A STUDY OF THE

PHYSICAL FACTORS INVOLVED IN THE SWIFT STABILITY TEST FOR FATS*

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OF THE many test proposed for determining the susceptibility of fats and oils to oxidation, or in a more practical sense, of predicting the keeping quality, the one sometimes referred to as the Swift[1] Test appears to be gaining fairly wide acceptance, and bids fair to become a sort of standard method. It has many good features and has been the subject of cooperative study by a committee of this Society.[2] There is no need to describe the test again, but very briefly it consists in bubbling air through three portions of the sample, which are started at different times, until the one started first yields a rancid odor. Then the peroxide numbers of the test portions are plotted against time, and the stability is expressed as the number of hours that the fat maintains a peroxide number below some arbitrary value. Since the success of this sort of test so frequently depends upon a rigid adherence to the particular set of conditions chosen, the authors of the original publication emphatically cautioned against departing from these. The temperature is 208° F. (97.8° C.), the rate of air flow 2.33 cc./scc., and 20 cc. of fat are treated in 1-in. test tubes in the dark.

The writer's first efforts to use this test produced some erratic results, and since he had departed somewhat from the exact conditions specified in the original paper, it appeared desirable to study the method carefully with respect to these conditions, partly with the object of determining the magnitude of error that might result from any variations in them, and partly to ascertain if some modification might not yield results in a shorter time. This seemed especially important, since the duration of the test for very stable fats of the all hydrogenated type might be in the neighborhood of 100 hours, or four days. This circumstance not only limits the capacity of the apparatus, but renders the test practically useless for control purposes and makes it a slow tool for experimental testing. This was recognized by the stability test committee, the report of which in 1932 indicated its intention to examine the possibility of using metals to further accelerate the onset of the end point.

In the course of the work being reported here certain slight modifications of the apparatus were made which are believed to be improvements in certain respects and are presented for the benefit of those who wish to make their own apparatus at an appreciable saving in cost.

The Apparatus

There are two principal changes. (1) The substitution of oil color tubes for the 1-in. test tube, and (2) the elimination of the oil bath. The oil color tubes are more durable than test tubes; they are much cheaper, require less sulphuric acid-chromate solution for cleaning, and are more easily handled during cleaning in quantity. Also a smaller sample is required for the test. When it was found that these would, with a few individual exceptions, fit snugly into 1-in. standard copper pipe (⅞-in. I. D.), a heating apparatus not requiring oil suggested itself. Five inch lengths of the pipe, closed at the lower end, are soldered at the upper end into the cover of a rust resisting closed container in which water is boiled and retained by refluxing. This apparatus may be made quite compact, and requires only a single 500 watt heater to mtaintain boiling. In the case of the writer's, a cover was soldered on a cheap, drum shaped refrigerator drip pan 14 inches in diameter. For studying the effect of light on the test this shape was required so that all the tubes would be equidistant from the light source. It is heated by an electric iron costing $1.50. The temperature of the fat in the tubes is 99.5° C. (211° F.). This difference of 3° F. from the temperature of the Swift test required the determination of the temperature coefficient of the test results to obtain a correction to apply, making the writer's results comparable to others. The use of smaller tube and less fat necessitated changing the rate of flow so that the rate of flow of *air per cc. of fat* would be the same as in the Swift test. Fourteen cc. of fat permits the air delivery tube to be 2 inches below the surface, and 1.63 cc./sec. gives the correct flow. Somewhat smaller air delivery tubes are used because of the smaller holes in the stoppers. Finally, the detection of the rancid odor has been facilitated in the following way: 50 cc. extraction flasks are left hung over the air outlet tubes. When testing for the end point, these are removed and the contents inhaled. The odor of the accumulated gases leaves no doubt as to when the test is "out." The apparatus is shown in Plate I.

