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Improved Techniques for Testing Fats and Oils by the Oxygen Bomb Method

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GEARHART *et al.* (2) have presented a comparison of methods for testing the oxidative stabilities of fats, oils, and fatty foods. An Oxygen Bomb Method adapted from an A.S.T.M. Method (1) for determining the stability of gasoline under accelerated oxidation conditions was described and compared with the Active Oxygen Method (4, 5) and the Schaal Oven Method (3), which are now in use throughout the food industry. This Oxygen Bomb Method involves subjecting the material being tested to an elevated temperature in an atmosphere of oxygen under pressure (usually at greater than atmospheric pressure) in a closed system. A continuous record of the pressure within the system is maintained, and the end of the induction period of the test material within the bomb is indicated by an abrupt decrease in pressure within the system.

In this early work a number of merits and some limitations of the Oxygen Bomb Method, as applied to testing food products, were brought to light. The notable advantages of the bomb method over the stability test methods were its greater speed, precision, and range of products that could be tested by this one method. The principal limitation seemed to be concerned with the lack of uniformity in judging the end-point of the induction period regardless of the type of material being tested. This difficulty apparently stemmed from significant variations in oxidative reactivity of different fats and oils and also from variations in the levels and reactivities of lipides present in different types of food products. In general, it was believed on the basis of the initial work that this Oxygen Bomb Method was largely limited to use in testing fats and oils of a highly reactive nature and food products containing such reactive fats.

After extensive preliminary work with this Oxygen Bomb Method had been completed, it became obvious that this method held great potential as a tool for control and research in the food industry, particularly, if some of its shortcomings could be overcome. Improvements in basic techniques which permit an increase in the number of products successfully evaluated by the Oxygen Bomb Method and which make possible the preparation of standard procedure for testing various fats, oils, and food products by the Oxygen Bomb Method are described in this paper.

Experimental

During the early work with the Oxygen Bomb Method it was observed that the end-point obtained when foods containing appreciable quantities of fat were tested was sharper (a more abrupt or clear-cut decrease in pressure within the bomb at the end of the induction period of the sample) than the end point obtained when the fat itself was tested. This observation indicated that, if a means of expanding the surface area of the fat or oil in the bomb could be devised, the reactivity of the fat or oil in the bomb would be greatly increased. Presumably this increased reactivity would result in a shorter induction period and a sharper end-point and would make possible the testing of relatively nonreactive fats and oils. Various methods for increasing the surface area were investigated, and it was found that a porous cellulosic material, having complete inertness itself under the conditions of the test and having good absorptive qualities, would be suitable. Any of a number of similar materials would probably serve equally well; however in our tests we used a packing material widely used throughout various industries.[1]

A statistically designed experiment was prepared to determine the effects of expanded surface area of the test media upon the precision and scope of the Oxygen Bomb Method as applied to fats and oils. No attempt has been made in this recent work to improve the techniques, as described in the original paper (2), for evaluating various finished food products containing appreciable levels of fat. However, in the interest of presenting a complete summary of work to date on this method, there will be some discussion in this paper (based on earlier work) of the application of the Oxygen Bomb Method to testing finished food products.

For the studies with fats and oils, suitable quantities of lard, cottonseed oil, and a hydrogenated vegetable oil shortening were obtained from commercial sources. The necessary concentrations of commercially available phenolic antioxidants were added to portions of the different types of fats and oils to permit observation of the effect of expanded surface area on the bomb-test results at varying levels of oxidative stability. These different stability levels were also necessary for the statistical analysis of the results. Preliminary investigations had revealed six grams of the fat or oil dispersed on a 5- x 9-cm. (approximately 1.5 g.) rectangle of Kimpac to be convenient working quantities; hence that ratio of fat to dispersant was used in these tests. In evaluating the fat or oil without benefit of the dispersant, six-gram samples were used. The samples of animal fats or hydrogenated vegetable oil were subjected to 50 p.s.i. of initial oxygen pressure in the bombs while the vegetable oil, because of its higher natural reactivity, was sub-

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[1] Kimpac, a Kimberly-Clark Corporation product.

