PHOTOCHEMICAL STUDIES OF RANCIDITY

by

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Much attention has been directed to the use of the peroxide value for estimating the stability of an oil or fat. Generally during the commercial manufacture of oil products there is no particular precaution exercised to guard against the effect of light, and consequently oil products of varying peroxide values reach the consumer. As peroxides develop in oils stored in tin containers, which exclude all light, one might say that peroxides are not the result of exposure to light, but are due to natural aging of the oil. As a matter of fact, light accelerates the formation of peroxides, and it is possible that the oil which has been more or less exposed to light and air throughout its manufacture may only need time for the peroxides and also the compound causing rancidity to develop.

It has been shown in a previous article[3] that if cottonseed or corn oil has been protected from light by wrapping the glass containers with metal foil, opaque black paper or a green wrapping material whose permeability to light is limited to the interval from 4,900 to 5,800 Angström units, rancidity does not appear even though the peroxide value reaches approximately 60 millimoles per kilo of oil. If the oil has not been protected from light, rancidity appears at this stage. Our experiments show that a protected oil may have a peroxide value of nearly 200 without being rancid as determined organoleptically, i.e., by the sense of taste and smell.

The observation that the development of rancidity can be appreciably delayed by adequate protection from certain wave-lengths of light[4] naturally has raised the question which part of the visible spectrum is most active in bringing about this form of spoilage in an oil or fat. The purpose of this paper, therefore, is to show the effect of various color filters of known light transmission on the formation of peroxides and the development of rancidity.

The ideal method of obtaining this information is with a specially designed spectrophotometer having a dispersion great enough to irradiate individual samples at definite wave-lengths. Not having access to this type of equipment, however, the results given in this paper were obtained by means of color filters.[5]

Experimental

Cottonseed oil was placed in each of twelve crucibles which were light-proof to all light except that transmitted by the color filter that covered it. All samples were placed on the inner sill of a south window. The color filters were selected and arranged to absorb known wave-lengths so that the whole visible spectrum was utilized selectively for irradiation. The color filters were arranged as follows:

1. A clear glass (transmission falls to 5% at 3,100 Å).

[1]Food Research Division Contribution No. 224.

[2]Read at the meeting of the American Oil Chemists Society, Oct. 13, 1933.

[3]Coe, Mayne R., and J. A. LeClerc. Photochemical Studies of Rancidity—Peroxide Values of Oils Affected by Selective Light. Ind. & Eng. Chem. 26:245-248, 1934.

[4]Coe, Mayne R., and J. A. LeClerc. Photochemical Action a Cause of Rancidity. Cereal Chemistry, Vol. 9, No. 5, p. 519, 1932.

[5]Filters were not adjusted to transmit light of equal energy.

TABLE 1. PEROXIDE VALUE AND RANCIDITY[1] OF SELECTIVELY IRRADIATED COTTONSEED OIL AND LARD

Filter		Cottonseed Oil[2]						Lard[3]			
		May 9		May 18		June 28		July 25		August 26	
Color	Transmission falls to 5% of light at Å units	Peroxide value	Rancidity (Organoleptic)	Peroxide value	Rancidity (Organoleptic)	Peroxide value	Rancidity (Organoleptic)	Peroxide value	Rancidity (Organoleptic)	Peroxide value	Rancidity (Organoleptic)
1 Clear	3,100	314.9	V.R.	472.2	V.R.	801.0	V.R.[4]	54.7	R.	305.2	V.R.[4]
2 Blue	5,600	86.7	R.	275.0	V.R.	837.0	V.R.[4]	0.5	N.R.	331.0	V.R.
3 Yellow	4,000	78.4	R.	77.5	R.	538.8	V.R.	0.4	N.R.	197.0	V.R.
4 Deeper yellow..	4,150	72.3	R.	73.5	R.	200.8	V.R.	0.4	N.R.	40.7	R.
5 Deeper yellow..	4,410	64.9	R.	65.1	R.	106.5	R.	0.4	N.R.	39.6	R.
6 Deeper yellow..	4,650	47.0	N.R.	59.4	R.	97.9	R.	0.3	N.R.	lost	
7 Deeper yellow..	4,840	45.2	N.R.	57.0	R.	95.5	R.	0.2	N.R.	18.0	R.
8 Deeper yellow..	5,150	38.7	N.R.	51.7	N.R.	lost	R.	0.1	N.R.	23.3	R.
Green	5,090	26.8	N.R.	34.7	N.R.	75.1	N.R.	0.1	N.R.	0.3	N.R.
Orange red	5,650	35.9	N.R.	47.6	N.R.	76 4	S.R.	0.1	N.R.	0.7	S.R.
Medium red	6,120	28.9	N.R.	39.6	N.R.	75.2	S.R.	0.1	N.R.	0.6	S.R.
Far red	6,310	29.3	N.R.	39.7	R.	81.1	R.	0.1	N.R.	19.1	R.

