Evaluation of Tests for Rancidity in Edible Packaged Oils*

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TESTS made by means of odor and taste are generally considered to be the most reliable criteria of rancidity, but such tests are difficult to evaluate on a quantitative basis. Other objections common to organoleptic tests, such as individual variation, the lack of a permanent standard, and sensorial fatigue, make a reliable quantitative chemical or physical test highly desirable.

Many chemical and physical measurements have been proposed for the detection and measurement of rancidity. None of these tests has proved entirely satisfactory, but many are used either alone or to supplement organoleptic tests. Most of the work on these tests has been done on fats which are aged while exposed to air. In the present investigation an attempt was made to evaluate several tests as to their reliability in measuring quantitatively the extent to which rancidity has developed in oils stored in sealed containers. This type of rancidity is thought to differ from ordinary autoxidative rancidity which develops in fats exposed to air.

All oils used in these tests were obtained directly from the refiner and packed immediately on receipt. All lots were judged to be of good fresh organoleptic quality when packed. The following terms were used to describe the organoleptic state of the different samples:

Good—Fresh quality oil.
Trace Rancid—An edible oil but a trace of rancidity detectable by careful comparative tests.
Slightly Rancid—Rancidity detectable by some but not all people.
Rancid—Inedible.
Very Rancid—Repugnant.

The Methylene Blue Reduction Test

The procedure used was essentially that described by Royce (1). Two milliliters of 0.025% methylene blue chloride in aldehyde-free absolute alcohol was added to 25 milliliters of oil. According to Bickford and Markley (2), the amount of dissolved oxygen has a marked influence on the fading time, therefore all samples were mixed in the same manner by inverting 25 times. Incubation was at 88° C. and the end-point was judged visually.

Determinations were made of the methylene blue fading times of corn and cottonseed oil packs stored for one and three months at 4°, 21°-26° (room temperature), and 38° C. in 12-ounce sealed flint and amber glass bottles in the dark. Similar samples were exposed to diffused light and to direct sunlight at room temperature. The containers were commercial bottles sealed with a pulp and vinylite lined metal screw cap. The packaging procedure consisted of filling the containers to overflow at 52° C. and sealing them immediately.

At the end of one month rancidity had begun to develop in all samples except those stored at 4° C. in the dark. The samples ranged in organoleptic quality from good to very rancid; but no significant decrease in the fading time took place except in the case of oils stored in flint bottles and exposed to direct sunlight. The latter oils were very rancid. The methylene blue fading time also failed to indicate the development of rancidity in both corn and cottonseed oils stored for three months under the above conditions. The fading time did decrease after this storage period, but there was no significant difference between the values of rancid and good samples.

Fresh corn oil sealed in 12-ounce flint glass bottles was aged in the dark in a hot-air oven at 100° C. and also by exposure to General Electric S-4 type sunlamps at 38° C. and 500 foot-candle intensity. Fifty milliliter samples of the oil were placed in open four-ounce containers and also aged under the same conditions to determine the effect of exposure to air on the methylene blue fading time. The results of these tests are recorded in Table I.

The methylene blue fading time decreased with the development of rancidity in corn oil aged in the dark at an elevated temperature (100° C.) both in sealed and in open containers, but the sensitivity of the test was low in the case of the oils in which rancidity was induced by heat without exposure to air. In the samples exposed to sunlamps at 100° C. the fading time of the oil also decreased with the length of exposure in open containers, but there was no significant change in the sealed samples. Apparently the methylene blue fading time depends upon the presence of oxygen during storage at moderate temperatures rather than on the organoleptic quality of the oil.

Since the methylene blue test appeared to be most reliable in the case of oils which had been exposed to the air during the development of rancidity, oils which had aged in sealed containers were first incubated in contact with air before the test was made. This incubation procedure failed to produce any changes in the fading time which could be correlated with the different organoleptic states of the oils.

On a basis of the results obtained the presence of excess oxygen or a high temperature appears to be necessary to cause a change in the fading time to accompany the development of rancidity. As far as is known, all previous investigators who have reported the successful use of this test used it on fats which had aged in unsealed containers. It appears that the changes in an oil which influence this test take place along with the development of rancidity under certain conditions but that there is not necessarily a direct relationship between these two properties.

