THE RELATION BETWEEN THE IODINE VALUES AND REFRACTIVE INDICES OF SOME HARDENED VEGETABLE OILS.

PART I.

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INTRODUCTION

The hardening or hydrogenation of a fixed oil consists in the addition of hydrogen to the molecules of unsaturated glycerides present in the oil. This addition takes place at the olefine linkings present in the acyl portion of such glycerides as glyceryl oleate, glyceryl linolate and glyceryl linoleate and the final product in these three cases is glyceryl stearate. Other unsaturated constituents of oils are glyceryl erucate in rape-seed oil, glyceryl ricinoleate in castor oil and glyceryl clupanodonate in fish oils, and these compounds on reduction yield respectively glyceryl behenate, glyceryl hydroxystearate[1] and glyceryl stearate. The customary method of determining the degree of hardness or the percentage reduction is by estimating the iodine (bromine) values of the original oil and of the hardened product. The drawback of this method is that it takes some time for completion; even when Winkler's method[2] is used about 2·5 hours are required, and, as in the study of the reduction of an oil work is frequently simplified if the degree of hydrogenation can be rapidly ascertained, a quicker method is highly desirable.

Ubbelohde and Svanoe[3] have drawn attention to the fact that othe physical constants such as melting point and refraction number of partially hardened oils bear a definite relationship to the iodine values, and that any one of these physical constants may be used for ascertaining the degree of hardening. These authors themselves studied the relationship between iodine value, refraction number and melting point of the following oils :—Cottonseed, linseed, castor, tung and whale.

Undoubtedly the simplest physical constant to determine is the refractive index, as with the aid of an Abbé refractometer a determination requires less than five minutes and the approximate correction of the index for temperature change is well known.

[1] If the hydroxyl groups are also reduced the final product is glyceryl stearate.
[2] Cf, this Journal, 1916, **1**, 173.
[3] *Zeitsch. angew. Chem.*, 1919, **32**, 276.

As we considered the relation between the refractive indices of hardened vegetable oils and their iodine values or degree of unsaturation of great importance in connection with work on the hardening of Indian oils we have started a series of experiments, the object of which is to determine the refractive index/iodine value curves for all ordinary Indian oils, and the present communication gives the tables and curves for the following vegetable oils :—

Cottonseed	Coconut
Linseed	Sesamé
Ground-nut	Castor
Mohua (*Bassia latifolia*)	Hongay (*Pongamia glabra*)

and also for West Coast sardine oil.

Purification

All the oils used were submitted to a preliminary refining process before hydrogenation. The acid value was first determined and about 10 per cent more than the calculated quantity of caustic soda required for neutralization added in the form of a 10 per cent aqueous solution to the previously warmed oil. In the case of fish and ground-nut oils 5 per cent solutions were found more satisfactory. The mixture was maintained at 70°C. for half an hour and continuously stirred. It was then allowed to stand until the soap separated. The oil was washed with warm water, dried by heating gently and finally clarified by warming to 70°C. with 3 to 5 per cent of Fullers' earth, and filtering while still hot.

Hydrogenation

The method of preparing the hydrogen, the apparatus for hydrogenation and the preparation of the nickel catalysts are described in the Appendix (p. 60). In the case of each oil a series of reductions was carried out during varying periods of time, so that samples of hardened oil were obtained with different degrees of unsaturation. After reduction the oils were filtered, in order to remove the catalyst, and the iodine value and refractive index of each sample determined.

In some experiments the filtration of the oil occasioned some difficulty. This was largely due to the fine state of division of the catalyst and the blocking of the pores of the paper. This difficulty was especially noticeable in the case of the catalyst prepared from nickel nitrate and sugar, and also with the nickel powder produced from the carbonate after the catalyst had been used several times. On the other hand, the catalyst obtained by depositing nickel on Kieselguhr was readily removed by filtration.

Iodine Values

These values were determined by Winkler's method.[1] In the earlier experiments considerable discrepancies were noticed in the case of duplicate experiments. Such discrepancies were found to be due to the loss of bromine vapour when removing the stoppers of the bottles containing the solutions in order to add potassium iodide solution just before the titrations. The mixing, with the exception of the addition of acid, was generally performed in the laboratory, the bottles removed to a dark room, the acid added and the bottles kept for the requisite time in the dark room. As this room was appreciably warmer than the laboratory, on removing the stopper in order to add the potassium iodide solution, air escaped from the bottle and carried bromine vapour with it. Any error due to this cause was eliminated by cooling the bottles in ice water just before removing the stoppers, and by the introduction of this device it was found that duplicate experiments gave concordant results.

In the case of hardened castor oil, however, the method was found quite unreliable. For the original oil values were obtained which agreed very closely with those found by Wijs' method, but after hydrogenation, the apparent iodine value actually rose slightly even although the oil was converted into a hard solid. Duplicate determinations gave approximately the same values, but in subsequent experiments under slightly different conditions, values were obtained which differed very widely. For example, one sample of oil gave the values 80·0, 80·8, 27·2, 48·8, 84·3 by the Winkler method and a value of 6·9 by Wijs' method. The acetyl value of this particular sample was 72 and that of the original oil 154·5. These discrepancies are no doubt to some extent due to the presence of the hydroxyl group, but it is difficult to see why reliable figures are obtained for the original oil but not for the hardened samples.

Refractive Indices

The instrument used for determining refractive indices was an Abbé refractometer, the accuracy of which was checked from time to time by means of a glass plate of known refractive index ($n_D = 1{\cdot}5168$). When adjusted to give the correct reading with the glass plate, the correct value for the refractive index of water was also obtained, but on measuring the index of a sample of oil ($n_D^{25} = 1{\cdot}471$) on the Abbé refractometer and on a Pulfrich refractometer, which also gave correct readings with the glass plate and with water, a difference of

[1] Cf. this Journal, 1916, I, 173.

0·0004 was observed, the Pulfrich giving the higher value. As no means were avilable of determining which instrument was correct, the readings given by the Abbé refractometer have not been altered and hence may be subject to a constant error of the order of 0·0004.

A heating arrangement was used in connection with the instrument as many of the products had moderately high melting points and the temperature of observation was always several degrees above the melting point of the sample. The majority of the determinations were made at temperatures between 50° and 65° and for purposes of comparison the values found have been calculated to 60°. The formula used for this calculation was that given by Joseph,[1] namely adding or subtracting 0·00036 for a rise or fall of each degree of temperature.

A few experiments were made with the oils under investigation, both unhardened and partially hardened, and the use of this coefficient for ranges of temperature not exceeding ten degrees was found to give an error not exceeding 0·0001.

When making measurements at 60° a small correction + 0·0003 had to be introduced for the change in the refractive index of the glass, and a second correction due to the fact that the temperature of the prisms was found to be about 0·3° below the temperature of the water in the jacket. The latter value was determined by placing a small quantity of pure palmitic acid melting at 62·6, between the prisms and very gradually raising the temperature until liquefaction was observed. A similar experiment at 70° with *o*-nitraniline gave a corresponding figure. The total correction thus amounted to + 0·0002.

