Stability Tests on Fats Containing Oxidation Accelerators and Inhibitors

H. D. Royce

Although the food industries have probably long recognized the significance of the pioneer researches on antioxidants, commercial developments along this line have not kept pace with the practical utilization of stabilizers in some of the other fields, notably the rubber and the petroleum industries. Newton (5) has made the observation that many of the well known commercial antioxidants, especially the polyhydroxy phenols, are undesirable in foods on account of toxicity and failure to carry over their stabilizing action into the finished product. Newton and Richardson (6) propose the addition of carotene to susceptible fats, and favor palm oil as a source of this material. According to their claims, a small percentage of palm oil in lard exerts a definite stabilizing action and delays the onset of rancidity. No figures are given for the keeping quality of palm—cottonseed oil mixtures. Musher (4) proposes the admixture of crushed sesame seed with milk and dairy products for the purpose of inhibiting rancidity. The practical value of this process is apparently limited to those applications in which the flavor and presence of bulky inert ingredients are not objectionable. It is generally conceded that crude vegetable oils possess greater stability than most refined oils or animal fats, due to the presence of naturally occurring antioxidants, and the above process may be interpreted on that basis.

Mattill and co-workers (2) (3) (7) have investigated the antioxidant properties of a large number of compounds, in connection with the oxidative destruction of the fat soluble vitamins. Vitamin E particularly has been shown to be very susceptible to oxidation, and rancid fats are likely to be deficient in this factor. An antioxidant was found in the unsaponifiable lipids of lettuce in the course of their investigation, and its possible role as a protector of the accompanying vitamin E was discussed. That the peroxides formed in fat oxidation tend to destroy vitamins A and E, is also brought out by the work of Waddell and Steenbock (10), in which the strongly proöxidant effect of iron salts on fats caused destruction of the vitamins in animal rations treated with ferric chloride. Vibrans (9) has given a good review on the history of anti-oxidants, including a summary of the Moureau and Dufraisse theory, and presents data showing the stabilizing action of a few commercial antioxidants added to lard.

The purpose of the present paper centers on the stability of fats containing both pro- and antioxidants, and the development of a rapid method for the evaluation of antioxidants. The methylene blue reduction method (8) and a modification of the M.M.A. accelerated oxidation apparatus (11) have been used in most cases to obtain the following stability curves. The use of copper and irradiation as accelerators to shorten the aging period in evaluating fat stabilizers is described. A majority of the stability tests have been made on cottonseed oil and hydrogenated cottonseed oil, employing gossypol[1] as the stabilizer.

Experimental

The apparatus and procedure for conducting the methylene blue keeping quality test have been described in a previous paper (8). Peroxide values are determined according to Wheeler's method (11), and the ac-

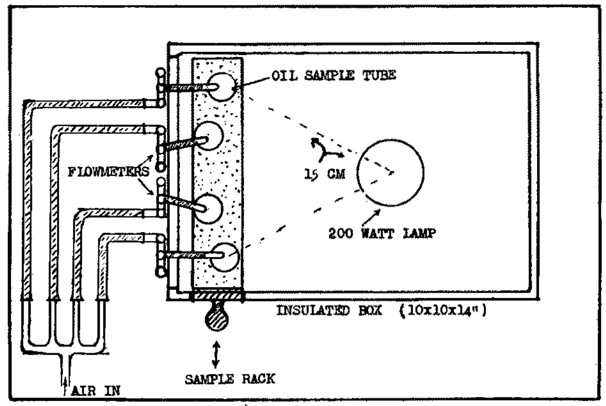
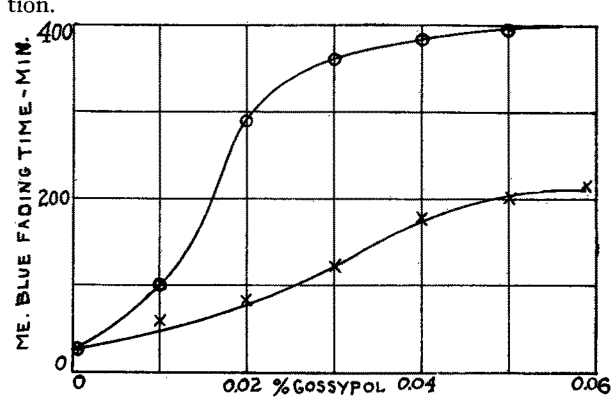