Presence of Aldehydes

The aldehydes present in corn and cottonseed oils stored in sealed containers under the same conditions as used in the evaluation of the methylene blue test were estimated by the bisulfite method proposed by Lea (3).

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TABLE I

Comparison of Organoleptic and Methylene Blue Tests, Aldehyde Contents, and Chlorophyll Values of Corn Oil Stored in Open and Sealed Containers Under Accelerated Conditions

Storage Time (Hours)	Organoleptic Quality		Methylene Blue Fading Time (Minutes)		Aldehydes **		Chlorophyll Value	
	Sealed	Open	Sealed	Open	Sealed	Open	Sealed	Open
Stored at 38° C. Under Sunlamps *								
0	Good	Good	94	94	7	7	9	9
6	Rancid	Rancid	100	49	14	6	15	14
12	Very Rancid	Very Rancid	100	47	13	6	20	20
24	Very Rancid	Very Rancid	99	47	12	71	22	26
36	Very Rancid	Very Rancid	100	35	18	79	30	47
Stored at 100° C. in the Dark								
0	Good	Good	94	94	7	7	9	9
6	Rancid	Very Rancid	100	54	8	5	7	4
12	Rancid	Very Rancid	73	32	8	6	8	7
24	Very Rancid	Very Rancid	76	21	10	85	9	11
36	Very Rancid	Very Rancid	69	15	10	90	9	11

* Intensity of light, 500 foot candles.
** As p.p.m. carbonyl group.

After three months under the various storage conditions the samples of oil stored in screw-cap bottles exhibited all stages of rancidity; however, there was no significant change in their aldehyde content. It may be seen from Table I that the fresh corn oil, aged artificially in the presence of air, showed an increase in its aldehyde content when rancidity was induced by light or heat. However, the test was not sensitive enough to detect the early stages of spoilage. Storage of oil in sealed containers prevented the formation of large amounts of aldehydes.

The formation of aldehydes appears to depend on or is influenced by the presence of oxygen, however, incubation tests, in the presence of air, failed to reveal any correlation between the original organoleptic state of the oil and the rate of formation of aldehydes.

The formation of aldehydes, as determined by the bisulfite method, appeared to depend more on the presence of oxygen than on the actual development of rancidity. In open containers the well-known fact that large amounts of aldehydes are formed during the oxidation of fats was observed. If these products were produced during the early stages of rancidity, they were broken down as fast as they were formed. In many instances an actual decrease in aldehyde content occurred during storage of oil in sealed containers under natural conditions. Pool (4) reported similar decreases in Kreis test values on oils stored in hermetically sealed containers.

Viscosity

Viscosity measurements were made on corn and cottonseed oils stored in 12-ounce flint and amber glass screw-cap bottles under various conditions. The determinations were made by taking the time necessary for the oil to flow through a capillary at a constant temperature of 25° C.

Samples were stored in the dark at 4° C., at room temperature, and at 38° C., while other samples were exposed to direct sunlight and to diffused light at room temperature. After storage for one month these samples varied in organoleptic quality from good to very rancid. No significant change in the viscosity, as measured by this method, took place until the later stages of the development of rancidity.

The viscosity of very rancid oil which had been exposed to direct sunlight did increase slightly; however, this change was not as sensitive as the organoleptic change and not sensitive enough to detect the early stages of deterioration. Similar results were obtained when cottonseed oil was packed in sealed containers and aged by exposure to sunlamps.

Film Pressure

The vertical film balance, as described by Boyd and Harkins (5), was used to determine the film pressure of a unimolecular film of various samples of corn and cottonseed oils. (The film pressure is the difference between the surface tension of the clean surface of the subphase and that of the subphase when covered by the film.) Distilled water was used as the subphase and the monomolecular film was formed by adding the oil diluted one to ten with redistilled petroleum ether. An arbitrary scale was set up several feet from the instrument, and readings were made by means of a beam of light reflected from a small mirror placed over the knife-edge of the balance. The film pressure was represented by the number of scale divisions (one division equals 2.5 mm.) deflection caused by spreading monomolecular film of the oil over the surface of the distilled water.

