Photochemical Studies of Rancidity: The Chlorophyll Value in Relation to Autoxidation[1]

MAYNE R. COE

Agricultural Chemical Research Division, Bureau of Agricultural Chemistry and Engineering, U. S. Department of Agriculture

The problem of rancidity, from a scientific point of view, has heretofore been rendered more difficult by the fact that the ultimate standards to which all data must be referred have been based on taste and smell. It is true that the senses of taste and smell may be developed to a remarkable degree of sensitivity and consistency; nevertheless this method of differentiating the degree of rancidity leaves much to be desired.

The well-known chemical methods generally used for following the changes in the oxidative type of rancidity of an oil or fat have likewise proven inadequate, because they fail to give a quantitative knowledge of the state of oxidation. They also fail to enable one to detect and to follow the very earliest stages in the process of rancidification and do not always make possible a comparison of the potential keeping qualities of any two or more oils or fats. Recent investigations of the "chlorophyll value test" (1) for following what is regarded as autoxidation of an oil seem to indicate that all three of these requirements for a test may be fulfilled.

Theory

It is well known that fresh oils fluoresce when placed under the ultraviolet lamp equipped for fluorescence studies. This fluorescence would indicate that certain reacting substances are present. It has been observed that, in different stages of development of rancidity, the intensity of the natural fluorescence of an oil decreases with increased oxidation indicating that a loss of the reacting substances has taken place. The decrease in fluorescence is so gradual, however, that the degree of change due to oxidation as observed under the lamp is practically impossible to follow. A means for measuring this change with greater precision becomes necessary.

It was conceived that chlorophyll, known for its property as a photosensitizer (2), would when added to an oil give up its excitational energy to those acceptor molecules in the oil which fluoresce and which, so long as these molecules remain in the reacting state, are believed to be responsible for rancidity autoxidation. When the acceptor molecules, or reacting substances, are progressively oxidized, as when an oil becomes rancid, they lose the property of quenching the fluorescence of chlorophyll. Advantage has been taken of this property of oils toward chlorophyll in following rancidity autoxidation, by titrating a given amount of chlorophyll with the oil under examination. The number of c.c. of oil necessary to quench the red chlorophyll fluorescence is called the "chlorophyll value."

Every investigator working in the field of rancidity will recall that when an oil begins to look bleached, it is usually rancid. According to the mechanism of rancidification as proposed recently (3), chlorophyll or chlorophyll-like pigments in the oil serve as photosensitizers and react in the presence of light and air to form active HO:OH. It is believed that when this reaction takes place the oil starts to bleach and to become rancid. It is reasonable to believe that at this point, due to rancidity autoxidation, the chlorophyll value of the oil increases. This marks the beginning where a decrease takes place in the transfer of the energy of the added chlorophyll to the acceptor molecules. In other words, the acceptor molecules should begin to oxidize and thus decrease. This is borne out by experiment. It is quite possible that the slightest increase in chlorophyll value is the first indication of rancidity oxidation; that is, a forerunner of organoleptic rancidity. If that is true the chlorophyll test may be regarded as being more significant than any test so far devised.

The principle underlying the chlorophyll value method for evaluating the rancidity autoxidation follows a fundamental phenomenon of nature and is believed to be quantitative in reaction. An explanation of this phenomenon may be stated as follows:

(1) A fresh oil containing reactive substances (x), when examined under an ultra-violet light, shows a natural light-blue fluorescence due to the presence of the (x).
(2) Chlorophyll alone, under the same conditions, fluoresces red.
(3) When a fresh oil containing reactive substances (x) and added chlorophyll is placed under an ultraviolet light, the red fluorescence of the chlorophyll is quenched.
(4) When a rancid oil, in which the reactive substances (x) are oxidized, plus added chlorophyll is examined under an ultraviolet light, the red fluorescence of the chlorophyll persists. The lesser the amount of the reactive substances (x) remaining in the oil, the greater the intensity of the red fluorescence of the chlorophyll.

Unlike other tests that are based on the measure of certain compounds evolved during the development of rancidity, e.g., fatty acids, peroxides, aldehydes, etc., the proposed method is virtually a measure of the reactive substances (as yet unclassified) left in the oil and still unchanged by photochemical oxidation. A low chlorophyll value means that the reactive substances of the oil have undergone little or no oxidation with respect to the development of rancidity and the oil is organoleptically considered fresh. A high chlorophyll value of that particular oil which has become rancid means that the reacting substances have become oxidized with a corresponding loss in quenching power. The degree of rancidity is indicated by the number of c.c. of oil required to quench a definite amount of standard chlorophyll.

