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THE RELATION BETWEEN THE IODINE VALUES AND REFRACTIVE INDICES OF HARDENED OILS. PART II.

BY

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THE RELATION BETWEEN THE IODINE VALUES AND REFRACTIVE INDICES OF HARDENED OILS. PART II.

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In part I¹ it has been shown that the curves representing the relation between the iodine value and refractive indices of oils varying in degree of hardness are nearly coincident for a number of different oils. The investigation has now been extended to the following oils:—

Argemone (*Argemone mexicana* Linn.), English mustard, Rocket (*Eruca sativa* Lam.), Indian rape (*Brassica campestris* Linn. sub-species *Napus*), Cashew kernel (*Anacardium occidentale* Linn.), Soya bean (*Dolichos soja* Linn.), Poppy seed (*Papaver somniferum* Linn.), Rayan (*Mimusops hexandra* Roxb.), Olive (*Olea Europea sativa* Linn.), Seal and Cod-liver.

The methods of hydrogenation and determination of the iodine values and refractive indices were the same as those described in Part I, with the exception that, in determining the iodine values of the harder samples by Winkler's method,² it was found desirable to use 20 cc. of carbon tetrachloride instead of the usual 10 cc. With the smaller quantity of solvent the very hard samples did not always dissolve completely, and in such cases the iodine value found was apt to be a few units low. With the larger quantity accurate values were obtained when analysing known mixtures of tristearin and triolein, with iodine values ranging from 0 to 10.

The slight uncertainty in the absolute value of the refractive index referred to in Part I was eliminated by using a piece of fluorite of known refractive index ($n_D^{20} = 1.43375$) for checking the refractometer. Both this and the glass piece ($n_D = 1.5168$) previously used gave concordant values within the limit of experimental error, so that it appears probable that the values previously given are correct.

All the oils were purified before hydrogenation in the manner described in Part I. The oils of the mustard group were found to require special treatment in order to avoid rapid poisoning of the catalyst. An account of these experiments will be given in a future paper.

The values obtained by experiment are shown in Tables I to XII.

¹ This *Journal*, 1922, 5, 47.

² Cf. this *Journal*, 1916, 1, 173

DISCUSSION OF RESULTS

The results in general are similar to those previously given in Part I, as may be seen from a few typical curves in Fig. 1. There are, however, certain differences to which attention may be drawn.

1. The oils of the rape or mustard group, viz., rocket, mustard and rape oils, have higher refractive indices for a given iodine value than those of all other oils so far examined with the exception of castor, hongay and argemone oils. This is due to the presence of considerable quantities of glycerides of erucic acid. These oils also have comparatively high acetyl values varying from 19 to 25 in the various samples examined, and although these appear to be due mainly to the presence of mono- or di-glycerides, glycerides of hydroxy-acids also are probably present, and these would contribute towards the raising of the refractive index. The composition of these oils is under examination and the question of the refractive index will be dealt with more fully when the results are complete.

2. Argemone oil has a high refractive index for a given iodine value, and the iodine value—refractive index curve in some ways resembles those of the rape oils. The oil, however, does not appear to contain any appreciable quantity of erucic acid, and it seems probable that the high refractive index is due to the presence of di-glycerides and of glycerides of hydroxy-acids. The acetyl value of the sample examined was 40 and some difficulty was found in obtaining consistent iodine values. The composition of the oil is now being examined.

