PHOTOCHEMICAL STUDIES OF RANCIDITY:

ANTIOXIDANTS VS. GREEN LIGHT PROTECTION

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WHILE the use of certain compounds for the purpose of inhibiting oxidation is old, it was not until the results of Moureu[1] and Dufraisse were published that a decided effort was made to find an antioxidant capable of delaying that form of oxidation known as rancidity. The problem of rancidity is a serious one because many of the oil-bearing foods, the annual production of which in the United States is valued at nearly two billions of dollars, are subject to this form of spoilage.

In many instances, the use of an antioxidant would be most advantageous. For that reason investigators are eagerly in search of a compound that is edible and at the same time has the ability to inhibit oxidation. Since there are a number of antioxidants which are used for delaying the oxidation of commodities other than foods, it occurred to the authors that a comparison of the protection afforded by some of the common antioxidants with that of protective green wrappers or containers might prove of interest.

Antioxidants: In dealing with the oxidation of oils and fats, it has been observed that the development of rancidity is accompanied by the formation of peroxides. An antioxidant added to oils or fats tends to prevent this peroxide formation. As the protective action of the antioxidant disappears, peroxides increase and rancidity develops. According to the conceptions of Moureu and Dufraisse with regard to antioxygenic activity, the peroxide A (O_2) (A being the auto-oxidizable substance and O_2 atmospheric oxygen) oxidizes the antioxygen B with the formation of a peroxide B (O) while it, itself, is transformed into another peroxide A (O). These two peroxides are then said to be mutually antagonistic and thus to destroy each other with the regeneration of the three original components A, B and O_2 in their initial state. A representation of antioxygenic action is

$$A + O_2 \rightarrow A(O_2);\ A(O_2) + B \rightarrow A(O) + B(O);\ A(O) + B(O);\ \rightarrow A + B + O_2$$

For direct oxidation of the antioxygen, the following is representative:

$$A + O_2 \rightarrow A(O_2);\ B + O_2 \rightarrow B(O_2);\ A(O_2) + B(O_2) \rightarrow A + B + 2O_2$$

Compounds which are known to exhibit antioxygenic action belong to the ortho- and para-dihydroxyphenols or their substitution products and to some of the unsaturated polybasic aliphatic acids. The antioxidants used in this investigation are: maleic acid, phthalic acid, hydroquinone, pyrogallol, cathechol and guaiacol.

Green Light: Certain wave lengths of radiation may act photo chemically upon substances that absorb it. This applies not only to foods and numerous other manufactured products, but also to numerous pure chemicals and certain pharmaceuticals. It has been found that certain oils and fats show strong absorption in the ultra-violet and blue regions and to a lesser extent in the yellow and red regions of the spectrum. Each part of the spectrum, however, can have an oxidizing or reducing effect, depending upon the nature of the light sensitive substances. In all cases the chemical action of light comes under the law of Grotthus[1] that only those rays of light which are absorbed can produce chemical action.

Thus, when oil-bearing foods subject to rancidity are enclosed in green wrappers of a proper shade, the wave lengths of light which promote rancidity—that is, those in the ultra-violet, blue and red regions, are absorbed by the wrapper or container instead of by the substance itself. Repeated experiments have established that certain commodities protected from light retain their color, freshness, flavor and aroma appreciably longer than when unprotected. However, up to the present time no data have been published showing a comparison of green light protection vs. antioxidants.

It is doubtful if oils or fats which have been heated to temperatures such as those used in frying potato chips and doughnuts and also in baking crackers and cookies and which may have been treated previously with an antioxidant would still remain free from rancidity when exposed to light. So far as we know this has not been determined. Experimental evidence shows that if commodities containing oil thus treated are enclosed in protective green wrappers, they will remain fresh for a much longer period owing to the protection afforded by the green container. Therefore, even though an acceptable antioxidant were found, it would no doubt still be advantageous to protect from light, either by total exclusion of light or by the use of green wrappers, foods that contain oils or fats treated with the antioxidant.

EXPERIMENTAL

In the first experiment, corn oil having an initial peroxide value of 3.0 was used. To 100 cc. samples were added 0.1 per cent of hydroquinone and maleic acid, respectively. One 50-cc. portion of each sample containing the antioxidant was transferred to a clear bottle and wrapped with protective green paper, and the other portion was kept in a clear bottle unwrapped. Untreated oil samples, one in a clear bottle unwrapped, and the other in a clear bottle wrapped in green paper, were exposed to light under the same conditions. The peroxide values obtained after 72 days' exposure are given in Table 1.

