The Change in the Peroxide Values of Corn and Cottonseed Oils Under Various Storage Conditions

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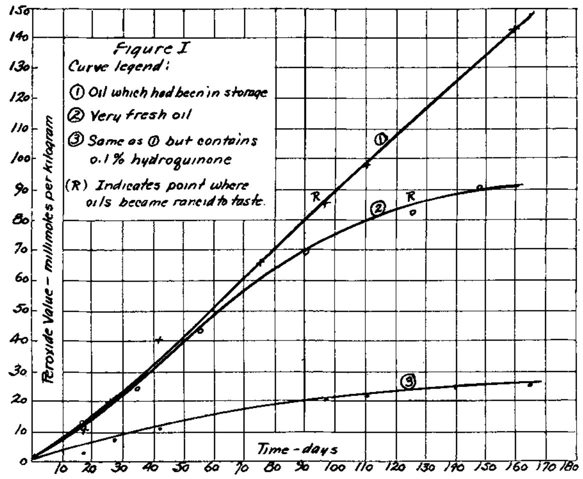
IT was shown in a paper[1] from this laboratory, presented at the October meeting of the Oil Chemists Society last year, that the peroxide content of an oil changed regularly throughout its aging at an elevated temperature. The method used in that paper was a modification of Lea's method[2] which he used to show the regular way in which the peroxide values of fats changed when exposed to light. Szahlender had been independently developing a method identical to that of Lea's and presented it in an address[3] before the Belgian Pharmaceutical Society at Budapest October 9 last year. All of these papers contain the same fact; the development of taste rancidity is connected directly with a rise of the peroxide number to a value many times greater than that of the same oil or fat when it is fresh. This fact should, therefore, be of considerable assistance in rating the age of an oil or fat. Certainly no other analytical value shows such a wide and regular change over the range between a fresh and a rancid fat as does the peroxide value. This paper is a report of the results of experiments designed to follow the rate of change of the peroxide value in corn and cottonseed oils under abnormal storage conditions in order to determine whether the above general statement always holds true, namely, that rancidity must be preceded by a sharp rise in the peroxide value.

It will be recalled that the work reported here last year from this laboratory was done at an elevated temperature, e.g., 100° F. Figure I shows how the peroxide value rose smoothly and regularly to a definite maximum and then fell off. The elevated temperatures were used in order to accelerate the reaction and shorten the experimental time.

It is to be noted from the shape of this curve that an attempt to calculate a bimolecular reaction constant would end in failure. Therefore, several reactions must be taking place simultaneously, with one reaction probably predominating. Also it is logical to believe that this speeding up of these reactions by elevated temperatures and by producing a large surface by air blowing, that the predominating reaction would largely mask the effects of the more secondary ones.



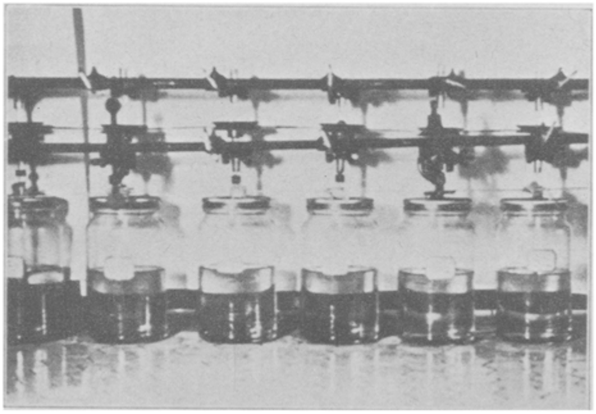
It was, therefore, thought advisable to follow the development of taste rancidity in oils by means of the change in the peroxide value using three types of storage conditions which would show more clearly how the peroxide value changes during the aging process. These conditions are:

1. At room temperature and with constant stirring to give infinite surface exposed to the air.
2. Sealed under nitrogen after the oil had been thoroughly evacuated to remove all occluded and dissolved air.
3. Sealed bottles stored in the dark and at refrigeration temperatures.

