with the test. Heated oils may interfere. However, such oils are not likely to be present in olive oil sold for food purposes.

Note:

Since this paper was written there has been reported in the July issue of Food Industries,[13] a method used by the Federal Food and Drug Administration for the last few months.

This method has been tried by the authors who find that the color resulting does not last long enough to permit of easy comparison with standards, and second that some olive oils give a pink color reaction which can be mistaken as indicating the addition of some tea seed oil.

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Photochemical Studies of Rancidity: Induction Period of Protected and Non-Protected Oils*

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THE induction period of oils or fats and its significance in determining their keeping quality have long been active subjects for investigation. Usually in the process of refining and in handling for the market, oils are more or less exposed to deleterious agents, especially finely divided metals, as well as unfavorable temperature and light conditions, all of which play an important part in altering the induction period.

Under normal conditions, an oil of good keeping quality is characterized by a long induction period and a low peroxide value. Under such conditions, when the oil is not in contact with metals, the peroxide value will increase to about 30 or 60 before the oil becomes rancid. This usually takes from one week to one month. If an oil is exposed to light of more than ordinary intensity, under certain conditions the induction period may be shortened to a few days only. In general, as rancidity develops the peroxide value increases. Consequently, many investigators have undertaken to correlate rancidity and the induction period with the peroxide value. Numerous observations have shown, however, that oils or fats protected from light, for example, by means of a green wrapper or container, may have a peroxide value equal to or even greater than an unprotected oil or fat that has become rancid and still be organoleptically free from rancidity.[1]

*Food Research Contribution No. 299.

[1]1934. Coe, Mayne R., and J. A. LeClerc. Photochemical Studies of Rancidity: Peroxide Values of Oils as Affected by Selective Light. Ind. Eng. Chem., Vol. 26, Page 245.

Preliminary Experiment

Corn oil through which moisture-laden air[1] had been bubbled for six months, during which time it had been protected from light with opaque black paper, was transferred to two tubes, one of which was wrapped with protective green (delimited by 4,900 to 5,800 Ångström units) paper while the other was unprotected. The tubes were then exposed to the light in an east window. After such exposure for about seven weeks, it was found that, although the peroxide value of the two samples was about the same, the unprotected sample was rancid while the oil protected by green paper was still free from rancidity. This preliminary experiment indicated that the reaction which gives rise to the rancid taste or odor may have no connection with the formation of peroxides. That the development of rancidity in these experiments is a photochemical change is also indicated by the fact that when oils are protected from harmful light the original mobility and color of the oil, as well as the taste and odor, are to a large extent preserved.

[1]A very adverse treatment.

The results noted above have raised the questions: (1) "What influence does protection from harmful light have on the induction period of a fresh oil?" (2) "Does 'protective green,' as defined above, extend the keeping quality or induction period of an oil?" (3) "Does the process concerned with the development of rancidity begin when the oil is first exposed to light, i.e., does this mark the beginning of the induction period?" (4) "Does the peroxide value of a protected oil modify the induction period of that oil when the oil is exposed to light?" It may be possible to answer some, if not all, of these questions.

Experimental

An experiment was made to determine whether rancidity develops at about the same time in a fresh oil as in an oil which, for a time, had been exposed to light but had been protected by this special green wrapping. Cottonseed and corn oils were used. The initial peroxide value of the former was 1.0; that of the latter was 1.5.

Two eight-ounce bottles of clear glass containing cottonseed oil and two containing corn oil were each provided with a two-hole cork stopper. One bottle of each set was wrapped with protective green paper; the remaining bottle of each set was not wrapped. Through one hole of the stopper was inserted a glass tube which was connected with a flow meter delivering six liters of moist air per hour. The apparatus was adjusted so that, as nearly as possible, all four samples received the same amount of air. This experiment lasted five weeks, during which time the samples were exposed to the light of a south window. Each week the peroxide values were determined, and an organoleptic test for rancidity was made. These tests were continued until the oil protected by the green wrapper had developed a peroxide value equal to that of the unprotected oil at the time rancidity was first noted. At that stage the oil that had been protected was exposed without wrappers to light and at the same time and under the same conditions fresh samples of cottonseed oil and corn oils, respectively, taken from the original cans which had been kept in a household mechanical refrigerator, were exposed to light. The initial peroxide value of the fresh cottonseed oil was 3; that of the corn oil was 11. The time required for each of these samples to become rancid was noted. The data in Tables I and II show the results of this experiment.

