PHOTOCHEMICAL STUDIES OF RANCIDITY: RATE OF PEROXIDE DEVELOPMENT UNDER CONSTANT INTENSITY OF LIGHT*

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THE peroxide value, which at present is used as a measure of the freshness and keeping quality of an oil, has gained considerable vogue among oil chemists. A more detailed study of the conditions under which peroxides are developed has, however, seemed desirable. In a previous paper, (1) it was shown that an oil which has been protected from light and which has developed a certain amount of peroxides without having become rancid, will itself become rancid in about the same interval of time as will a fresh sample of the same oil when the two are exposed side by side in normal daylight.

This investigation is a continuation of the one previously reported, the object being to study the rate of development of peroxide in oils treated as mentioned above, excepting that 500-watt CX Mazda lamps (tungsten filament in ultra-violet transmitting glass) were used instead of sunlight for irradiation of the oils. While the spectral distribution of radiation from these lamps only roughly approximates that of sunlight, their constant intensity and ease of control assure more uniform results.

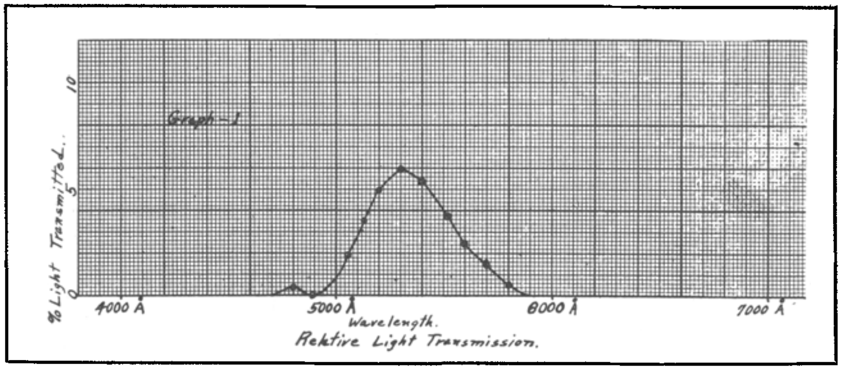
Experimental

Refined and deodorized cottonseed oil with an initial peroxide value of 5.0, and refined corn oil with an initial peroxide value of 0.0 were used. Four crocks, each four inches deep, held the respective oils; two contained cottonseed oil and two contained corn oil. One crock of each set was covered with a sextant green filter, the transmission of which is shown in Graph I. The other crock of each set was covered with water-white cellophane, which transmits light freely from the lamps. These four crocks were placed under a battery of four CX, 500-watt, Mazda lamps which, besides emitting light in the visible spectrum, also emit an abundance of infra-red and a small amount of near ultra-violet radiation. The position of the crocks was changed each day so that each sample of oil was subjected, on the average, to the same intensity of light. Under such conditions of illumination, rancidity and peroxide development take place at more constant rates and more rapidly than in ordinary sunlight. The development of peroxides and of rancidity in cottonseed- and corn-oils when thus subjected to the photochemical action of light from CX lamps is shown in Table I.

The development of peroxides and of rancidity in fresh cottonseed and corn oils and in the same oils which had previously been protected with a sextant green filter is shown in Table II. In this experiment small bottles were used to hold the oils. These oils were exposed to light on all sides instead of only through the top and that may account for the more rapid development of peroxides in the bottles as compared with oils in the crocks.