Effect of Modified Flow Conditions on the Results and the Reproducibility of Results

It was suspected that the use of a smaller delivery tube might make for a shorter test time because such produces smaller air bubbles, with consequent considerable increase of contact area between gas and fat (since the area of a spherical bubble varies with the square of the radius). In order to test this and

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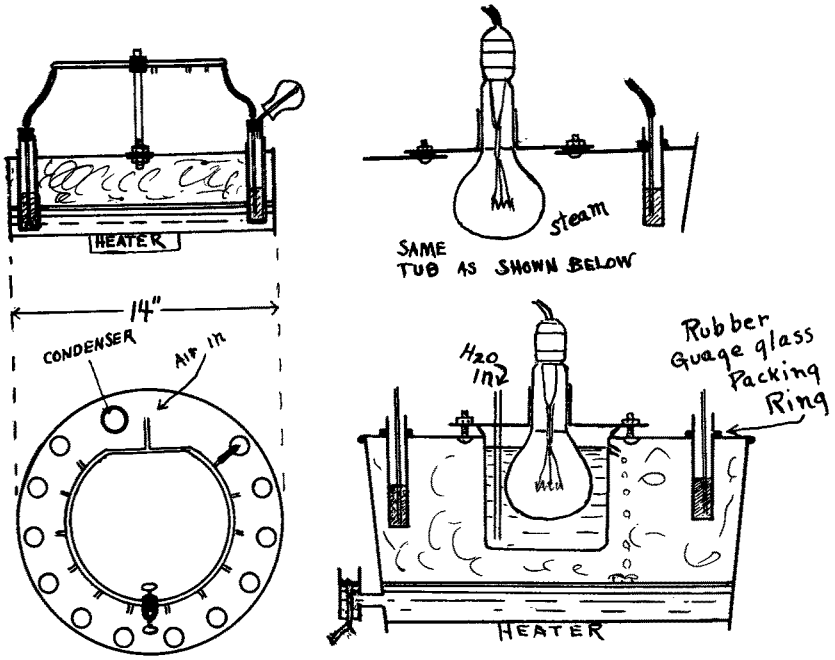


PLATE I—APPARATUS

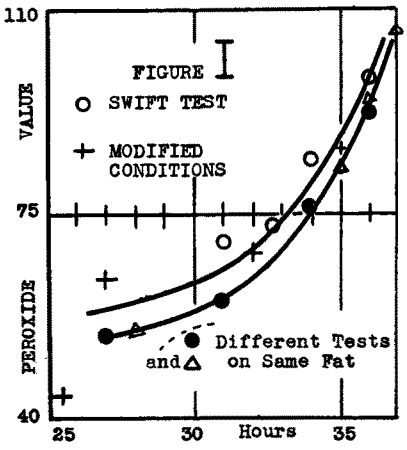
to check the validity of the assumption of the compensating effect of a smaller air flow rate with a smaller amount of fat, the following experiment was made: A sample was tested in strict accordance with the Swift method. At the same time the sample was run according to the conditions just described. Also a repeat run was made on another sample which had been stored in the ice box a day or so between tests. The results are shown in Figure 1. It is evident that the method is capable of very good precision and that the writer's modification yields results in line with others. These results are summed up in the following table:

TABLE I

	Swift Method	Present Modification
Volume of fat	20	14 cc
Rate of air flow	2.33	1.63 cc/sec
Diameter of inlet tube	0.40	0.25 cm
Test time	34	34 hrs.

Now careful consideration of the factors involved in a reaction between a gas and a liquid, through which the gas is bubbled, leads to the obvious conclusion that the dimensional elements that would be expected to influence the rate is the area of gas bubble surface contacting unit quantity of liquid in unit time. By this standard the flow conditions just tabulated are not the same, for, as suggested above, the gas inlet tube in the writer's apparatus, being smaller, releases a given amount of air in a given time in the form of more bubbles, and these have a greater total surface. Since, however, the same keeping test was obtained in the two cases, the implication is that the value of the rate of air flow might not be of much consequence to the results. Although this conclusion was checked and verified by direct test, as will be reported, the magnitude of the differences in surface just mentioned were calculated after making a rough determination of the rate of bubble formation from different sized tubes. The equations used and data for the two conditions are given in Table Ib, as well as two equations relating the number of bubbles formed and the total bubble surface to the size of the tube.

