

# Peroxide Formation as a Measure Of Autoxidative Deterioration

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**I**N spite of the enormous amount of valuable research which has been reported on the subject, the nature of the chemical reactions involved in the deterioration of vegetable oils is yet largely conjectural. Many phases of these reactions have been examined; the products produced during deterioration; analytical methods of determining these products; the factors influencing the reaction rates, and other aspects of the whole phenomena of rancidity have been carefully considered. A complete review of all this work would be beyond the scope of this paper. However, an attempt is here made to bring together that material from the literature

of rancidity which bears upon the investigation reported below.

Oxidation by the oxygen of the air, aided by such agents as light, heat and certain metallic or organic compounds, is generally considered responsible for the development of rancidity. (Such a case, where molecular oxygen enters into a chemical reaction is termed "autoxidation.") While bacterial action has been considered as a possible factor<sup>1 2 3</sup> it is now generally conceded that the primary change occurring during the aging of an oil or fat is a strictly chemical oxidation. The majority of investigators have therefore directed their attention towards means of studying both quantitatively

and qualitatively the action of oxygen and the products formed during the deterioration.

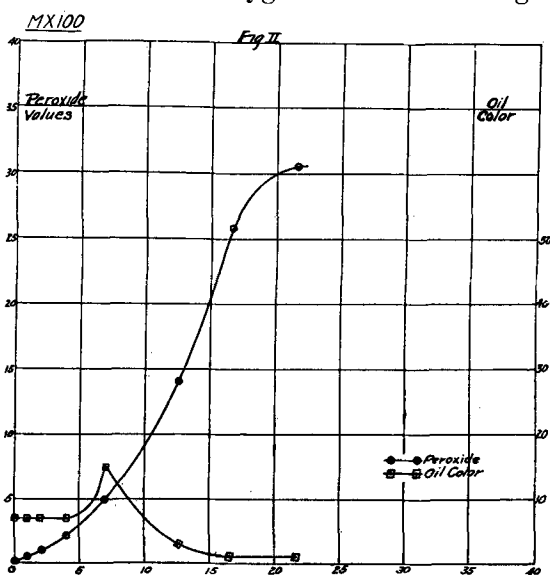
Greenbank and Holm<sup>4</sup> studied the susceptibility of fats towards autoxidation by measuring the rate of oxygen absorption by a given amount of fat or oil under reproducible conditions. This technique has been used in modified forms by other workers for studying autoxidation.<sup>5 6 7 8 9 10</sup>

A recent improved apparatus for following oxygen absorption is described by Milas<sup>11</sup> in which he overcomes the following objections to previous methods:

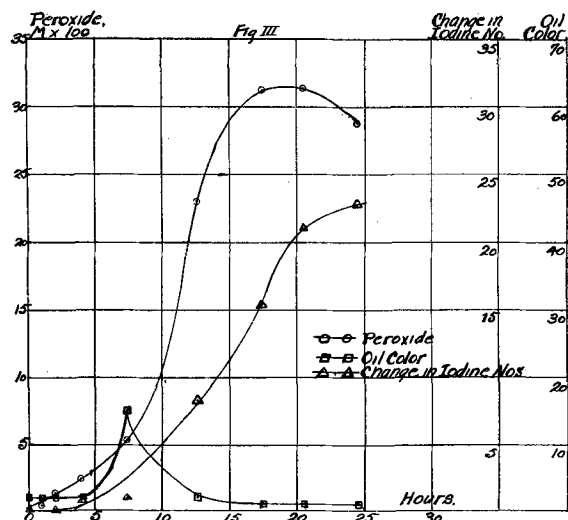
1. Changes in rate of absorption due to changes in pressure of the oxygen.
2. Failure to maintain a true equilibrium between the oil and oxygen gas.
3. Formation of oxidation products which may be gases and hence decrease the apparent absorption rate. The presence of volatile products which may otherwise affect the reaction.

