Photochemical Studies of Rancidity:

Factors Which Increase the Rate of Oxidation of Fats and Oils With Special Reference to the Role of Light[1] [2]

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The enormous losses incurred in oil-bearing foods by the development of rancidity have made it a matter of intense importance among oil investigators to study the causes of this form of spoilage and to find some means for reducing it. Rancidity as discussed in this paper is a form of oxidation; the speed of its reaction is influenced by numerous factors.

Under normal conditions, a fat or oil has an induction period; that is, a phase of change which precedes rapid oxidation. It is the ambition of every investigator to discover some means by which to lengthen that period during which the oil or fat will remain fresh. Until recently this period of induction has been largely measured by the rate of peroxide formation. The "chlorophyll value" test (6) has recently been proposed as being very useful in following this chemical change. The factors which are known to accelerate oxidation in oils and fats are numerous; the most important ones which affect the life of a fat or oil as found on the market today may be classified under two main heads; namely, (a) the primary factors, such as metals and light, and (b) the contributory factors of air, moisture, temperature, photosensitizers, etc.

Effect of Metals

Metals play an important role especially as related to the processing and packaging of oils and fats. It is well known that metals and metallic salts in solution, e.g., copper, iron, nickel, cobalt, chromium, and manganese accelerate oxidation in oils and fats. According to King, Roschen, and Irwin (20), Lea (23), and others, copper is much more effective than any of the other metals. As little as two parts per million of copper is enough after six days' ordinary storage to induce oxidation in lard. Lead, iron, and zinc appear to be intermediate in activity (13), while tin and aluminum, according to Davies (7), (8), (10), seem to be inactive even in concentrations of 100 parts per million. Emery and Henley (13) found that metals produced rancidity in the dark at about the same rate as it is catalyzed by light alone.

The oxidation of oils if due to the catalytic action of metals and metallic salts may be explained according to a recent theory of rancidification (5) which implies that hydrogen peroxide (HO.OH) in the active state must be produced before this form of oxidation can take place. This follows quite logically from the work of Kufferath and Merckens (21) and of Merckens alone (25). These authors were able to obtain photographic images with magnesium, zinc, cadmium, nickel, cobalt, and lead, when these metals were placed close to a photographic plate in the dark. They explained the darkening of the plate by these metals on the basis that the oxidation of the active metal produced hydrogen peroxide which acted on the plate. Russell (29) attributed this action to metallic oxidation in moist air and also found that on supplying to the metallic surfaces more moisture than it would normally obtain from the atmosphere surrounding the photographic plate, the activity was much increased. Dombrowsky's (12) experiments also seem to show that metals alone were not active in the production of active H_2O_2 except in the presence of moisture and oxygen. Lengyel (24) believed that hydrogen formed in the presence of moisture on the metallic surface might be considered the active agent. This idea follows very closely that of Fisher (14) who states that hydrogen is liberated (15) as the result of the photochemical action of light on chlorophyll (26) or chlorophyll-like pigments.

It would seem, therefore, on the basis of what has been stated above, that the production of rancidity in the presence of metals may be due to the formation of hydrogen. Chlorophyll which is normally found in an oil, thus produced hydrogen by photochemical action and the metals produce hydrogen by contact with moist atmosphere and subsequently in the presence of air both form loosely combined H_2O_2. Consequently, any means or steps taken which will exclude entirely certain active metals or metallic compounds from contact with oils and fats will appreciably lengthen their keeping quality. This suggests the question: "Which metals may be recommended for the utilization of oil in the food or other industries?"

Copper, being the most active catalyst for oxidation, should not be used for oils unless heavily tinned. Iron, though not so active in catalyzing rancidity, should be replaced with tin or aluminum where possible. Because mere traces of such active metals suffice to produce oxidation, the kind of metal employed in the making of equipment to be used in connection with oils and fats should be given first consideration.

Effect of Light

It is common knowledge among investigators of rancidity problems that light is one of the main factors in accelerating the oxidation of oils and fats. Experiments were conducted by Browne (1), (2) for measuring the rate of change in the weight of butterfat, which, over a period of years, had been exposed to light and to darkness. A uniformly greater percentage increase in weight was noted in the fat exposed to light than in the fat kept in darkness. Kerr (19) concluded after a series of tests of different fats and oils stored under controlled conditions of light, temperature, and access of air, that under no conditions does rancidity develop in the absence of oxygen, but that when oxygen is present light will accelerate rancidity. It is his claim that moisture, especially in the presence of light, promotes spoilage of fats. Kerr (19) and Emery and Henley (13) and others found

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that storing oils or fats in the dark noticeably delayed the development of rancidity.

Salkowski (30) found that in the absence of light very little oxygen is consumed by an oil or fat and that rancidity results from the combined activity of atmospheric oxygen and light, the speed of the process depending upon the intensity of light. These findings seem to corroborate those of Ritsert (28).