[1]Organoleptic test, expressed thus: V.R. = very rancid; R = rancid; S.R. = slightly rancid; N.R. = not rancid.
[2]Original peroxide value, 14.8 on April 26.
[3]Original peroxide value, 0.1 on July 14.
[4]Also viscous.

2. A lantern blue filter transmitting violet, blue and a portion of the green (transmission falls to 5% at 5,600 Å).

3 to 8. A series of yellow filters selected to absorb in sequence the region of violet and blue light, so that the series finally excludes all the blue end of the spectrum (transmission falls to 5% in each of the filters at 4,000 Å, 4,150 Å, 4,410 Å, 4,650 Å, 4,840 Å, and 5,150 Å, respectively).

9. A special green filter which absorbs all the blue, yellow, orange and red (shorter wave-length transmission falls to 5% at 5,090 Å; maximum wave-length transmission at 5,380 Å; longer wave-length transmission falls to 5% at 5,880 Å).

10. An orange red filter which absorbs all the blue end of the spectrum up to the yellow green (transmission falls to 5% at 5,650 Å).

11. A medium red filter which absorbs still more of the blue end including the orange red (transmission falls to 5% at 6,120 Å).

Table 1 shows the relation of wave-lengths of light included in the visible spectrum to the production of rancidity and to the development of peroxides in cottonseed oil and lard, as demonstrated by the use of these filters.

It will be noticed that the development of peroxides and of rancidity in both cottonseed oil and lard is influenced similarly by light from the respective color filters.

In another experiment cottonseed oil and corn oil were exposed simultaneously under the same conditions to direct sunlight from May 1 to May 19, 1933, using a set of Corning glass color filters. These filters were clear (Corex D); violet; lantern blue; dark blue green; signal green; sextant green; lemon yellow (Noviol C); yellow, medium shade; yellow, red shade; 142% red; and sextant red (virtually black).[6]

The purpose of this experiment was to compare the influence of selected light with the formation of peroxides and the development of rancidity in the two oils irradiated simultaneously. The results are given in Table 2.

Discussion

The foregoing tables of results show very strikingly that under the conditions of these experiments the blue end of the spectrum is appreciably active in the formation of peroxides and the development of organoleptic rancidity. Table 1 shows that with a few days irradiation the samples of cottonseed oil and lard under the clear filters developed peroxides and rancidity much faster than the samples under the color filters, but at the end of the experiments the samples irradiated with blue light exceeded those irradiated by clear light with respect to peroxide development. Since there is no certain means of measuring rancidity except organoleptically, it is difficult to distinguish, with any degree of precision, the difference in amount of rancidity developed in the samples under the above-mentioned filters.

The rate of peroxide formation decreases in the oil, irradiated by the succeeding filters as successive portions of the blue end of the visible spectrum are excluded. The minimum peroxide formation as well as absence of organoleptic rancidity are consistently characteristic of an oil protected entirely from light or protected by a green filter. In other words, the peroxide value of the oil protected by the green filter is less than that of the same kind of oil which has been irradiated by other light, especially by filters transmitting varying amounts of blue.