TABLE II

Relative Film Pressures of Cottonseed Oil Stored Under Various Conditions in Sealed Bottles for Six Months

Sample	Organoleptic Quality	Relative Film Pressure (Arbitrary Scale Units)
Dark		
4° C.	Good	24.0
21°-26° C.	Trace Rancid	24.5
38° C.	Slightly Rancid	24.0
Diffused Light, 21°-26° C.		
Flint Glass	Very Rancid	24.0
Direct Sunlight, 21°-26° C.		
Flint Glass	Very Rancid	19.5
Amber Glass	Very Rancid	17.5

Little change in the film pressure of monomolecular layers of corn or cottonseed oils was found to take place with the development of rancidity when the oils were stored in sealed containers, except in the later stages of rancidity. The data in Table II are typical of the results found for edible oils stored under these conditions. Similar results were obtained when the oils were aged artificially in sealed bottles by exposure to sunlamps.

Cottonseed oil was also aerated by a steady stream of air while held at 100° C. The film pressure was determined at intervals. From Table III it can be seen that the film pressure changed much more quickly and was a better index of rancidity under these conditions than when the oil was aged in sealed containers. These changes are similar to those ob-

served by Clark and Rugg (6) who obtained significant changes in the drop-spreading pressures of soybean oil, as measured by means of a hydrophilic balance, right from the time aeration of the oil at 100° C. was begun. Oils which had been stored out of contact with air did not show such striking changes in their film pressure with changes in the organoleptic quality of the oil. It appears that the change in film pressure is not wholly dependent on the organoleptic quality of the oil but is influenced by the oxidation products formed in the presence of excess air.

TABLE III

Relative Film Pressures of Cottonseed Oil Aerated at 100° C.

Aeration Time (Hours)	Organoleptic Quality	Relative Film Pressure (Arbitrary Scale Units)
0	Good	16.8
0.5	Good	17.0
1	Good	14.3
2	Good	13.4
4	Trace Rancid	10.6
6.5	Slightly Rancid	7.0
11	Slightly Rancid	6.8
17	Rancid	3.3

In the sealed samples only those oils which had been exposed to direct sunlight showed changes in their surface tension. Therefore both light and air appear to influence the change in the film pressure of cottonseed oil. Although the development of rancidity is influenced by these same two factors, the results reported here show that the changes in the oil which cause rancid odors and flavors, at least during the early stages of rancidity, differ from those changes which affect the film pressure.

Light Transmission

It is well known that bleaching of edible oils takes place during oxidative changes, especially at the end of the induction period. It was thought that this loss of color might be a means of following quantitatively the oxidative changes occurring in edible oils.

A Coleman Universal Spectrophotometer, equipped with 20 mm. curvettes, was used in making all light-transmission measurements between 335 and 800 millicrons wave lengths. Transmissions of over 100% in the infrared region are due to the use of distilled water as the reference standard.

The color of both corn and cottonseed oils faded when they were exposed to light in sealed containers. The light transmission curves of these oils have a minimum (maximum absorption) between 340 and 365 millimicrons. This minimum did shift with the color changes in the oil, but the shift was not significant as far as the organoleptic quality of the samples was concerned.

The curves were found to shift throughout their entire length as the oil in sealed containers changed color. The greatest change occurred in the transmission of light below 600 millimicrons. Figure 1 shows typical curves of corn oil which had been aged in sealed bottles in the presence and absence of light for 12 months. Similar curves were obtained for cottonseed oil.

Most of the fading of the color of corn and cottonseed oils took place during the first three months of the storage period and seemed at first to correlate with the development of rancidity, the degree of bleaching and organoleptic quality depending on the

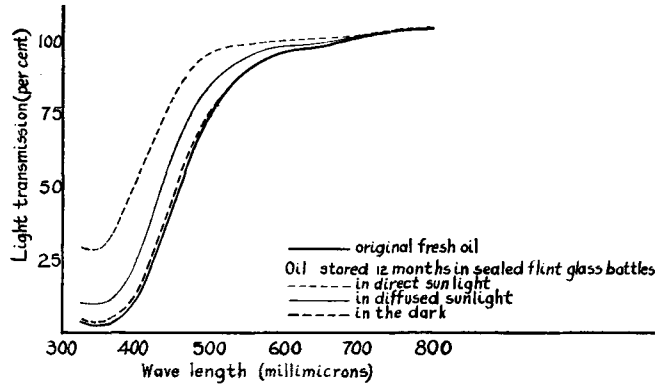

FIG. 1. Light transmission of corn oil stored at 24° C.

intensity of the light to which the oil was exposed. Amber glass containers were very effective in retarding these harmful effects of light. However, darkening was found to occur sometimes, especially in samples not exposed to light. That is, the color of corn and cottonseed oils was found to depend on the storage conditions but not on their odor and taste.