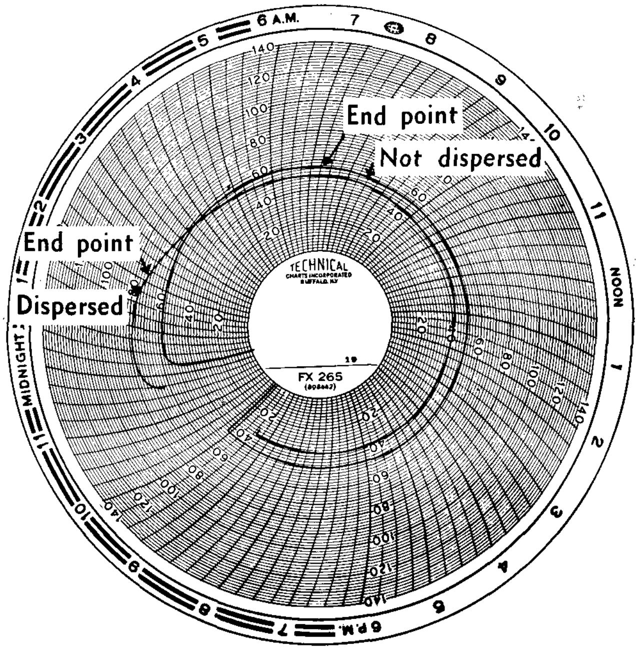

FIG. 1. Effect of dispersion on induction period of lard.

jected to 30 p.s.i. of initial oxygen pressure. All samples were subjected to a temperature of 210°F. (the temperature of boiling water in our locality) after the bombs had received their initial charge of oxygen. In summary, then, each type of fat or oil at the various levels of oxidative stability, as provided by the added antioxidants, was evaluated by the Oxygen Bomb Method with and without the benefit of the dispersant. Each type of fat at each stability level was also evaluated by the Active Oxygen Method in order that comparative data would be available.

For the studies of the oxidative stability of fats and oils in finished food products, samples of potato chips, pastry, and crackers were prepared by standard laboratory procedures. These products represent deep-fat-fried foods, baked foods with high fat content, and baked foods with relatively low fat content and alkaline in reaction. Thirty-gram portions of these products, broken into particle size convenient for the bombs (¼–½ in.) were tested by the Oxygen Bomb Method. Particle size of food products has little significant influence on the results of the bomb tests because of the small variation in fat dispersion accomplished by variations in food-particle size. This point will be investigated in future work. Samples of foods prepared with animal fats or hydrogenated vegetable oil were subjected to 100 p.s.i. of initial oxygen pressure in the bombs while foods prepared with vegetable oil were subjected to 50 p.s.i. of initial oxygen pressure. All bomb tests on food products were run at 210°F. after the bombs had received their initial charge of oxygen. Each type of food was evaluated by the Schaal Oven Method in order that comparative data would be available.

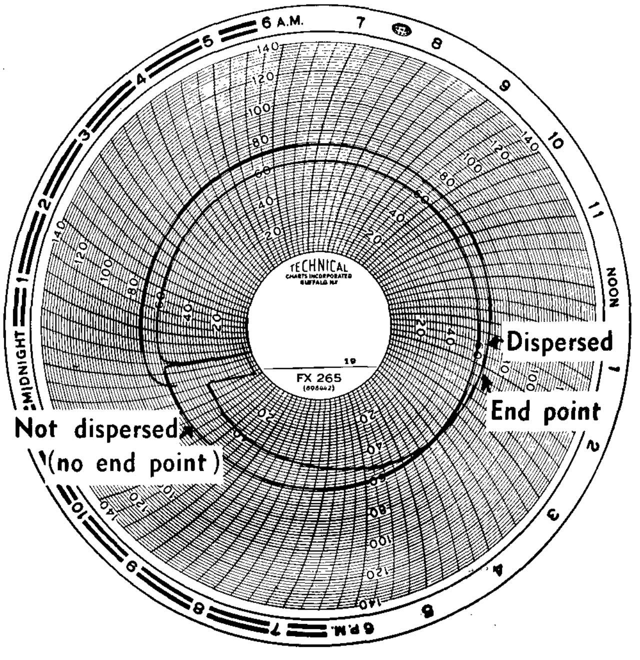

FIG. 2. Effect of dispersion on induction period of vegetable shortening.