The apparatus used to correct these errors is, of course, quite complicated.

Another method of following the amount of oxygen absorbed is by observing the gain in weight of an oil on exposure to oxygen. Delore<sup>12</sup> used this procedure to compare several oils. Täufel and Müller<sup>13</sup> also employed it as a means of comparing certain known methods now used for qualitatively measuring rancidity. The use of the gain in weight method as a true index of the amount of oxygen absorbed during the



development of rancidity is also open to objections. Browne<sup>14</sup> has demonstrated in the case



of butter fat that volatile products may escape, causing a loss in weight; further, that hygroscopic substances may be formed which take up moisture from the air, thus causing an increase in the weight result obtained.

A third method of attack upon the problem of autoxidation has been made by taking advantage of the fact that some of the reducing substances produced (presumably aldehydes) are volatile and may be removed from the oils or fats by steam or air currents. The quantity of these products may then be estimated, at least comparatively, by determining the amount of permanganate necessary to oxidize them. Issoglio<sup>15</sup> appears to be the first to have used this procedure. More recently Grettie and Newton<sup>16</sup> have described an improved apparatus for such a determination.

A general variation on the above method consists in detecting the aldehydes without removing them from the oils or fats. The von Fellenberg<sup>17</sup> test for aldehydes using the familiar fuchsin-sulfur dioxide reagent under definite concentrations and conditions is such an example. The test has been given a quantitative aspect by comparing the color depth produced to that produced by known concentrations of acetaldehyde under similar conditions. The values are, of course, reported in terms of acetaldehyde units. Arbitrary color standards have also been used made from permanganate solutions. It has been objected (cf. ref. 13) that this test is too uncertain for a quantitative method, and in general it does not seem to have attained great popularity. This may be due to

the fact that it is so sensitive and that the reagent is rather unstable.

The Kreis test<sup>18</sup> probably is the most widely used single test for detection of incipient rancidity. The depth of red color developed in this hydrochloric acid-phloroglucinol test has been estimated in various ways. Kerr<sup>19</sup> dilutes the oil with kerosene until color is no longer obtained, and thus determines the dilution of oil which just fails to give an observable color. Holm and Greenbank<sup>20</sup> similarly determine the minimum amount of oil necessary to produce a given degree of color by using various amounts of an ethereal solution of the oil of known concentration. They report that using this method, the intensity of color is proportional to the amount of oxygen absorbed, and that "no case has been noted where there has been appreciable oxidation without giving a Kreis test."

C. H. Lea<sup>21</sup> proposed a modification of the Kreis test for fats in which the fat (l. g.) is dissolved in benzene (2 cc.), concentrated hydrochloric acid (1 cc.) is added and the mixture shaken one minute. A 0.1 per cent solution of phloroglucinol in ether is then added, shaking continued for another minute, and after centrifuging the pink aqueous layer is compared with a set of permanganate standards. The Wiedman modification<sup>22</sup> of the Kreis test merely substitutes acetone for ether and concentrated sulfuric for hydrochloric acid. The methods recommended by A. S. Richardson<sup>23</sup> is perhaps the most easily performed method of getting a numerical indication of the intensity of color.

Certain objections have been raised to the Kreis test. Thus it has been shown by Kobert<sup>24</sup> that many substances besides those which could be present in oils may form a red condensation product. W. B. Smith<sup>25</sup> and others have pointed out that there are certain natural substances in cottonseed oil, which may give a red color in the Kreis test. This seems to be especially true of crude cottonseed oil. Powick<sup>26</sup> clarified these difficulties by pointing out that these red condensation products could be differentiated from that formed in rancid oil by spectroscopic examination. His work indicates that the substance which is formed in the Kreis test is a condensation product of epihydrine aldehyde with the phloroglucinol. Without going further into the various articles for and against

the Kreis test it may be noted that the fat analysis commission of Germany has rejected it as well as the Wiedman modification.<sup>27</sup> The chief objection which is usually offered is that extremely old and rancid fats fail to give a positive test. Such an objection hardly seems reasonable, since the test finds practical use in the range of deterioration previous to development of odor and taste rancidity. While there may be exceptions, it is usually found that conditions which lead to deterioration of the oil lead to a positive Kreis test of the oil. A further consideration of the significance of the Kreis test will be given in a discussion following the experimental part of this paper.