Effect of Light and Oxygen on the Color of the Oils

In order to check the results found in the storage tests, corn and cottonseed oils were aged artificially in the dark at 100° C. and also by exposure to sunlamps at 38° C. in both open and sealed bottles. When corn oil was heated in the dark, rancidity de-

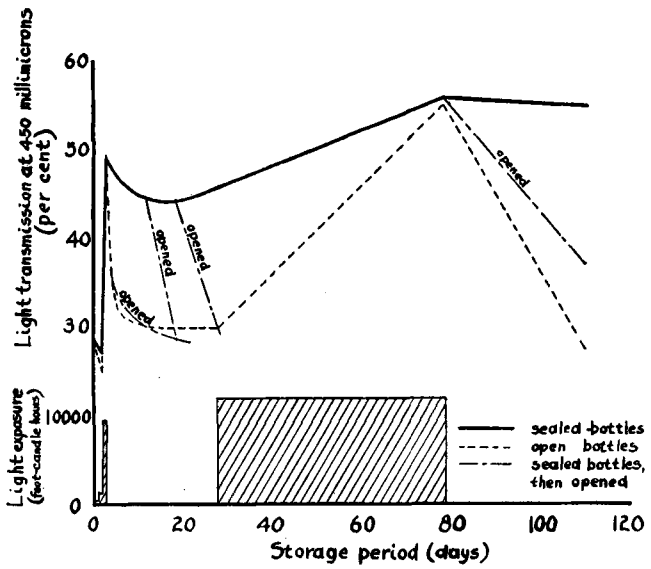

FIG. 2. Color changes of corn oil during storage in two-ounce flint glass bottles at 24° C.

veloped rapidly whether the oil was exposed to the air or not. In the case of the oil stored in sealed containers little change in the color took place. The oil aged in the presence of air darkened at first after which bleaching occurred.

The samples exposed to sunlamps at 38° C. also deteriorated rapidly in organoleptic quality whether exposed to the air or not. Considerable bleaching of the sealed samples occurred, but exposure to air slowed up this action considerably. These results indicate that light is the main factor causing the fading of corn and cottonseed oils with rancidity playing

a minor role. The darkening of the oils is evidently caused by the pressure of excess oxygen and is accelerated by heat.

Reversibility of the Color Change

The reversibility of the color change is demonstrated by the results shown in Figure 2. The light transmission at 450 millimicrons was used as the index of color because the color change was greatest at this wave length. In this test fresh corn oil was packed in sealed and unsealed two-ounce flint screw-cap bottles at room temperature (24° C.). Several samples of each type were stored so that a new sample could be used for each examination.

First the series of sealed and unsealed bottles of oil were exposed to direct sunlight. The first two days were cloudy, and the amount of light falling on the samples was 355 and 1600 foot-candle-hours respectively as measured by a General Electric Exposure Meter equipped with special masks. The slight darkening of the oils which occurred during this period was probably due to utilization of dissolved oxygen by the oil. On the third day the amount of light falling on these samples was 9,000 foot-candle-hours and bleaching of both sealed and exposed oils occurred. The exposed sample did not bleach as much as that protected from the air.

The samples were stored for the next 25 days in the dark. Slight darkening followed by a slight bleaching of the sealed oil occurred. The open samples darkened almost to their original color in about nine days under these conditions. Sealed samples which were opened during this period also darkened in a few days to about the same extent as the original open samples. This change in light transmission took place through the whole wave band between 335 and 800 millimicrons. At the end of a total storage period of 18 days the sealed samples were a trace rancid, the open ones were slightly rancid. After 28 days' storage the samples were slightly rancid and very rancid, respectively. In both cases the sealed samples were bleached much more than the samples exposed to air. This is another instance where the development of rancidity did not parallel the loss of color. The quality of both oils continued to deteriorate up to the end of the test.

From the 28th to the 79th day of storage the samples were exposed to direct sunlight. As can be seen, bleaching occurred in both the sealed and open bottles. During the last 31 days of the test the oils were stored in the dark during which time darkening took place. From the 79th to the 110th day a sealed sample, a sealed sample which was opened on the 79th day, and an original open sample were stored in the dark. As can be seen from Figure 2 the change in transmission of the oil which had been exposed to air during the whole storage period was greater than the change taking place in the oil which was exposed for only the last 31 days. The sealed sample showed relatively little change.