Experimental

It has been pointed out by many investigators, especially by Szahlender (loc. cit.) that the development of rancidity is a surface reaction and that great care must be exercised in obtaining a representative aliquot from a sample of fat. In fact, it is impossible to actually obtain a truly representative aliquot for the reason that the stage of oxidation at the surface layer is probably very different from that at a lower level. And furthermore, even if the whole sample is thoroughly mixed, the value obtained from the mixture does not show how far the oxidation has proceeded in the most deteriorated part and that is what counts in regard to taste rancidity. The best way appears to be that of giving the oil an infinite surface exposed to the air continuously causing the whole sample to change together and thus eliminating the questionable surface error. It was further thought that although air blowing the sample is the simplest method to give it infinite surface, the air may distill away some very volatile products of the reaction and would not thus give the true results.

A battery of six glass stirrers of the inverted "T" type, about 2″ in diameter, was set up using pint jars for the containers. The stirrers passed through loose fitting holes in the lids, and were all driven from one belt, passing over all the stirrer pulleys, thus insuring a



Battery of Stirrers Used in Experiment

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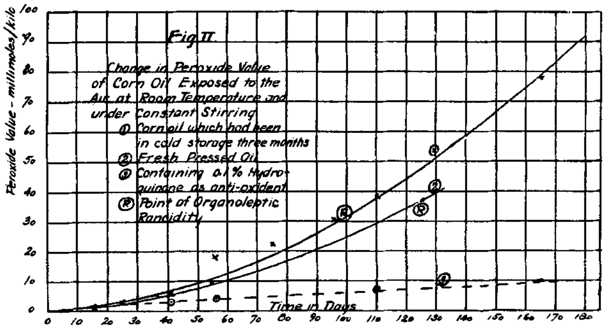
[1] Wheeler, OIL AND SOAP, May, 1932.

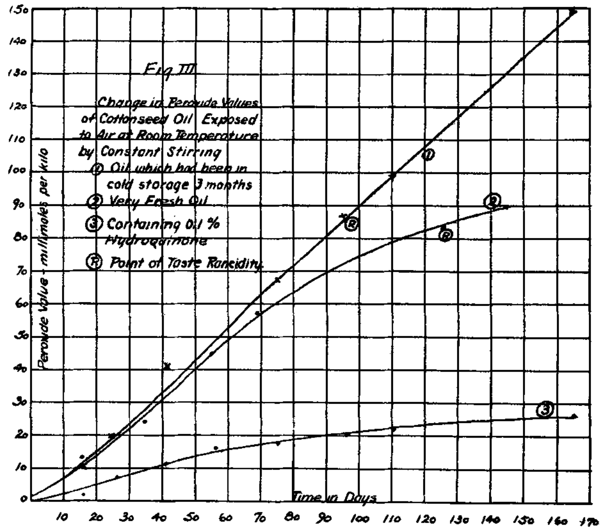
[2] Proc. Royal Soc. 108B, 175-189 (1931).

[3] Magyar Gyogyszeresztudomanyi Tarsasag Est. pp. 58-69 Jan. (1932).

uniform stirring action in all the samples. The stirring rate was just fast enough to keep the surfaces of the samples in continuous motion with no beating or whipping effects, and ran day and night.

Samples were withdrawn by a pipette from the various containers and the peroxide values determined. The results are shown in Figures II and III. These curves indicate clearly that a gradual rise in the peroxide value precedes the development of a rancid taste which points are marked by a circled "R" on each curve. Further than that, in the case of curve 4 where a strong inhibitor of rancidity, hydroquinone, was used, the rise of the peroxide value was also checked decidedly. This indicates that under atmospheric oxidation both with and without an anti-oxidant, the rate of development of a rancid flavor and the rise of the peroxide value appear to be directly related.





Tschirch and Barber[4] were the first to propose an accurate mechanism of the oxidation of a fat so as to account for the products obtained by the many investigators in this field. The formation of a labile peroxide which broke down into shorter chains was the main part of their theory. This assumed the absorption of oxygen, the rate of absorption of which has been used by Greenbank and Holm[5] as a measure of the speed of the oxidation. However, the rate of this absorption is not regular and does not appear to continue to the rancid point.