Crude oils have a low chlorophyll value due presumably to the presence of an abundance of the reactive substances. Refined oils have a higher chlorophyll value while a finished oil usually has a still

[1] Food Research Unit Contribution No. 511.

higher chlorophyll value, indicating that the reactive substances may have been largely lost during refining. The chlorophyll value end point of a "finished" oil is easy to determine. However, for crude and refined oils the presence of certain substances that fluoresce yellow under a mercury light make it more difficult to determine their chlorophyll values. It is well known that the degree of refining has a great influence on the induction period. As the induction period is affected by this refining process, there is the possibility of refining an oil to a known chlorophyll value. An oil with a low chlorophyll value should have a longer induction period than one with a high chlorophyll value.

Equipment and Reagents

Any high intensity mercury vapor lamp equipped for fluorescence studies is suitable for use in estimating chlorophyll values.

The magnesium chlorophyll that was used in these investigations is of the fluorescing type. Standard "A" solution is made with 0.3 gm. of magnesium chlorophyll made up to 200 c.c. with non-fluorescing mineral oil. It must be kept from *all light*.

A second standard "B," which must be prepared for each variety of oil examined, is made by adding first a certain quantity of chlorophyll to the oil and then bringing the oil solution to the neutral point by adding chlorophyll standard "A" solution drop by drop until the final solution, when examined under the ultraviolet lamp, gives a neutral color which is just short, by one drop, of giving a pink fluorescence. This standard must be kept from *all light*, preferably in a refrigerator.

Other Apparatus and Material

(a) Non-fluorescing mineral oil for making up standard "A."
(b) Burette graduated in 1/20 c.c. for standard "A."
(c) Burette graduated in 1/20 c.c. for holding oil to be tested.
(d) Porcelain crucibles of 5 or 10 c.c. capacity in which to carry out test.
(e) Stirring rod for mixing standard "A" and oil.

Method

Run 0.250 c.c. of standard "A" solution into a crucible. Titrate with oil under examination until the neutral point is reached, as determined by matching the glow of the oil with standard "B" when both are placed under a mercury lamp equipped for fluorescence studies. The number of c.c. of oil needed to match standard "B" is called the "chlorophyll value."

A qualitative method for the detection of rancidity based upon the chlorophyll value has been devised as follows:

In the case of "finished" cottonseed oil, take 2 c.c. of oil in a porcelain crucible and to this add 0.1 c.c. of standard "A" chlorophyll solution. Stir thoroughly and observe the character of fluorescence under the ultraviolet lamp equipped for fluorescence studies. For 0.1 c.c. of standard chlorophyll 2 c.c. of fresh cottonseed oil is usually just enough to produce the neutral color under the ultraviolet lamp. However, if the oil is rancid 0.1 c.c. of chlorophyll will continue to fluoresce red and the shade of red will depend on the progress of oxidation.

In this work duplicate determinations may be run by adding another aliquot of chlorophyll standard solution to the same crucible containing the determination of the first test and then titrating with the oil as before.

For those who may have difficulty in matching the neutral standard exactly, a "lantern yellow" polished glass color filter 3⅛ inches square, will appreciably assist the eye to match the pink fluorescence of the standard and the samples while being observed under the lamp. However, unless the most accurate information is desired, one or two drops over or under the end-point will not make a serious difference in the chlorophyll value.

Experimental

Considerable experimentation has been done in order to determine the usefulness of the chlorophyll value as a measure of autoxidation. Finished oil has generally been used. In one experiment, duplicate samples of finished cottonseed oil were prepared in two Erlenmeyer flasks, for exposure to light of an east window of which one was protected with sextant green paper and the other was unprotected. The chlorophyll values and peroxide values were determined at certain intervals over a period of three months. (The Kreis test proved to be valueless for following the oxidation of the oil and consequently was dropped after a few tests.) See Table I.

TABLE I

The Chlorophyll and Peroxide Values of "Finished" Cottonseed Oil, Protected and Unprotected From Light of an East Window

Length of exposure Days	Wrapped in green		Unprotected	
	Chlorophyll value	Peroxide value	Chlorophyll value	Peroxide value
Initial 0	2.2	3.0	2.2	3.0
2	2.1	6.0	3.9SR	7.5SR
4	2.0	11.5	5.2R	14.5R
5	2.1	15.0	6.8R	18.0R
6	2.1	17.5	7.5R	22.0R
7	2.1	20.0	7.6R	26.0R
19	2.2	45.5	....	....
25	2.1	60.0	....	....
32	2.2	65.0	....	....
39	2.6	74.0	....	....
47	2.6	83.0	....	....
55	3.6SR	90.5SR	....	....
60	3.8R	97.5R	....	....
67	3.8R	102.5R	....	....
75	6.6R	110.0R	....	....
81	6.7R	125.5R	....	....