These color changes occurred throughout the entire light transmission curve and were reversible except in the case of the samples which had been stored for 79 days or longer in open bottles. These oils had changed to a yellow-orange color and were evidently highly oxidized. They behaved similarly to fresh oils in their light transmission above 480 millimicrons, but at shorter wave lengths the change in transmission during subsequent storage was much less.

It appears that the color changes of corn oil between 335 and 800 millimicrons are reversible. In the case of severe oxidation, where corn oil was exposed to air for long periods of time, this reversibility appears to have been destroyed.

From the above results oxygen appears to be the principal factor causing darkening of corn and cottonseed oils. The darkening of oils on exposure to oxygen and their bleaching when subjected to light suggests a reaction which may be a step in the chain of reactions resulting in the development of rancidity as light catalyzes both the development of rancidity and the bleaching of the oils. The darkening of oils may be due to the formation of the first oxidation products which in turn break down and oxidize the oil further to form products which cause rancidity.

Induction Period

The induction period of fats has been used extensively to evaluate their quality or potential keeping quality. Oils which have become rancid cannot possess an induction period in the strict sense of the term; however, it was thought that the time necessary for oils which had been stored in sealed containers to reach a given peroxide value might be used to evaluate their organoleptic quality.

The induction period tests were carried out by incubation in a hot-air oven at 80° C. (The oil (250 ml.) was stored in open Pyrex containers of standard dimensions and one-gram samples were removed at intervals. The peroxide content was determined by the method described by Lea (7). The end of the induction period was taken as that time when 10 millimoles of peroxide per kilogram of fat had accumulated. This is lower than the values at which fresh corn or cottonseed oils become rancid in an oven test (35 to 45 millimoles), but most of the samples had already become rancid during storage in sealed containers; therefore these values had no significance. It was found that the peroxide content of stored oil increased rapidly in the oven test after it had reached about 6 millimoles per kg. of fat, especially when antioxidants were used, and that the 10 millimoles end-point gave good relative stability values.

No correlation could be found between the organoleptic quality and the induction period of corn and cottonseed oils stored in sealed bottles at various temperatures in the dark or exposed to strong or diffused sunlight. The original peroxide value was also useless as an indicator of rancidity.

In many cases it was found that oils which had been exposed to light and had become rancid possessed longer induction periods than oils of the same lot which were of good organoleptic quality after storage for the same length of time in the dark. An examination of the peroxide values of corn and cottonseed oils aged under natural conditions indicated that the length of the induction period was dependent on the initial peroxide value, which in turn was influenced by exposure of the oils to light.

The original peroxide value and the induction period of cottonseed oil which had been stored in the presence of air under refrigeration in the dark is recorded in Table IV. This oil was still of good organoleptic quality and possessed a peroxide value of 5.69 millimoles per kilogram of oil. This oil was

then packed in sealed two-ounce flint glass bottles and exposed to sunlamps at 38° C. As can be seen from the table the organoleptic quality of the oil fell rapidly and the peroxide values decreased. On the other hand, the induction period increased almost four-fold in 55 hours. This confirms the observation made in the storage tests that the induction period of oils, stored in sealed containers, depended on the original peroxide content. The destruction of peroxide by light would explain the longer induction periods of oils stored in the presence of light in comparison to those of oils of better organoleptic quality stored in the dark.

Chlorophyll Value

The chlorophyll values of corn and cottonseed oils were determined by the method proposed by Coe (8). A solution of 0.15 grams of a highly refined magnesium chlorophyll in 100 milliliters of redistilled

TABLE IV

Relationship Between Peroxide Values and Induction Periods of Cottonseed Oil in Sealed Containers During Light Exposure (38° C., 500 foot candles light intensity)

Exposure Period (Hours)	Organoleptic Quality	Peroxide Value (Millimoles of Peroxide per Kg.)	Induction Period (Hours)
0	Good	5.69	2.0
0.5	Good	5.09	2.5
1	Good	4.31	3.0
2	Good	3.99	4.5
4.5	Good	4.53	3.5
6	Trace Rancid	3.13	4.0
9	Slightly Rancid	3.63	5.0
12	Rancid	2.77	5.0
24	Very Rancid	2.69	5.0
48	Very Rancid	1.58	7.0
55	Very Rancid	1.85	7.0

petroleum ether was used as the standard solution. One-half milliliter of this solution was placed in low-form porcelain micro-crucibles, and the oil to be tested was added dropwise with stirring from a standard one-milliliter pipette until the red fluorescence of the chlorophyll solution under ultraviolet light just disappeared. Observations were made with the naked eye.