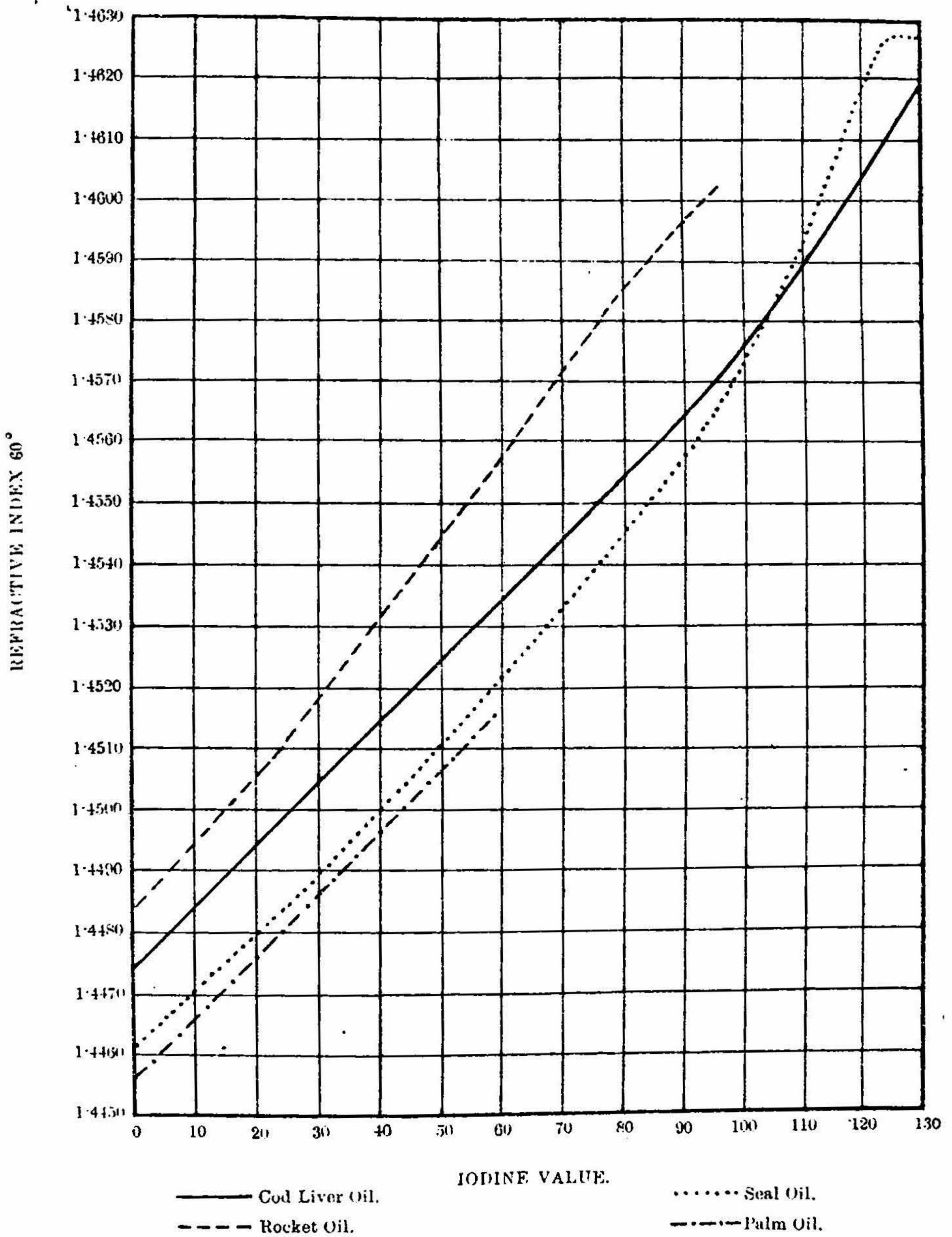
3. The refractive indices of the completely hardened oils, other than argemone and the rape oils, vary considerably more than those given in Part I. The figure for olive oil is 1.4463, which corresponds almost exactly with that of the purest tristearin we have been able to obtain, viz., 1.4462 for a sample from Kahlbaum carefully repurified and with melting point 71–72°, and also for a sample synthesised in the laboratory with melting point 71.4–72°. These results do not agree with Scheij's¹ value 1.4473. Completely hardened cod-liver oil has a high refractive index, while palm oil yields a product with low refractive index as might be expected from the quantity of palmitic acid it contains. The exact reason for these variations is not known in the majority of cases and further experiments are necessary to ascertain if the refractive index of the completely hardened sample is characteristic of the oil or only of the particular sample examined.

4. The curves representing the relation between iodine value and refractive index are not always straight lines for iodine values

¹ *Rec. trav. Chim.*, 1899, 18, 188.