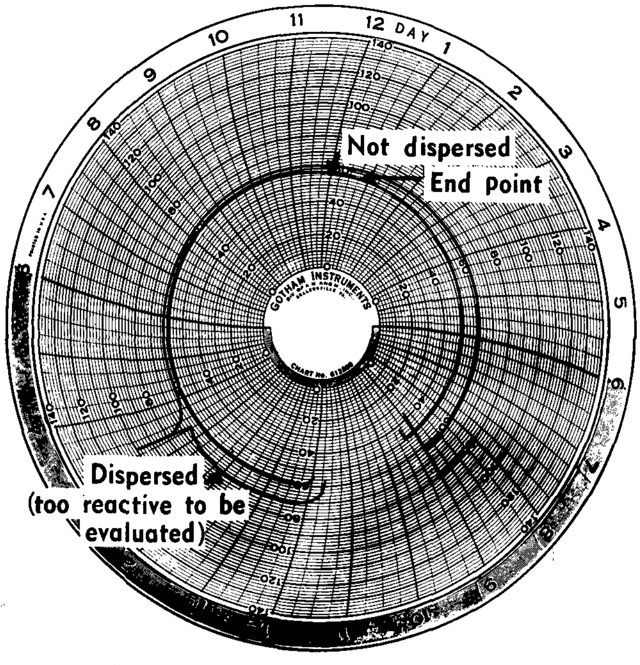

FIG. 3. Effect of dispersion on induction period of vegetable oil.

Results and Discussion

When animal fats were evaluated by the Oxygen Bomb Method, it became apparent that the use of a dispersing agent provided a sharper end-point and also shortened the time required for the test. Figure 1 shows this finding in the case of a lard tested with and without a dispersant. In earlier attempts it had been impossible to evaluate hydrogenated vegetable oil by the Oxygen Bomb Method; however it appears that with a dispersing agent this type of product can be successfully tested (Figure 2). This same situation exists with grease and tallow. In testing vegetable oil by the Oxygen Bomb Method, the use of a dispersant was found to be undesirable because of the extreme activity (high degree of unsaturation) and explosive nature of the oil under such conditions (Figure 3). Satisfactory results with vegetable oil were obtained without using a dispersing agent.

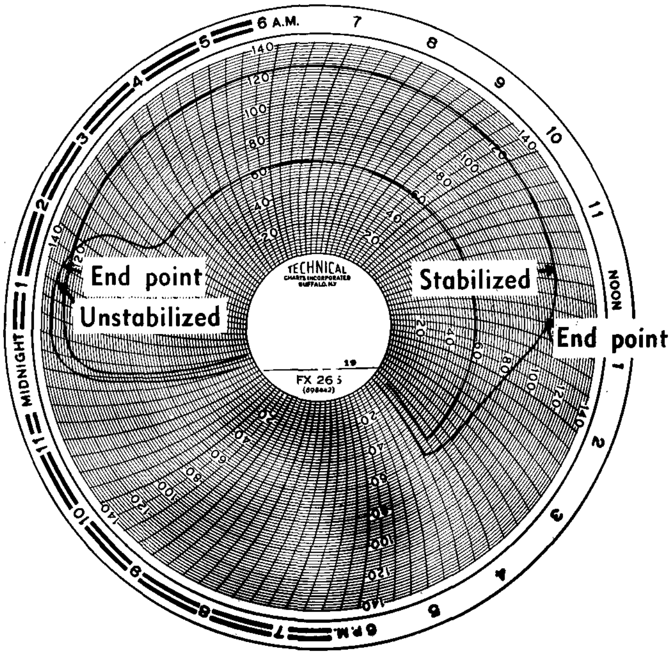

FIG. 4. Effect of antioxidant on induction period of pastry.

A general summary (Table I) of the results of the recent studies on fats and oils demonstrates the wide applicablity of the Oxygen Bomb Method, with the aid of the dispersing technique, to the evaluation of various types of fats and oils and gives some indication of the relationship between AOM results and Oxygen Bomb results (with and without dispersing agent) at various levels of oxidative stability.