The values obtained for the iodine numbers and refractive indices of samples of hardened products obtained from the following oils

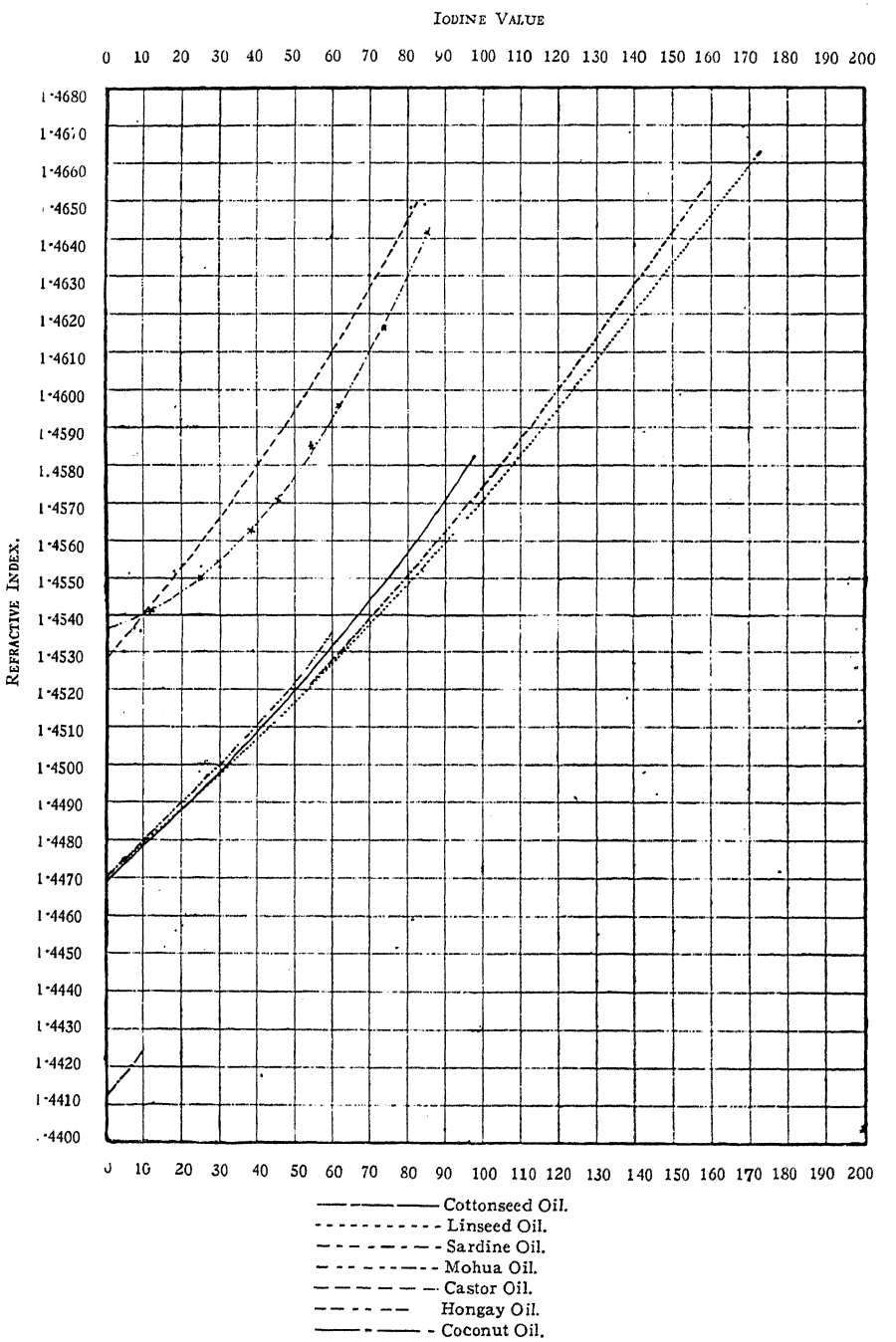
Cottonseed	Linseed
Ground-nut	Sardine
Sesamé	Castor
Mohua	Hongay

Coconut

are given in Tables I to VIII, and the relations are represented graphically in the curves given in Diagram I. The curves for ground-nut oil and sesamé oil are almost coincident with those for cottonseed oil and sardine oil respectively, so they have not been reproduced. The curves for castor oil and hongay oil as explained later are only approximations.

[1] *J. Soc. Chem. Ind.*, 1920, **39**, 66 T.

FIGURE I


Iodine Value
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
Refractive Index.
1·4680
1·4660
1·4650
1·4640
1·4630
1·4620
1·4610
1·4600
1·4590
1·4580
1·4570
1·4560
1·4550
1·4540
1·4530
1·4520
1·4510
1·4500
1·4490
1·4480
1·4470
1·4460
1·4450
1·4440
1·4430
1·4420
1·4410
1·4400
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200
Cottonseed Oil.
Linseed Oil.
Sardine Oil.
Mohua Oil.
Castor Oil.
Hongay Oil.
Coconut Oil.

Discussion of Results

1. In the case of oils which consist solely of mixtures of the glycerides of stearic, oleic, linolic, linolenic and clupanodonic acids it is highly probable that for any particular iodine value the refractive index will be approximately constant and independent of the nature of the oil.

The conditions for absolute independence are—

(*a*) That the refractive index of a mixture of glycerides is identical with the mean refractive index of the constituents.

(*b*) That the refractive index of a mixed glyceride is the same as that of a corresponding mixture of mixed glycerides.

(*c*) That the addition of two atoms of hydrogen to the molecule of any member of the series of acids, oleic-clupanodonic, produces a constant change in the refractive index.

It is intended to investigate these conditions in detail at a later date, but meanwhile it may be remarked that all oils of this type yield the same final reduction, product, tristearin, and hence the refractive indices of the completely hardened oils should be identical.

The presence of the glycerides of other fatty acids, such as palmitic, would affect the absolute refractive index, but would not alter the rate of change on hardening, as this is due to the reduction of the unsaturated acids allied to stearic acid. In other words, it might be expected that all curves would be parallel.

2. Of the oils examined, cottonseed, ground-nut, sesamé, mohua, linseed and sardine may be said to belong to the class under consideration, although they probably contain small amounts of glycerides derived from palmitic acid, and in the case of ground-nut oil of arachidic and lignoceric acids. The composition of the latter oil has been investigated by Jamieson, Baughman and Brauns.[1] The curves for these oils are nearly coincident, and the values of $n_D^{60°}$ calculated for the completely hardened oils are respectively 1·4468, 1·4468, 1·4467, 1·4470, 1·4469 and 1·4468, which may be considered identical within the limit of experimental error. Scheij's values for tristearin and tripalmitin are 1·4473 and 1·4455. The presence of 5 per cent. of glycerides of palmitic or arachidic acid would consequently produce an alteration of about 0·0001 in the refractive index of the completely hardened oil.

3. For iodine values below 50 the curves for these oils are linear and parallel, a difference of 1 unit in the iodine value corresponding

[1] *J. Amer. Chem. Soc.*, 1921, **43**, 1372.

with a difference of 0·00010 in the refractive index, so that within this range the curves may be represented by the formula—

$$n_D = H + (I.V.) \times 10^{-4}$$

where H is the refractive index of the completely hardened oil and I. V. is the iodine value of the given sample.

4. The curves for linseed and sesamé oil appear to form an exception to the above rule as they cross some of the other curves at low iodine values, but this may be due to experimental error as there are only a few available determinations for linseed oil and the figures for sesamé oil do not agree very well among themselves.

5. At higher iodine values the curves tend to bend upwards, indicating that the glycerides of the more unsaturated acids, which are reduced first, have a higher rate of change of refractive index with iodine value than the glycerides of oleic acid. The steepest portion of all the curves is the initial part of the curve for sardine oil, where a difference of 1 unit in the iodine value produces a difference of 0·00014 in the refractive index. This is probably due to the presence of glycerides of clupanodonic acid.

6. In the case of cottonseed oil a number of experiments have been made using different classes of catalysts[1] and consequently hardening for different times to obtain the same iodine value. From Table I it will be seen that the relation between iodine value and refractive index is independent of the nature of the catalyst and of the time of hardening for the range of temperature employed.

7. The curve for coconut oil is much below all the others owing to the presence of glycerides derived from acids of low molecular weight.