A second experiment was conducted in the same manner with

[1]The Negative Catalysis of Auto-oxidation, Antioxygenic Activity, by Charles Moureu and Charles Dufraisse, in Jour. Soc. Chem. Ind., 47, 819-28, 1928.

[1]Scientific Memoirs, by John W. Draper, p. 412 (1878).

TABLE I

Comparison of the Peroxide Values of Untreated Corn Oils and Corn Oils to Which 0.1 gm. Antioxidant Had Been Added. Room Temperature.

Initial Peroxide Value	Original oil in Refrigerator 40° F.	Untreated Clear bottle	Untreated Green wrapped bottle	Hydroquinone Clear bottle	Hydroquinone Green wrapped bottle	Maleic Acid Clear bottle	Maleic Acid Green wrapped bottle
3.0	18.9	186.0*	85.3	74.9*	18.5	24.0*	18.9

* Organoleptically rancid.

corn oil having an initial peroxide value of 1.5 In this experiment 0.01 per cent of the antioxidants was added and the oils were exposed to 12 days of June sunlight. A comparison of peroxide values is shown in Table 2.

TABLE 2

Comparison of the Peroxide Values of Untreated Corn Oils and Corn Oils to Which 0.01 Percent of Antioxidant Had Been Added. Room Temperature.

Initial Peroxide Value	Original Oil in Refrigerator 40° F.	Untreated Clear bottle	Untreated Green wrapped bottle	Hydroquinone Clear bottle	Hydroquinone Green wrapped bottle	Maleic Acid Clear bottle	Maleic Acid Green wrapped bottle	Pyrogallol Clear bottle	Pyrogallol Green wrapped bottle	Phthalic Acid Clear bottle	Phthalic Acid Green wrapped bottle
1.5	12.4	65.0*	14.4	33.4*	6.5	49.0*	7.5	23.5*	4.0	54.2*	7.5

* Organoleptically rancid.

A third experiment was conducted essentially in the same manner with corn oil having an initial peroxide value of 1.5. Peroxide values were determined after 41, 68, and 154 days, respectively. A comparison of antioxidant protection is shown in Table 3.

TABLE 3

Comparison of the Peroxide Values of Untreated Corn Oils and Corn Oils to Which 0.01 Percent Antioxidant Had Been Added. Room Temperature.

Days Exposed	Initial peroxide Value	Original Oil in Refrigerator 40° F.	Untreated Clear bottle	Untreated Green wrap'd bottle	Hydroquinone Clear bottle	Hydroquinone Green wrap'd bottle	Maleic Acid Clear bottle	Maleic Acid Green wrap'd bottle	Pyrogallol Clear bottle	Pyrogallol Green wrap'd bottle	Phthalic Acid Clear bottle	Phthalic Acid Green wrap'd bottle	Catechol Clear bottle	Catechol Green wrap'd bottle	Guaiacol Clear bottle	Guaiacol Green wrap'd bottle
41 days	1.5	6.0	57.0	20.5	44.8†	9.0	44.5*	9.0*	18.5	4.0	62.8*	17.5	55.0*	20.5	70.0*	27.0
68 days	..	11.5	138.0*	43.5	122.5*	19.5	122.0*	22.5	52.5†	8.0	151.5*	43.0	123.5*	40.0	173.0*	56.0
154 days	..	9.0	...	61.5	306.0*	23.0	286.5*	37.0	200.5*	7.5	322.0*	53.0	301.0*	44.0	...	...

*Organoleptically rancid. †Slightly organoleptically rancid.

In order to learn whether results similar to those obtained with corn oil could be obtained with an animal fat, lard was treated with the antioxidants used in the third experiment except guaiacol. The initial peroxide value was zero. These results are shown in Table 4.

TABLE 4

Comparison of the Peroxide Value of Untreated Lard and Lard to Which 0.01 Percent Antioxidant Had Been Added. Room Temperature.