The ease with which a fat reduces methylene blue to the colorless state is the basis of the photoelectric methods of Greenbank and Holm<sup>28</sup> and of H. D. Royce.<sup>29</sup> The rate at which an oil or fat will reduce methylene blue, catalyzed by light, measures the rate of reaction of the initial oxidation of the fat and hence is considered a measure of the keeping quality of the oil. While this method appears to be an excellent method of testing oils, the apparatus is rather complicated and expensive.

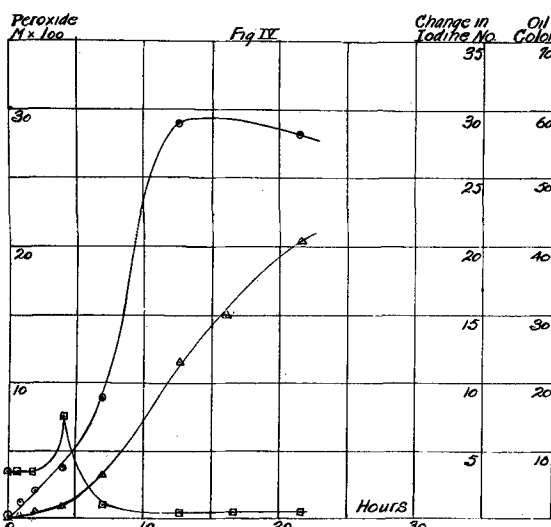
Bailey and Ebert<sup>30</sup> determine the time necessary to produce the Schiff test for aldehydes in comparing the keeping qualities of oils.

Stamm<sup>31</sup> claims that if an oil is heated with a solution of diphenyl carbazide (formed by condensing phenylhydrazine and urethane), a red color indicates that rancidity will soon develop.

The investigations of Bolton and Williams<sup>32</sup> on the iodine number of the unsaponifiable matter of oils shows that this value is lowered quite noticeably in rancid oils, and might be made the basis of a test for rancidity.

The fact that normal deterioration of an oil is caused by oxygen leads to the important question of the fate of the oxygen which is taken up by the oil. It undoubtedly attacks the double bonds of the unsaturated acids which are present as glycerol esters and also, no doubt, at matter, as shown recently by Bolton and Williams.<sup>32</sup> A fact which seems of the utmost importance is that "active" or "liable" oxygen, presumably in the form of organic peroxides, is detectable in oils which have been exposed to the air under conditions which would lead to

development of rancidity. Qualitative means of detecting this "active oxygen" have been known for some time. Vintilesco and Popesco<sup>33</sup> apparently were the first ones to detect this