FIGURE I.

RELATION BETWEEN IODINE VALUE AND REFRACTIVE INDEX.



below 80 to 90, but in several cases, notably argemone, soya cashew-nut, seal and rayan oils, they are appreciably convex to the iodine-value axis.

5. All the curves are steeper at the higher iodine values and in several cases, as already observed with other oils, there is a distinct break near the value 90. Most of the curves are approximately parallel, seal oil, however, is a marked exception. The curve is very steep and crosses nearly all the others.

6. There are indications that in some cases hydrogenation for a very short time alters the iodine value without appreciably affecting the refractive index. This was first noticed in the case of seal oil and seems to occur also in argemone and linseed oils. Further experiments are required to ascertain what reaction takes place.

7. In order to enable rapid comparison to be made between different oils Table XIII has been drawn up. In this table values are given for all the oils so far examined, with the exception of castor and coconut. The numbers represent smoothed values of refractive indices for differences of ten units in iodine values. It will be observed that although it is not yet possible to deduce very much regarding the composition of an oil from these figures, yet, in the case of a new oil, they may serve as a guide to indicate the presence of abnormal constituents.

In conclusion we wish to thank the following gentlemen for the data connected with the oils mentioned after their names :—

- Mr. S. Narayana Iyer : argemone and linseed oils.
- Mr. V. M. Mascarenhas : mustard oil.
- Mr. T. J. Mirchandani : rocket and poppy-seed oils.
- Mr. N. R. Damle : rape oil.
- Mr. S. M. Mudbiri : cod-liver oil.
- Mr. R. G. Pradhan : soya-bean oil.
- Mr. C. K. Patel : cashew-nut, olive and rayan oils.
- Mr. K. M. Sheth : seal oil.
- Mr. D. S. Naidu : olive oil.
- Mr. A. Subrahmanyam : palm oil.

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TABLE I.
ARGEMONE OIL.

Relation between iodine value and refractive index

No. of sample	Iodine value. Winkler	n_D^{60} observed	n_D^{60} calculated. $1.4480 + (I.V.) \times 10^{-4}$	Difference	Time of hydrogenation in hours.
Original oil.	121.8	1.4614	1.4602	+ 12	...
2	108.1	1.4612	1.4588	+ 24	0.25
3	104.7	1.4607	1.4585	+ 22	0.4
4	100.2	1.4598	1.4580	+ 18	0.6
5	96.3	1.4593	1.4576	+ 17	0.75
6	90.5	1.4582	1.4571	+ 11	1.0
7	84.7	1.4574	1.4565	+ 9	1.25
8	80.2	1.4568	1.4560	+ 8	1.5
9	78.7	1.4565	1.4559	+ 6	1.75
10	66.7	1.4549	1.4547	+ 2	2.0
11	46.3	1.4527	1.4526	+ 1	2.5
12	36.6	1.4514	1.4517	- 3	3.0
13	26.9	1.4506	1.4507	- 1	3.5
14	13.6	1.4497	1.4494	+ 3	4.0
15	8.5	1.4494	1.4489	+ 5	4.5
	0.0		1.4480		

TABLE II.
MUSTARDSEED OIL.

Relation between iodine value and refractive index.

No. of sample	Iodine value. Winkler	n_D^{60} observed	n_D^{60} calculated $1.4488 + (I.V.) \times 10^{-4}$	Difference	Time of hydrogenation in hours
Original oil.	110.0	1.4605	1.4598	+ 7	0
1a	96.1	1.4590	1.4584	+ 6	0.5
2a	93.6	1.4589	1.4582	+ 7	1.0
1	89.5	1.4584	1.4578	+ 6	0.3
3a	87.6	1.4579	1.4576	+ 3	2.0
2	80.5	1.4575	1.4569	+ 6	0.7
5a	71.6	1.4558	1.4560	- 2	4.0
3	60.4	1.4547	1.4548	- 1	1.3
6a	59.7	1.4546	1.4548	- 2	5.0
7a	47.0	1.4535	1.4535	0	6.0
4	44.8	1.4530	1.4533	- 3	1.7
8a	21.7	1.4509	1.4510	- 1	8.0
5	6.7	1.4496	1.4495	+ 1	2.2
6	5.5	1.4494	1.4494	0	3.0
7	2.5	1.4492	1.4491	+ 1	4.0
8	1.0	1.4488	1.4489	- 1	6.0
	0.0	...	1.4488

TABLE III.