8. The position of the castor oil curve is undoubtedly due to the presence of the hydroxyl group in the glycerides, and the position of the hongay oil curve is so near to that of castor oil, although its acetyl value is only 24 as compared with 150 for castor, that an examination of the constituents present in this oil has been started.

9. In the case of castor oil (Table VII) the refractive indices have been calculated according to the formula

$$n_D^{60} = 1{\cdot}4527 + (I.V.) \times 10^{-4}$$

and it will be noted that the agreement between the observed and calculated values is not nearly as good as with most of the other oils.

[1] For details of preparation of each type, see p. 61.

The discrepancies may be due to the presence of the hydroxyl groups present in the acyl radicle. It would thus be possible to have two samples of the hardened oil with the same iodine value but with different acetyl values and hence different refractive indices. According to Grün and Woldenberg [1] on reduction with palladium as catalyst at the ordinary temperature the hydroxyl groups are not affected. With a nickel catalyst the results vary according to the temperature. Jurgens and Meigen[2] state that above 200° both addition to the olefine linking and reduction of the hydroxyl groups occur side by side, but that at 200° the hydroxyl groups are reduced more readily than the olefine linking.

It is hoped to carry out further experiments on the hardening of castor oil in order to study the effect of the hydroxyl groups.

10. The case of hongay oil appears similar to the above. The series of figures given refers to one set of experiments only. Subsequent experiments have given different results and consequently the curve reproduced must only be regarded as typical.

Comparison with other Observations

Among recent researches dealing with the present subject the experiments of Kahbenberg and Ritter[3] on the reduction of cottonseed oil with different catalysts may be mentioned. The catalysts used have given only partial hardening, the lowest iodine value obtained being about 60 as compared with 108 for the original oil or about 44 per cent reduction. Within the limits of their experiments there appears to be no definite relationship between iodine value (Hanus) and refractive index (Abbé refractometer). In some cases an increase of 10 to 12 units in the iodine value produces an increase of 0·0001 in the refractive index, in other cases an increase of 0·0004 and in others 0·0020 and in one case an increase of 4 in the iodine value produces a decrease of 0·0013 in the refractive index.

Pickering and Cowlishaw [4] have drawn attention to the relation between the refractive index and the iodine value of oils and fats. They show that for most oils of the ordinary type, e.g. linseed, soyabean, cottonseed, ground-nut, the relation

$$n_D^{40} = 1{\cdot}4515 + 0{\cdot}0001171 \times \text{I. V}$$

but this does not hold good for palm-kernel or coconut oil. By

[1] *J. Amer. Chem. Soc.*, 1909, **31**, 49.
[2] *Chem. Umschau Fett. Ind.*, 1916, **23**, 90.
[3] *J. Physical Chem.*, 1921, **25**, 89.
[4] *J. Soc. Chem. Ind.*, 1922, **41**, 74 T.

taking into account the saponification number (S. V.) and the acid number (A.V.) of the oil, it is found that the following equation

$$n_D^{40^\circ} = 1{\cdot}4643 - 0{\cdot}000066 \times \text{S.V.} - \frac{0{\cdot}0096\ \text{A.V.}}{\text{S.V.}} + 0{\cdot}0001171 \times \text{I.V}$$

holds good for practically all oils with the exception of castor oil, provided the oils are fresh and have not undergone oxidation. It will be observed that the factor 0·0001171 is greater than the one we have adopted. This is because the oils in question are not hardened and the larger factor is more accurate than ours at the upper and steeper portions of the curves. The refractive index at 60° for a completely hardened oil is approximately 1·4443 according to the above formula, whereas the actual experimental value is 1·4468, and hence it must be recognised that the formula can only be used through a limited range of iodine values. For a more extended range a parabolic formula is necessary and this may be written,

$$n_D^{60} = 1{\cdot}4468 + 1{\cdot}03 \times 10^{-4}\ (\text{I.V.}) + 7{\cdot}3 \times 10^{-8}\ (\text{I.V.})^2$$

This holds good within five units in the fourth place for all the oils under consideration except castor, hongay and coconut.

The work of Ubbelohde and Svanoe (*loc. cit.*) is of a similar nature to ours, but they have not correlated their results.

Fig. II shows the results obtained by them for cottonseed, linseed and castor oils reduced to a temperature of 60°. It will be seen that their curves approximate closely to our own except in the case of castor in which less reduction of the hydroxyl group seems to have taken place. The absolute values of the completely hardened oils are lower than any we have found and the curves are of a different shape.

P. Pascal[1] has measured the refractive indices of tripalmitin, tristearin and triolein and of some of their binary and ternary mixtures at 70°, and it might be expected that his values could be represented by curves approximating very closely to those based on the data obtained with hardened natural oils. Unfortunately neither the absolute values for the pure glycerides nor yet the temperature coefficients given by him agree with those obtained by other observers, e.g. Scheij [2] and Partheil and Velsen [3] and doubt arises as to the value to be attached to his figures. For the sake of comparison a curve representing the relation between the refractive indices of mixtures of tristearin and triolein and their iodine values is shown in

[1] *Bull. Soc. Chim.*, 1914, (iv), **15**, 360.
[2] *Rec. trav. Chim.*, 1899, **18**, 188.
[3] *Arch. pharm.*, 1900, **238**, 261.

