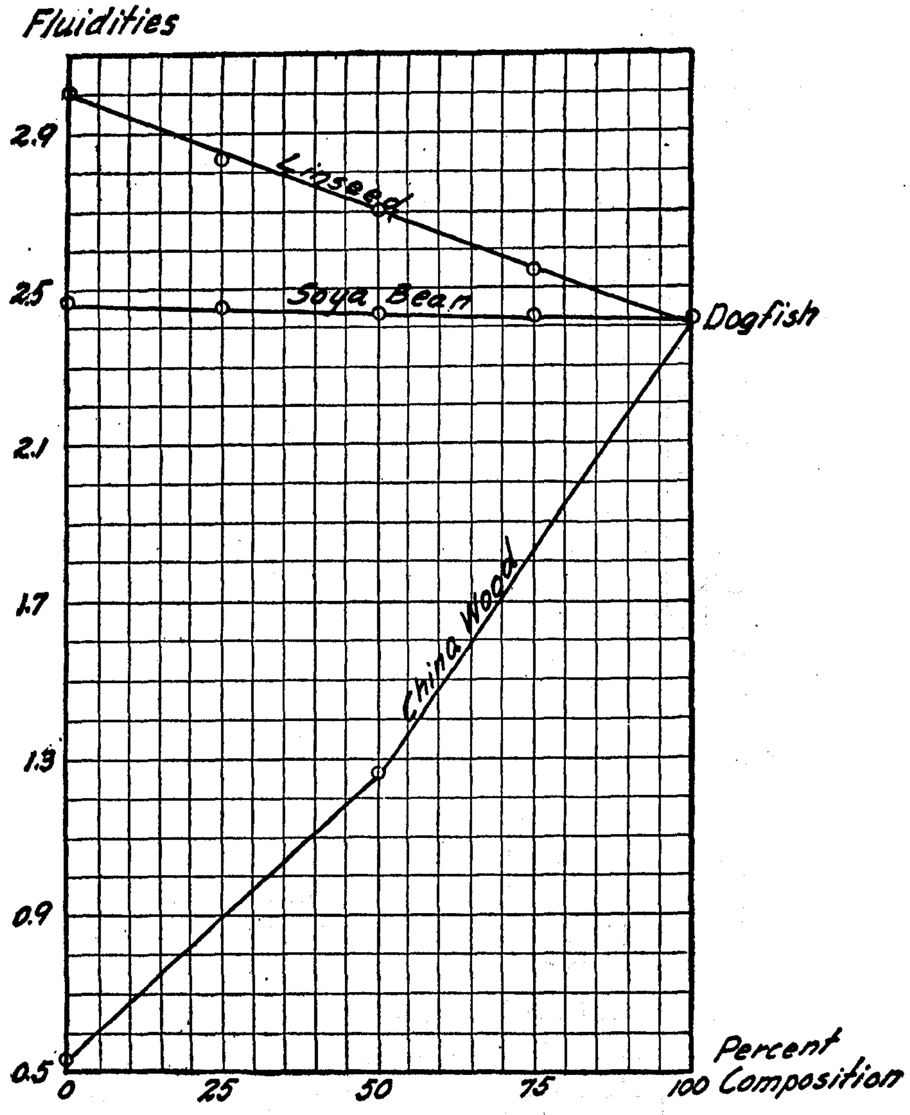

FIG. 3.—Fluidity curves, 30°.

are linear functions of the temperature over the range at which we worked, except with the China-wood oil, the composition of which changes on heating. Linseed and dogfish-liver oil mixtures have additive densities at 30° while the other mixtures do not. This data was of value to us principally in our calculation of the viscosities.