Since cottonseed oil and lard, when irradiated by light from the same color filters, react similarly with respect to the formation of peroxides and to the development of rancidity, it is possible that the same or similar compounds are present in both animal and vegetable oils or fats which cause them to become rancid.

In the experiments reported in Table 2 the formation of peroxides and the development of rancidity in the oils exposed to light of the blue end of the spectrum were greater than in the oils exposed to the red end. At the blue end of the spectrum a violet filter was used which transmitted mostly violet and some blue light while at the red end of the spectrum a sextand red filter (virtually black) was used which transmitted only infra-red. The latter gave protection because the active wave-lengths of light were absorbed by it, indicating that the infra-red rays are apparently not conducive to the development of rancidity.

In these experiments the peroxides formed more slowly in the corn oil than in the cottonseed oil, but the relative effect of irradiation by the different color filters was the same.

All these experiments have shown that the blue end of the visible spectrum appears more active in the formation of peroxides and in the development of rancidity than the other portion. The question then arises, is this a matter of wave length or of energy transmission? Does the sextant green filter protect because it transmits less energy than the blue filter or is it because of exclusion of wave lengths of light in the blue end of the spectrum? This problem forms the next step in our study.

In good commercial practice, containers or wrappers intended to protect foods from rancidity should have the property, especially, of excluding light of both the blue and the red ends of the spectrum. The green container or wrapper transmitting light delimited by 4,900 to 5,800 Ångström units has been found to be best suited for oil-bearing foods.[4]

Conclusions

1. Experiments with oils irradiated by means of color filters selected so that successive portions of the visible spectrum are absorbed show that blue light is more conducive to the formation of peroxides and the development of rancidity than the red end of the spectrum for the same time of irradiation.

2. The results of these experiments seem to indicate that the formation of peroxides and the development of rancidity are accelerated in proportion to the amount of blue light transmitted by the filter.

3. The development of rancidity does not necessarily parallel the formation of peroxides. This is shown by the fact that an oil protected by green and not organoleptically rancid may have a peroxide value as high as, or higher than, an oil which has not been so protected and which is rancid.

4. Experiments show that, with respect to the formation of peroxides and the development of rancidity, lard, and animal fat, responds to selective light in the same way as do corn and cottonseed oils.

5. Containers or wrappers designed for enclosing oil-bearing foods should exclude both ends of the visible spectrum, more especially the blue, in order to prevent or delay the development of rancidity.

6. The color which affects the development of rancidity the least is green delimited by 4,900 to 5,800 Ångström units.

[6]Specifications for these filters may be found in Corning Glass color filter catalog.

TABLE 2. PEROXIDE VALUES AND DEVELOPMENT OF RANCIDITY IN COTTONSEED OIL AND CORN OIL IRRADIATED SIMULTANEOUSLY FOR 19 DAYS

Filter	Transmission falls to 5% Angström Units	Cottonseed Oil Peroxide Values	Cottonseed Oil Rancidity	Corn Oil Peroxide Values	Corn Oil Rancidity
Clear (Corex D)	2,600	164.7	R[1]	120.5	R
Violet	4,700	221.0	R	91.7	R
Lantern Blue	5,300	245.3	R	149.0	R
Dark Blue Green	5,800	256.4	R	151.0	R
Signal Green	6,200	113.3	R	117.0	R
Sextant Green	4,900	87.6	NR[2]	69.0	NR
Lemon Yellow (Noviole C)	4,800	114.0	R	89.6	R
Yellow, Medium Shade	5,300	85.8	R	85.7	R
Yellow, Red Shade	5,500	102.8	R	84.8	R
Red (142%)	5,900	90.6	R	79.3	R
Sextant Red[3]	7,600	96.4	NR	68.6	NR

[1]R = rancid.
[2]NR = not rancid.
[3]This filter is virtually black to the eye. It transmits infra-red freely.