Davies (9) was one of the first, in discussing the development of taint in oil-bearing foods, to emphasize the necessity of taking strict precaution at all stages of manufacture to guard against undue exposure to strong sunlight. He further stated that although the effects of strong light in shortening the induction period may not be at once apparent, he found that once autoxidation has been initiated the subsequent storage of the product in the dark does not in any way arrest the development of rancidity.

Lea (22) conducted an elaborate investigation of the effect of light on the oxidation of fats, covering such points as the relative susceptibilities of fats to oxidation, the effect of various intensities of illumination, the autocatalytic nature of oxidation, the differences in susceptibility to oxidation, the bleaching action of light and the influence of oxidation on free acidity. These changes during oxidation were followed by estimating the amount of peroxide formed during the autoxidation of the fat. In summarizing he states:

> "Oxidation is accelerated sensibly by weak artificial light, while exposure for a few minutes to direct sunlight is sufficient to produce rancidity.
>
> "The reaction is autocatalytic and even brief exposure to light accelerates the subsequent oxidation."

His conclusions are very significant, because they support well the observations that the cause of oxidative rancidity is more often a photochemical phenomenon.

It is claimed by Wagner, Walker, and Oestermann (31) that light alone, even in the absence of air, is capable of producing rancidity. However, Holm, Wright, and Greenbank (17) offer an explanation by saying that the keeping quality of oils stored in vacuum is largely dependent upon the inherent quality of the fat, the nature of which is due to some type of loosely bound oxygen, which cannot be removed by vacuum and which is sufficient to oxidize the fat and to cause perceptible odors and flavors.

In order for light to play an active part in producing a change in an oil or fat there must be present a photosensitizer which acts as a light absorber. This brings about reactions of other components of the system which of themselves may not be affected by light. According to the "Grotthus-Draper absorption law," only light which is absorbed can produce chemical changes. In that case the active light is limited to those wavelengths which are absorbed by the photosensitizer. The photosensitizer in this case (5) is believed to be chlorophyll or a chlorophyll-like pigment. Curves (26) showing the light transmission of various vegetable oils seem to indicate the presence of chlorophyll. Experiments have shown that when this photosensitizer or chlorophyll is removed as much as possible by adsorption, e. g., by passing the oil through a column of finely powdered sugar, the induction period of the oil is lengthened. It has been demonstrated also that the oil occluded in the upper part of the column soon becomes rancid while that at the lower end of the column remains fresh for an appreciable time.

Although it has been known for some time that light plays an important role in the development of oxidative rancidity, only during recent years has attention been directed to the role played by the different regions of the spectrum. The first paper (3) on this subject revealed that light (green) delimited by 4900 to 5800 Ångström units is the least active photochemically in promoting rancidity. Greenbank and Holm (16) published a paper soon after, which stated that the blue region of the visible spectrum was the least effective in accelerating oxidation. Also, the same authors published a paper (18) recently in which they rescind their former claims regarding the effectiveness of blue light and state that the catalytic activity of the spectrum decreases with increases in wavelength.

Davies (11) made a study of the light transmission of a number of colored (a) transparent and other wrapping materials and noted the differences in the degree of protection they afforded oil-bearing foods when exposed to light. He concluded that for the preservation of oil-bearing foods in colored transparent cellulose, "It is on the whole the depth of color and not the actual tint which is of importance."

Morgan (27) carried out numerous experiments with transparent cellulose films and corroborates our findings that the blue and invisible ultraviolet wavelengths of light materially accelerate the development of rancidity. He claims, however, that visible light, such as red and yellow, has little effect in catalyzing rancidity, and makes the statement, "Consequently rancidity retarding wrappers may be of any visible color except blue."

Experimental

Although it has been repeatedly demonstrated in our investigations that the region of the visible spectrum delimited by 4900-5800 Ångström units is the least active in promoting rancidity, it should be noted that no account has thus far been taken of the actual amount of radiant energy received by the oil or fat. Experiments of this kind have been conducted to show the effect of irradiating oils with light from filters so adjusted that they transmit light of equal energy, as measured by the thermopile and galvanometer. Spectral regions a few hundred Ångström units wide and which together included the whole visible spectrum were selected for this experiment. Ultraviolet light was screened out by means of color filters so selected that only the desired regions of the visible spectrum were admitted. Infrared was excluded from all samples except one by means of a three-inch thickness of water and by means of an "Aklo" heat-absorbing filter (the latter only where needed). The amount of radiation transmitted by each filter was adjusted to the same intensity so that the only limiting factor in the experiment was the