Initial Peroxide Value	No. of Days' Exposure	Original Oil in Refrigerator 40° F.	Untreated Clear bottle	Untreated Green wrapped bottle	Hydroquinone Clear bottle	Hydroquinone Green wrapped bottle	Maleic Acid Clear bottle	Maleic Acid Green wrapped bottle	Pyrogallol Clear bottle	Pyrogallol Green wrapped bottle	Phthalic Acid Clear bottle	Phthalic Acid Green wrapped bottle	Catechol Clear bottle	Catechol Green wrapped bottle
0.0	21	0.0	•64.5*	1.5	11.0*	1.5	39.5*	1.5	8.0	1.3	19.0*	2.0	9.0*	1.5
...	83	0.0	139.0*	3.5	13.0*	3.0	97.0*	4.5	10.5	1.0	81.0*	3.5	11.5*	1.5

*Organoleptically rancid.

DISCUSSION

The foregoing tables indicate that the exclusion of injurious wavelengths of light under conditions of the experiments proved to be a more effective means of controlling the development of rancidity than the use of antioxidants. Pyrogallol seems to be an exception, especially in the case of lard (see Table 4), but obviously such an antioxidant has no place in food products. The commercial advantage of eliminating light, either entirely or by using protective green as a container or wrapper, is that foods retain their original flavor, aroma and color without the necessity of adding a foreign substance. The data show further that if a green wrapper is used in conjunction with an antioxidant, the peroxide formation is appreciably inhibited and the development of rancidity retarded. However, the experiments just reported indicate that organoleptic rancidity may nevertheless manifest itself even with a low peroxide value. An untreated oil or fat protected from light with green may have a higher peroxide value than an oil or fat which has been treated with antioxidants, and yet the rancid taste or odor may not develop in the former. From the data obtained it is evident that the development of rancidity does not always run parallel with the formation of peroxides, although peroxides are always present in rancid samples. The antioxidant seems to be mainly operative in checking peroxide formation.

The original fat or oil kept in the refrigerator at a low temperature and protected from light by its tin container remained fresh throughout the experiment. The peroxide value of this fat or oil varied but little, even five months after the can had been first opened.

Whether 0.01 or 0.1 per cent of the antioxidant was used, the peroxide formation and rancidity development was relatively the same. One objection to the antioxidants used, with the exception of pyrogallol, is their slight solubility in oil. Pyrogallol is easily soluble, and its marked antioxigenic properties may, in part, be accounted for by this intimate contact of the antioxidant with the unsaturated molecules in the oil.

Table 5 gives the relative protective factor of the antioxidants used compared with that of green paper after 41 days' exposure to light. The values are based on the formula devised by Greenbank and Holm:[1]

[1]Ind. Eng. Chem., **26**, 243, 1934.

TABLE 5

Protective Factors of Antioxidants as Compared with that of Green Paper.

	Maleic Acid	Phthalic Acid	Hydroquinone	Pyrogallol	Guaiacol	Catechol	Green Wrapper	Refrigerator
Table I Corn Oil.......	7.8	..	2.5	..	..	..	2.1	9.3
Table II Corn Oil.......	1.3	1.2	2.0	2.8	..	..	4.6	5.4
Table III Corn Oil.......	1.3	0.9	1.3	2.8	0.8	1.0	2.7	9.0
Table IV Lard	1.6	3.4	5.9	8.0	..	7.1	43.3	65.0

*Preliminary percentage for 1933 and 1934 computed on returns from more than 90 per cent of the privately-owned commercial light and power enterprises.
**Operating figures are not yet available as regards the years 1933 and 1934

Protective Factor=

$$\frac{\text{Millimoles of peroxide per kilogram of untreated oil}}{\text{Millimoles of peroxide per kilogram of treated oil}}$$

This formula cannot be applied to oils or fats that have been enclosed in a green or opaque container or wrapper because such oils or fats may develop even higher peroxide values than unprotected oils or fats and still be free from rancidity. The protective factor for the green wrapper is higher in every instance than for the antioxidants used with the exception of that for maleic acid after 72 days' and for pyrogallol after 41 days' exposure. If the peroxide value were a direct measure of rancidity the protective factor would be significant, but according to the experiments reported in this and earlier papers such a protective factor may be misleading, especially when the peroxide values have been derived from oil treated as shown in this investigation.