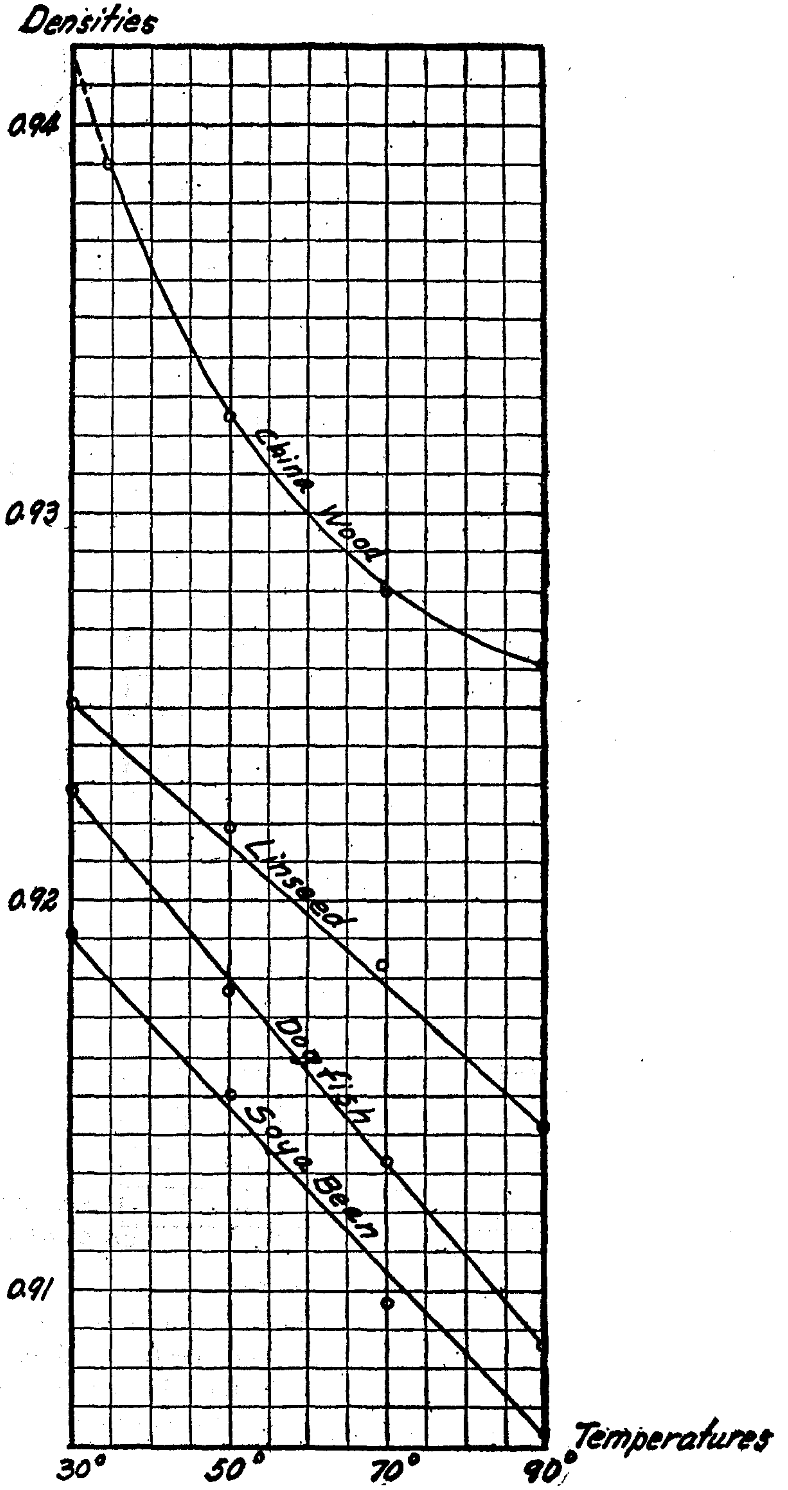

FIG. 4.—Density curves, 30°–90°.

TABLE VIII.—DENSITIES OF OILS AT GIVEN TEMPERATURES.