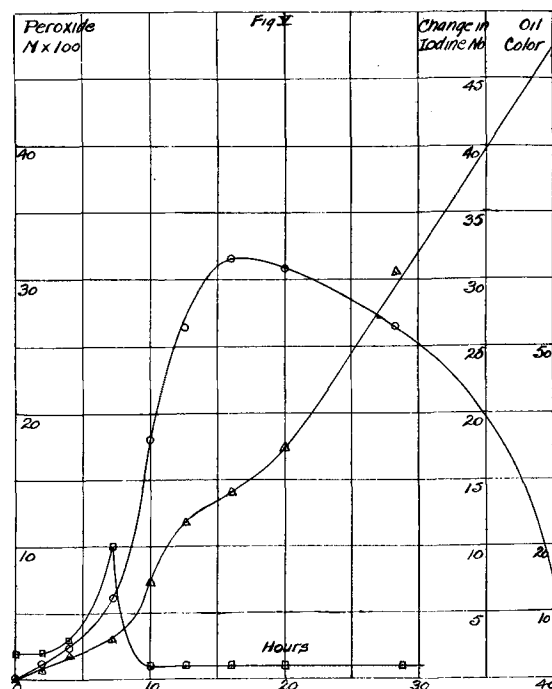


"active" or "labile" oxygen by the action of rancid fats on easily oxidized substances with production of colored materials. Guaiac is the substance often used. Prescher<sup>34</sup> and Kerr and Sorber<sup>35</sup> use this test in a qualitative manner. Very little attention has been given until recently toward development of a convenient quantitative determination of this labile oxygen in oils.

The liberation of iodine from acid potassium iodide solution has been used qualitatively as a test for peroxides in oils. The liberated iodine is detected with a starch indicator solution. Powick,<sup>26</sup> Tschirch and Barben,<sup>36</sup> Holde, Bleyberg and Brilles<sup>37</sup> and others have thus used it qualitatively. It is only in the last year that any attempts have been made to determine quantitatively and conveniently the amount of "active oxygen" or peroxides in edible oils and fats with the view of using this value as a quantitative measure of the degree of deterioration of the oil or fat. This is rather remarkable in view of the fact that almost every theory of oxidation of fats and oils postulates a peroxide as the compound which is first formed when oxygen attacks the molecule of fat containing a double bond.

Taffel and Revis<sup>38</sup> studied the liberation of iodine by oils containing peroxides from acid potassium iodide solutions. They found that the iodine was liberated slowly and incompletely

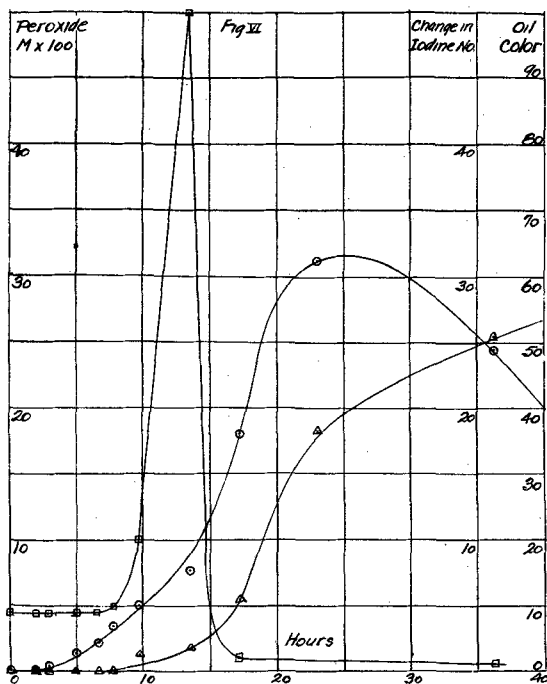
if an acidified aqueous solution of potassium iodide was used. However, if a few cc. of concentrated potassium iodide solution were added to glacial acetic acid and the oil, evolution of iodine was rapid and complete in five minutes' time if the mixture was shaken. Solid barium iodide could be used in place of the potassium iodide. They showed that the potassium iodide and the barium iodide prevented the oil from absorbing free iodine which would occur in their absence. Working with ground-nut oils, they found that if the oil had been treated with oxygen at temperatures below 120° C. (that is, subject to ordinary oxidation), it contained principally peroxides which would release iodine from the reagent at room temperature unless very rancid, when a short period of heating was necessary. Oils which had been treated with oxygen at higher temperatures (170° C.) contained a more difficultly reducible peroxide which could be determined by using a large excess of reagent and boiling for half an hour in an atmosphere of carbon dioxide. The liberated iodine was titrated with N/10 sodium thiosulfate.