That is, within the error of these measurements, the volume of the bubbles, for a given flow, is proportional to the square of the diameter of the delivery tube. Or the area

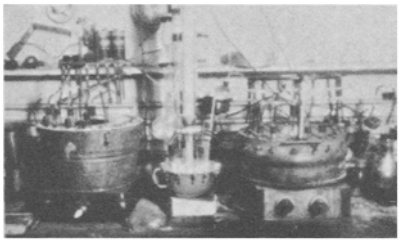


of the bubbles is proportional to the 4/3 power of the diameter of the tube, which may be shown to follow from the above relations.

Thus, increasing the reacting surface by 33% of the regular value had no measurable effect on the results. This suggested that a lot of time might have been wasted in careful calibration of capillary flow tubes. To verify this conclusion by actually using different rates of flow in the same apparatus the data in Table II were obtained. Their reliability is indicated by curves and in Figure I. These conincide almost exactly in Test I.

Therefore, changing the rate of flow by 100% produces no difference in the test results, at least for the particular samples studied. It is realized that these experiments ought to be made on other types of fats and oils before drawing final conclusions regarding this effect, but the following theoretical considerations are in support of the results just presented.

In the case of reactions of the third order, the reaction rates follow the law for monomolecular re-



actions when two of the reactants are present in great excess relative to the third. The hydrogenation of oils is a typical example. Here, in the general case, the oil and catalyst occur in such high excess over the hydrogen at the points of reaction that the concentration of the latter alone governs the rate. If we can picture a reacting system in which oil is dissolved in extremely dilute solution in some solvent through which hydrogen is bubbled in great excess, then we would expect that the rate, assuming also an abundance of catalyst, would depend on the oil concentration. Or if the catalyst, instead of the oil, were present in extremely small amounts, its concentration would govern the rate. This last is analogous to the state we have in the stability test. The oxidation of the fat is essentially catalytic, the catalyst or catalysts being some compounds resulting from the breakdown of the original reaction products, or the

RELATION OF VOLUME AND AREA OF BUBBLES AND RATE OF BUBBLE FORMATION TO DIAMETER OF TUBE PRODUCING THEM

TABLE 1a

	Swift[2]	Freyer[1]	Freyer
Tube diameter = d	0.40 cm.	0.25 cm	0.25
Volume of fat	20 cc.	14	14
Rate of flow	140 cc./min.	98 cc.	140
No. bubbles/min. = n	475	795	1135
Volume of bubbles = v	0.295 cc.	0.123	0.123
Area = $4.85v^{2/3}$ = a	2.15 sq. cm.	1.20	1.20
Sq. cm./min.	1030	955	1360
Sq. cm./min./cc. fat	51.5	68.0	97
Ratio $\frac{Sw}{Fr}$	.75		

TABLE 1b

$$v = 4.19\,r^3 \quad , \quad a = 12.6\,r^2$$

$$r^2 = \left\{\frac{v}{4.19}\right\}^{2/3} \quad , \quad a = \frac{12.6\,v^{2/3}}{4.19^{2/3}} = 4.85\,v^{2/3}$$

$$\left\{\frac{d_2}{d_1}\right\}^2 = \frac{0.0625}{0.16} = 0.39 \text{ and } \frac{n_1}{n_2} = \frac{0.123}{0.295} = 0.42$$

$$\frac{0.42 - 0.39}{0.42} \times 100 = 7\%, \text{ difference}$$

$$\text{Therefore, } \frac{n_1}{n_2} = \left\{\frac{d_2}{d_1}\right\}^2$$

$$\text{Also, } \left\{\frac{d_2}{d_1}\right\}^{4/3} = .54, \text{ and } \frac{a_2}{a_1} = .56, \text{ so } \frac{a_2}{a_1} = \left\{\frac{d_2}{d_1}\right\}^{4/3}$$

reaction products themselves. Calculation shows that the amount of these is very small in comparison with the supply of available oxygen passing through the fat; so that at least a two-fold variation in the latter should not make any appreciable difference in the rate of the reaction. This depends more by far on other factors, notably temperature, as shall be shown, and accidental catalysts.