Fig. 1. Accelerated Aging Apparatus with Irradiation Feature

celerated oxidation tests are carried out in a modification of the M.M.A. apparatus (Fig. 1). The compressed air and flowmeter assembly of the M.M.A. apparatus was adapted to the constant temperature irradiation chamber of the methylene blue unit, so that the essential change consisted in the use of intense irradiation in addition to aeration at high temperature. Standard A.O.C.S. oil color tubes are used in place of the test tubes in the original setup, and the air delivery capillaries extend to the bottom of the color tubes. The latter are filled with oil to the 25 ml. mark, and air flow regulated in the usual manner, with stopcocks on the flowmeters. The sample rack holds six tubes equidistant (15 cm) from a 200 watt lamp. Thus in changing from accelerated oxidation to determination of methylene blue fading time, it is only necessary to withdraw the air capillaries, and change intensity of illumination by replacing the 200 watt lamp with a 100 watt daylite bulb. Temperature is adjusted and thermostatic control is maintained by hot air circulation as in the original metylene blue assembly. Unless otherwise indicated, the accelerated oxidation rates were determined at 100° C., with air flow of 10 liters per hour. Methylene blue fading time tests were made at 70°C., with 0.001 per cent dye concentration.



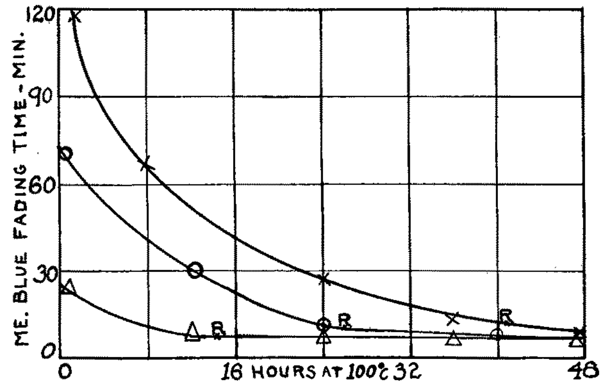
X—Crude Gossypol. O—Pure Gossypol

Fig. 2a. Antioxidant Effect of Gossypol Added to C. S. Oil

Pure crystalline gossypol was prepared for this work by Clark's modification (1) of the Carruth method. Purity was checked by melting point and molecular weight

[1]The toxicity of gossypol precludes its use in edible products.

determination on the compound itself, and on the dianiline derivative. Figure 2a shows the antioxidant effect of pure gossypol and crude gossypol at low concentrations in deodorized cottonseed oil. The crude gossypol represents the precipitate obtained when the crude gossypol acetate in ether solution was agitated and warmed with 4 volumes of water. The relatively low stabilizing value of the crude compound indicates the presence of a proöxidant which is removed by the purification process.



X—0.02% Gossypol. O—0.01% Gossypol. △—Control. R—Rancid Flavor

Fig. 2b. Accelerated Aging Curves for C. S. Oil with Added Gossypol

The aging curves for pure gossypol in cottonseed oil (Figure 2b) are in good agreement with the fading time—concentration curves. The samples were aged in open beakers without aeration at 100°, and it will be seen that the development of rancid flavor has been extended from 14 hours for the control to 41 hours for the sample containing 0.02 per cent added gossypol. Further confirmation of the powerful antioxidant effect of gossypol may be seen in the peroxide value[1]-aging curves of Figure 3. A good comparison of the methylene blue with

