phate industry. These developments relate to the concentration of low-grade phosphate ores by flotation and to the manufacture of phosphorus in the blast furnace. The production capacity of a blast furnace by the so-called one-step method of phosphoric acid manufacture by the Victor Chemical Works at Nashville, Ala. (*2*), is approximately 125 tons phosphorus pentoxide per day, but the furnace is designed to produce orthophosphoric acid. Some phosphorus pentoxide is obtained in this furnace in the dust-collecting equipment.

One experimental blast furnace in Florida produced elementary phosphorus. As far as is known, no further development work has been done on this method of manufacture of phosphorus, and the plant is closed.

Since there is no special call for phosphorus pentoxide for technical applications, the price is still on a high level of about $400 per ton. As with all pioneering and epoch-making industrial developments, it will take some time for the market prices to decrease.

Even with this high price of phosphorus pentoxide the cost of refining some gasolines is very low because of the small amount required. This amount is 0.1 per cent of phosphorus and would be equivalent to 0.25 pound per barrel and a cost of 5 or 6 cents per barrel.

The cost of coke (which can be recovered) is not large. Additional operating costs would then be the normal cost of redistilling gasoline which depends on the cost of fuel, running from 4 to 5 cents per barrel. The direct cost of the total treatment would be somewhere around 10 cents per barrel, excluding general overhead.

Literature Cited

(1) Brown and Berry, *J. Phys. Chem.*, 29, 1312 (1925).
(2) Easterwood, H. W., *Trans. Am. Inst. Chem. Engrs.*, 29, 1–20 (1933).
(3) Malishev, B. W., *J. Am. Chem. Soc.*, 57, 883 (1935).
(4) Malishev, B. W., *Petroleum Z.*, 28, No. 17, 7–10 (1932).

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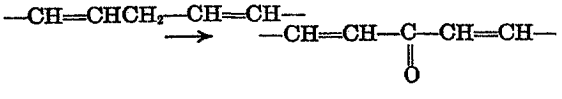
Studies in the Drying Oils

XIX. Oxidation of Linseed Oil[1]

ROBERT S. TAYLOR AND JUDSON G. SMULL
Lehigh University, Bethlehem, Pa.

THE nature of the chemical process by which linseed oil molecules, under the influence of oxygen, are built up to colloidal dimensions has been the subject of several theories. Scheifele advanced the theory that film formation was entirely the result of the condensation of the oil molecules containing conjugated double-bond systems (*10*). That this is not a complete explanation of the film-forming process was pointed out by Scheiber (*7*) who subsequently developed this theory more fully (*9*). His theory states that the preliminary oxidation of all the drying oils—with the exception of tung and related oils—results in the formation of conjugated double-bond systems throughout the oil, and it is about these centers of activity that condensation and polymerization occur. The mechanism proposed for this reaction is:



This theory has been extended by Scheiber and others to account for the changes which occur in the formation of "stand oils" (*3*, *6*, *8*). Kappelmeier believes that the condensation which results from the conjugation may be ascribed to the "diene synthesis" (*5*) of Diels and Alder.

Conjugate systems, in general, show the following characteristic properties:

1. A conjugated system has a higher refractive index than that of a nonconjugated isomer.
2. A conjugated system has a lower heat of combustion than that of a nonconjugated isomer.
3. A conjugated system reacts with halogenating agents relatively slowly (*1*).
4. A conjugated system reacts readily with maleic anhydride, and, so far as is known, the nonconjugated system does not react.

Data under the first three headings are submitted in so far as they help to confirm the more important results under the fourth heading.

Complete data under the first three headings are not obtainable because it is practically impossible to prepare the nonconjugated oxidized isomers for comparison. Under the fourth heading, however, chemical reaction is shown when examination of the constants is carefully made. The curves show perhaps more clearly the decided changes that have taken place. These changes are explained later in more detail.

This study followed the changes in refractive index, heat of combustion, and iodine number resulting from the oxidation of linseed oil. In addition, the reaction of Diels and Alder

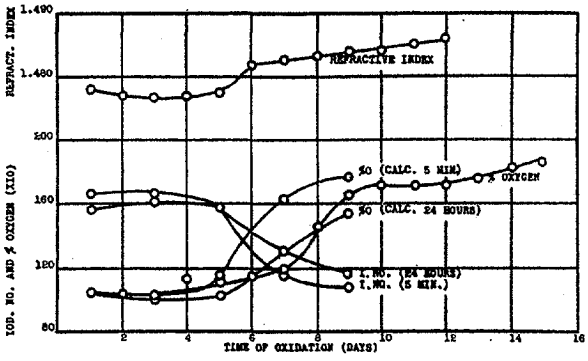


FIGURE 1. CHANGE IN REFRACTIVE INDEX, OXYGEN ABSORBED, AND IODINE VALUE WITH TIME

[1] The first seven articles of this series appeared as unnumbered papers in IND. ENG. CHEM. as follows: 17, 138, 905 (1925); 18, 1245, 1252 (1926); 19, 62, 901, 903 (1927). Parts VIII to XVIII appeared in Volumes 20 to 26 (1928 to 1934), inclusive.