Oils.	30°	35°	50°	70°	90°
Dogfish-liver	0.9228	....	0.9175	0.9131	0.9082
Linseed	.9251	....	.9219	.9183	.9141
Soya-bean	.9191	....	.9149	.9095	.9063
China-wood	.9411	0.9389	.9324	.9279	.9260
Dogfish-liver:					
25 per cent linseed	.9237	....	.9158	.9120	.9090
50 per cent linseed	.9235	....	.9124	.9051	.8986
75 per cent linseed	.9245	....	.9169	.9100	.9051
25 per cent soya-bean	.9200	....	.9158	.9111	.9082
50 per cent soya-bean	.9200	....	.9149	.9076	.9055
75 per cent soya-bean	.9191	....	.9141	.9103	.9046
25 per cent China-wood	.9268	.9237	.9149	.9209	.9074
50 per cent China-wood	.9300	.9289	.9255	.9230	.9188
75 per cent China-wood	.9348	.9322	.9245	.9230	.9204

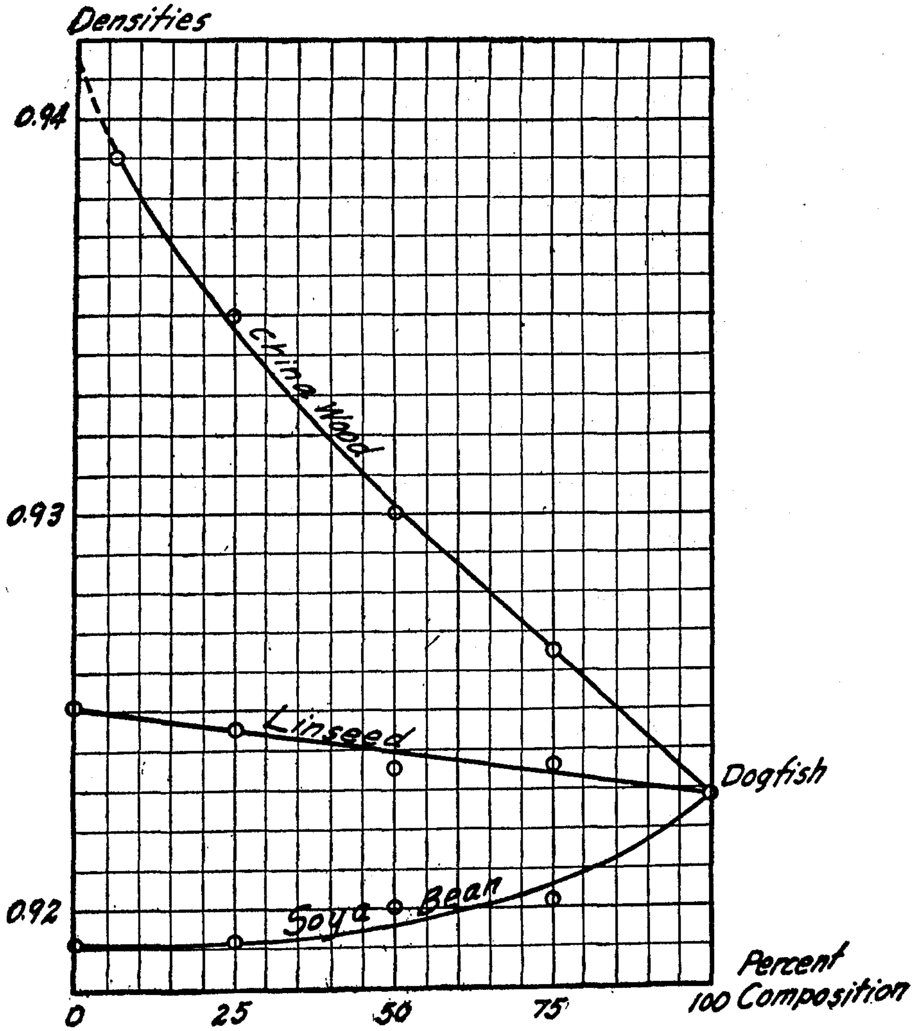

FIG. 5.—Density curves, 30°.

INDEX OF REFRACTION.