FIGURE II

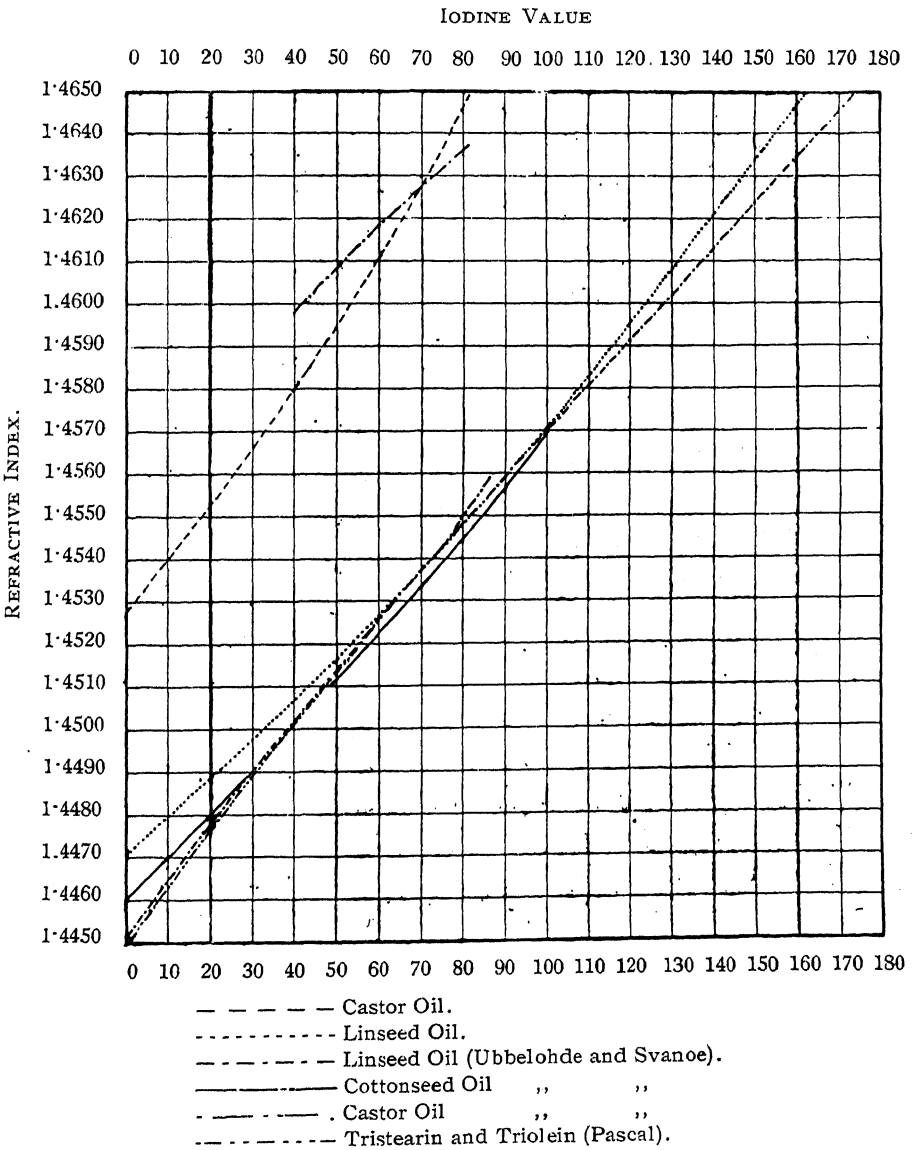

Iodine Value
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180
Refractive Index.
1·4650
1·4640
1·4630
1·4620
1·4610
1.4600
1·4590
1·4580
1·4570
1·4560
1·4550
1·4540
1·4530
1·4520
1·4510
1·4500
1·4490
1·4480
1.4470
1·4460
1·4450
0 10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180
— — — — — Castor Oil.
- - - - - - - - - - Linseed Oil.
— - — - — - — Linseed Oil (Ubbelohde and Svanoe).
———·——— Cottonseed Oil ,, ,,
- ——— - ——— . Castor Oil ,, ,,
—— - - — - - - — Tristearin and Triolein (Pascal).

Fig. II; the calculation to 60°, however, has been made by adding 0·0036 to the values as measured by Pascal at 70° and not by using his temperature coefficients. It will be observed that the curve approximates very closely to the curve for linseed oil obtained by Ubbelohde and Svanoe.

Table I

COTTONSEED OIL (INDIAN)

Relation between Iodine Value and Refractive Index

No. of Sample	Iodine Value Winkler	$n_D^{60°}$ observed	$n_D^{60°}$ calculated 1·4468 + I.V.10⁻⁴	Difference	Time of hydrogenation in hours	Catalyst
Original oil	98·0	1·4582	1·4566	+16	0	...
3	77·8	1·4553	1·4546	+ 7	3	A
1	75·0	1·4551	1·4543	+ 8	3	A
9	73·8	1·4549	1·4542	+ 7	4	A
16	67·8	1·4540	1·4536	+ 4	2	B
20	66·2	1·4539	1·4534	+ 5	2	B
6	63·6	1·4536	1·4532	+ 4	6	A
7	62·2	1·4535	1·4530	+ 5	4	A
29	60·8	1·4533	1·4529	+ 4	0·5	C
2	60·3	1·4532	1·4528	+ 4	4	A
8	59·0	1·4530	1·4527	+ 3	8	A
28	54·9	1·4523	1·4523	0	0·5	C
4	52·1	1·4522	1·4520	+ 2	6	A
19	51·8	1·4522	1·4520	+ 2	4	B
15	50·3	1·4520	1·4518	+ 2	4	B
5	49·6	1·4520	1 4518	+ 2	8	A
48	48·9	1·4519	1·4517	+ 2	1	C
30	48·7	1·4518	1·4517	+ 1	1	C
21	47·8	1·4517	1·4516	+ 1	12	B
10	47·5	1·4517	1·4516	+ 1	8	A
31	45·4	1·4515	1·4513	+ 2	2	C
22	44·1	1·4513	1·4512	+ 1	12	B
27	43·9	1·4511	1·4512	− 1	1	C
47	40·5	1·4507	1·4509	− 2	2	C
18	38·5	1·4506	1·4507	− 1	8	B
17	38·2	1·4506	1·4506	0	12	B
32	33·0	1·4502	1·4501	+ 1	2	C
26	32·7	1·4503	1·4501	+ 2	2	C
54	31·0	1·4499	1·4499	0	2	D
11	30·2	1·4497	1·4498	− 1	8	E
12	30·0	1·4497	1·4498	− 1	12	A
52	28·7	1·4495	1·4497	0	2	D
13	28·0	1·4495	1·4496	− 1	12	A
14	24·8	1·4492	1·4493	− 1	8	B
46	18·7	1·4484	1·4487	− 3	4	C
24	12·9	1·4480	1·4481	− 1	4	C
25	10·0	1·4480	1·4478	+ 2	4	C
56	7·0	1·4474	1·4475	− 1	2	C
55	5·0	1·4472	1·4473	− 1	4	D
53	4·0	1·4468	1·4472	− 4	4	D
58	1·0	1·4469	1·4469	0	2	C
57	0·0	1·4469	1·4468	+ 1	4	C
64	0·0	1·4469	1·4468	+ 1	1	C
66	0·0	1·4469	1·4468	+ 1	2	C

Table II

GROUND-NUT OIL

Relation between Iodine Value and Refractive Index

No. of Sample	Iodine Value	$n_D^{60°}$ observed	$n_D^{60°}$ calculated 1·4468 + I.V.10⁻⁴	Difference	Time of hydrogenation in hours	Catalyst
Orginal oil	86·0	1·4562	1·4554	+8	0	...
11	65·2	1·4533	1·4533	0	0·5	C
2	63·5	1·4535	1·4532	+3	0·5	C
7	52·9	1·4524	1·4521	+3	3	C
10	50·7	1·4520	1·4519	+1	1	C
9	43·5	1·4510	1·4512	−2	2	C
4	43·2	1·4510	1·4511	−1	1	C
3	30·0	1·4499	1·4498	+1	1	C
6	28·0	1·4495	1·4496	−1	2	C
8	5·9	1·4475	1·4474	+1	4	C
5	3·0	1·4472	1·4471	+1	4	C
1	2·8	1·4471	1·4471	0	4	C
12	0·0	1·4468	1·4468	0	4	C

Table III

SESAME OIL

Relation between Iodine Value and Refractive Index

No. of Sample	Iodine Value Winkler	$n_D^{60°}$ observed	$n_D^{60°}$ calculated 1·4467 + I.V. 10⁻⁴	Difference	Time in hours
Original oil	110·0	...	1·4577	...	...
N 1	103·0	1·4577	1·4570	+7	0·3
N 2	91·8	1·4564	1·4559	+5	0·7
N 3	84·3	1·4552	1·4551	+1	1·0
n 12	78·4	1·4546	1·4545	+1	0·2
N 4	75·8	1·4542	1·4543	−1	1·3
N 5	70·4	1·4537	1·4537	0	1·9
p 1	66·9	1·4533	1·4534	−1	...
N 6	65·5	1·4530	1·4533	−3	2·3
N 7	61·7	1·4528	1·4529	−1	3·0
n 4	61·2	1·4526	1·4528	−2	0·5
p 4	61·2	1·4525	1·4528	−3	2·0
n 8	60·2	1·4524	1·4527	−3	0·3
p 9	58·9	1·4526	1·4526	0	2·0
p 6	50·4	1·4513	1·4517	−4	1·0
n 3	31·4	1·4496	1·4498	−2	1·0
p 5	29·5	1·4494	1·4497	−3	4·0
n 11	24·7	1·4490	1·4492	−2	1·0
p 10	20·5	1·4488	1 4488	0	3·0
p 2	17·9	1·4484	1·4485	−1	3·0
n 2	16·7	1·4483	1·4484	−1	2·0
p 11	10·6	1·4485	1·4478	+7	4·0
p 15	9·3	1·4481	1·4476	+5	4·0
p 12	8·5	1·4480	1·4476	+4	5·0
n 9	8·4	1·4476	1·4475	+1	2·0
p 17	3·7	1·4477	1·4471	+6	6·0
p 14	3·6	1·4474	1·4471	+3	3·0
n 7	3·3	1·4472	1·4470	+2	3·0
n 10	2·4	1·4472	1·4469	+3	4·0
p 16	2·3	1·4469	1·4469	0	...
n 6	1·8	1·4473	1·4469	+4	4·0
n 13	1·5	1·4475	1·4469	+6	5·0
...	0·0	...	1·4467	...	...