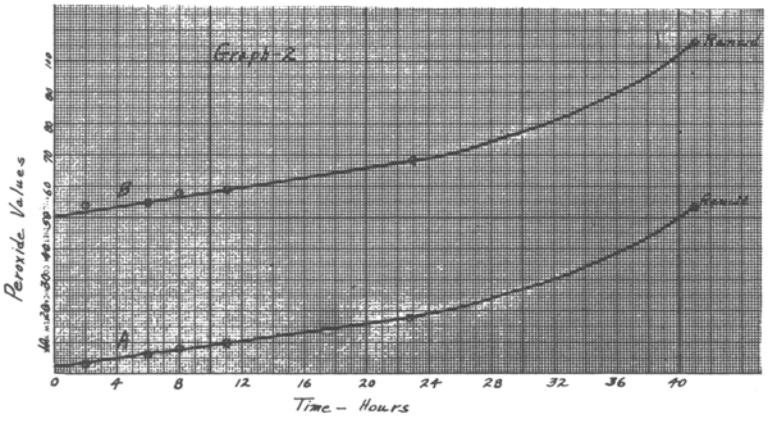
The data in Table III are similar to those of Table II except that the determinations of peroxides were made at shorter intervals. Corn oil with a peroxide value of 50.0 was used for comparison.

From Data given in Table III Graph 2 was drawn by plotting peroxide values against the hours of exposure to light.



A. Peroxide Development Curve for Corn Oil Taken from Can in Cold Room and Then Irradiated in a Clear Bottle with CX Lamps.

B. Peroxide Development Curve for Corn Oil Taken from the Same Can and Irradiated in a Clear Bottle, But Starting with a Peroxide Value of 50 Which Had Been Developed Under a Green Filter.



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[1] Coe, Mayne R. (1936). Photochemical Studies of Rancidity: Induction Period of Protected and non-Protected Oils. OIL AND SOAP, 13, no. 8, pp. 197-199.

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TABLE I.
PEROXIDE VALUES OF OILS IRRADIATED BY CX LAMPS

	Cottonseed Oil		Corn Oil	
Time of Exposure, in Days	Clear cellophane	Sextant green filter	Clear cellophane	Sextant green filter
0	5.0	5.0	0.0	0.0
3	25.0 R	11.0	16.0	3.0
5	42.5 R	16.5*	31.0	4.5
10	88.5 R	24.5	61.0	10.5
17	167.5 R	33.5*	86.0 R	15.5
20	263.0 R	43.5	172.5 R	20.5*
24	....	49.5*	177.5 R	24.5
30	....	59.5	....	30.5
32	....	64.0	....	35.0*
36	....	64.0	....	41.5
44	....	...	....	50.0*
Refrigerator sample at end of test (44 days)	11.5	...	1.5	...

*At this point a sample was taken for irradiation alongside of a sample still low in peroxide value of the same oil which had been kept in the dark in a cold room (temperature 54°-55° F.). (See Table II.)
R = rancid.

TABLE II.

Comparison of the rate of peroxide development in sextant-green previously protected oils with that of samples still low in peroxide value of the same oils when the two are exposed simultaneously to full light of CX lamps.

COTTONSEED OIL

	Test 1—2 days Peroxide Values		Test 2—3 days Peroxide Values		Test 3—1 day Peroxide Values	
	Fresh Oil	Protected Oil*	Fresh Oil	Protected Oil*	Fresh Oil	Protected Oil*
Initial	5.0	16.5	5.0	33.5	6.2	49.5
Final	40.0 R	59.5 R	46.5 R	80.5 R	21.5 R	65.0 R
Gain in Peroxides	35.0	43.0	41.5	47.0	16.5	15.5

CORN OIL

	Test 1—6 days Peroxide Values		Test 2—1 day Peroxide Values	
	Fresh Oil	Protected Oil*	Fresh Oil	Protected Oil*
Initial	0.0	20.5	1.5	35.0
Final	46.0 R	72.0 R	39.5 R	72.0 R
Gain in Peroxides	46.0	51.5	38.0	37.0

R = rancid.
*See Table I.

TABLE III.
PEROXIDE VALUES IN CORN OIL

Comparison of the rate of peroxide development in sextant green previously protected corn oil with that of a fresh sample of the same oil when the two are exposed in simultaneously to full light of CX lamps and are examined at frequent intervals.