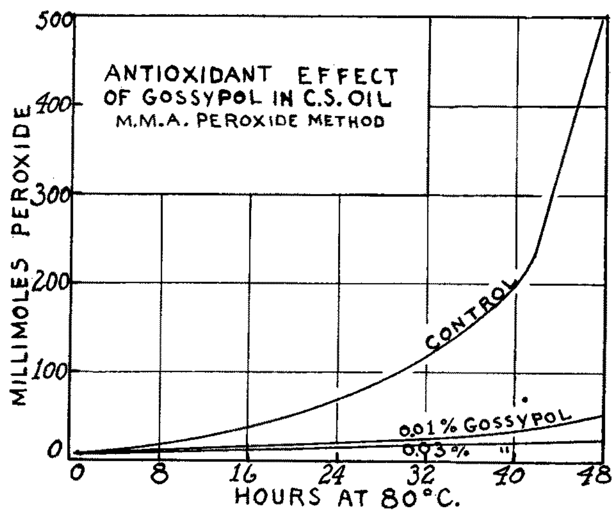
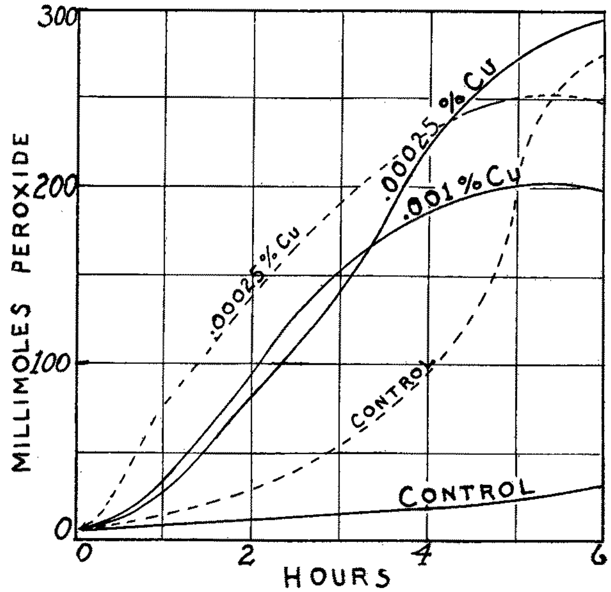


Fig. 3. Accelerated Oxidation of Cottonseed Oil, Using Air Flow of 10 Liters per Hour at 80° C.—No Light

the peroxide method for following oxidation of fats is also afforded by Figure 2b and Figure 3.

Figure 4 shows the accelerated oxidation of cottonseed oil promoted by copper, with and without irradiation. In the case of the high copper concentration (0.001%),

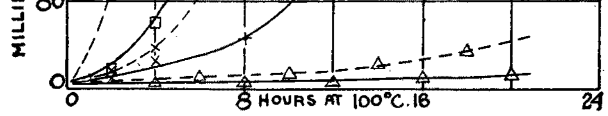


- - - - 200 W. Light at 15 Cm. ——— No Light

Fig. 4. Proöxidant Effect of Copper in C. S. Oil—Aged at 100° C.

the copper evidently catalyzes the decomposition of peroxide, giving a low maximum in the curve, and a smaller percentage is more desirable for the purpose at hand. Naturally the combined effect of copper and irradiation causes a marked decrease in the induction period, and practical fat stability measurements on commercial fats using light as an accelerator may be completed in a few hours. Under such conditions the average fat or salad oil will develop a rancid flavor in less than six hours, and a maximum peroxide value in 8 to 10 hours.