In order to control the end-point of the titration three standards made up of different proportions of the chlorophyll solution and the type of oil being tested were prepared for each series of determinations. To one standard enough oil was added so that the red fluorescence just disappeared. The other two standards had one drop less and one drop more oil added to them than the first standard. By this means duplicate titrations checked within two drops of the oils. The "chlorophyll values" are expressed in terms of the number of drops of the oil needed to neutralize the red fluoresence of 0.5 milliliters of the chlorophyll solution.

In general the chlorophyll value of corn and cotton seed oils when aged, either in the presence or absence of light, at temperatures between 4° C. and 38° C. increased gradually with the length of storage and extent of the development of rancidity. However, there were some discrepancies between the chlorophyll values and the organoleptic qualities of the oils, especially when the chlorophyll value of oils exposed to light were compared with those of oils of similar quality aged in the dark.

The results of approximately 400 determinations of the chlorophyll value of corn and cottonseed oils in sealed containers, aged under various conditions of light and heat are summarized in Table V. It is apparent from the range of values found for oils in the various stages of rancidity that the organoleptic state of the oils is not the only factor governing its chlorophyll value.

TABLE V

Chlorophyll Values of Edible Oils Aged in Sealed Glass Bottles Both in the Presence and Absence of Light at Temperatures Hanging From 40° C. to 38° C.

Organoleptic Quality	Chlorophyll Value	
	Corn Oil	Cottonseed Oil
Good	8-12	14-24
Trace Rancid	9-26	16-25
Slightly Rancid	8-15	16-25
Rancid	9-19	17-34
Very Rancid	9-90	19-46

Factors Influencing the Chlorophyll Value

Fresh corn oil was aged in both sealed and open 12-ounce bottles by exposure to sunlamps at 500 foot-candles intensity at 38° C. and by incubation at 100° C. in the dark in a hot-air oven in order to determine the effect of exposure to air and light on the chlorophyll value (see Table I).

Air did not appear to have any effect on the chlorophyll value of corn oil exposed to sunlamps for periods up to 12 hours. Oils which had been exposed 24 to 36 hours had higher chlorophyll values when aged in contact with air. But the organoleptic state of these oils was definitely worse than that of the samples stored in sealed bottles. Although the flavor of the oil continues to deteriorate after it has become very rancid, no distinction has been made in this investigation between such oils in presenting the results of organoleptic tests. Air also appeared to accelerate the changes in the chlorophyll value of corn oil stored in the dark at elevated temperatures. Again the samples aged in contact with air had deteriorated more than those stored in sealed containers.

The oil exposed to light showed a regular increase in its chlorophyll value in contrast to a preliminary decrease and finally a slight increase when exposed to heat in the absence of light. Although the oils aged under the two conditions deteriorated in flavor at approximately the same rate, there was a great difference in the rate of increase of their chlorophyll values. Evidently light has more influence on the increase in chlorophyll value of an oil than on its organoleptic quality. In many oils which had been aged artificially under sunlamps, opened, then stored at room temperature in the dark, the organoleptic state changed markedly during storage in the dark with little or no change in the chlorophyll values.

Further evidence that the increase in the chlorophyll value is apparently due in a large degree to exposure to light rather than to a change in the organoleptic state was also shown by the fact that 6-palmitoyl-l-ascorbic acid and catalase slowed up the development of rancidity in oils exposed to light for a short period but had no effect on the chlorophyll value.

The fact that the chlorophyll value did not correlate with the organoleptic quality of edible oils is in agreement with the work by French and Lundberg (9). In the present investigation oils which had been exposed to intense light became very rancid, became bleached, lost much of their fluorescence, and had high

chlorophyll values. These results seem to support the above authors' findings that the absorption of light by oils and their fluorescence influence the chlorophyll value. They stated that the fluorescent quenching is not a chemical reaction but an optical phenomenon due to (1) the internal filter action of the oil and (2) the fluorescence of the oils themselves.