The second storage condition was, therefore, designed to test whether rancidity would develop in the absence of oxygen, and also whether peroxides would develop simultaneously. In order to do this the oil had to be completely evacuated so that all traces of oxygen would be removed. This was done by pumping the occluded air out of the oil at less than a millimeter pressure for eight hours at room temperature, after which the vacuum was released with pure nitrogen. The apparatus used for this is shown in Figure IV. By means of the double two-way stop-cocks of large bore it was possible to draw the de-oxygenated oil into the ampoule under a high vacuum. When enough oil had entered the ampoule the vacuum that remained was released by means of pure nitrogen when the lower stop-cock was turned. The ampoule was then pulled out of the rubber connection until it was possible to seal off the neck between the rubber connection and the bottle proper. By bending the rubber connection before sealing, the filling tube D which extends down inside the neck of the ampoule was broken off and allowed to fall into the ampoule. This prevented any drops of oil from wetting the inside of the neck of the ampoule so that it would be burned when the seal was made. After the tube D had fallen into the ampoule the neck was then sealed off using a sharp pointed oxygen-gas flame.

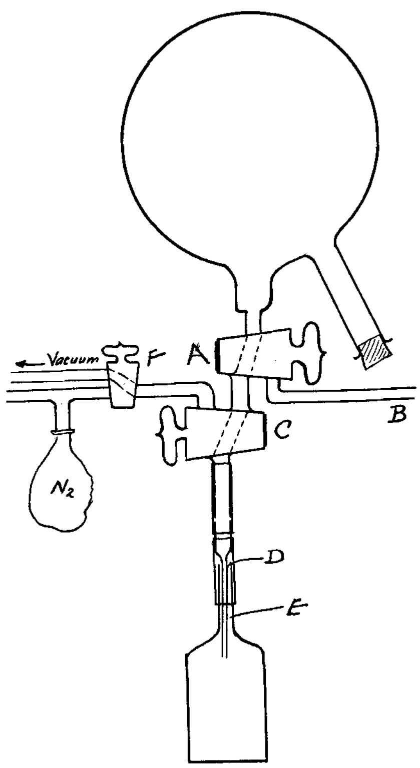


Fig. IV
Apparatus For Filling Ampoules Under Nitrogen or a Vacuum

Two sets of control samples were also filled with cottonseed oil. The first set was filled in air and sealed in air by simply using a small funnel. The second set of controls were filled by the same method as described under the nitrogen sealing process except that the oil had not been previously evacuated and filled with nitrogen. In other words, they were simply a vacuum sealed "fill" of ordinary oil.

The filled ampoules were allowed to stand in the light near a window in the laboratory for about four months. One ampoule of each series was opened at intervals and

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[4] Chem. Umschau 31, 141-5 (1924).
[5] *Ind. Eng. Chem.* 17, 625 (1925).

the peroxide number run on it. These results are shown in Table I.

TABLE I.

Cottonseed Oil

Description of Sample	Peroxide values (Millimoles/kilo) after 45 days	65 days	105 days	125 days	Taste at 125 days
A) Control under air	2.3	6.2	7.0	2.1	Rancid
B) Control under vacuum	2.1	...	2.0	...	Rancid
C) Evacuated oil sealed under nitrogen	0	0	0	0	Flat but not rancid

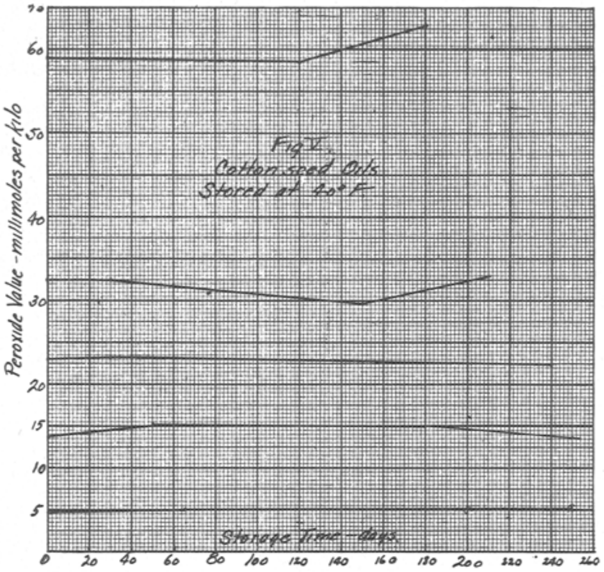
It will be noted in connection with the control samples, "A," that the peroxide values did not reach a very high maximum, 7.0, before it fell off and became rancid. The value at which organoleptic rancidity became marked in the case of similar oil which was exposed to the air as shown above, was about 80 millimoles peroxide per kilo of oil. Here it is only 7.0. This fact appears to coincide well with the theory of rancidity put forward by Tscirch and Barber (loc. cit.) and referred to above. Those unsaturated bonds which are capable of forming peroxides with the oxygen of the air have in the case of the control samples removed all the oxygen available from the limited supply of air in the ampoules and thus are not able to rise to a very high peroxide content. The splitting of the peroxides to form compounds of lower molecular weight then sets in and rancidity develops. This splitting lowers the peroxide content obviously, as shown by the falling of the values at the end of the storage period.