Table IV

MOHUA OIL

Relation between Iodine Value and Refractive Index

No. of Sample	Iodine Value Winkler	$n_D^{60°}$ observed	$n_D^{60°}$ calculated 1·4470 + I.V. 10^{-4}	Difference	Time in minutes
Original oil	59·5	1·4535	1·4530	+5	...
C 6	54·0	1·4525	1·4524	+1	...
C 5	53·0	1·4524	1·4523	+1	...
A 2	52·1	1·4526	1·4522	+4	...
C 7	52·0	1·4523	1·4522	+1	...
C 10	52·0	1·4526	1·4522	+4	...
C 16	52·0	1·4529	1·4522	+7	...
A 3	50·2	1·4525	1·4520	+5	...
B 2	49·1	1·4527	1·4519	+6	15
C 8	47·0	1·4519	1·4517	+2	...
A 1	45·2	1·4515	1·4515	0	...
C 11	42·0	1·4514	1·4512	+2	...
C 13	38·3	1·4509	1·4508	+1	...
C 21	38·3	1·4507	1·4508	−1	...
B 3	35·3	1·4506	1·4505	+1	20
C 14	35·0	1·4505	1·4505	0	...
C 22	34·0	1·4505	1·4504	+1	...
C 12	32·5	1·4505	1·4503	+2	...
B 3*a*	30·3	1·4500	1·4500	0	15
C 15	30·0	1·4500	1·4500	0	...
C 24	24·0	1·4496	1·4494	+2	...
C 25	24·0	1·4495	1·4494	+1	...
A 4	22·3	1·4491	1·4492	−1	...
B 4	17·8	1·4489	1·4488	+1	30
C 19	17·0	1·4486	1·4487	−1	...
B 5	12·9	1·4484	1·4483	+1	40
C 26	10·9	1·4483	1·4481	+2	...
B 6	10·3	1·4479	1·4480	−1	50
C 20	9·1	1·4482	1·4479	+3	...
B 7	5·0	1·4475	1·4475	0	60
B 8	4·4	1·4473	1·4474	−1	70
B 9	3·7	1·4473	1·4474	−1	90
...	0·0	...	1·4470	...	...

Table V

LINSEED OIL

Relation between Iodine Value and Refractive Index

No. of Sample	Iodine Value Winkler	$n_D^{60°}$ observed	$n_D^{60°}$ calculated 1·4469 + I.V. 10^{-4}	Difference	Time of hydrogenation in hours	Catalyst
Original oil	173·0	1·4663	1·4642	+21	0	C
1	109·5	1·4582	1·4579	+ 3	1	C
2	80·8	1·4549	1·4550	− 1	2	C
3	24·3	1·4492	1·4493	− 1	4	C
4	3·0	1·4472	1·4472	0	6	C
...	0·0	...	1·4469	...	...	C

Table VI

WEST COAST SARDINE OIL

Relation between Iodine Value and Refractive Index

No. of Sample	Iodine Value Winkler	$n_D^{60°}$ observed	$n_D^{60°}$ calculated 1·4468 + I.V. 10^{-4}	Difference	Time of hydrogenation in hours
Original oil	159·6	1·4654	1·4628	+26	...
M 2	152·2	1·4645	1·4620	+25	0·3
K 17	149·7	1·4642	1·4618	+24	...
K 14	149·6	1·4640	1·4618	+22	...
M 3	148·0	1·4638	1·4616	+22	0·5
K 1	142·3	1·4631	1·4610	+21	...
A 9	138·9	1·4629	1·4607	+22	...
M 4	138·8	1·4626	1·4607	+19	0·8
K 15	136·0	1·4619	1·4604	+15	...
M 5	131·7	1·4617	1·4600	+17	1·0
K 16	120·5	1·4600	1·4589	+11	...
M 6	114·9	1·4594	1·4583	+11	1·3
K 3	113·2	1·4589	1·4581	+ 8	...
K 2	109·7	1·4585	1·4578	+ 7	...
M 7	104·3	1·4580	1·4572	+ 8	1·5
K 8	104·1	1·4578	1·4572	+ 6	...
M 8	91·5	1·4564	1·4560	+ 4	1·8
K 5	90·1	1·4560	1·4558	+ 2	...
M 9	81·3	1·4553	1·4549	+ 4	2·0
K 4	80·1	1·4550	1·4548	+ 2	...
A 5	78·2	1·4548	1·4546	+ 2	1·0
K 9	76·7	1·4547	1·4545	+ 2	...
M 10	74·2	1·4544	1·4542	+ 2	2·5
M 11	64·2	1·4533	1·4532	+ 1	3·5
M 12	57·7	1·4525	1·4526	− 1	4·0
K 6	56·7	1·4523	1·4525	− 2	...
A 8	51·8	1·4523	1·4520	+ 3	1·0
M 13	48·4	1·4515	1·4516	− 1	2·3
A 4	42·0	1·4513	1·4510	+ 3	...
M 14	40·7	1·4507	1·4509	− 2	2·5
K 11	36·9	1·4505	1·4505	0	...
A 6	36·0	1·4506	1·4504	+ 2	...
M 15	35·9	1·4503	1·4504	− 1	2·8
K 12	18·1	1·4486	1·4486	0	...
M 16	18·0	1·4487	1·4486	+ 1	3·0
K 10	17·1	1·4486	1·4485	+ 1	...
A 2	16·7	1·4488	1·4485	+ 3	...
A 3	13·5	1·4485	1·4482	+ 3	...
K 13	12·1	1·4480	1·4480	0	...
A 7	10·5	1·4482	1·4478	+ 4	4·0
...	0·0	...	1·4468	...	...

Table VII

CASTOR OIL

Relation between Iodine Value and Refractive Index

No. of Sample	Iodine Value Wijs.	$n_D^{60°}$ observed	$n_D^{60°}$ calculated 1·4527 + I.V. 10-4	Difference	Time in hours
Original oil	84·6	1·4649	1·4614	+35	...
63	81·4	1·4648	1·4608	+40	0·13
62	69·9	1·4630	1·4597	+33	0·25
64	53·8	1·4586	1.4581	+ 5	0·50
59	30·3	1·4553	1·4557	− 4	0·50
65	25·0	1·4553	1·4552	+ 1	0·75
66	18·7	1·4552	1·4546	+ 6	0·63
60	9·6	1·4536	1·4537	− 1	6·0
61	6·9	1·4537	1·4534	+ 3	6·0
58	6·5	1·4545	1·4534	+11	1·0
57	5·3	1·4546	1·4532	+14	2·0
56	4·7	1·4530	1·4532	− 2	3·0
...	0·0	...	1·4527	...	...

Table VIII

HONGAY OIL

Relation between Iodine Value and Refractive Index

No. of Sample	Iodine Value Winkler	$n_D^{60°}$ observed	$n_D^{60°}$ calculated 1·4525 + I.V. 10-4	Difference	Time in hours
Original oil	87·3	1·4642	1·4612	+30	0
1	74·0	1·4616	1·4599	+17	0·25
2	62·3	1·4596	1·4587	+ 9	0·50
3	54·0	1·4585	1·4579	+ 6	0·75
4	44·9	1·4571	1·4570	+ 1	2·0
5	38·2	1·4563	1·4563	0	5·0
6	24·7	1·4550	1·4550	0	7·0
7	12·1	1·4541	1·4537	+ 4	9·0
...	0·0	...	1·4525	...	...