ROCKET OIL.

Relation between iodine value and refractive index.

No. of sample	Iodine value. Winkler	n_D^{60} observed	n_D^{60} calculated $1.4484 + (I.V.) \times 10^{-4}$	Difference.	Time of hydrogenation in hours
Original oil.	96.0	1.4602	1.4580	+ 22	...
Do. sulphur free.	78.1	1.4584	1.4562	+ 22	...
26	67.1	1.4564	1.4551	+ 13	0.2
19	62.0	1.4560	1.4546	+ 14	0.4
27	54.0	1.4549	1.4538	+ 11	0.5
28	45.5	1.4539	1.4530	+ 9	1.0
20	41.9	1.4534	1.4526	+ 8	0.8
21	34.0	1.4524	1.4518	+ 6	1.2
22	25.7	1.4515	1.4510	+ 5	1.5
23	18.8	1.4504	1.4503	+ 1	2.0
29	16.1	1.4499	1.4500	- 1	2.3
24	9.9	1.4495	1.4494	+ 1	2.5
30	3.3	1.4488	1.4487	+ 1	3.5
25	2.0	1.4486	1.4486	0	3.0
	0.0		1.4484

TABLE IV.
RAPE OIL.

Relation between iodine value and refractive index.

(a) English sample

No. of sample	Iodine value. Winkler	$n_D^{60^\circ}$ observed	$n_D^{60^\circ}$ calculated $1.4480 + (I.V.) \times 10^{-5}$	Difference	Time of hydrogenation in hours
Original oil	98.2	1.4582	1.4578	+4	
1	93.8	1.4570	1.4574	-4	
2	78.9	1.4562	1.4559	+3	
15	78.4	1.4561	1.4558	+3	
16	74.3	1.4555	1.4554	+1	
7	65.8	1.4542	1.4546	-4	
6	51.5	1.4529	1.4532	-3	
13	24.5	1.4501	1.4505	-4	
8	8.5	1.4489	1.4489	0	
9	5.8	1.4488	1.4486	+2	
11	3.7	1.4484	1.4484	0	
4	0.7	1.4481	1.4481	0	
	0.0	...	1.4480	...	

(b) Sample pressed in laboratory.

Original oil	91.5	1.4583	1.4574	+9	
K	83.3	1.4567	1.4565	+2	
H	78.6	1.4557	1.4561	-4	
L	76.0	1.4556	1.4558	-2	
M	60.6	1.4539	1.4542	-3	
A	53.9	1.4529	1.4536	-7	
B	34.9	1.4515	1.4517	-2	
N	33.9	1.4513	1.4516	-3	
C	17.7	1.4496	1.4500	-4	
D	2.2	1.4485	1.4484	+1	
G	1.6	1.4484	1.4484	0	
	0.0	...	1.4482	...	

TABLE V.
COD LIVER OIL.

Relation between iodine value and refractive index.