TABLE I

Stabilities of Animal Fats and Vegetable Oils as Determined by the Oxygen Bomb and Active Oxygen Methods

Fat or oil	Oxygen bomb method		AOM stability
	Without dispersant	With dispersant	
	hrs.	*hrs.*	*hrs.*
Lard control	6.25	1.25	9
Lard + antioxidant A	28.0	3.25	41
Lard + antioxidant B	55.0	6.25	66
Yellow grease control	......[a]	1.25	1
Yellow grease + antioxidant A	......[a]	3.25	8
Yellow grease + antioxidant B	......[a]	19.5	150+
Cottonseed oil control	11.5	......[b]	8
Cottonseed oil + antioxidant A	14.25	......[b]	12
Cottonseed oil + antioxidant B	21.0	......[b]	31
Vegetale shortening control	......[a]	13.5	68
Vegetable shortening + antioxidant A	......[a]	16.5	139
Vegeable shortening + antioxidant B	......[a]	18.5	190

[a] Not sufficiently reactive to be evaluated by this method

[b] Too reactive to be evaluated by this method.

A statistical analysis of the results from these studies with fats and oils revealed that the Oxygen Bomb Method involving the dispersing technique is no less precise than the Oxygen Bomb Method involving no dispersing agent. Also, on the basis of data from these studies, a good correlation (coefficient of 0.945) was found to exist between the Oxygen Bomb results obtained with and without a dispersing agent when lard was tested. In view of the correlation (coefficient of 0.86) previously found to exist for AOM and Oxygen Bomb results with lard, it is believed that a suitable correlation should exist between AOM results and Oxygen Bomb results when a dispersing agent is used. Also, a satisfactory correlation between test method and results should exist when other types of fats or oils are tested; however additional work should be done to prove this point.

Typical results obtained from Oxygen Bomb evaluation of pastry is shown in Figure 4. It was noted that sharp end-points can be expected with potato chips and pastry; however crackers do not provide such a sharp end-point, possibly because of the low fat content of this product. A comparison of results obtained from Oxygen Bomb and Schaal Oven evaluations of these products is shown in Table II.

TABLE II

Stabilities of Some Fat-Containing Foods as Determined by the Oxygen Bomb and Schaal Oven Method

Food	Oxygen Bomb Method	Schaal Oven Method
	hrs.	*days at 145°F.*
Potato chips fried in		
control animal fat	1	3
stabilized animal fat	10	42
Potato chips fried in		
control vegetable oil	8	10
stabilized vegetable oil	12	15
Pastry prepared with		
control lard	2	2
stabilized lard	15	37
Crackers prepared with		
control lard	10	9
stabilized lard	16	28

Since the statistical evaluation of data from these two methods has already been reported (2), it will suffice now to re-emphasize only the marked increase in precision offered by the Oxygen Bomb Method. The results in Table II illustrate the markedly shorter time required for the Oxygen Bomb Method when compared with the Schaal Oven Method.

On the basis of the recent and previous studies the following conditions of oxygen pressure, sample size, and physical condition should be applicable in testing most fats or oils and fat-containing foods for oxidative stability by the Oxygen Bomb Method. The temperature should be held constant (about 210°F.) for all products.

a) Animal fats, mixed animal and vegetable shortenings, and vegetable shortenings (or other fats or oils of relatively stable nature)
Sample: Six grams on a dispersing agent
Initial oxygen pressure: 50 p.s.i.

b) Vegetable oils (or other similar highly reactive fats or oils)
Sample: 15 grams
Initial oxygen pressure: 100 p.s.i.

c) Food products containing animal fats, mixed animal and vegetable shortenings, or vegetable shortenings (or other fats or oils of relatively stable nature)
Sample: 30 grams of convenient particle size
Initial oxygen pressure: 100 p.s.i.

d) Food products containing vegetable oil or similarly reactive fat or oil
Sample: 30 grams of convenient particle size
Initial oxygen pressure: 50 p.s.i.

Ideally the end-point or end of the induction period is taken as that point, in the pressure-time curve, which is preceded by a pressure drop of at least 2 p.s.i. within 15 min. and succeeded by a drop of not less than 2 p.s.i. in 15 min. (taken from the A.S.T.M. method [1]). When the test material is not sufficiently reactive to provide the above pressure drop, the end-point should be taken as the midpoint of the first hour where a 2-p.s.i. drop in oxygen pressure occurs, followed by a 2 p.s.i. or greater drop in the succeeding hour.

The Oxygen Bomb Method has been used quite effectively in the laboratory to develop information on the oxidative characteristics of a wide variety of products. The wide applicability of this method in the food industry has been demonstrated by successful evaluations of products such as fish scrap, fried chicken, various types of nuts, egg solids, butter oil, fish sticks, pastry and cake premixes, and fatty acids. A number of other materials not successfully evaluated with present techniques, possibly because of low fat content or extreme stability of oxidizable components, are some cereal products, some animal feeds, coffee, and some candies.