TABLE I—PEROXIDE VALUES OF PROTECTED AND UNPROTECTED OILS

Length of Time of Exposure Days	Cottonseed Oil: Clear Glass	Cottonseed Oil: Green Wrapper	Corn Oil: Clear Glass	Corn Oil: Green Wrapper
0	1	1	1.5	1.5
7	36 (SR)	9	22	12
14	68 (R)	19	38	19
20	89 (R)	26	49 (SR)	25
35	132 (R)	48	93 (R)	41
42	192 (R)	60	104 (R)	50

SR=Slightly rancid.
R=Rancid.

TABLE II—PEROXIDE VALUES IN RELATION TO INDUCTION PERIODS

Length of Time of Exposure Days	Cottonseed Oil: Fresh	Cottonseed Oil: (Previously protected with green)	Corn Oil: Fresh	Corn Oil: (Previously protected with green)
0	3	60 (a)	11	50 (a)
10	31	60	23	52
17	51 (R)	81 (R)	33	52
24	..	..	44	65
31	..	..	54 (R)	78 (R)

(a) These samples had been protected with a green wrapper for 42 days previously.
R=Rancid.

A variation of this experiment was conducted with new lots of cottonseed and corn oils and also with peanut oil. Air was not bubbled through these oils. This time, samples of the respective oils were taken at various stages of peroxide development from the bottles which had been protected with green wrappers, and these were exposed to the light in an east window along with fresh samples of the same oils taken from the refrigerator. Tables III and IV show the results of this experiment.

TABLE III—PEROXIDE VALUES OF PROTECTED AND UNPROTECTED OILS

Length of Time of Exposure Days	Cottonseed Oil: Clear Glass	Cottonseed Oil: Green Wrapper	Corn Oil: Clear Glass	Corn Oil: Green Wrapper	Length of Time of Exposure Days	Peanut Oil: Clear Glass	Peanut Oil: Green Wrapper
0	2.5	2.5	0.25	0.25	0	0.0	0.0
17	23 (R)	14*	24	5	..	..	..
24	37 (R)	22	35	7	7	8	4
41	67 (R)	42*	59	18*	31	62 (R)	9*
48	78 (R)	48*	66 (R)	23	46	..	16
62	..	68*	..	37*	74	..	28*
91	..	..	..	72*	117	..	48*

R=Rancid.
*=Peroxide value when sample was taken for exposure with fresh samples from the refrigerator.

TABLE IV—PEROXIDE VALUES IN RELATION TO INDUCTION PERIODS

Test No.	Initial Peroxide Value: Fresh Oil	Initial Peroxide Value: Protected Oil	Exposure After Removal of Wrapper, Days	Peroxide Value: Fresh Oil	Peroxide Value: Protected Oil
Cottonseed Oil					
1	3	14	7	28 (R)	46 (R)
2	3	42	7	26 (R)	61 (R)
3	5	48	7	29 (R)	86 (R)
4	7	68	7	34 (R)	99 (R)
Corn Oil					
1	Less than 1.5	18	7	Not Rancid	Not Rancid
1	Less than 1.5	18	14	79 (R)	102 (R)
2	Less than 1.5	37	6	Not Rancid	Not Rancid
2	Less than 1.5	37	19	85 (R)	136 (R)
3	Less than 1.5	72	7	Not Rancid	Not Rancid
3	Less than 1.5	72	14	86 (R)	152 (R)
Peanut Oil					
1	Approximately ..2	9	8	Not Rancid	Not Rancid
1	Approximately ..2	9	13	80 (R)	103 (R)
2	Approximately ..4	28	6	Not Rancid	Not Rancid
2	Approximately ..4	28	14	149 (R)	205 (R)
3	Approximately ..5	48	6	Not Rancid	Not Rancid
3	Approximately ..5	48	9	50 (R)	116 (R)

R=Rancid.

Discussion

The induction period of an oil, as usually understood, acquires a new interpretation in view of the experiments here recorded. Our results show (Table I) that when a sample of oil protected from light had developed a peroxide value equal to that of an unprotected sample of the same oil when rancidity was first noted, and this protected oil was afterward exposed to clear daylight along with a fresh sample of the same oil, the two became rancid at about the same time. Even though moist air was bubbled through the oil, the green wrapper provided protection from photochemical action.

A variation of this experiment was carried out with cottonseed oil, corn oil and peanut oil (Table IV). Samples of these oils were protected with green wrappers until they had acquired certain peroxide values and were then exposed to daylight along with fresh samples of the same oils. In each instance, the fresh and the previously protected samples became rancid after approximately the same length of time.