C. H. Lea,<sup>21</sup> in his investigations on the effect of light on the oxidation of fats, used a method of determining active oxygen. This method consisted of heating the oil or fat in a solvent mixture of glacial acetic acid (two volumes)

and chloroform (one volume) in the presence of solid potassium iodide. Oxidation of the reagent or fat during the process is prevented by previously filling the tube with nitrogen, while the steady evolution of chloroform vapor prevents diffusion of oxygen back into the tube. The reaction mixture is cooled, poured into five per cent potassium iodide and titrated with N/500 sodium thiosulfate.

A trial of these methods on samples of cottonseed oil and corn oil brought forth the following facts: In the method of Taffel and Revis,<sup>28</sup> the oil does not completely dissolve in the acetic acid, and shaking is necessary. Unless protected from oxygen by an atmosphere



of inert gas, this will undoubtedly lead to high values. Also, the necessity of shaking during the reaction is an inconvenience. In the method of Lea<sup>21</sup> the solid potassium iodide which is added remains largely undissolved and here again shaking and heating are necessary.

It occurred to the author that if a procedure could be found whereby a homogeneous mixture of the oil, acetic acid and potassium iodide could be obtained the reaction should be much more rapid and complete and would require no shaking, so protection from the oxygen of the air would not be so necessary. After trying a number of substances in mixture with glacial acetic acid, the following procedure, using a

solvent mixture of glacial acetic acid and chloroform was found to accomplish the desired effect:

Three to ten grams of oil are dissolved in 50 cc. of solvent mixture (60 per cent glacial acetic acid, 40 per cent chloroform) and 1 cc. of saturated potassium iodide solution added. The mixture is stirred by giving a rotary motion to the flask. After exactly one minute from the time of addition of the potassium iodide, 100 cc. of water are added and the liberated iodine is titrated with 0.1 N or 0.01 N sodium thiosulfate, depending on the amount of iodine liberated. Starch is added toward the last as an indicator. Vigorous shaking is necessary at the very last to remove the last traces of iodine from the chloroform layer. The results may be conveniently expressed as moles of peroxide per 1,000 gm. of oil, calculated according to the following formula:

$$\text{Moles of peroxide, } M = \frac{.5 \times \text{cc.} \times N}{\text{gm.}}$$

cc. = cc. of thiosulfate

N = normality of thiosulfate

gm. = grams of oil

In carrying out this procedure, a slight precipitate of potassium iodide will separate out, but most of it will remain in solution. The evolution of iodine is rapid, the majority being formed in the first 5 or 10 seconds after addition of potassium iodide.

The following experiment was carried out to confirm the protective action of the potassium iodide in preventing the oil from absorbing iodine after it is released:

a. 25 cc. of a solution of free iodine in glacial acetic acid required 21.1 cc. of 0.1 N. thiosulfate.

b. To 25 cc. of the same solution of iodine were added 5 cc. more of glacial acetic acid, 20 cc. of chloroform, 1 cc. of saturated potassium iodide and then 8.7 gm. of cottonseed oil. After standing 5 minutes, 22.9 cc. of 0.1 N. thiosulfate were required.

c. The same amount of the same oil was then treated with the regular reagent without any free iodine. 1.9 cc. of 0.1 N thiosulfate were required. Subtracting the titration in (c) from that in (b) one obtains 21.0 cc. which is practically identical with that obtained in (a)

or, in other words, the oil absorbed iodine equivalent to only 0.5 per cent of the total amount present, even when a large amount of iodine was present such as would be released by only a very rancid oil.

The time limit of one minute was chosen as it was found that this gave the same result as when the sample was allowed to react for over an hour (protected from oxygen by an atmosphere of nitrogen). This agreement is no doubt due to a balancing of errors, the short time tending to cause a slightly low value, the fact that no protection from oxygen is used tending to cause a slightly high value. The two errors are slight and balance, and the simplification of procedure is a great advantage. When the peroxide content is very great (titration over 25 or 30 cc. of 0.1 N thiosulfate) it is necessary to use a small sample of oil, while on fresh oils, more accurate titrations may be obtained with a larger amount of oil.