R = rancid, as determined organoleptically.
SR = slightly rancid.

In the course of this study, an experiment was conducted in order to test the behavior of an oil that had been protected from light for 25 days by a green filter. The oil at that time had attained a peroxide value of 60.0 and a chlorophyll value of 2.1. The oil was divided into two portions; one was exposed to light unprotected while the other was protected by a green wrapper. The results of this experiment are recorded in Table II.

TABLE II

The Chlorophyll and Peroxide Values of "Finished" Cottonseed Oil Which Had Been Protected With a Green Wrapper
(See Table I)

Length of exposure Days	Protected with green		Unprotected	
	Chlorophyll value	Peroxide value	Chlorophyll value	Peroxide value
Initial 0	2.1	60.0	2.1	60.0
4	2.2	68.5	7.6R	79.0R
7	2.2	67.3	7+R	112.8R

R = rancid, organoleptically.

The next experiment was conducted in the same manner with eight different samples of finished cottonseed oil all having different initial chlorophyll and peroxide values. The Kreis test was omitted because of its lack of significance. The results are shown in Table III.

The effect on the chlorophyll and peroxide values of heating oils or of using them for deep frying likewise has been studied. The samples of oils used in this experiment were collected from a local potato chip factory and are representative of oils used in deep frying under commercial conditions. The results of this experiment are shown in Table IV.

TABLE IV

The Effect of Heating or Deep Frying on Chlorophyll and Peroxide Values

History of the cottonseed oil	Before exposure to light		After 13 days' exposure to light	
	Chlorophyll value	Peroxide value	Chlorophyll value	Peroxide value
No. 1, Fresh oil, unused	2.4	2.0	3.9R	15.5R
No. 2, Fresh oil, heated to 200° F	2.4	2.5	3.4R	19.0R
No. 3, Fresh oil, heated to 300+° F	2.4	2.5	3.4R	16.0R
No. 4, Oil after frying one hour	1.4	4.5	2.0R	13.5R
No. 5, Oil after frying two hours	1.1	1.5	1.9R	9.0R
No. 6, Oil after frying three hours	1.1	2.0	1.7R	10.0R
No. 7, Oil after frying four hours	1.1	2.0	1.7R	9.5R
No. 8, Oil after frying five hours	1.1	1.5	1.6R	8.0R
No. 9, Oil after frying six hours	1.0	1.5	1.5R	1.10R
No. 10, Oil after frying seven hours	0.8	2.0	1.7R	9.0R
No. 11, Oil after frying eight hours	0.8	1.0	1.3R	9.5R
No. 12, Oil after frying nine hours	0.8	1.5	1.3R	10.0R
No. 13, Oil after frying ten hours	0.8	1.5	1.3R	10.5R
No. 14, Oil after frying 10½ hours (1½ bbls. new oil added)	0.8	2.0	1.4R	10.5R
No. 15, After cooling overnight	0.9	11.0	1.4R	10.5R
No. 16, After frying two hours	0.6	1.5	0.9R	9.0R
No. 17, Part of oil used three weeks	0.6	11.5	1.1R	22.0R
No. 18, Same as No. 1, kept in 130° C. oven two weeks	0.2VR	5.0VR	....	....
No. 19, Same as No. 17, kept in 130° C. oven two weeks	0.15VR	5.5VR	....	....

R = rancid, organoleptically.
VR = very rancid, organoleptically.

In order to determine the sensitivity of the chlorophyll value test in detecting rancid oil added to fresh oil, increasing amounts of rancid oil having a chlorophyll value of 12.6 were added to decreasing amounts of a fresh oil whose chlorophyll value was 2.9. The results obtained in the chlorophyll value test are shown in Table V.

A number of "finished" cottonseed oils were then examined for their chlorophyll values, which were found to vary from 1.70 to 3.05. Assuming that the induction period of oils might vary inversely with the chlorophyll value, the following method was devised to test this assumption:

Six drops of the oils to be tested were added to strips of blotting paper of the same size. The individual strips were then placed in bottles of the same shape and size. These strips were irradiated, in the closed bottles, with one CX Mazda lamp. In that way the gaseous constituents which were evolved during irradiation were confined within the bottles, making it quite easy to detect any organoleptic differences. The samples with chlorophyll values of 1.70, 1.85, 1.90 after a certain time of exposure, were not rancid, while the samples with higher chlorophyll values, namely, 2.75, 2.85, 3.05, were definitely rancid.