The refractive indices were measured by the use of a microscope, the apparent and true depths of a column of liquid being compared. Figure 6 shows that the index of refraction is not a good criterion of the purity of linseed and soya-bean oils when being tested for the presence of fish oil, but it should be valuable in the case of China-wood oil,

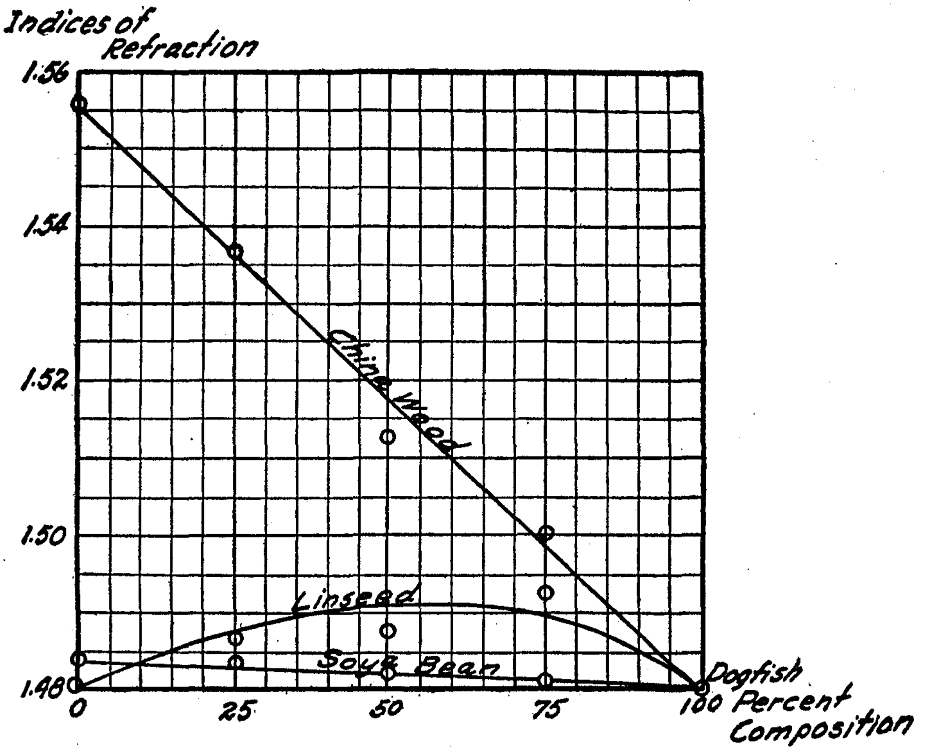

FIG. 6.—Index of refraction curves, 25°.

the refractive index of which is considerably greater than that of the other oils. This has been brought out by the work of Wise[a] in a recent study of this oil.

ACID, SAPONIFICATION, AND IODINE NUMBERS.

The results of the acid, saponification, and iodine number measurements are presented in table IX and figures 7 to 9. The first two numbers represent the milligrams of potassium hydroxide necessary for 1 gram of oil, while the iodine numbers were obtained by Hübl's method, being per cent iodine required by the oil.

[a] Wise, L. E.: On the indices of refraction of China-wood oil. Journal of Industrial and Engineering Chemistry, vol. 4, 1912, p. 497–498. Easton, Pa.

The acid numbers are seen to be additive generally for the mixtures, while the saponification numbers offer no general behavior. The iodine numbers are additive for