Coe (10) stated that heating an oil, evidently in contact with air, lowered its chlorophyll value. This was the opposite effect to that which he expected. In several instances in this investigation the chlorophyll value of an oil decreased on storage especially when exposed to heat and air in the absence of light. In most cases this decrease was accompanied by an increase in the fluorescence under ultraviolet light and an increase in the absorption of light by the oil. The organoleptic quality of the oil did not improve in any case.

From theoretical considerations Bickford *et al.* (11) atributed the quenching of the fluorescence of chlorophyll to the presence of dissolved oxygen in the oils, and the increase in the chlorophyll value during the development of rancidity to the consumption of this oxygen. However, in this investigation vigorous shaking of oil, which had been stored in sealed containers, with air failed to change the chlorophyll value. Fresh and rancid samples of sealed corn and cottonseed oils exposed to air in the dark at 4° C. also failed to show a decrease in their chlorophyll values as would be expected if the dissolved oxygen was the reactant.

It appears that the chlorophyll value of an oil is governed primarily by exposure to light rather than by its organoleptic state. This and the reversibility of the chlorophyll value without a corresponding change in the organoleptic state alone preclude its general use as a reliable test for rancidity.

Miscellaneous Tests

Preliminary determinations of the spectral transmission curves* of corn oil in the ultraviolet and infrared regions revealed no significant differences which could be attributed to changes in the oil due to the development of rancidity.

Polarograms of aqueous and alcoholic extracts of corn and cottonseed oils in various stages of organoleptic deterioration were made by means of a Heyrovsky Polarograph, Model XI, using a saturated calomel reference electrode. Oils which had aged in contact with air as well as samples which had become rancid while stored in sealed containers were studied, but no evidence of any substance present in these extracts was found which was due to the development of rancidity. The use of other extractants may prove more successful.

The water extractant was a 0.1N KCl solution made up of redistilled water. The ethyl alcohol was redistilled and saturated with potassium chloride. It was found advisable to saturate the alcohol with potassium acid phthalate as a buffer. The extraction was carried out by shaking the oil with the extractant in the dark in glass stoppered containers. The resultant emulsion was filtered to remove the free oil before the solution was placed in the reaction vessel. Polarograms were obtained with the dropping mercury electrode both as the anode and as the cathode. These were made on the untreated solutions as well as on those which had been washed with nitrogen.

An attempt was made to use the fluorescence of the oil itself as a measure of the degree of rancidity which had developed in an oil. The amount of fluorescence was determined by means of a Coleman Universal Spectrophotometer fitted with the ultraviolet illuminator attachment. Light of both 365 and 436 millimicrons wave length was used. The reference standard was a solution of 0.3 mg. of quinine sulphate in 0.1N sulfuric acid.

The fluorescence of oils stored in sealed containers and exposed to intense light, such as direct sunlight, decreased in intensity. This decrease appeared to parallel the bleaching of the oil and the development of rancidity, however, oils protected from light showed little change in their fluorescence, even in samples which were in advanced stages of rancidity.

Summary

Organoleptic tests, in spite of their limitations, were the most satisfactory methods of determining the quality of corn and cottonseed oils which had aged in sealed containers. The chemical and physical tests used in this investigation were influenced more by storage conditions, such as exposure to light or the presence of air, than by the actual organoleptic state of the oil.

Changes in the methylene blue fading time of an oil were dependent on the presence of air or a high temperature during storage. Aldehydes, as determined by the bisulfite method, increased in oils exposed to air but their formation in oils in sealed containers was very slow even with extensive development of rancidity. No significant changes in the film pressure of oil in sealed containers took place except in samples exposed to light for several months, however, aeration of an oil at 100° C. resulted in a rapid change in film pressure. Exposure to light caused the color of the oils to fade, exposure to air caused darkening, yet both factors contributed to the development of rancidity. The induction period of the oils stored in sealed containers depended upon their original peroxide value which in turn was influenced by exposure to light. Exposure of sealed samples of oil to light caused a destruction of peroxides. The chlorophyll value of oils and the fluorescence changed rapidly when they were exposed to light; however, oil could be made rancid in the absence of light with little or no significant change in its chlorophyll value.

Preliminary polarographic and light transmission studies in the ultraviolet and infrared regions of the spectrum failed to reveal any changes in the oils which could be correlated with the development of rancidity.

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