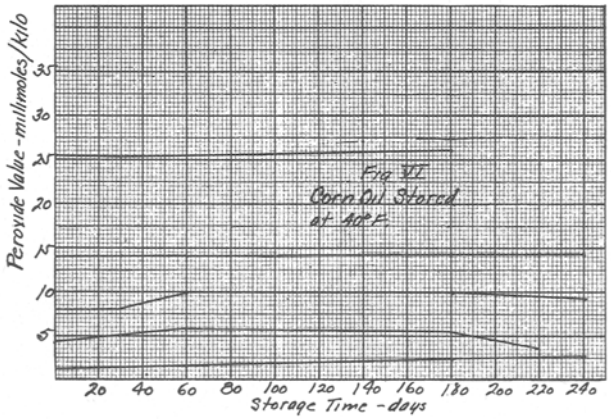
The "C" samples which were filled from oil containing no oxygen and which were sealed under nitrogen show markedly different results. Since there is no oxygen present there is no peroxide formation. In fact, these samples would not give even a feeble test for peroxides when starch solution was used. But more important than this is the fact that when no peroxide formation took place in the light and at room temperature there was no development of rancidity. The samples tasted flat as has been recorded, but the evacuating process is largely responsible for this change in flavor. Furthermore, in the case of the control samples the peroxide value *did* rise and the samples then became rancid. Thus under these abnormal storage conditions it appears that the development of rancidity is preceded by a rise in the peroxide values, and a direct relation exists between the two phenomina.

In the third series of experiments here presented an attempt was made to determine first, whether refrigeration temperatures which are well known to delay rancidity will also delay the formation of peroxides. And second, it was thought advisable to ascertain the effect of raising the peroxide values of cottonseed and corn oils by air blowing and then storing under refrigeration. In other words, will the presence of a high peroxide value accelerate the development of rancidity by breaking down to rancid forming products when it is no longer possible to take up oxygen from the air. Will an old oil keep just as well under refrigerated conditions as a fresh one?

Four two-liter bottles each of corn and cottonseed oils were blown at room temperature with moist air for various periods of time and the peroxide values run on each bottle. This gave a wide range of oils, from fresh to almost rancid. Four two-ounce glass stoppered bottles were then filled from each of the above artificially aged oils and were hermetically sealed and stored at 40° F. In addition to this a set of controls were also stored making 40 samples in all.

These samples were removed from storage from time to time and opened and examined for their peroxide content. The results are shown in Figures V and VI. None of the samples had a rancid taste after the long storage period. Since the samples showed little or no change in the peroxide values during this storage it is to be assumed there was no splitting up of the peroxides already present as a result of the aging treatment prior to storage. And if there was no splitting of the peroxides to form rancid compounds there should be no rancid flavor. This was exactly the case as shown by the results. This means therefore that the process of rancidity consists first in the formation of peroxides from a reaction of the oxygen of the air with the unsaturates of the oil. These peroxides then begin to split and the two reactions occur simultaneously, the formation preponderating at the start, then later, the splitting reaction begins to proceed faster and the peroxide content falls off and taste rancidity ensues. Refrigeration delays the speed of both reactions.





Summary

The relation between the formation of peroxides in corn and cottonseed oils and the development of rancidity have been studied under three types of storage conditions. A direct relation was shown to exist between them but the exact peroxide value at which organoleptic rancidity sets in depends upon such conditions as the amount of oxygen available, the temperature and the amount of surface exposed. Light exerts an accelerating influence upon the formation of peroxides as is shown by other work of the author's now in the course of publication.