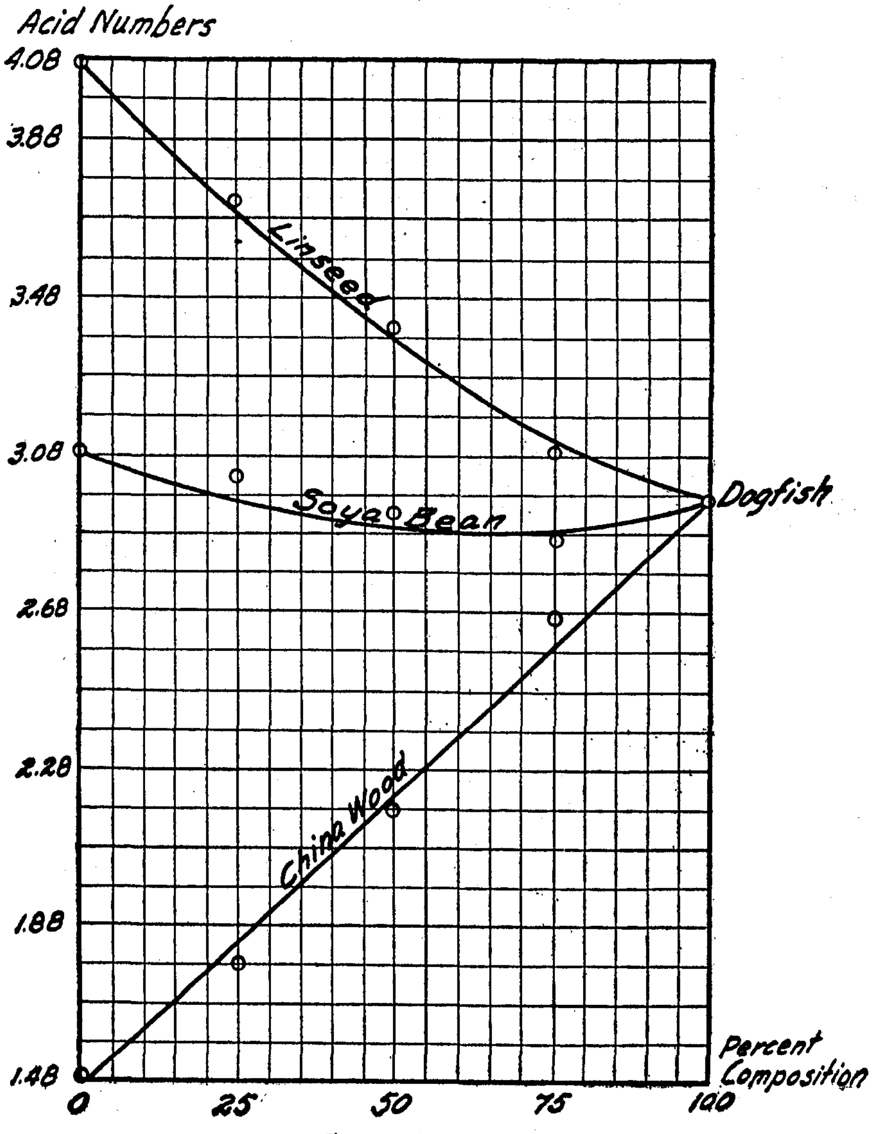

FIG. 7.—Acid number curves.

the linseed and soya-bean mixtures, the China-wood mixtures, however, giving a hyperbolic curve. As the iodine number of the linseed is so much higher than that of the dogfish-liver oil, this, as is well known, furnishes good evidence of the purity of the former.

The values for the other vegetable oils are so near those of the fish oil that great value can not be placed in this test. Reference may be made to the work of McIlhiney [a] for a method of examining China-wood oil.