One sample of cottonseed oil protected from light had acquired a peroxide value of 14 (Table IV), another similarly protected had developed a peroxide value of 68. Both these samples were exposed to light beside fresh samples of cottonseed oil taken from the original can kept in the refrigerator. In seven days' exposure all four samples had become rancid, indicating that oils which have been protected from light, even though they have acquired a relatively high peroxide value, become rancid in approximately the same time as do fresh samples of oil when both are exposed to light. This is very significant, because if the peroxide value were a measure of the susceptibility of the oil to rancidity, the cottonseed oil which had a peroxide value of 14 would have taken appreciably longer to develop rancidity when exposed to light than the one having a peroxide value of 68.

The data given in Table IV show further that the four samples fresh from the refrigerator exposed to light at different times acquired nearly the same peroxide value before they became rancid. Also, the difference between the peroxide value of the previously protected samples at the time they were exposed to light and the peroxide value at the time they became rancid is strikingly near the peroxide value of the fresh refrigerator samples when they had become rancid.

This seems to suggest that the "compound" capable of becoming rancid remained unchanged during the time the oil was protected from harmful wavelengths of light, regardless of peroxide formation. On exposure of the oil to light the "compound" became susceptible to photochemical action leading to the development of rancidity.

It appears, therefore, that the normal induction period of an oil is influenced largely by the length of exposure and intensity of the light to which the oil has been subjected. The results obtained also indicate strikingly that the "compound" capable of becoming rancid is not so much affected by the development of peroxide as by exposure to light.

It is quite likely that different samples of the same kind of oil vary in their induction period because during the process of manufacture and marketing they have been exposed to different intensities of light for different lengths of time. Lea[1] has shown that once an oil or fat has been exposed to light for even a short period, placing it afterwards in the dark will not stop the development of rancidity. If an oil has had adequate protection from light the peroxide value developed at room temperature should not be given too great weight in estimating its induction period, for it is apparent that the induction period really begins when the oil is first exposed to light, irrespective of its peroxide value, and ends when the oil gives an organoleptic test for rancidity. The length of the induction period is also dependent to a greater degree than has been recognized heretofore upon the amount of light previously absorbed. Consequently protection from light is a potent means for extending the usual period during which an oil remains fresh.

Conclusions

1. The induction period of an oil is appreciably lengthened when the oil is kept in the dark, and it is likewise lengthened when oils are protected from light by a green wrapper delimited by 4,900 to 5,800 Ångström units.

2. An oil which has been protected from light for a certain period and then exposed to light will develop rancidity in about the same time as will a fresh sample of the same oil exposed to light under the same conditions.

3. The development of peroxides in oils protected from light by means of a green wrapper is no indication of the rate at which rancidity will develop in unprotected oils. The idea heretofore held that the time required for rancidity to develop is associated with the peroxide value is no longer tenable, except in the case of accelerated tests.

4. The results indicate that rancidity of an oil has no necessary correlation with the development of peroxides.

5. A high peroxide value in an oil does not mean that the induction period will be short. This is especially true if the oil has been adequately protected from light.

6. The time required for an oil which has been protected from light to become rancid is, under like conditions, the same regardless of the acquired peroxide value.

7. There is apparently a relationship (see Table IV) between the numerical increase in the peroxide value of an oil previously protected from the time it is exposed to light until it becomes rancid and the peroxide value of a fresh sample of the same oil when it becomes rancid.

[1]Effect of light on Oxidation of Fats. Lea, Colin H. Proc. Roy. Soc. (London), B 108, page 175-89 (1931).

Oil Resistant Protective Coatings

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IN the storing and packaging of fats and oils there has long been a desire to procure an effective coating composition which would resist the penetration and be proof against the action of these substances. There are of course a number of products which are more or less suitable for this purpose, but nearly all of these possess one or more shortcomings. Relatively short useful life and high cost are the more prominent ones.

There are a number of substances, both inorganic and organic which have been used for this purpose; a variety of conditions dominating the choice as to when and where to use them. In this presentation we are particularly concerned with those types of products which will form a continuous non-porous or impervious adherent film on the container surface. The primary role played by these compositions is as a protector of the fat or oil, or the products containing same. If the material from which the container is made is metal or similar impervious substance, then the coating composition serves only to prevent any possible reaction which may take place between oil and the container material. However, if the material from which the container is made is more or less porous, includes non-liquid tight joints and is of relatively low mechanical strength, then there is required of the coating com-