TABLE V

The Effect on the Chlorophyll Value of Adding Rancid Oil to a Fresh Oil

Number	c.c. Fresh oil used	c.c. Rancid oil used	Chlorophyll value found	Chlorophyll value calculated
1	10	0	2.9	2.90
2	9	1	3.1	3.14
3	8	2	3.5	3.42
4	7	3	3.7	3.77
5	6	4	4.2	4.19
6	5	5	4.4	4.72
7	4	6	5.4	5.40
8	3	7	6.3	6.30
9	2	8	7.4	7.55
10	1	9	8.8	9.43
11	0	10	12.6	12.60

TABLE VI

Chlorophyll Values of "Finished" Cottonseed Oil as Received From Various Companies and Arranged in Descending Order of Stability

Samples from various companies	Chlorophyll values	Peroxide values
D	3.15	1.5
B	3.35	1.5
F	4.30	1.5
E	4.40	3.0
A	6.95	1.5

TABLE III

Chlorophyll Values of Various Samples of "Finished" Cottonseed Oil After Exposure to Light

Days exposure	Sample No. 1				Sample No. 2				Sample No. 3				Sample No. 4			
	Green wrapper		Unprotected		Green wrapper		Unprotected		Green wrapper		Unprotected		Green wrapper		Unprotected	
	Chlorophyll value	Peroxide value	Chlorophyll value	Peroxide value	Chlorophyll value	Peroxide value	Chlorophyll value	Peroxide value	Chlorophyll value	Peroxide value	Chlorophyll value	Peroxide value	Chlorophyll value	Peroxide value	Chlorophyll value	Peroxide value
Initial values																
0	2.1	17.5	....	....	2.4	25.5	....	....	3.3	17.0	....	....	2.6	20.0	....	....
1	3.0	22.75	7+R	31.0R	3.0	29.5	13.0R	38.0R	4.0	23.5	21.0R	29.0R	3.0	25.5	16.0R	32.5R
3	3.0	27.0	18.0R	92.0R	3.0	33.0	16.0R	54.5R	4.0	28.0	30.0	47.0	4.0	28.0	27.0	49.5
6	3.0	33.5	Discontinued		3.0	39.0	....	....	Lost		....	....	4.0	33.0	....	....
13	3.0	53.5	....	....	3.0	58.5	....	....	....	....	....	....	3.0	50.5	....	....
19	3.5	69.0	....	....	4.0	78.0	....	....	....	....	....	....	3.0	61.5	....	....
26	4.0	69.3	....	....	7.0R	92.5R	....	....	....	....	....	....	7.0R	63.5R	....	....
	Sample No. 5				Sample No. 6				Sample No. 7				Sample No. 8			
Initial values																
0	3.5	20.5	....	....	3.5	14.0	....	....	2.0	29.0	....	....	3.1	10.0	....	....
6	4.0	28.0	29.0R	32.0R	4.0	23.5	26.0R	32.5R	2.5	37.5	11.0R	39.0R	4.0	19.0	19.5R	26.0R
14	4.5	38.0	....	....	4.0	30.5	....	....	2.0	48.5	....	....	4.0	28.5	....	....
19	4.0	45.0	....	....	4.0	38.0	....	....	2.0	57.5	....	....	4.0	36.0	....	....
27	6.0SR	53.5SR	....	....	6.0SR	45.0SR	....	....	3.0	65.0	....	....	5.0SR	40.5SR	....	....
33	6.5R	58.5R	....	....	8.0R	51.0R	....	....	3.0	74.5	....	....	5.5R	45.5R	....	....
42	7.0R	71.0R	....	....	7.0R	61.5R	....	....	3.0	83.0	....	....	5.5R	54.5R	....	....

R = rancid, organoleptically.
SR = slightly rancid, organoleptically.

Another experiment was conducted to learn the effect of the presence of metal in oil. Copper wire was placed in each of two samples of cottonseed oil. One sample was exposed to light. The other sample was placed in a dark closet. Eleven days afterward the chlorophyll value was determined. The first sample had a chlorophyll value of 7.0 and was rancid, while the one in the dark was 2.7 and sweet. The initial value was 2.0.