Summary

The use of a dispersing agent to expand the surface area, thus providing an increase in reactivity of fats and oils under the conditions of the test, has been investigated. This dispersion technique permits the testing of a wider range of products, decreases the test time, and results in sharper end-points. These improvements should serve to increase the applicability of the Oxygen Bomb Method as a tool for oxidation studies and quality control in the food industry. A general comparison of the Oxygen Bomb Method with the AOM and Schaal Oven Method has been presented to illustrate the relationship between results obtained by these various methods. The dispersion technique has been combined with previously established bomb techniques, and procedures for testing a wide variety of fats, oils and food products by the Oxygen Bomb Method are suggested.

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Plasticizer Properties of Some Acrylonitrile-Eleostearate Adducts and Their Hydrogenated Derivatives

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In an earlier publication (1) we have described the Diels-Alder reaction of the *n*-butyl esters of *alpha*- and *beta*-eleostearic acids with acrylonitrile and fumaronitrile and at the same time have reported the plasticizer properties of the adducts. It was found that acrylonitrile reacts readily with the eleostearates and that the resulting products, although not entirely suitable as primary plasticizers, were quite satisfactory as secondary plasticizers. In conjunction with dioctyl phthalate or tricresyl phosphate the acrylonitrile adducts contributed a number of desirable features to the vinyl chloride-vinyl acetate copolymer.

In view of these considerations it appeared of importance to ascertain whether or not the plasticizing qualities could be improved by modification of the acrylonitrile adduct to produce a material with suitable properties as a primary plasticizer.

It was observed that the presence of appreciable amounts of a polyunsaturated or of a completely saturated, long-chain moiety impairs compatibility (2), particularly in glyceridic materials (3). Improved compatibility results from the reduction of polyunsaturation. Saturation of the cyclic and exocyclic ethylenic linkages of certain adducts of the eleostearates also results in an enhanced compatibility of the material (4). Accordingly an investigation was undertaken to establish optimum conditions for the hydrogenation of the ethylenic bonds of the acrylonitrile adducts with minimum reduction of the nitrile group and to determine the plasticizing properties of the hydrogenated derivatives.

Experimental

The procedures employed for the preparation of the esters of tung oil fatty acids, acrylonitrile adducts of the eleostearic acid esters, and selective hydrogenation of these adducts were essentially the same for the methyl, ethyl, and butyl derivatives. A typical series of experiments is described in detail.

Preparation of the Esters of Tung Oil Fatty Acids. Tung oil (1,200 g.) was added to a solution of sodium alcoholate, which had been prepared previously by dissolving metallic sodium (6.6 g.) in the appropriate absolute alcohol (400 g.). This mixture was refluxed with frequent shaking over a period of 2 hrs. The glycerol layer which separated from the reaction product on cooling was removed, and the crude esters were washed successively with two 500-ml. portions of N/2 HCl and then with several 250-ml. portions of water until free of acid. The esters were freed from volatile materials by vacuum-stripping on a steam cone, employing a stream of carbon dioxide. The resulting product was distilled through a short-path column at reduced pressure, yielding a main fraction which weighed approximately 875 g. The products obtained had the following characteristics: methyl esters—b.p. 152°C./5 microns, n_D^{20} 1.4925, 73% methyl *alpha*-eleostearate, 3% methyl *beta*-eleostearate;[2] ethyl esters—b.p. 156°C./100 microns, n_D^{20} 1.4928, 49% ethyl *alpha*-eleostearate, 18% ethyl *beta*-eleostearate; butyl esters—b.p. 173°C./350 microns, n_D^{20} 1.4915, 60% butyl *alpha*-eleostearate, 4% butyl *beta*-eleostearate.

The esters were stabilized with 0.05% of hydroquinone and stored in a refrigerator at 5°C. until required.

Reaction of Acrylonitrile with the Eleostearates. A mixture of 250 g. of the appropriate esters (*ca.* 0.65 mole), 75 g. of acrylonitrile (1.40 moles), and 1 g. of hydroquinone was refluxed for 96 hrs. At this time

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[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] Eleostearates were determined by the method of Hoffman *et al.* (5).