No. of sample	Iodine value. Winkler	n_D^{60} observed	n_D^{60} calculated $1.4474 + (\text{I.V.}) \times 10^{-4}$	Difference	Time of hydrogenation in hours
Original oil	147.9	1.4647	1.4622	+ 25	...
1	143.0	1.4640	1.4617	+ 23	0.25
21	143.0	1.4639	1.4617	+ 22	0.10
22	142.2	1.4637	1.4616	+ 21	0.25
1A	135.3	1.4627	1.4609	+ 18	0.33
23	134.3	1.4625	1.4608	+ 17	0.4
3	125.7	1.4615	1.4599	+ 16	1.0
24	123.2	1.4610	1.4597	+ 13	1.0
2A	122.0	1.4608	1.4596	+ 12	0.67
4	116.1	1.4596	1.4590	+ 6	1.5
3A	112.7	1.4594	1.4587	+ 7	1.33
4A ₂	102.5	1.4580	1.4577	+ 3	1.75
5A ₂	91.5	1.4565	1.4566	- 1	2.25
5	71.1	1.4544	1.4545	- 1	2.5
4A	59.0	1.4533	1.4533	0	2.0
6	28.8	1.4505	1.4503	+ 2	3.5
5A	22.8	1.4497	1.4497	0	3.0
7	12.0	1.4486	1.4486	0	4.5
8	9.9	1.4484	1.4484	0	6.0
6A	6.1	1.4479	1.4480	- 1	4.0
9	3.1	1.4477	1.4477	0	7.0
10	1.5	1.4476	1.4476	0	8.5
11	0.4	1.4475	1.4474	+ 1	10.0
	0.0	...	1.4474	...	

TABLE VI.
SOYA BEAN OIL.

Relation between iodine value and refractive index.

No. of sample	Iodine value. Winkler	$n_D^{60^\circ}$ observed	$n_D^{60^\circ}$ calculated $1.4466 + (I.V.) \times 10^{-4}$	Difference	Time of hydrogenation in hours
Original oil	130.6	1.4600	1.4597	+3	...
1	126.1	1.4590	1.4592	-2	0.25
2	119.1	1.4581	1.4585	-4	0.5
3	100.2	1.4561	1.4566	-5	0.75
4	85.4	1.4550	1.4551	-1	1.0
2a	82.1	1.4542	1.4548	-6	1.0
5	78.9	1.4538	1.4545	-7	1.5
6	68.4	1.4528	1.4534	-6	2.0
7	52.6	1.4511	1.4519	-8	2.5
3a	48.7	1.4510	1.4515	-5	2.0
8	42.3	1.4505	1.4508	-3	3.0
9	32.3	1.4495	1.4498	-3	3.5
10	27.1	1.4490	1.4493	-3	4.0
13	19.3	1.4483	1.4485	-2	6.0
7a	10.7	1.4477	1.4477	0	6.5
14	10.3	1.4475	1.4476	-1	7.0
9a	3.2	1.4469	1.4469	0	9.0
10a	1.1	1.4467	1.4467	0	10.0
...	0.0	...	1.4466

TABLE VII.
CASHEW KERNEL OIL.

Relation between iodine value and refractive index.

No. of sample	Iodine value. Winkler	$n_D^{60^\circ}$ observed	$n_D^{60^\circ}$ calculated $1.4465 + (I.V.) \times 10^{-4}$	Difference	Time in hours
A.1	83.5	1.4551	1.4549	+2	0
B.1	82.0	1.4549	1.4547	+2	0
A.2	78.4	1.4545	1.4543	+2	0.17
B.2	77.3	1.4542	1.4542	0	0.17
B.3	71.2	1.4534	1.4536	-2	0.33
A.3	69.5	1.4533	1.4535	-2	0.42
B.4	63.1	1.4524	1.4528	-4	0.50
A.4	56.9	1.4517	1.4522	-5	0.75
B.5	54.4	1.4514	1.4519	-5	0.75
A.11	47.6	1.4508	1.4513	-5	0.20
A.12	44.7	1.4505	1.4510	-5	0.25
B.6	40.8	1.4501	1.4506	-5	1.00
A.5	38.1	1.4498	1.4503	-5	1.17
A.9	35.5	1.4496	1.4501	-5	0.42
B.7	27.7	1.4487	1.4493	-6	1.25
A.10	26.6	1.4488	1.4492	-4	0.32
B.8	19.0	1.4481	1.4484	-3	1.50
A.6	13.4	1.4476	1.4478	-2	1.75
B.9	8.4	1.4470	1.4473	-3	1.75
B.10	3.2	1.4467	1.4468	-1	2.00
A.7	2.4	1.4467	1.4467	0	2.42
A.8	1.2	1.4466	1.4466	0	3.25
...	0	...	1.4465

TABLE VIII.