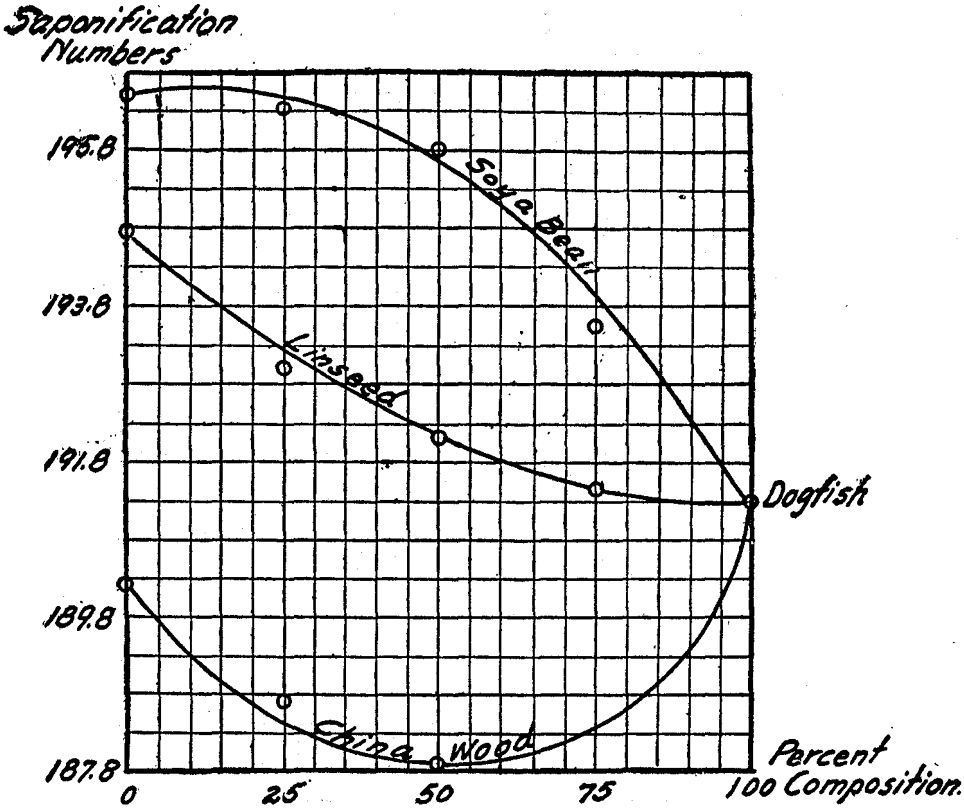

FIG. 8.—Saponification number curves.

TABLE IX.—INDEX OF REFRACTION, ACID, SAPONIFICATION, AND IODINE NUMBERS.

Oils.	Index of refraction at 25°.	Acid number.			Saponification number.			Iodine number.		
		1	2	Average.	1	2	Average.	1	2	Average.
Dogfish-liver	1.4801	2.91	2.94	2.93	191.3	191.2	191.3	122.7	120.3	121.5
Linseed	1.4805	3.98	4.01	4.00	194.0	195.3	194.7	152.1	152.7	152.4
Soya-bean	1.4837	3.08	3.08	3.08	196.7	196.4	196.5	130.5	125.1	127.8
China-wood	1.5560	1.47	1.49	1.48	190.1	190.2	190.2	(124.4?)	137.1	137.1
25 per cent linseed	1.4948	3.06	3.06	3.06	191.4	191.6	191.5	129.2	....	129.2
50 per cent linseed	1.4872	3.41	3.43	3.42	192.0	192.4	192.1	137.9	139.1	138.5
75 per cent linseed	1.4870	3.75	3.68	3.72	191.0	194.9	193.0	144.3	145.1	144.7
25 per cent soya-bean	1.4790	2.85	2.85	2.85	193.5	193.5	193.5	123.3	123.1	123.2
50 per cent soya-bean	1.4819	2.94	2.92	2.93	195.6	195.9	195.8	123.1	122.1	122.6
75 per cent soya-bean	1.4834	3.00	3.03	3.02	196.4	196.1	196.3	126.9	127.7	127.3
25 per cent China-wood	1.4997	2.60	2.72	2.66	193.2	193.0	193.1	128.0	126.4	127.2
50 per cent China-wood	1.5120	2.14	2.19	2.17	187.6	187.9	187.8	133.2	131.4	132.3
75 per cent China-wood	1.5363	1.78	1.76	1.77	188.5	188.9	188.7	135.6	136.5	136.1

[a] McIlhiney: A method of examining China-wood oil. Journal of Industrial and Engineering Chemistry, vol. 4, 1912, p. 496–497. Easton, Pa.