Table IX

COCONUT OIL

Relation between Iodine Value and Refractive Index

No. of Sample	Iodine Value Winkler	$n_D^{60°}$ observed	$n_D^{60°}$ calculated 1·4413 + I.V. 10⁻⁴	Difference	Time of hydrogenation in hours	Catalyst
Original oil	10·1	1·4424	1·4423	+1	0	...
7	2·5	1·4418	1·4416	+2	0 08	C
1	1·7	1·4416	1·4415	+1	1·0	A
4	1·4	1·4416	1·4414	+2	1·0	A
2	0·4	1·4414	1·4413	+1	3·0	A
6	0·4	1·4414	1·4413	+1	0·5	C
5	0 0	1·4413	1·4413	0	2·0	C
8	0·0	1·4413	1·4413	0	3·0	C

Appendix

GENERATION OF HYDROGEN AND PREPARATION OF CATALYSTS FOR LABORATORY EXPERIMENTS

ON the commercial scale hydrogen is usually manufactured from water gas and occasionally electrolytically, e.g. by means of an Oerlikon electrolyser.

For laboratory purposes the electrolytic method is the most convenient, especially when the oxygen can be collected and utilised.

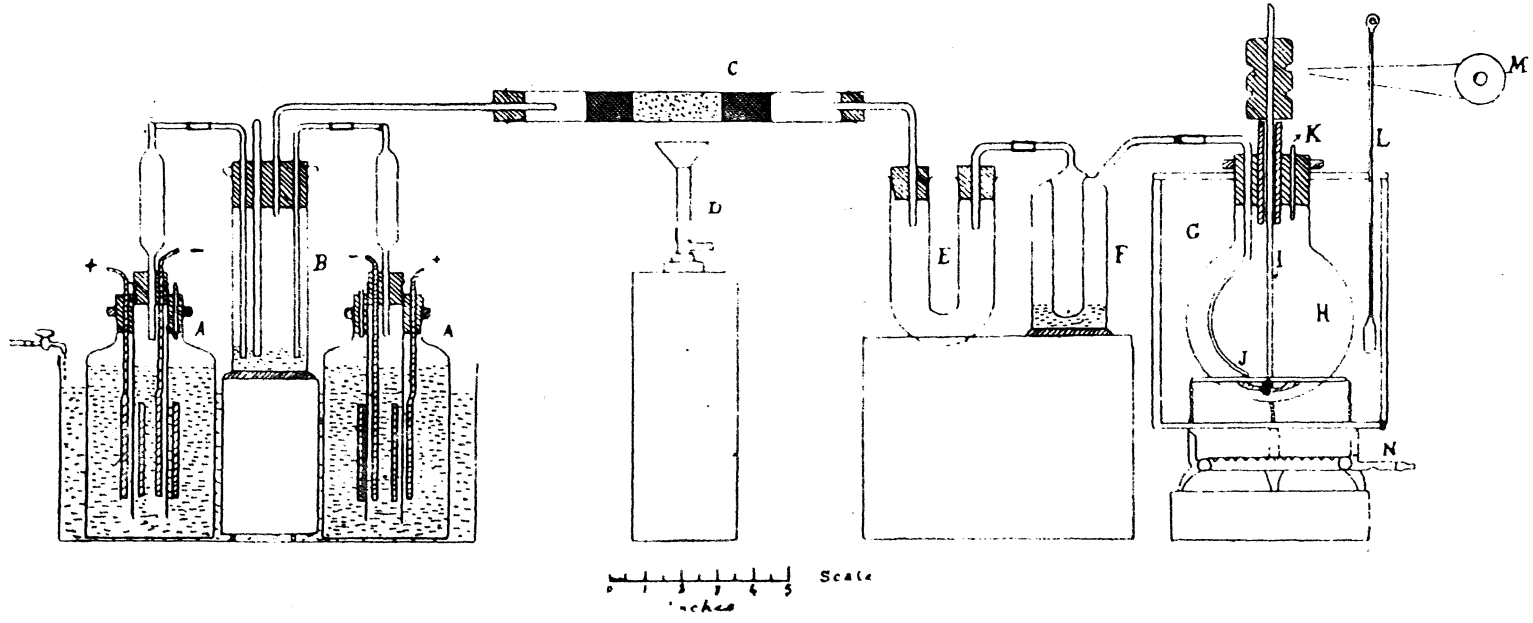
During the progress of this work Palmer [1] has described a laboratory apparatus for preparing electrolytic hydrogen, in which nickel electrodes are used with a 5 per cent potassium hydroxide electrolyte at 25–30°. The anode is steeped in concentrated nitric acid for half an hour before use as otherwise it is readily attacked and disintegrated when large currents are employed.

The apparatus which has been used for several years in these laboratories is shown in Diagram III. It consists of a battery of six electrolytic cells containing sulphuric acid, sp. gr. 1·12 and arranged in series. Each cell is a wide-mouthed bottle of 750 c.c. capacity. The electrodes are strips of sheet lead bent into the form of cylinders, the anode is placed outside and the cathode inside a wide glass tube (0·9″ diameter) passing through the cork, which also carries a glass tube through which the lead to the anode passes. The oxygen

[1] *J. Soc. Chem. Ind.*, 1920, **39**, 316 T.

FIGURE III

LABORATORY APPARATUS FOR THE HYDROGENATION OF OILS



A & A'—Electrolytic cells. (A battery of six cells in series, of which only two have been shown.)
B & F—Sulphuric acid wash bottles.
C—Hard glass tube containing copper turnings.
D & N—Burners.
E—Calcium chloride U tube.
G—Air bath.
H—Reaction vessel.
I—Glass stirrer.
J—Hydrogen inlet.
K—Hydrogen outlet.
L—Thermometer.
M—Electric Motor.

is allowed to escape into the air. The wide glass tube dips into the electrolytic liquid well below the level of the electrodes in order to minimise admixture of the hydrogen and oxygen due to pressure changes. The six hydrogen delivery tubes are sealed to the three main tubes passing into the sulphuric acid wash bottle, and the hydrogen after leaving this bottle is passed over copper turnings strongly heated in a hard glass tube. This removes traces of oxygen and the gas is then dried and passed into the reducing vessel, which is a round bottomed flask provided with a stirrer, a gas inlet and a gas outlet.

The reduction vessel is placed in an asbestos air bath heated by a gas flame to the temperature required for the reduction. In most cases a temperature of 180° was maintained, but was varied in one or two instances in order to see if alteration of temperature affected the relation of iodine value to refractive index. In all cases the vessel was filled with hydrogen while cold, the temperature then raised to 180° and afterwards the stirrer started and a continuous current of hydrogen passed and the time calculated from that point.

The current required was supplied from the 100 volt mains and was adjusted by means of resistances to give 4 amps. corresponding with a total of 200 c.c. of hydrogen per minute measured at 25° and 680 mm., i.e. 0·9 grams of hydrogen per hour. The resistance of the cells was considerable, each requiring about 10 volts and consequently the whole battery was immersed in cold running water to prevent overheating.

CATALYSTS

Numerous catalysts are described in the literature and many of these have been patented. We have prepared several of the commoner types in order to compare their efficiencies in the apparatus we have used when working at atmospheric pressure.

Catalyst A.—Finely divided nickel prepared by the action of nickel nitrate on sugar.