Effect of Light on the Rate of Peroxide Formation

Royce[3] studied the effect of strong light on the rate of increase of peroxide number in oils, using a 200 watt lamp at 15 cm. More recently Evans,[4] investigating the antioxidant effects of vegetable lecithin, gives comparative data for peroxide formation both in light and dark. These tests were made at room temperature on oils and were accelerated by dissolved cobalt.

At the beginning of the present study it was felt that the use of strong light offered the best and most constant means of accelerating the oxidation, so that results could be obtained in a shorter time. Bearing in mind that the present stability test had as yet received no official recognition the writer was particularly anxious to develop some simple modification that would shorten the test without introducing any serious complications, especially of apparatus. This proved to be more of a problem than was expected, two principal difficulties being encountered: (1) Line voltage fluctuations, resulting in considerable variation of the illumination (5% change of voltage produces a 20% change of illumination). (2) Interference with temperature control by heat radiation from the light source. For example, a tube of oil in the dark thermostat assumed the temperature of the medium, but when the light was turned on, the oil temperature rose 5° C., whereas the air or steam of the thermostat, showed no change of temperature, provided this were read with a properly shielded and well ventilated thermometer. In the case of the air thermostat the temperature may be easily regulated to any desired value, but this type of apparatus lacks simplicity, and, unless very well designed and constructed, is subject to annoying breakdowns when doing continuous duty. An apparatus (shown in Plate I) was built which used steam as the thermostatic medium. The lamp was fitted into the steam space through a close fitting collar soldered on to a plate, which was bolted over a gasket on to the cover of the tub. However, to permit working at 100° C. it was necessary to modify this arrangement by providing an optical filter to absorb the infra-red radiation from the lamp, a result accomplished by having the lamp immersed in a large beaker of water, which it was necessary to renew continuously to prevent boiling. Nevertheless, scale showed a tendency to form on the lamp, a very serious objection; so that in any further work with this apparatus it will be imperative to circulate distilled water around the lamp and through a heat exchanger. Thus, still more apparatus.

Absolute constancy of line voltage is an ideal never actually attained in a laboratory where heavy loads are frequently and irregularly thrown on. Voltage regulators that will handle the 300 watt load necessary are quite expensive. However, it is possible by proper selection of a circuit, to keep the variations small enough to avoid serious interference with the test; but in any case it would be necessary to check the illumination photometrically every few hundred hours during the life of the lamp. This would not be difficult with the small photoelectric foot candle meters now available.

All of these considerations led to the writer's abandoning of further efforts to shorten the test time by using light, especially when it was found that the same result could be attained very simply by increasing the temperature.

In Table III are given the results of two comparisons of the stability test run in the dark and in different values of illumination. The fat was an all-hydrogenated shortening. A similar comparison is included, which was interpolated from Royce's[3] two curves on cottonseed oil. In Figure II the data are plotted. It had to be assumed that Royce's lamp was operated at rated voltage and that it had the same characteristis as this writer's. If his voltage had any value below rated, then the curve would be flatter at the higher foot-candle values. The illumination values were meas-

TABLE II

Effect of Rate of Flow on the Stability Test.

TEST I

Sample	Time	Peroxide No.	Result
All-hydrogenated	26 hrs.	58 M.E./kg.	
Flow: 0.82 cc./sec.	29	80	
	31	112	29 hrs.
Same sample	26	60	
Flow: 1.63 cc./sec.	29	82	
	31	112	29 hrs.

TEST II

Same, 3 wks. earlier. Flow: 1.63 cc./sec	35.5 hrs.
Same, 3 wks. earlier. Flow: 2.28 cc./sec	36.5 hrs.

ured with a photoelectric photometer borrowed from the light company. Extrapolating the curve out to a per cent reduction in test time of 67 we obtain an illumination value of 1120 foot candles, which would be furnished by a 250 or 300 watt lamp operated at some voltage below rated. Thus, tests results would be completed in one-third the time required in the dark. In Table IIIb are given data showing the error that would result from a relatively slight variation in the voltage. These are calculated from Figure II and from curves, not given, showing the variation of illumination with voltage changes.