This method has been used to study the autoxidation of cottonseed and corn oils; deter-

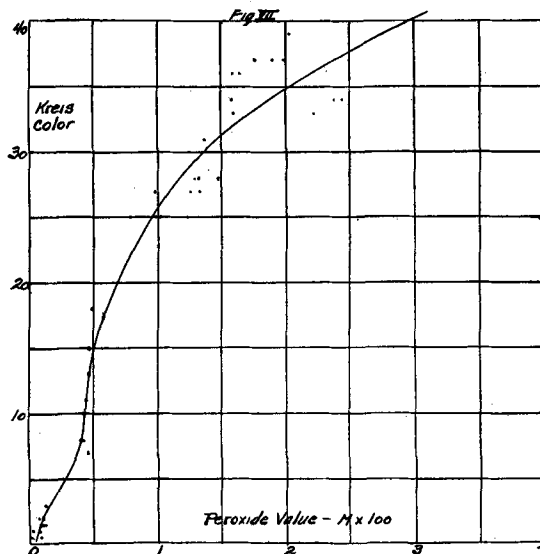
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The evolution of iodine is rapid, the bulk being released in the first five or ten seconds after addition of potassium iodide.

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mining the course of peroxide concentration as the oils are oxidized and studying the relation of peroxide concentration to certain other properties of the oils. The method used consisted of passing air with a definite vapor pressure through samples of the oil under identical conditions, for varying lengths of time and determining the peroxide concentration and other properties of these samples. The apparatus is diagrammed in figure I. The water pump delivers air (saturated with water vapor at the temperature of the water) under a slight pressure to the reservoir, where separate leads deliver it to the corresponding flowmeters which were made with identical calibrations. The air bubbles through the oil at a definite rate (10 liters per hour was used in all the runs), controlled by the stopcock on the flow meter. The tube which leads the oxygen into the oil is a

6 m.m. tube which extends 40 m.m. below the surface of the oil. The oil (20 cc.) is contained in 25 x 150 m.m. test tubes with an inside diameter of 22 m.m.  $\pm$  0.5 m.m. The bath is maintained at such a temperature that the temperature of the oil in the tubes is 100° C.  $\pm$  0.2°.



After being placed in the bath, the sample is allowed ten minutes to come to the correct temperature, then air is passed in. After the desired length of time, the tube is removed, stoppered and placed in cold water. The following experiment shows that the procedure gives identical conditions. Duplicate samples treated for 3.08 hours showed values for M. of 0.0248 and 0.0250. Duplicate samples after 4.6 hours showed 0.0342 and 0.0334, while another set of duplicates after 5.6 hours showed values of 0.0395 and 0.0399.

This procedure was then used to study the course of peroxide concentrations and other properties as shown in the following tables of data and in the graphs of these data. The Hanus method was used for determining iodine number, while the color of the oil is expressed as per cent of 0.1 N. potassium dichromate solution. The latter gave a fairly accurate and convenient method of numerically expressing the color of the oil. The Kreis colors were determined with Lovibond color glasses, according to the method mentioned described by Richardson (loc. cit.). The results of the more complete runs on several samples of cottonseed oil and a sample of corn oil were as follows:

## COTTONSEED OIL

<i>Hours</i>	<i>M</i>	<i>Oil Color</i>	<i>Remarks</i>
0	0.000865	7	Kreis color of 1
1	0.00554	7	
2.08	0.0103	7	
4.16	0.0202	7	
7.0	0.0449	15	Sl. rancid odor and taste
12.67	0.141	3	Very rancid odor and taste
16.66	0.257	1	Very rancid odor and taste
21.66	0.304	1	Very rancid odor and taste

These results are shown graphically in figure II.