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(a) An examination of these transparent films obtained through the courtesy of Dr. Davies showed that, with the exception of the darkest red film, most of them transmitted copious amounts of ultraviolet, violet, and blue light. Comparison was also made of the protective properties of these films with those of protective green glassine, using potato chips as the oil-bearing food. Little or no protection was afforded (as judged organoleptically) by any of the films except the dark red one (which excluded all light below 7400 Angström units) and the green glassine. This particular red proved to be as protective as the Corning Sextant Red filter mentioned in a previous paper, (4), its spectral transmission comparing very well with that filter.

light of the particular region of the spectrum studied. The light source was a 500-watt C. X. Mazda lamp immersed in a round glass jar containing water. The water was kept cool by a coil. The effect of the respective regions of the spectrum in accelerating the oxidation of the cottonseed oil irradiated was followed by means of the peroxide value, the chlorophyll value, and the organoleptic tests. This experiment was conducted during a period of 133 days. Results appear in Table I.

In two repeat experiments with cottonseed oils from another source, conducted in the same manner, a copper wire of the same size and length was placed in each sample of one set of oils in order to accelerate the reaction and thus shorten the duration of the experiment. Also a measured amount of chlorophyll was added to each sample of the other set of oils for the same purpose. The relative effect of the spectral regions was essentially the same as that shown in Table I.

TABLE I

The Chlorophyll Values and Peroxide Values of Samples of Finished Cottonseed Oils[1] Irradiated by Light From Color Filters Adjusted so as to Transmit Equal Intensities of Light[4]

Filters Limiting and Peak Transmissions in Angström Units	11 days	60 days	73 days		133 days	
	Chlorophyll value	Chlorophyll value	Chlorophyll value	Peroxide value	Chlorophyll value	Peroxide value
No. 1 Violet 4000-4300-4800	3.0	6.0R	8.3R[2]	106.0R	18.5R	175.0R
No. 2 Blue 4200-4600-5200	2.0	5.0R	5.0R	80.5R	10.0R	125.0R
No. 3 Blue-green 4700-5000-5600	2.0	3.0	4.0SR[3]	64.5SR	6.5SR	113.5SR
No. 4 Blue-green 4600-5200-5700	2.0	3.0	4.0SR	84.0SR	6.0SR	125.0SR
No. 5 green 5250-5440-6100	2.0	3.0	3.5	66.5	4.5	109.0
No. 6 Yellow-green 5500-5700-6200	2.0	4.0	4.5SR	77.5SR	8.0R	120.5R
No. 7 Orange-yellow 5900-6200-7000	2.0	4.0	3.5	69.5	6.5SR	117.5SR
No. 8 Red 6300-6600-7500	2.0	3.0	3.5	70.0	7.0R	117.5R
No. 9 Infrared 7400	2.0	3.0	3.5	66.5	4.0	110.5
No. 10 Clear 4000-5800-7400	2.5	5.0R	5.0R	79.5R	8.0R	128.0R
Oil kept in can in refrigerator	2.0	3.0	3.0	6.5	3.0	15.5

[1] Initial chlorophyll value 2.0; peroxide value 1.5.

[2] R means rancid.

[3] SR means slightly rancid.

[4] One 500-watt C. X. Mazda lamp was used as the light source.

General Discussion

All indications seem to substantiate the data previously reported that the cause of oxidative rancidity in oils is more commonly due to the naturally occurring factors, i.e., either to the presence of finely divided metals in the oil or more especially to the undue exposure of the oil to light. It is of the utmost importance that serious consideration be given to the kind of metal of which the equipment and receptacles are made. For example, butter should not be processed in anything that is copper-lined because it is a well-known fact that spoilage often results from minute amounts of copper in the butter. Potato chips fried in a copper kettle have appreciably less keeping qualities as a result of the oil being contaminated with seemingly negligible amounts of that metal.

According to general knowledge aluminum and tin appear to catalyze rancidity the least. They should, therefore, make the best receptacles to be used for deep frying. Iron is commonly used for the same purpose, but there is always a question whether the products cooked in oils or fats in contact with that particular metal will survive the sales period before rancidity appears.

Discussion of Experimental Data

The results (See Table I) show that under equal intensities of incident light the region below 4900 Ångström units (including the ultraviolet which is generally known to be active) is the most active portion of the visible spectrum for promoting rancidity and that the regions embraced by filter No. 5 and No. 10 (See Table I) around 5500 and 7500 Ångström units promote rancidity the least. Intermediate regions at 5700 and 6600 Ångström units do not appear quite so active as the blue region for promoting rancidity. The filters having a peak transmission of light at 5000, 5200, and 6200 Ångström units transmit light which promotes rancidity but to a lesser extent than light of the blue, yellow, and the middle visible red regions. It is obvious that the exclusion of all light would be the most effective method of packaging for preventing or delaying rancidity. However, a sales story is lacking in the opinion of the retailer when the commodity cannot be seen.