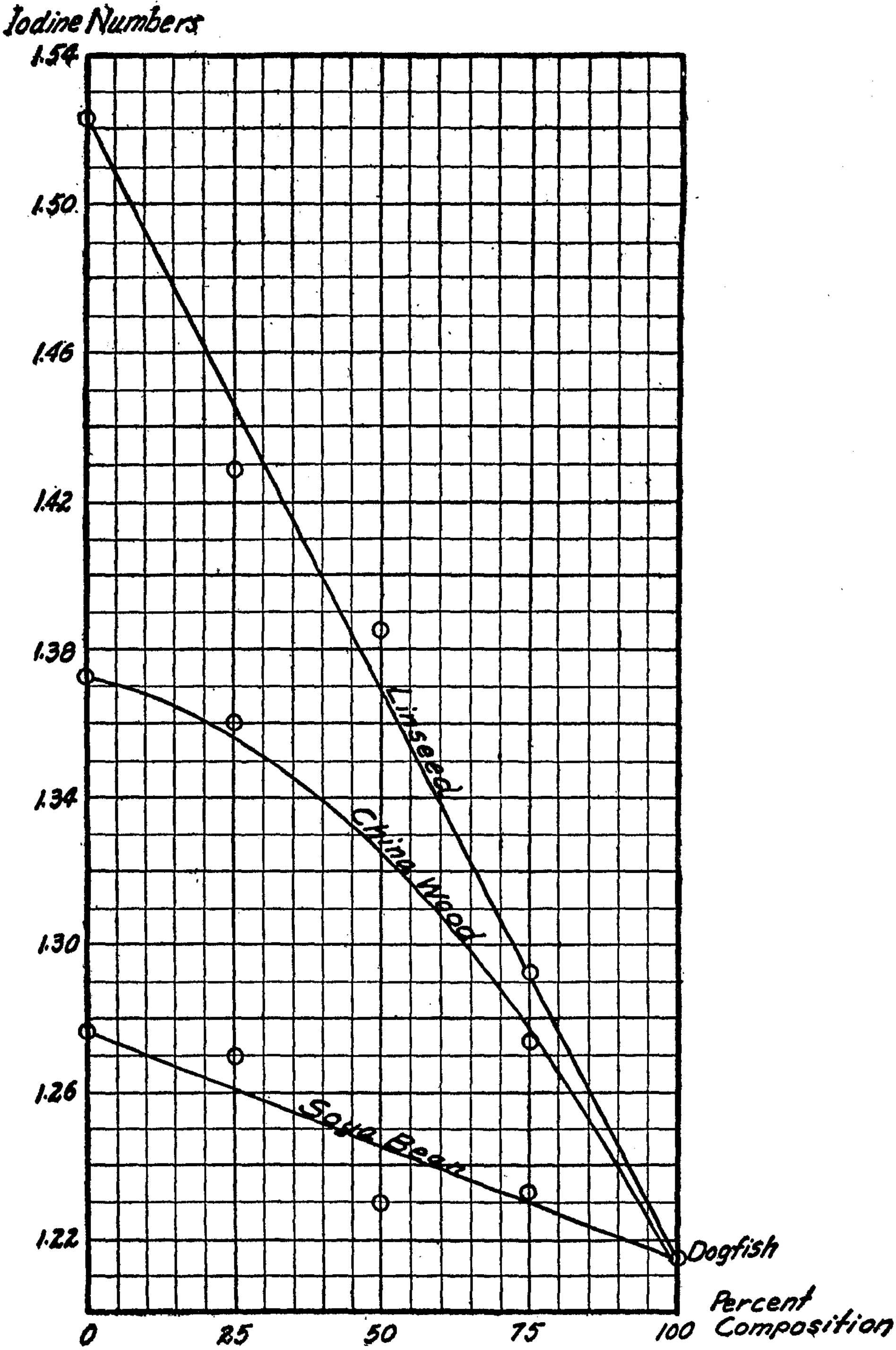

FIG. 9.—Iodine number curves.

SUMMARY.

1. The fluidities of fish and vegetable oil mixtures are additive, except where there is decomposition of either component on heating.

2. The viscosities of these mixtures are also additive when the values for the components approximate each other closely.

3. The fluidities of vegetable oils are nearly linear functions of the temperature. It has been previously shown that this holds true for various fish oils.

4. The fluidity of China-wood oil is a good test of its purity, as it is unusually low.

5. The specific gravities of the mixtures are approximately additive and vary linearly with the temperature. The density of China-wood oil is very high.

6. The index of refraction, acid number, and saponification number of the mixtures do not allow any general conclusions. The acid number of linseed oil is high and that of dogfish-liver oil is low compared with that of China-wood oil. The refractive index of China-wood oil is lowered by the introduction of small amounts of fish oil.

7. The low iodine number of the dogfish-liver oil makes the presence of this oil in vegetable oils known by marked lowering of their iodine values.