The method used was as follows:—10 grams of nickel nitrate crystals and 1·65 grams of sugar were dissolved in 15 c.c. of water and the solution allowed to drop on to a nickel dish heated to dull redness. The reaction is vigorous, and a voluminous, extremely light residue of nickel oxide is formed. It is advisable to allow each drop to decompose before a further quantity of solution is allowed to drop on to the dish, and as the oxide formed is very light and is easily carried away by the liberated gases, it is advantageous to cover the dish with a lid. The oxide is collected and reduced in a current of hydrogen at

250°, an operation which usually takes 2·5 hours. During this reduction the colour changes from black to a yellowish colour and finally to black again. It is allowed to cool to 180°, the oil to be reduced, added and the reduction started.

Traces of nitrogen compounds are apt to destroy the activity of this type of catalyst.

Catalyst B.—Finely divided nickel prepared by the reduction of the oxide. A solution of 10 grams of nickel nitrate or 9·8 grams of nickel sulphate in 50 c.c. of water is precipitated at 60° with a solution of 6 grams of sodium carbonate in 25 c.c. of water. The precipitate is washed free from carbonate, dried at 105° and heated in a nickel dish to a dull red heat in order to convert the nickel carbonate to oxide. Observations show that the temperature to which the carbonate is heated in order to bring about this change has a considerable effect on the activity of the catalyst. The oxide is finally reduced in a current of hydrogen at 250°. The time required is about two hours and the colour changes are the same as those observed in the case of Catalyst A.

Catalyst C.—Finely divided nickel obtained by precipitating the carbonate on Kieselgühr and subsequent reduction. The method of preparation of the carbonate is similar to that described under Catalyst B with the exception of the addition of six grams of Kieselgühr to the nickel sulphate solution. The final conversion into nickel was accomplished in three different ways—

(1) The mixture of carbonate and Kieselgühr was heated to dull redness to convert the carbonate to oxide, which was then reduced at 250° and preserved under the oil to be hardened.

(2) The mixture of carbonate and Kieselgühr was reduced directly in a current of hydrogen at 250° and then preserved under oil.

(3) Similar to C 2, but a temperature of 300° was used during reduction.

Catalyst D.—The method of preparation was similar to that used for Catalysts C 2 and 3, with the exception that the precipitant was borax (8 grams in 20 c.c. of water). When reduced at 250° the catalyst is inactive, but it becomes active when reduced at 300°.[1]

[1] For details and discussions on borate catalysts, *see* H. Schönfeld, *Seifensied. Zeit.*, 1914, **41**, 945; Erdmann and Rack, *Ibid.*, 1915, **42**, 3 and 75; Norman, *Ibid.*, **46**, 191; Bosshard and Fischli, *Zeitsch. angew. Chem.*, 1915, **28**, i, 365; G. Frerichs, *Arch. pharm.*, 1915, **253**, 512; *Seifensied. Zeit.*, 1916, **43**, 782; H. Schönfeld, *Zeitsch. angew. Chem.*, 1916, **29**, i, 39. It is generally agreed that a certain amount of metallic nickel is formed during reduction.

Catalyst E.—This was a sample of commercial catalyst prepared by a method similar to that used for C 2. It was received from England preserved in cottonseed oil.

Several series of experiments have been made with these catalysts and the results are given in Table X.

Table X

Comparative Activity of Catalysts A–D

100 grams of cottonseed oil of iodine value 98·0 and acid value 0·03 were used in each experiment. The current of hydrogen was kept constant at 200 c.c. per min. and the stirring was kept constant at 800 revolutions.

In each case the catalyst contained two grams of nickel and the activity was measured by the diminution of the iodine value.

Catalyst	Time of Hydrogenation in hours					
	0·5	1	2	3	4	8
A (*a*)	...	...	...	75·0	62·2	47·5
A (*b*)	...	...	...	78·2	63·6	49·6
B (*a*)	...	...	67·8	...	50·3	24·8
B (*b*)	...	...	66·2	...	51·8	25·0
C 1 (*a*)	55·0	48·0	40·5	...	18·7	...
C 1 (*b*)	60·0	48·9	45·3	...	...	...
C 2 (*a*)	...	41·5	32·7	...	10·0	...
C 2 (*b*)	...	45·0	33·0	...	12·9	...
C 3	...	20·0	7·0	...	0·0	...
D (*a*)	...	...	31·0	...	5·0	...
D (*b*)	...	...	28·7	...	4·0	...

These experiments prove that a catalyst of the type C is the most efficient of those tried,[1] and also that the conversion into oxide before reducing with hydrogen is unnecessary. They show that if the nickel-carbonate Kieselgühr is first dried and then heated in an atmosphere of hydrogen at 300° a very active catalyst is obtained.

[1] According to Armstrong and Hilditch (*Proc. Roy. Soc.*, 1921, A, **99**, 490) nickel obtained by reduction on Kieselgühr occupies a much greater volume than when reduced in the absence of Kieselgühr and is much more active than nickel produced by other methods. They conclude that the variations in the catalytic power of reduced nickel are to be ascribed to the different surface areas of the free nickel exposed.

Two further sets of experiments were made with catalysts of the type C 3, but containing different proportions of nickel. Three different catalysts were used, viz. :—

C 3 *a* containing 10 per cent nickel and 90 per cent Kieselgühr
C 3 *b* ,, 20 ,, ,, 80 ,, ,,
C 3 *c* ,, 30 ,, ,, 70 ,, ,,

In one set of experiments four grams of catalyst was used in each case and thus the ratio of nickel to oil was different in each experiment. In the second set the quantity of nickel per 100 grams of oil was kept constant, viz. 1 gram, but the total quantity of catalyst used was different in each experiment.

The results obtained are summarised in Table XI.

Table XI

Comparative Activity of Nickel-Kieselgühr Catalysts, C 3

Weight of Catalyst in grams	Weight of Nickel in grams	Iodine Value after reduction	
		1 hour	2 hours
4	0·4	51·0	35
4	0·4	44·0	...
4	0·8	15·0	0
4	0·8	18·5	...
4	1·2	7·0	0
10	1·0	29·0	23
5	1·0	2·5	0
3·3	1·0	12·0	0

The conclusions to be drawn from these experiments appear to be—

1. Diminishing the amount of nickel in the catalyst from 30 to 20 per cent, but using the same weight of nickel in each experiment increases the activity of the nickel, whereas a further reduction to 10 per cent diminishes the activity. The latter phenomenon may be due to the negative catalytic activity of Kieselgühr.

2. If, however, the total weight of catalyst is kept constant, but the weight of nickel varied, then there is an increase in activity from 10 to 30 per cent nickel content in the catalyst, but the increase

from 10 to 20 per cent has a more marked effect than the increase from 20 to 30.

3. Of the catalysts tried one of the type C 3 containing 20 to 25 per cent of nickel appears to be the most efficient.

In all the experiments so far described a current of hydrogen was passed through the apparatus at atmospheric pressure (680 mm.) and all unused hydrogen was allowed to pass into the atmosphere. A series of experiments has been made in which the exit tube from the reduction vessel was closed, and a mercury seal attached to the shaft of the stirrer. In all other respects the apparatus was identical with that already described. The supply of hydrogen was automatic as immediately pressure was generated in the reduction flask the electrolyte was forced down in the cathode compartment and gas ceased to be evolved. As the hydrogen was used up by the oil in the reduction vessel the electrolyte flowed back and as it came into contact again with the electrode hydrogen was evolved.

During the course of the experiments it was noticed that at the beginning of each reduction the rate of hydrogenation was greater than the rate of generation of the hydrogen so that a partial vacuum was created in the reduction vessel and there was a risk of the electrolyte being sucked into the sulphuric acid wash bottle. This was avoided by stirring the oil very slowly during the first fifteen minutes.

Table XII gives the results obtained in two sets of experiments.