	Peroxide Value		Gain in Peroxides	
Time of Exposure in Hours	Fresh	Previously Protected	Fresh	Previously Protected
0	1.5	50.0	..	..
2	3.0	54.0	1.5	4.0
6	6.0	55.0	4.5	5.0
8	8.5	58.5	7.0	8.5
11	10.0	59.0	8.5	9.0
24	18.0	65.8	16.5	15.8
66	53.5	106.0	52.0	56.0

Discussion

The results of the experiments here recorded confirm those given in a former paper (1) and likewise seem to indicate (assuming that peroxides are related to the development of rancidity) that the peroxides developed in oils under a sextant green filter have different characteristics from those which are developed under full light of CX lamps. In the first place the formation of peroxides is slower when an oil is placed under a sextant green filter than when it is exposed to full light. In the second place the rate of peroxide formation proceeds uniformly when samples of the same oils are exposed simultaneously to full light even though one oil may be fresh and have a low peroxide value, while the other may be a high peroxide oil, the peroxide having been developed under a sextant green filter. This is true even when the oil, which had been protected by a sextant green filter as stated has a peroxide value practically equal to that at which the unprotected oil becomes rancid. It was found also that the compound or compounds which develop the rancid odor accompany only those peroxides which are formed after the oil is exposed to full light. In other words, it takes just as long for rancidity to develop in an oil formerly protected with a sextant green filter and possessing a high peroxide value as it does in a fresh oil, when the two are exposed to the same light.

This indicates very clearly that the process involved in the development of rancidity begins just as soon as the oil is exposed to light and is independent of the amount of peroxides that may have been formed in the oil while protected by a sextant green filter. To support this view mention should be made of the results obtained in experiments in which air was bubbled through oil protected by a sextant green filter and in which rancidity did not develop even though high peroxide values had been acquired(2).

There is reason to believe that the process involved in the formation of peroxides is accelerated when the oil is exposed to full light, and that there is a photosensitizer in the oil which, in the presence of light, gives rise to a reacting molecule which later brings about rancidity development, since a normal induction period always precedes the appearance of rancidity even when the protected oil already has a high peroxide value.

The results of Table I show that corn oil develops rancidity much more slowly than does cottonseed oil under the same constant light source and temperature. The results given in Table II likewise show that under controlled light intensity and temperature, the numerical increase in peroxide values, with both unprotected and previously protected oils, is approximately the same when the two oils become rancid. Since, in one of these samples, rancidity had developed at the end of the first day's irradiation, (Table II) it was planned to determine the peroxide values at intervals of a few hours. For this experiment corn oil instead of cottonseed oil was selected because the initial peroxide value of the former was low, viz., 1.5. At each interval throughout the experiment the numerical increase in peroxide values was essentially the same in both the fresh oil and in the oils which had been previously protected.

The peroxide values of these oils as given in Table III are plotted in Graph II. This graph indicates beyond a doubt, first, that when a fresh oil of a low initial peroxide value is compared with an oil which had previously been protected by a sextant green filter and which had attained a high peroxide value, the relative rate of increase of the formation of peroxides in both oils is the same; second, the length of the induction period is likewise the same in both oils even though at the beginning of the experiment the oil which had been protected with a sextant green filter had developed

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[2] Coe, Mayne R., and J. A. LeClerc (1934). Photochemical Studies of Rancidity: Peroxide Values of Oils Affected by Selective Light. Ind. Eng. Chem., 26, no. 3, pp. 245-248.

a peroxide value of 50.0; and third, it would appear that the same process which takes place when a fresh oil becomes rancid also takes place in another portion of the same oil which had previously acquired a relatively high peroxide value as a result of having been protected by a sextant green filter.

Just why the peroxides that have developed under a green filter do not exhibit the characteristics of those developed under full light is now being studied.

Conclusions

(1) Peroxides in oils increase at a uniform rate when the oils are irradiated with light from a constant source, such as CX lamps.