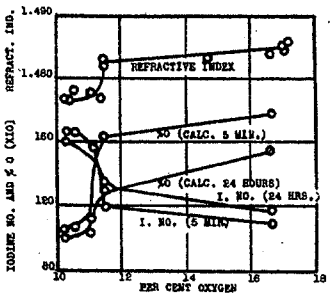


FIGURE 2. CHANGE IN REFRACTIVE INDEX AND IODINE VALUE WITH OXYGEN CONTENT

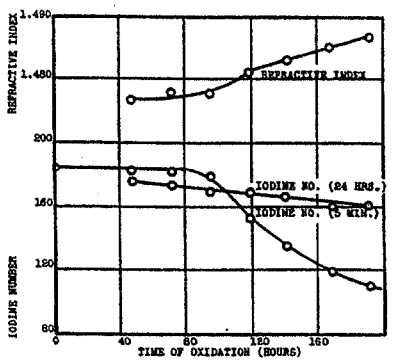


FIGURE 3. CHANGE IN REFRACTIVE INDEX AND IODINE VALUE WITH TIME

involving maleic anhydride and conjugated compounds was applied to the oil in various degrees of oxidation (*4*).

Methods

The refractive index was determined by means of an Abbé-Zeis refractometer at 25° C. Heats of combustion were measured in an Emerson bomb calorimeter. Ultimate analyses were made by the standard combustion method. Iodine numbers were determined by the Bolton-Williams method (pyridine dibromide sulfate solution in glacial acetic acid) (*2*).

The oils used were alkali-refined linseed oils. Oxidation was carried out by bubbling air through the oil in glass percolators. The temperature was regulated by an electric resistance which was enclosed in glass and immersed in the oil.

Results

The results obtained are given in Table I and are plotted in Figures 1 and 2.

In Tables I and II the 5-minute and 24-hour iodine-number columns refer to the time of reaction between the halogenating agent and the oil.

The results given in Table II are plotted in Figure 3, those in Table III are plotted in Figures 4 and 5, and those in Table IV in Figures 6 and 7.

The columns headed "Calculated Oxygen" were computed on the assumption that one iodine atom was equivalent to one oxygen atom in the oxidation.

Owing to the uncertainty as to the exact mechanism of oxygen addition to the molecule, the results given for calculated oxygen are empirical and yet, when compared with the determined oxygen values, the correlation is quite good.

The method of calculation was to use the determined oxygen value of 10.6 (1-day period) as the basis for the subsequent values. Then the iodine numbers of each sample were subtracted from the original 1-day values, and this difference was converted to oxygen, which was then added to the 10.6 to give the calculated figure. Because the 5-minute and 24-hour iodine values for samples (1-day) differ by 10 points, the calculated oxygen values for the 5-day sample are different, even though the determined iodine values on the 5-day sample are identical.

The Diels and Alder reaction was carried out

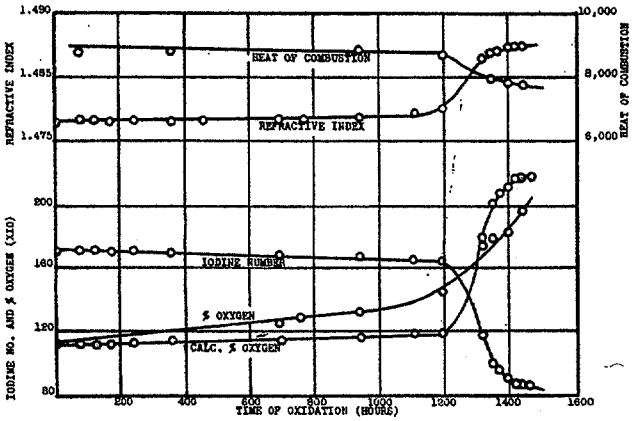


FIGURE 4. CHANGE IN HEAT OF COMBUSTION, REFRACTIVE INDEX, AND OXYGEN ABSORBED WITH TIME

TABLE I. DATA ON MONTH-OLD OIL SAMPLES OXIDIZED AT 50° C.