## COTTONSEED OIL

<i>Hours</i>	<i>M</i>	<i>Iodine No.</i>	<i>Oil Color</i>	<i>Remarks</i>
0	0.00070	109.8	2	Kreis color of 2
1	0.00773	109.4	2	
2.08	0.0137	109.8	2	
4.0	0.0242	109.1	2	
7.41	0.053	108.8	15	Sl. rancidity
12.66	0.230	101.5	2	Marked rancidity
17.4	0.312	94.5	1	Marked rancidity
10.5	0.314	88.7	1	Marked rancidity
24.5	0.287	87.1	1	Marked rancidity

These results are shown graphically in figure III.

## COTTONSEED OIL

<i>Hours</i>	<i>M</i>	<i>Iodine No.</i>	<i>Oil Color</i>	<i>Remarks</i>
0	0.00264	106.4	7	Kreis color of 5
1	0.0126	106.2	7	
2.08	0.0208	105.8	7	
4.16	0.0381	105.6	15	Sl. rancidity
7.0	0.895	103.2	2	Marked rancidity
12.67	0.290	94.8	1	Marked rancidity
16.16	.....	91.5	1	Marked rancidity
21.66	0.283	85.7	1	Marked rancidity

These results are shown graphically in figure IV.

## COTTONSEED OIL

<i>Hours</i>	<i>M</i>	<i>Iodine No.</i>	<i>Oil Color</i>	<i>Remarks</i>
0	0.000246	110.6	2	Kreis color of 1
2	0.0129	109.9	2	
4	0.0246	108.9	3	
7.25	0.0620	107.6	20	
10	0.181	102.9	1	Marked rancidity
12.67	0.264	98.8	..	Marked rancidity
16	0.316	96.5	..	Marked rancidity
20	0.307	92.8	..	Marked rancidity
28.4	0.265	80.1	..	Marked rancidity
40.3	0.069	63.9	..	Marked rancidity

These results are shown graphically in figure V.

## CORN OIL

<i>Hours</i>	<i>M</i>	<i>Iodine No.</i>	<i>Oil Color</i>	<i>Remarks</i>
0	0.00074	127.0	9	Kreis color 0*
2	0.00192	126.9	9	
3	0.0056	126.9	9	
5	0.0146	126.9	9	
6.67	0.0229	126.9	9	

CORN OIL				
<i>Hours</i>	<i>M</i>	<i>Iodine No.</i>	<i>Oil Color</i>	<i>Remarks</i>
7.83	0.0350	126.9	10	
9.75	0.0502	125.7	20	
13.55	0.0764	125.3	100	
17.17	0.191	121.5	2	Marked rancidity
23.0	0.312	108.8	2	Marked rancidity
36.33	0.245	101.6	2	Marked rancidity

These results are shown in figure VI.

\*This oil produced an appreciable color when shaken with the HCl, so the blank used consisted of acid, oil and ether, without phloroglucinol. In fact this procedure was used in all the Kreis tests reported. The phloroglucinol reagent was tested with conc. HCl and found to produce no color.

An inspection of the above tables and graphs reveals several interesting facts. Under the conditions of the experiment, the peroxide concentration rises to a maximum of a little over 0.3 and then falls off. The color of the oil makes a sudden rise and fall. This peak occurs at a peroxide concentration of about 0.05 in the case of cottonseed oils and at a somewhat higher value in the corn oil examined. It is most remarkable that it was just beyond this point that marked rancidity was noted in every case. The values for the change in iodine number show that a certain peroxide concentration builds up before appreciable change in this values occurs. The curves showing the change in iodine number show a slight tendency to drop at a point about where the peroxide value has reached its maximum, but figure 5 shows that this value then rises again. This probably means that after peroxides no longer form, some other process of breaking down of the double bonds is occurring. Complete explanation of this phenomena will require further investigation. This occurs far beyond the point when marked rancidity has developed. It can be seen that peroxide concentration is a delicate method of determining the amount of oxidation which has occurred in an oil, and that it is an indication of how far the oil is toward a condition of rancidity. As an indication of the *keeping* quality of a *fresh* oil, a determination of peroxides cannot be said to be a reliable single test, but after appreciable oxidation has occurred, and before marked rancidity has set in.

it does indicate how far the oil has proceeded in the oxidation process. It could readily be used to compare keeping qualities of fresh oils by exposing them to air under controlled conditions for definite lengths of time *then* and comparing the peroxides formed.