(2) An oil which has been protected by a sextant green filter and which has already developed a certain amount of peroxides will, when exposed simultaneously to light of CX lamps with a fresh sample of the same oil, continue to develop peroxides, and at the same rate as that of the fresh oil.

(3) The induction period of an oil which has been protected by a sextant green filter is unaffected by the peroxides which were developed during protection and is equal to that of a fresh sample of the same oil.

(4) The development of rancidity in oils that have been protected by a sextant green filter proceeds independently of the peroxides that may be already formed.

(5) Peroxides which develop under a sextant green filter do not increase the susceptibility of the oil to become rancid.

Acknowledgment

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REPORT OF REFINING COMMITTEE AMERICAN OIL CHEMISTS' SOCIETY 1936-1937

THE personnel of the Refining Committee was increased this year to 15 members. The general interest in refining problems is evidenced by the excellent cooperation given the chairman by the entire group.

The study of Soya Bean Oil refining occupied the entire attention of the committee this year. A proposed plan for the study of this problem was sent to the committee on November 3, 1936, and the work, which was later carried on by Mr. H. L. Kevern in Swift & Company's Chemical Laboratory from January 5, 1937, to March 6, 1937, followed the suggestions outlined in this plan.

The detailed particulars of the Soya Bean Oil refining tests carried on in the Swift Laboratories were furnished to the committee in a report dated April 14, 1937. The refining study led to procedures which appeared to give satisfactory results with Expeller and Hydraulic type oils. The methods which were accepted for cooperative study were as follows:

Crude Soya Bean Refining—Expeller and Hydraulic Types

The apparatus and general procedure shall be the same as prescribed for hydraulic pressed crude cottonseed oil, with the following exceptions:

Strength of lye shall be 12° for expeller soya bean oil and 20° for hydraulic soya bean oil. Two tests shall be made on each oil using the maximum amount of sodium hydroxide as calculated from the formula $\frac{\text{F.F.A.}}{5.2} + .54$ and ⅔ of this maximum quantity of sodium hydroxide.

Expeller soya bean oil shall be agitated at 20-24° C. for 90 minutes from the time the sodium hydroxide solution is added with the agitator running 250 r.p.m. ± 10. It shall then be immediately transferred to 65° C. bath and stirred at 70 ± 5 r.p.m. for exactly 12 minutes. Temperature of oil must then be 65° C. ± 2° C., adjusting the temperature of the water bath if necessary within the limits specified to obtain this final oil temperature.

Hydraulic soya bean oil shall be agitated at 20-24° C. for 45 minutes from the time the sodium hydroxide solution is added with the agitator running 250 r.p.m. ± 10. It shall then be immediately transferred to 65° C. bath and handled as directed under Expeller soya bean oil.

At the end of the slow agitation period of refining both Expeller and Hydraulic soya bean oils shall be allowed to settle in the 65° bath for one hour. Cool by setting in a cold water bath at 20-24° C. for one hour. The oil shall then be allowed to set over night before pouring off. If the oil has become warm over night it should be chilled in a bath at 20-24° C. for 30 minutes.

The soapstock may be hardened by chilling in water at a temperature of 20-24° C. if necessary to permit draining the oil from the soapstock.

Cooperative samples of Expeller and Hydraulic soya bean oil were sent to the committee on March 22, 1937. The results obtained in this cooperative study, using the method outlined above, are given on the attached tabulations. These results may in general be considered quite satisfactory for a cooperative study of this kind.

The method suggested for Expeller and Hydraulic oils did not appear to give the most satisfactory results on Extracted oil. A longer period of slow agitation, however, led to considerably improved results, but the study of this type of oil was not considered to be of sufficient extent to permit definite conclusions.

Recommendations

The committee recommends (1) that the method for refining Expeller and Hydraulic soya bean oil as outlined above be suggested as a tentative method to replace the one now given in the American Oil Chemists' Society Methods; (2) that the work on Extracted soya bean oil be continued next year.

H. S. MITCHELL, Chairman.