Discussion

Chlorophyll acts as a photosensitizer (4) (5) and when exposed to light in the presence of the reacting substance found in an oil it is able to transfer light energy into chemical energy. Thus, when an oil is treated with chlorophyll and is exposed to light it soon develops rancidity. A low intensity of natural fluorescence of the oil after irradiation indicates a greatly reduced number of molecules of the reacting substances present in the oil. This is believed to be a result of autoxidation. Since the reacting substances in the oil are not apt to oxidize completely, one is able to estimate the unchanged portion quantitatively. Chlorophyll fluorescence is quenched in proportion to the amount of the reacting substance present. Therefore, as an oil oxidizes, the power to quench the fluorescence of the photosensitizer diminishes proportionately. Advantage is taken of this phenomenon to determine the progress of oxidation by titrating a definite quantity (0.250 c.c.) of standard chlorophyll solution with the oil in question. The larger the number of c.c. of oil needed to quench the standard chlorophyll, the more oxidized is the oil with respect to the development of rancidity. Thus, the number of c.c. of an oil required to quench a measured quantity of standard chlorophyll is called the "chlorophyll value" of an oil. The higher the chlorophyll value the less reactive substances there are in the oil and vice versa. This value is not a direct proportion with respect to the freshness of an oil, but is an inverse relationship. However, it is in direct relationship to the oxidized reactive substances of an oil.

The initial Kreis test on the oil used in Table I produced a slight pinkish color even though the oil was organoleptically fresh. After one day's exposure to light both oils (one sample protected and the other unprotected from light) became slightly more pink, the unprotected sample being noticeably more so. After four days' exposure to light, the oil being still fresh organoleptically, the Kreis test was discontinued because the color, increasing in intensity as the experiment continued, gave a false indication of the state of the oil with reference to the development of rancidity as measured by the organoleptic tests and the chlorophyll value test. The protected oil maintained a chlorophyll value of 2.0 to 2.2 for 32 days without becoming rancid even though the peroxide value had increased from 3 to 65. On the other hand, the unprotected sample after only four days' exposure was rancid, the chlorophyll value having increased from 2.2 to 5.2 and the peroxide value from 3.0 to 14.5.

These results (Table I) show, in other words, that when an oil is protected by a sextant green wrapper, the chlorophyll value remains essentially the same until the oil begins to become rancid, at which stage there is a sudden rise in chlorophyll value. As the degree of rancidity increases the chlorophyll value increases likewise. As has been shown in previous experiments, the peroxide values of unheated oils or fats protected from light do not necessarily parallel the development of rancidity. When the sample of oil protected by green wrapper finally became rancid, its peroxide value was six times as high as that of the unprotected sample when it became rancid (Table I).

The results included in Table II are significant because they show again that so long as the oil which is protected from harmful light remains fresh the chlorophyll value continues practically the same, even though the peroxide value increases.

The characteristics of the samples of cottonseed oil shown in Tables III (a) and VI (b) as judged by the chlorophyll and peroxide values, are essentially the same as those shown in Table I. The results indicate that the chlorophyll value of an oil bears a definite relation to the induction period. It is apparent also that the peroxides, aldehydes, etc., do not interfere with the chlorophyll value. The constituents that are related to the development of rancidity seem rather to be those that affect the chlorophyll value chiefly, and not until these constituents are altered does the chlorophyll value increase.

The effect of heat, as in deep frying in oils, on the chlorophyll and peroxide values is shown in Table IV. Under such heat conditions, the significance of the chlorophyll value seems to be quite different from that of unheated oils. Heating of an oil seems to increase its ability to quench the fluorescence of the chlorophyll and as a consequence the more the oil is heated the lower is the chlorophyll value, the opposite of what might have been expected. On the other hand, it has been observed that even though the chlorophyll value decreases, as it does with continued heating of the oil, this same low chlorophyll value begins to increase as soon as the oil is exposed to light, indicating that due to light there is a loss of the reacting substances. Thus far, it has been impossible to interpret results of this kind or to state how the chlorophyll value test can be utilized by the potato chip-, doughnut-, and other industries using oil or fat for frying.

The effect on the chlorophyll value of adding rancid oil to a fresh oil, as shown in Table V, seems to indicate that the mechanism underlying the proposed test for the autoxidation of an oil is sensitive enough to be affected by the addition of even a small amount of rancid oil to a fresh oil. In this case a total of 10 c.c. of a mixture of fresh and rancid oils was used. The chlorophyll value of a mixture of oils of different chlorophyll values may be calculated in accordance with the following formula:

$$\frac{10}{\frac{\text{no. c.c. fresh oil}}{\text{chlorophyll value (fresh oil)}} + \frac{\text{no. c.c. rancid oil}}{\text{chlorophyll value (rancid oil)}}} = \text{Calculated chlorophyll value.}$$

The accuracy of this titration method is shown by the close agreement of the determined chlorophyll values with the theoretical values.