Time	Iodine No. 5 min.	Iodine No. 24 hr.	Oxygen	Calcd. Oxygen 5 min.	Calcd. Oxygen 24 hr.	Refractive Index
Days			%	%	%	
1	166	156	10.6	10.6	10.6	1.478
2	...	...	10.4	..	..	1.477
3	167	161	10.3	10.4	10.0	1.477
4	...	...	11.4	..	..	1.477
5	158	158	11.1	11.6	10.3	1.4778
6	...	...	11.5	..	..	1.482
7	120	135	11.5	16.4	13.2	1.4828
8	...	...	14.7	..	..	1.4835
9	109	117	16.6	17.8	15.5	1.4842
10	...	...	17.1	..	..	1.4843
11	...	...	17.1	..	..	1.4851
12	...	...	17.2	..	..	1.4862
13	...	...	17.7	..	..	....
14	...	...	18.3	..	..	....
15	...	...	18.6	..	..	....
16	...	...	18.7	..	..	....
17	...	...	19.0	..	..	....

TABLE II. DATA ON TWO-MONTH-OLD OIL SAMPLES OXIDIZED AT 45° C.

Time	Iodine No. 5 min.	Iodine No. 24 hr.	Refractive Index
Hr.			
48	181	175	1.4766
72	181	172	1.4779
96	178	169	1.4778
120	153	168	1.4815
142	136	167	1.4832
170	120	160	1.4857
192	110	161	1.4868

TABLE III. DATA[a] ON IMMEDIATELY ANALYZED SAMPLES OF OIL OXIDIZED AT 25° C.

Time	Oxygen	Calcd. Oxygen	Iodine No.	Heat of Combustion	Refractive Index
Hr.	%	%		*Cal./g.*	
0	11.2	11.2	170.6	...	1.4777
72	..	11.2	170.6	8800	1.4782
118	..	11.1	170.8	..	1.4782
166	..	11.2	170.1	..	1.4779
238	..	11.2	170.4	..	1.4781
358	..	11.4	169.2	8825	1.4782
454	..	..	..	..	1.4782
694	12.5	11.4	168.7	..	1.4783
766	12.9	...	...	...	1.4783
934	13.2	11.6	167.4	8880	1.4786
1103	..	11.8	165.5	...	1.4793
1198	14.5	11.9	165.1	8710	1.4799
1318	17.5	17.9	117.6	...	1.4879
1346	17.8	20.1	99.7	7980	1.4888
1366	..	20.7	95.4	...	1.4890
1394	18.2	21.1	91.7	7800	1.4896
1414	..	21.6	87.5	...	1.4898
1438	19.6	21.7	87.0	7740	1.4899
1462	..	21.8	86.1	..	....
1480	..	22.1	84.0	..	....

[a] From unpublished theses of R. Borton, I. Mills, and C. Bigelow, Lehigh University, 1935.

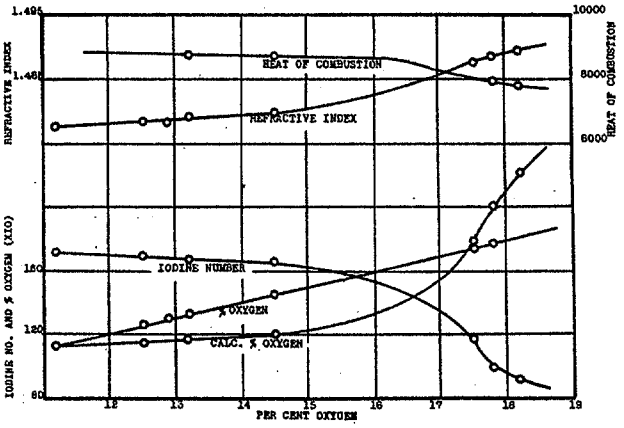


FIGURE 5. CHANGE IN HEAT OF COMBUSTION, REFRACTIVE INDEX, AND IODINE NUMBER WITH OXYGEN CONTENT

on the samples tabulated in Table III. Varying amounts of maleic anhydride were added to 10-gram portions of oil, and the mixtures were heated to 110° C. for 1.5 hours. The iodine numbers of these products were then determined. The results are tabulated in Table V.