CONCLUSION

1. The antioxidants used in this investigation showed antioxygenic activity in delaying the development of rancidity, but they were not so effective as green wrappers which absorb all light except that delimited by 4900-5800 Angstrom units.
2. The use of a protective green container or wrapper alone or in conjunction with an antioxidant increased the period during which the oil or fat remained fresh at room temperature and, incidentally, decreased the rate of peroxide formation.
3. Oils or fats stored at low temperatures and with light excluded remained fresh longer than if treated with an antioxidant or packaged in green and exposed to light at room temperature.
4. Packaging in green or opaque wrappers has a special advantage in that they can be used to protect those oil-bearing food products, such as shelled nuts and ground whole grain, to which it is difficult to add an antioxidant.
5. Protecting oil-bearing foods from rancidity by packaging in green or opaque containers is practical.

DISCUSSION

Pres. Hutchins: I am sure we all appreciate Mr. Coe's presentation of his paper. Are there any questions that any of the members wish to ask him?

Mr. Ganucheau: I would like to ask Mr. Coe if he used a yellow paper put out by the Sylvania Corporation?

Mr. Coe: I tested potato chips in that particular wrapper, and I found that it has protective advantages somewhat, but you cannot depend upon it because it lets through a lot of yellow and red light. Red light, I have found in my experiments with colored filters, causes rancidity, and this particular product does not protect from that kind of light. Therefore, it is not as good as the green that I hope to have accepted.

Mr. Ganucheau: We have a rather easy method of finding out the effect of the different wrappers. Take an ordinary developing out film that the photographers use and expose it. It will give you a very easy test, and we have found it quite effective. You can use different carbons for it and get different units from the different carbons. You can get the red, the ultra-violet, or the natural sunlight from these carbons. It is a very simple test and gives very nice results without any trouble.

Mr. Coe: Have you compared the two?

Mr. Ganucheau: We have compared green.

Mr. Coe: What sort of green did you use?

Mr. Ganucheau: I really could not say.

Mr. Coe: There is the point. If you do not get the proper green wrapper, you cannot get the results that I get. That is where the trouble comes in. There are a number of green wrappers on the market which protect very little.

Mr. Ganucheau: Is it any special company?

Mr. Coe: There is one put out by the Riegal Paper Company, and one by the Marathon Paper Company in Menasha. This particular company you have in mind lays a lot of stress on the influence of ultra-violet light. They think of it as the main cause. It undoubtedly is, but they are not also taking into account the effect of red light. Most oils, as I think you will be shown shortly, absorb considerably in the red and somewhat in the yellow. Where there is absorption, there is apt to be photo-chemical action of some kind, and that is taken care of by the particular green paper that I have recommended.

Dr. Newton: I have one or two points that seem pertinent in regard to the paper. The effect of light on the rancidity of fats has been known for a long time. When I first came into this field some twelve years ago, an old gentleman, Mr. Escher, in Swift's laboratory, told me of this effect, and that it was fairly generally accepted. He showed me samples that had been subjected then for a period of ten years, that he had been studying the effect of light on. Later Greenbank and Holm published some very interesting work showing the particularly active section of the spectrum.

The difficulty with the publicity that has come with Mr. Coe's work, as I see it, is that the people have misinterpreted it. He stated in this paper that the fat in closed tins stayed fresh throughout the experiment. We have had literally dozens of propositions offered to our commercial people for putting green liners inside packages that already exclude all the light, or green lacquers inside tin pails. I believe that some place in the publicity which has been given to this interesting work, they have failed to impress the fact that if you exclude all of the light, it is not necessary to take particular pains to exclude all but the green light.

I wish to correct another impression that I believe Mr. Coe is in error on. He says that no satisfactory edible antioxidants have yet been discovered. There are a number of the organic acids, such as citric, and several others that have been described, which, I think, have very fine antioxidant properties. In addition, some work in our own laboratory has shown gum guiac to be very effective, but entirely inactive physiologically. We have had some very complete tests made outside on physiologic activity, and we believe it is one of the active antioxidants that carries its activity over to finished baked goods. It seems to me that the practical application of the green wrapper is rather limited to such cases as glass containers for salad oils, wrapped potato chips, and things of that nature.

Mr. Coe: In reference to my statement about no antioxidants having been found, I take that from the viewpoint of the Food and Drug Administration. They have not recognized any yet, and of course I could not.