In addition to the above data, peroxide concentration and Kreis color number have been determined on a large number of samples of cottonseed and corn oils which had been exposed to air under various conditions, some by treating for short periods at 100° as in the above tests, others at room temperature and some of unknown history, being tested as received. In general a high peroxide value was always accompanied by a high Kreis color. The approximate relationship is shown in figure 7. With the methods used, no particular difference in the relationship was noticed for different conditions of exposure, so all the results are expressed in the one graph. Taffel and Revis,<sup>38</sup> as previously mentioned, state that they also found that high peroxide concentration was always associated with high Kreis color, and they suggest that the substance causing the Kreis test may be a peroxide. Attention is again called to the fact that Greenbank and Holm<sup>20</sup> found the intensity of the Kreis test to be proportional to the amount of oxygen absorbed. It is hardly possible that the substance which actually condenses with phloroglucinol in the Kreis test is a peroxide, or a more exact relationship between peroxide content and intensity Kreis test would be expected, but it does appear that the Kreis test is always associated in a roughly quantitative manner, with peroxides which will release iodine from hydriodic acid at room temperature. The fact that Lea<sup>21</sup> found that the relation of active oxygen to intensity of Kreis color varied markedly with conditions of temperature and illumination may be due to the



fact that in his method he heats the reaction mixture and may thus determine peroxides which are not active oxidizing agents at room temperature, as well as dissolved oxygen which may react on heating. It seems reasonable that the substance which actually condenses with phloroglucinol in the Kreis test is formed from peroxides in the test, or that the peroxides act on some other substance present in the oil or produced in the test, to produce the substance which does thus condense to produce the red color in the Kreis test.

#### Summary

1. A brief review of the literature of rancidity, especially methods of detecting and determining rancidity is given.

2. A rapid and convenient method of determining peroxides or "active oxygen" in vegetable oils has been developed.

3. A study of peroxide formation in cottonseed and corn oils at 100° C. was made. The relation of peroxide concentration to iodine number, oil color, and intensity of Kreis color is reported.

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### The Annual Golf Tournament

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thing that you can't afford to miss. Fine friendships start that way, and you get to know the other fellow better in that warm southern sunshiny afternoon, than in years of business association.

Last year the cup was won by that prince of good fellows, L. B. Forbes of Little Rock, which gives the commercial chemists a monopoly on it so far, the team of Barrow and Agee having won it in successive years previously, and it is said that the carpets in the Barrow and Agee homes have been worn smooth from indoor putting practice these winter evenings. Down at Houston, Andrew Schwartz has been practicing diligently all of this mild winter, and is said to be in the pink of condition (they say that the trees have suffered on those Houston golf courses from his vicious attacks).

Up at Chicago, John Vollertsen has been training on a new "fixed flavor" vitamin, said to improve the back swing. Watch out for him. W. H. Irwin has a new "premium" approach shot, which makes him dangerous, and L. M. Tolman has been taking up some "certified" exercises, which have him in the proper shape to give some of these commercial chemists a terrible battle this year.

John P. Harris is chairman of the Golf Committee this year, and it will be well worth the price to observe his fancy shots. He brought in a score of 98 last week and is going to play the other nine holes next week. A. F. Sanchez is in charge of the local arrangements, so you know that they will be well taken care of. Harry Trevithick and J. J. Vollertsen complete a committee which assures those contemplating attendance the most colorful competition yet.