The results seem to support strongly the idea that it is not the intensity of light alone that influences the development of rancidity, but rather that light of certain regions (including ultraviolet and the visible spectrum) exerts a greater catalytic effect than do others. They further show that the active regions appear to correspond roughly to the absorption curve of the oil. That is, the most active regions which promote rancidity are those where spectral absorption of light by the oil is appreciable. It will be noted that this experiment covered a long period of time before completion, because the low intensity of light transmitted by the color filters was slow in promoting oxidation.

Conclusions

1. Oils and fats keep longer from developing rancidity by excluding, as far as possible, noxious metals, copper being considered the most active.
2. When the intensity of light to which oil-bearing foods are exposed is the same, the ultraviolet, violet, and blue regions (below 4900 Ångström units) promote rancidity the most while the regions at about 5400 and above 7400 Ångström units promote rancidity the least. The yellow region around 5700 and the red region around 6600 Ångström units are less active than the blue region but nevertheless promote rancidity appreciably more than the green region.
3. The regions which are active in catalyzing rancidity seem to correspond with the light absorption regions of the oils.

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Solubility of Calcium Soaps of Gum Rosin, Rosin Acids and Fatty Acids

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When soap is used in hard water insoluble soaps (usually calcium and magnesium soaps) are formed. These insoluble soaps precipitate from the solution when there is not sufficient soap to keep them suspended. The hardness of a water is due principally to the soluble calcium and magnesium salts it contains. This study has been limited to the calcium soaps formed when a solution of a soluble calcium salt is mixed with a dilute soap solution.

The amount of insoluble soap formed when soap is used with hard water depends upon the hardness of the water. The ordinary bar, flake or powdered soap is made up of the sodium soaps of numerous fatty acids or fatty acids and rosin. The least soluble calcium or magnesium soaps of the fatty acids or rosin will form and will tend to precipitate as soon as the amount formed exceeds the solubility of the calcium or magnesium soap. This study was undertaken to determine which of the calcium soaps would be likely to precipitate first and to compare the solubility of the calcium soaps of the rosin acids with those of the fatty acids.

Gum rosin is made from the pine oleoresin that exudes from the longleaf and slash pine when the tree is wounded by cutting through the bark into the sap wood. Steam distillation of the pine oleoresin yields a volatile portion (gum turpentine) and a non-volatile portion (gum rosin). The gum rosin is about 90 per cent of rosin acids and about 10 per cent of resenes (neutral compounds and compounds difficult to saponify). The rosin acids are a mixture (5) of d-pimaric acid, l-abietic acid, dihydroabietic acid (4) and unidentified rosin acids. Rosin acids, such as d-pimaric and dihydroabietic acid, are stable toward oxygen at room temperature but rosin also contains rosin acids that are easily oxidized. Oxidation of these unstable acids may affect the properties of products made from rosin.

Experimental

The calcium soaps were precipitated from a hot dilute solution of the sodium soap[1] by the addition of a five per cent aqueous solution of calcium chloride (A.C.S. grade) slightly in excess of the amount needed for complete precipitation of the calcium soap. This solution was filtered through a Buchner funnel and the precipitate washed with distilled water. The moist cake was transferred to a glass-stoppered pyrex flask and distilled water added (100 c.c. to each 2 to 4 gm. of Ca soap). The flasks were then heated on a steam bath for five hours. During this period the flasks were frequently shaken. Immediately after heating the flasks were placed in an oven maintained at 50° C. After the flasks had been in the oven a week, a 20-c.c. sample was removed with a pipette[2] and placed in a weighed porcelain evaporating dish. The water was evaporated by placing the crucible on a steam bath. When the evaporation was apparently complete the crucible was placed in a vacuum oven at 100° C. for an hour. The crucibles were then placed in a vacuum desiccator and allowed to come to room temperature. The crucibles were weighed and the calcium soap in 20 c.c. of solution was determined. The calcium soap in 100 c.c. of solution was then calculated by multiplying by five.

Calcium soaps made from the following products as described above were tested for their solubility in water at 50° C.: Rosin (color grade WW) made from longleaf pine gum; rosin (color grade WW) made from slash pine gum; oxidized rosin[3]; d-pimaric acid ($[\alpha]^{20}_{D} + 55^\circ$, m.p. 211-213° C.) (6); dehydro-

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[1] Concentration of sodium caprylate solution was 0.7 per cent; all the other sodium soap solutions were less than 0.25 per cent.

[2] The end of the pipette was so covered with a folded filter paper that the solution was filtered before entering the pipette.

[3] The unstable rosin acids in the rosin (color grade WW) were oxidized by powdering the rosin and exposing it in a thin layer to air at room temperature for over two months.