Figure 5 shows the action of light as an accelerator on 3 different types of fats, indicating that the photocatalyzed reaction is similar to the dark reaction. Thus, comparative stabilities may be estimated by the former rapid procedure, and interpreted in terms of keeping quality under ordinary storage conditions. In the case of highly hydrogenated fats especially (hydrogenated



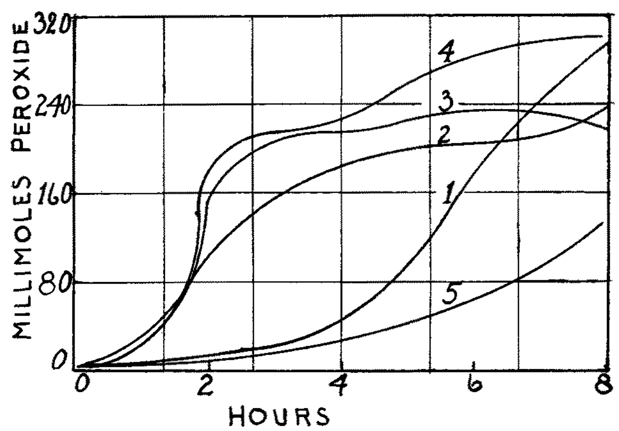
X—C. S. Oil (Control). □—Ref. Palm Oil (35y-22n). △ Hydrog. Palm Oil (I. No. 3.2). - - - - Light (200 W. at 15 Cm.). ——— Dark

Fig. 5. Effect of Light on Accelerated Oxidation Tests

palm oil in Figure 5), it is desirable to increase the rate of oxidation in order to shorten the test period. A comparison of the palm oil and cottonseed oil aging curves indicates superior stability of the latter, so that palm oil of this particular variety (Niger) would not be suitable as an antioxidant (2) for use in cottonseed oil.

The combined effect of copper and gossypol on the cotton seed oil aging curve shown in Figure 6, Curves

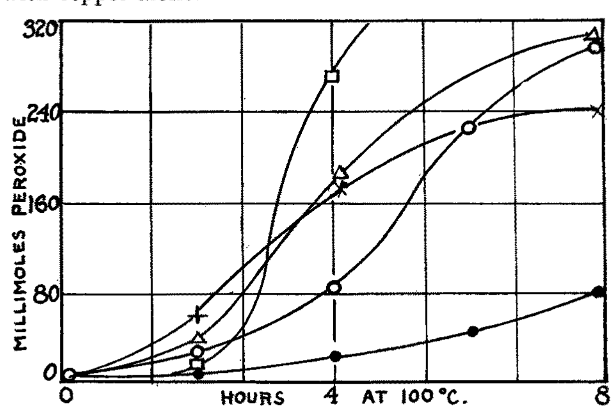
[1]All peroxide values were calculated to millimoles per kilogram of fat. Milli-equivalents of peroxide per kilogram of fat may be obtained by multiplying the recorded values by 2. (See King, Roschen and Irwin, this journal, 10, 6, p. 105, June, 1933, for details of calculation.)



1. C. S. Oil (Control). 2. C. S. Oil 0.00025% Cu. 3. Control + 0.00025% Cu. + 0.01% Gossypol. 4. Control + 0.00025% Gossypol. 5. C. S. Oil + 0.01% Gossypol

Fig. 6. Aging Curve for C. S. Oil Containing Both Pro and Antioxidants Aged at 100° C.—200 W. Lamp at 15 Cm.

3 and 4. The initial oxidation rate is slightly less than with copper alone, but after two hours the rate of peroxide formation increases rapidly and the peroxide values remain higher than with copper alone for the next few hours. This is interpreted to indicate that gossypol inhibits the tendency of copper to break down the peroxides, thus giving higher peroxide titration values, although the actual rate of fat oxidation may be less than with copper alone.