OLIVE OIL.

Relation between iodine value and refractive index.

No. of sample	Iodine value. Winkler	" $^{60^{\circ}}$ D observed	" $^{60^{\circ}}$ D calculated $1.4462 + (I.V.) \times 10^{-4}$	Difference	Time of hydrogenation in hours
Original oil.	83.6	1.4548	1.4546	+2	...
P.1.	74.4	1.4536	1.4537	-1	0.25
9	72.8	1.4538	1.4535	+3	0.33
1	71.6	1.4535	1.4534	+1	0.33
P.2.	67.7	1.4527	1.4530	-3	0.5
2	63.8	1.4524	1.4526	-2	0.67
10	58.1	1.4519	1.4520	-1	0.67
3	58.4	1.4516	1.4520	-4	1.0
P.3.	57.2	1.4515	1.4519	-4	0.83
4	43.7	1.4503	1.4506	-3	1.33
P.4.	41.6	1.4500	1.4504	-4	1.25
11	30.8	1.4493	1.4493	0	1.0
5	28.4	1.4489	1.4490	-1	1.67
P.5.	24.1	1.4484	1.4486	-2	1.8
6	20.4	1.4479	1.4482	-3	2.0
12	9.2	1.4470	1.4471	-1	1.33
7	6.1	1.4468	1.4468	0	2.33
13	1.4	1.4463	1.4463	0	1.8
P.6.	1.2	1.4465	1.4463	+2	2.5
8	1.1	1.4464	1.4463	+1	2.67
14	0.0	1.4462	1.4462	0	2.33

TABLE IX.

SEAL OIL.

Relation between iodine value and refractive index.

No. of sample	Iodine value. Winkler	n_D^{60} observed	n_D^{60} calculated $1.4462 + (I.V.) \times 10^{-4}$	Difference	Time of hydrogenation in hours
Original Oil	131.9	1.4626	1.4594	+32	...
1	123.9	1.4627	1.4586	+41	0.25
2	119.4	1.4616	1.4581	+35	0.5
3	114.8	1.4603	1.4577	+26	0.75
4	110.5	1.4594	1.4573	+21	1.0
5	100.4	1.4573	1.4562	+11	1.5
6	89.3	1.4557	1.4551	+ 6	2.0
7	72.9	1.4536	1.4535	+ 1	2.75
8	55.5	1.4516	1.4518	- 2	3.5
9	31.4	1.4489	1.4493	- 4	4.5
10	15.3	1.4475	1.4477	- 2	5.5
11	7.1	1.4467	1.4469	- 2	7.0
12	1.0	1.4463	1.4463	0	8.5
...	0.0	...	1.4462

TABLE X.
POPPY SEED OIL.

Relation between iodine value and refractive index.

No. of sample	Iodine value. Winkler	" 60° D observed	" 60° D calculated $1.4462 + (I. V.) \times 10^{-4}$	Difference	Time of hydrogenation in hours
Original Oil	137.8	1.4610	1.4600	+ 10	...
2	133.3	1.4604	1.4595	+ 9	0.5
11	131.3	1.4602	1.4593	+ 9	0.5
3	129.6	1.4600	1.4592	+ 8	1.0
12	129.1	1.4600	1.4591	+ 9	1.0
19	124.0	1.4592	1.4586	+ 6	0.75
4	115.0	1.4585	1.4577	+ 8	1.5
5	114.5	1.4584	1.4577	+ 7	2.0
13	112.5	1.4581	1.4575	+ 6	1.5
20	110.4	1.4578	1.4572	+ 6	1.3
6	100.4	1.4569	1.4562	+ 7	3.0
14	86.6	1.4552	1.4549	+ 3	2.0
7	69.6	1.4538	1.4532	+ 6	4.0
21	69.2	1.4534	1.4531	+ 3	2.7
22	65.5	1.4529	1.4528	+ 1	3.0
15	65.2	1.4529	1.4527	+ 2	3.0
16	54.6	1.4517	1.4516	+ 1	4.0
23	42.0	1.4503	1.4504	- 1	4.5
8	32.3	1.4494	1.4494	0	5.0
17	30.1	1.4493	1.4492	+ 1	5.0
9	10.3	1.4471	1.4472	- 1	6.8
10	2.5	1.4466	1.4465	+ 1	8.0
18	0.8	1.4463	1.4463	0	7.0
	0.0	...	1.4462		

TABLE XI.