Table XII

Comparative Hydrogenation in Closed and Open Vessels

Conditions of Experiment	Iodine Values of Cottonseed Oil after		
	1 hour	2 hours	3 hours
Hydrogen bubbling through oil ...	43·9	32·7	10·0
Exit to reduction vessel closed ...	55·9	40·4	17·5

Previous Work

One of the best accounts of the early history of the hydrogenation of oils is to be found in Ellis's paper.[1] Resumés of the whole subject are to be found in Ellis's *The Hydrogenation of Oils*, second edition, 1919, and Fahrion's *Die Hartung der Fette*, second edition, 1921.[2]

[1] *J. Soc. Chem. Ind.*, 1912, **31**, 1155.

[2] For technical aspects of hydrogenation, cf. E. R. Bolton, *J. Soc. Chem. Ind.*, 1922, **41**, 384 R.

One of the most interesting papers dealing with methods of hydrogenation and catalysts is that by Ubbelohde and Svanoe.[1] This gives a comparison of different methods of hydrogenation and also a comparison of different catalysts.

The authors have used three distinct methods of hardening and they claim that most of the methods described in the literature or patented fall into one of these three classes—

1. *Normann Method.* D.R.P. 141029 of 1902.—This is similar to the method we have used and described on p. 61. It consists in passing gaseous hydrogen at the rate of about fifty litres per hour through a suspension of the catalyst in the oil while the whole is vigorously stirred (3,200 revolutions).

2. *Wilbuschewitsch Method.* Eng. Pat. 30014 of 1900.—The reaction is carried out in an autoclave under a pressure of eight atmospheres. The suspension of oil and catalyst is pumped by means of a small centrifugal pump to the top of the autoclave and is there sprayed into an atmosphere of hydrogen and is withdrawn from the bottom of the autoclave by the pump for circulation. The hydrogen pressure is maintained at eight atmospheres by means of a valve.

3. *Erdmann Method.*—An aluminium vessel is filled with the catalyst which consists of nickel deposited on pieces of pumice the size of peas. The oil is dropped on to this catalyst and a stream of hydrogen is passed through the vessel.

The following catalysts were tried by the authors :—

1. *Germania Catalyst.*—A dark brown loose powder consisting of 15 per cent nickel and 85 per cent Kieselgühr. The catalyst was preserved in an atmosphere of carbon dioxide.

2. *Wilbuschewitsch Catalyst.*—A thick black liquid mass consisting of 6·7 per cent nickel, 19·9 per cent Kieselgühr and 73·4 per cent oil, i.e. 25 per cent nickel in the nickel-Kieselgühr mixture.

3. *Pure Nickel.*—This was obtained by decomposing the nitrate and reducing the oxide so formed at 300–310° in an atmosphere of hydrogen.

4. *Erdmann Catalyst.*—Pieces of pumice impregnated with 3 per cent of nickel oxide and reduced just before use.

[1] *Zeitsch. angew. Chem.*, 1919, **82**, 257-62, 269-72, 276-80.

The following are the more important generalisations which these authors draw from their experiments :—

1. The optimum temperature is 170–200°. At 120° the reduction is very slow and above 200° the rate again diminishes.[1]

2. In the Normann and Wilbuschewitsch processes the rate increases with the amount of catalyst present and is, as a rule, roughly proportional to the amount.

3. The rate of stirring has an effect on the velocity of reduction. An increase from 1,600 to 3,200 revolutions has an accelerating effect, but a further increase to 4,800 revolutions has no effect.

4. In the Normann apparatus increasing the current of hydrogen from 25 to 50 litres per hour per 150 grams of cottonseed oil used produces an increase in the rate of reduction, but a further increase in the hydrogen has no effect.

5. By using different pressures in the Wilbuschewitsch apparatus it was shown that the rate of reduction is nearly proportional to the pressure.[2]

6. A comparison of the efficiencies of the three processes shows that they follow the order Wilbuschewitsch, Normann, Erdmann. At 170° the Wilbuschewitsch process is five times as efficient as the Normann and by extrapolation it is shown that even under atmospheric pressure the former is more efficient than the latter.

As regards utilization of hydrogen the following figures are given :—

Wilbuschewitsch	...	88·6 per cent.
Normann	....	23·8 ,,
Erdmann	....	7·3 ,,

7. In the Normann apparatus the pure nickel catalyst is far less efficient than the Germania or Wilbuschewitsch : the ratios given are Germ. : Wilb. : pure Ni = 6 : 3 : 1.

The differences are not so marked, however, in the Wilbuschewitsch apparatus, and the Wilbuschewitsch catalyst retains its activity longer than the Germania. After three weeks very little deterioration can be detected, but after six months it is appreciable.

[1] For temperature curve, cf. Maxted, *J. Soc. Chem.Ind.*, 1921, **40**, 170 T.
[2] Compare Armstrong and Hildich, *Proc. Roy. Soc.*, 1921, A, **100**, 240.

8. Previous heating of the catalyst in an atmosphere of carbon dioxide at 145° or 200° produces slight deterioration. The diminution in activity of the catalyst during use cannot, however, be attributed solely to the heating effect.

9. According to Normann [1] it is not necessary that catalyst, hydrogen or oil should be specially pure, as appreciable amounts of substances which usually act as poisons to catalysts have but little effect.

Kahlenberg and Ritter [2] have carried out experiments with new catalysts, such as zinc-aluminium, bismuth-charcoal, nickel precipitated on zinc at the ordinary temperature and pure nickel from nickel chloride and hydrogen at 180–250°.

None of these catalysts appears, however, to possess the same efficiency as the nickel-Kieselgühr catalysts used in our experiments, as even after ten hours at 150–190° the iodine value of cottonseed oil was reduced from 108 to about 63, corresponding with a 44 per cent reduction.

GENERAL SUMMARY

1. Samples of cottonseed, linseed, ground-nut, mohua, sesamé, sardine, castor, hongay and coconut oils have been refined and hardened with the aid of a nickel catalyst at 180° and the relations between iodine value and refractive index determined.

2. Except in the case of castor and hongay oils the relations between the two physical constants is independent of the time and of the type of catalyst used.

3. In the case of the first six oils mentioned the curves representing the relation between iodine value and refractive index lie very close together and may be represented by the equation

$$n_D^{60°} = 1{\cdot}4468 + 1{\cdot}03 \times 10^{-4} \times (I.V.) + 7{\cdot}3 \times 10^{-8} (I.V.)^2$$

to an accuracy of about 0·0005.

4. The refractive indices at 60° of all six oils when completely hardened have practically the same value, viz. 1·4468.

5. The refractive indices of hardened coconut oil are much lower than those of other oils with the same iodine value.

[1] *Seifensied. Zeit.*, 1914, **41**, 645.
[2] *J. physical Chem.*, 1921, **25**, 89.

6. In the case of castor oil the relation between iodine value and refractive index is not independent of the type of catalyst or of the time of hardening owing to the varying extent to which the hydroxyl groups are reduced. It is possible that the case of hongay oil is similar.

7. A laboratory apparatus for the production of electrolytic hydrogen for hardening purposes is described.

8. A comparison of several types of nickel catalysts shows that the nickel-Kieselgühr (25 per cent nickel) is the most efficient of those examined and that it may be prepared by direct reduction of the Kieselgühr-nickel-carbonate mixture in hydrogen at 300°.

9. Such a catalyst can be used for about forty-four hours at 180° without appreciable deterioration.

10. The best proportions appear to be 20 to 25 per cent of nickel to 80 to 75 per cent of Kieselgühr.

11. A catalyst obtained by reducing a mixture of nickel borate and Kieselgühr in hydrogen at 300° is also extremely active.

In conclusion, we wish to thank the following gentlemen for assistance in carrying out some of the experiments :—

Mr. S. Bashirodien for work on mohua oil.

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