(a) These samples came from one company.
(b) These samples came from various companies.

It is worthy of note that according to the chlorophyll value test the oxidative type of rancidity, developed in the presence of metals, is apparently the same as that catalyzed by light. Our experiments seem to lead to the conclusion that this type of oxidative rancidity may not necessarily be associated with the production of the usual constituents of a rancid oil such as peroxides, fatty acids, and aldehydes, which products develop even in a fresh oil in the absence of light, but that it may be a form of oxidation closely related with the destruction of the reactive substances.

The variation in the chlorophyll value of oils from different sources seems to depend upon the conditions of refining (see Tables III and VI). It is well known that the induction period of an oil decreases with the degree of refinement. According to our experiments, the chlorophyll value increases in the same order. Since the chlorophyll value is believed indicative of the keeping quality of normal oil, it would seem entirely feasible for oil companies to adopt a certain chlorophyll value as a control factor in the refinement of their oils.

Another significant feature of the chlorophyll value test for rancidity is that it parallels quite well the indications obtained by the organoleptic method. Furthermore, our results show that as long as the oil is protected from light and remains fresh, the chlorophyll value remains substantially unchanged. Oil in the original can which was kept in the refrigerator and examined from time to time over a period of five months was found to retain essentially the same chlorophyll value throughout that time. The chlorophyll value seems to increase appreciably only when rancidity appears. Therefore, it is possible that all other tests have failed as a basis of estimating the development of rancidity because the products used as a measure of this form of spoilage may have little or no bearing on oxidative rancidity itself. In fact, the aldehydes, fatty acids, and peroxides may be the by-products of some other reaction than rancidity. It is suggested that the compound which is capable of autoxidation and which is associated with rancidity, is that substance in the oil which is capable of quenching the fluorescence of added chlorophyll. This thought naturally furnishes a new line of attack for the investigation of the rancidity problem.

Conclusions

1. The chlorophyll value of normally refined oils seems to indicate the degree of their autoxidation with respect to rancidity. It is dependent upon the property of the reacting substances of the oil to fluoresce.

2. The chlorophyll value of an oil remains essentially the same as long as the oil is organoleptically sweet. As it increases rancidity appears.

3. The chlorophyll value is a more significant and a more indicative means of expressing the degree of autoxidation of an oil with respect to rancidity than is the peroxide value obtained by whatever method, because the former measures the unoxidized or quenching portion of the reactive substances while the latter may be produced in an oil even though it is not rancid.

4. Experiments show that the lower the chlorophyll value for a given oil normally treated, that is, without excessive heat, the longer is the induction period of that oil.

5. Peroxides and aldehydes that are present in oils, either protected or unprotected from light, apparently do not interfere with the determination of the chlorophyll value.

6. Peroxides and aldehydes which are developed in oils in the presence of finely divided metals likewise do not interfere with the determination of the chlorophyll value.

7. Results seem to indicate that rancidity is a form of oxidation which is not necessarily correlated with the production of peroxides, fatty acids, and aldehydes.

8. A significant feature of the chlorophyll value test is that it parallels very closely the results obtained by organoleptic methods used to evaluate the development of rancidity.

9. The chlorophyll value test may be very accurately determined because it depends quantitatively upon the property of the reacting substances to quench chlorophyll fluorescence and upon the property of the chlorophyll fluorescence to persist as the reactive substances disappear.

10. The chlorophyll value is believed to be indicative of the keeping quality of a normal oil. Therefore, it would seem entirely feasible for oil companies to adopt a certain chlorophyll value as a control factor in the refinement of their oils.

BIBLIOGRAPHY

(1) Coe, Mayne R., Oil and Soap, *16*, 146-7 (1939).
(2) Franck, J., and Wood, R. W., Jour. Chem. Physics, *4*, 551-60 (1936).
(3) Coe, Mayne R., Oil and Soap, *15*, 230-6 (1938).
(4) Hirschlaff, E., Fluorescence and Phosphorescence, p. 26. Published by The Chemical Publishing Co., Inc., 1939.
(5) Coe, Mayne R., Oil and Soap, *15*, No. 9, pp. 230-6 (1938).