It was found that maleic anhydride exhibited no iodine number when treated by this method so that the reduction in iodine number was caused either by reaction or by the mere presence of the anhydride as an inert material. The column headed "Calculated Iodine Number" was computed on the basis of the anhydride acting as an inert material. The column headed "Discrepancy" lists the difference between this value and the actual value obtained. Any actual value greater than or equal to the calculated value indicates that no reaction has taken place, while values less than the calculated values indicate that reaction has taken place. Also, when the discrepancy reaches a constant value we can conclude that the reaction has been completed, and that the extra anhydride is merely acting as an inert material:

Hours of Oxidation	Maleic Anhydride Reacting
934	0
1198	0
1346	10
1394	12.5

The point at which the oil begins to exhibit reactivity with maleic anhydride is coincident with the point at which index of refraction, heat of combustion, etc., are changing rapidly.

A series of determinations of the acetyl values shows that the maleic anhydride did not react with the hydroxyl groups.

TABLE IV. DATA[a] ON IMMEDIATELY ANALYZED SAMPLES OF OIL OXIDIZED AT 60° C.

Time	Oxygen	Calcd. Oxygen	Iodine No.	Refractive Index
Hr.	%	%		
0	11.2	11.2	170.6	1.4777
11	..	11.4	169.1	1.4778
24	11.6	11.6	166.9	1.4780
49	15.5	15.8	134.0	1.4826
62	16.6	17.6	120.0	1.4839
70.5	16.8	18.0	116.1	1.4849
80.5	18.6	19.7	106.3	1.4861
94.5	18.8	22.0	84.7	1.4875

[a] Data from unpublished theses of R. Borton, I. Mills, and C. Bigelow.

TABLE V. RESULTS OF DIELS AND ALDER REACTION

Time	Maleic Anhydride	Iodine No.	Calcd. Iodine No.	Discrepancy
Hr.	%			
934	0	167.7	...	...
934	2.5	164.5	163	+1.5
934	5.0	159	159	0
934	7.5	157.5	156	+1.5
1198	0	165	...	...
1198	5.0	157.5	157	+0.5
1198	7.5	156	154	+2
1198	10.0	155	150	+5
1346	0	99.5	...	...
1346	7.5	86.3	92.6	−6.3
1346	10.0	83.5	90.5	−7.0
1346	12.5	81.5	88.5	−7.0
1394	0	91.7	...	...
1394	7.5	78.3	85.3	−7.0
1394	10.0	74.8	83.3	−8.5
1394	12.5	72.6	81.6	−9.0

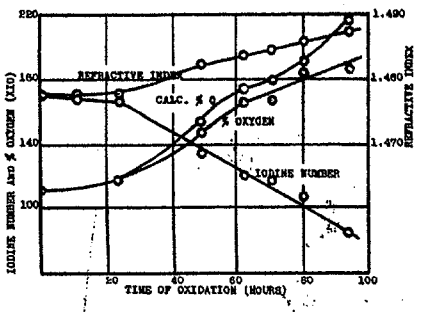


FIGURE 6. CHANGE IN REFRACTIVE INDEX, OXYGEN ABSORBED, AND IODINE NUMBER WITH TIME

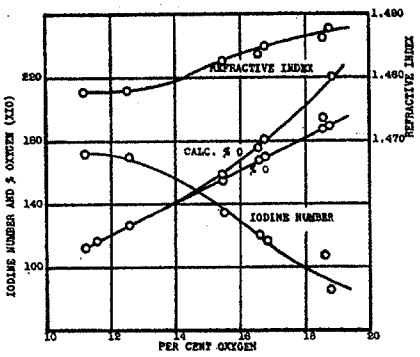


FIGURE 7. CHANGE IN REFRACTIVE INDEX AND IODINE NUMBER WITH OXYGEN CONTENT

Acknowledgment

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Literature Cited

(1) Boescken, J., and Gelber, E. T., *Rec. trav. chim.*, **46**, 158–71 (1927).
(2) Bolton and Williams, *Analyst*, 55, 5 (1930).
(3) Cutter, J. O., and Jordan, L. A., *J. Oil Colour Chem. Assoc.*, 18, 5–11 (1935).
(4) Diels, O., and Alder, K., *Ann.*, 348, 31 (1906).
(5) *Ibid.*, 460, 98–122 (1928).
(6) Kappelmeier, C. P. A., *Farben-Ztg.*, 38, 1018–20, 1077–9 (1933).
(7) Scheiber, J., *Farbe u. Lack*, **1929**, 477–8.
(8) *Ibid.*, **1929**, 585–7.
(9) *Ibid.*, **1930**, 51–3, 65.
(10) Schiefele, B., *Z. angew. Chem.*, **42**, 787–90 (1929).

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