RAYAN OIL.

Relation between iodine value and refractive index.

No. of sample	Iodine value. Winkler	" D_{60° observed	" D_{60° calculated $1.4461 + (I.V.) \times 10^{-4}$	Difference	Time of hydrogenation in hours
Original Oil	64.9	1.4527	1.4526	+ 1	...
A 1	61.5	1.4522	1.4523	- 1	0.2
A 2	55.2	1.4512	1.4516	- 4	0.4
A 3	48.4	1.4504	1.4509	- 5	0.7
A 4	44.1	1.4500	1.4505	- 5	1.0
A 5	37.5	1.4493	1.4499	- 6	1.2
A 6	28.8	1.4485	1.4490	- 5	1.4
A 7	22.7	1.4480	1.4484	- 4	1.7
A 8	13.0	1.4474	1.4474	0	2.0
A 9	1.1	1.4462	1.4462	0	3.0
...	0.0		1.4461		

TABLE XII.

PALM OIL.

Relation between iodine value and refractive index.

No. of sample	Iodine value. Winkler	$n_D^{60^\circ}$ observed	$n_D^{60^\circ}$ calculated $1.4456 +$ $(I. V.) \times 10^{-4}$	Difference	Time of hydrogenation in hours
Original oil	59.1	1.4517	1.4515	+2	0
2	55.4	1.4513	1.4511	+2	0.4
3	55.2	1.4512	1.4511	+1	0.6
4	49.3	1.4506	1.4505	+1	1.0
5	37.6	1.4493	1.4494	-1	1.5
6	37.5	1.4493	1.4494	-1	2.0
7	30.5	1.4486	1.4487	-1	2.5
8	18.7	1.4474	1.4475	-1	3.0
9	15.4	1.4472	1.4471	+1	3.5
10	6.6	1.4464	1.4463	+1	4.0
...	0.0	...	1.4456

TABLE

Refractive indices of hardened oils

Iodine value	Hongay	Argemone	Mustard	Rocket	Rape	Cod liver	Mohua	Linseed	Sardine
0	1.4525	1.4488	1.4488	1.4484	1.4481	1.4474	1.4470	1.4469	1.4468
10	1.4535	1.4495	1.4498	1.4494	1.4490	1.4484	1.4480	1.4479	1.4478
20	1.4545	1.4501	1.4507	1.4505	1.4499	1.4494	1.4490	1.4489	1.4488
30	1.4555	1.4509	1.4517	1.4518	1.4508	1.4504	1.4500	1.4499	1.4498
40	1.4565	1.4517	1.4527	1.4531	1.4517	1.4514	1.4511	1.4509	1.4508
50	1.4577	1.4528	1.4536	1.4544	1.4527	1.4524	1.4523	1.4519	1.4518
60	1.4593	1.4540	1.4546	1.4557	1.4537	1.4534	1.4535	1.4529	1.4529
70	1.4610	1.4553	1.4557	1.4571	1.4548	1.4544	...	1.4539	1.4540
80	1.4630	1.4567	1.4570	1.4585	1.4560	1.4554	...	1.4549	1.4551
90	...	1.4581	1.4583	1.4596	1.4574	1.4564	...	1.4561	1.4562
100	...	1.4598	1.4595	1.4576	...	1.4573	1.4574
110	...	1.4613	1.4605	1.4589	...	1.4585	1.4586
120	1.4604	...	1.4599	1.4599
130	1.4620	...	1.4614	1.4613
140	1.4635	...	1.4629	1.4628
150	1.4645	1.4642
160	1.4658	1.4654
170	1.4661	...

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