O—Deod. C. S. Oil (Control). X—Control + 0.00025% Cu. △—Control + 0.00025% Cu. and 0.025% Stabilizer S-23. □—Control + 0.00025% Cu. and 0.1% Stabilizer S-23. ●—Control + 0.025% S-23

Fig. 7. Stability Tests on C. S. Oil Containing Both Pro and Antioxidants

The same experiment was repeated, replacing gossypol with a more effective anti-oxidant, and the results were similar throughout (Figure 7). After aging 3 hours, the sample containing copper plus the highest per cent of antioxidant (0.1%) showed the greatest apparent rate of peroxide formation. Moreover, 0.025 per cent antioxidant S 23 is not sufficient to offset the proöxidant effect of 0.00025 per cent copper, even in the early stages of oxidation, since the rate of peroxide formation in this case can be seen to be greater than the rate for the control throughout the test.

On the basis of these results and others of a similar character, irradiation, with or without the addition of small percentages of copper (in oil-soluble form), has become a regular feature of our work on anti-oxidants and fat stability. Copper is generally used only with highly stabilized oils or all-hydrogenated fats, in which the aging period cannot be shortened to a convenient value by irradiation alone. Other metals, especially manganese, can be substituted for copper, and the preferred manner of rendering these metals oil-soluble comprises the formation of soap by heating the metal acetate with fully hydrogenated cottonseed fatty acids in an atmosphere of hydrogen.

This work was conducted under the direction of L. C. Haskell, to whom grateful acknowledgment is made.

Summary

1. Purified gossypol has been shown to have marked antioxidant strength at low concentration.
2. The combined effect of added pro- and antioxidants on the rate of peroxide formation in cottonseed oil is shown graphically.
3. A modification of Wheeler's accelerated oxidation apparatus is described, which shortens the aging period by means of irradiation.
4. The methylene blue test has been checked against peroxide titration for the estimation of fat stability.

Literature Cited

1. E. P. Clark, Oil and Fat Industries, *6*, p. 15, (1929).
2. M. J. Cummings and H. A. Mattill, J. Nutrition, *3*, 4, p. 421, (1931).
3. H. A. Mattill, J. Biol. Chem., *90*, 1, p. 141, (1931).
4. Sidney Musher, U. S. 1,841,842, January 19, 1932.
5. R. C. Newton, Oil and Soap, *9*, 11, p. 247, (1932).
6. R. C. Newton and W. D. Richardson, Can. 323,764, June 28, 1932.
7. H. S. Olcott and H. A. Mattill, Ibid., *93*, p. 65, (1931).
8. H. D. Royce, Ind. Eng. Chem., Anal. Ed., (1933), in press.
9. F. C. Vibrans, Oil and Fat Industries, *8*, 6 p. 223, (1931).
10. J. Waddell and H. Steenbock, J. Biol. Chem., *80*, 2, p. 431, (1928).
11. D. H. Wheeler, Oil and Soap, *9*, 4, p. 89, (1932).

Cooking Cottonseed Meats Containing High Moisture

The ordinary method of cooking cottonseed meats containing a high moisture content is to increase the steam pressure in the jackets of the cookers and lengthen the cooking time. This results in producing a dark-colored cake, owing to the high temperature to which the meats in immediate contact with the hot walls of the cooker are raised occasioned by the inadequate stirring devices usually present. To obviate this difficulty, and produce a light-colored soft cake and an oil having a lower refining loss with a better color, the following method was used:

The meats containing 14 per cent to 17 per cent moisture were being cooked in a five-high stack cooker. A half-inch open steam pipe was carried into the meats in the top three sections of the cooker. Through this pipe live steam under 80 pounds pressure was fed directly into the meats, maintaining the steam pressure on the jackets which would be used for cooking meats containing a normal amount of moisture. The temperature of the meats in the top section was quickly raised to 210° F. Until the temperature of the meats reached 210° F., the meats were becoming wetter due to the condensed open steam. After the meats reached 210° F., the additional heat in the steam above 210° F. acted to evaporate the moisture in the meats. The open steam likewise acted to assist the agitation of the meats. The fan was run at a high speed to carry off the excess steam from the cooker. The temperature of the meats in the second and third sections from the top reached 215° F. and 220° F. respectively. The temperature in