Effect of Temperature on the Rate of Peroxide Formation

After the observation was made that a sample with a stability test of 33 hours at 99.5° C. would last 49 hours at 93.5° C. (a boiling alcohol solution), it became apparent that increasing the temperature was the logical answer to the question of how to shorten the test. It should be remarked, however, that tests involving unstable antioxidants may not be strictly comparable when run at different temperatures. It appears, moreover, that the stability tests of different types of fats may have slightly different temperature coefficients. But in view of the amount of time it is possible to save by running at a somewhat elevated temperature, very serious consideration ought to be given to this factor when it becomes desirable for the Society to adopt some stability test as one of its tentative methods. No one condition is ideal in this test, and, at least within a range of a few degrees, one temperature is as good as another.

Again we face the problem of the design of a suitably simple apparatus. In addition to those already described, tests have been made at the temperature of a boiling saturated solution of common salt (108° C.) and at 115° C., the latter chosen as being one at which results are obtained in one-third the time required at 99.5° C. In the former case, design I, Plate I was used. The use of brine involves a corrosion problem, but it is hoped that this will be met in a new apparatus, recently built, but as yet untried, consisting of an enamelware container with a brass cover supporting the copper tubes in which the glass color tubes fit with small clearance. For higher temperatures, an oil bath is used, temperature being regulated by a Dekhotinsky bimetallic thermoregular, which breaks the current in a heavy duty magnetic relay (constructed at practically no expense in one day). This relay interrupts the current (about 8 amps.) in one element of a two-heat stove on which the apparatus rests. The other element burns continuously. An exposed element stove is used to insure rapid heat transfer to the oil bath; otherwise, with an embedded element hotplate, an appreciable time lag causes a too wide temperature variation during regulation, which should be within 1° C. Using copper color tube sheaths with 1/16-in. wall, it is necessary to maintain an oil bath temperature of 119° C. to have a test temperature of 115° C.

In Table IV and Figure III are given the results of the tests made at different temperatures.

The rate of change, that is, the slope, is seen to increase slightly with temperature, and it is evident that the coefficient is somewhat different for different types of fats. It would be expected to be different for a fat containing lecithin, since this substance is less stable at the higher temperature than at the lower and its protective qualities correspondingly impaired, but, in the one case where this was tested the change in the test's duration with temperature was the same regardless of the presence of lecithin.

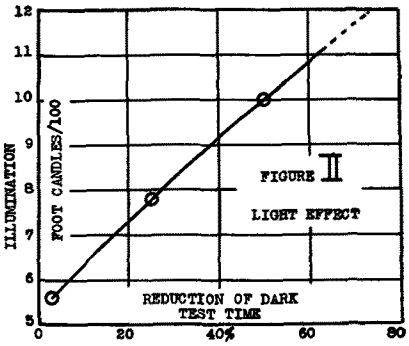


TABLE IV

Effect of Temperature on the Duration of the Stability Test

Sample	T_l Low Temp.	t_l Time	T_h High Temp.	t_h Time	$\frac{100\,(t_l - t_h)}{t_l\,(T_h - T_l)}$ Change per °C. in % of Low Temp.	Time
All-hydrogenated	93.5° C.	49 hrs.	99.5° C.	33 hrs.	5.45	$\frac{t_l}{t_h}$
All-hydrogenated	100.0	32	107.0	20	5.35	
All-hydrogenated	100.0	43.5	115	14.5	5.85	3.0
All-hydrogenated containing 0.06% lecithin	100.0	43.0	115	15.5	5.50	2.8
Bleached oil	100.0	9.5	115	3.7	5.30	2.6
All-hydrogenated (unstable)	100.0	26.0	115	9.3	5.50	2.8

TABLE IIIa

Effect of Light on Stability Test
Results obtained at, or corrected to 99.5° C.

Illumination	Time (light)	Time (dark)	Time reduction (% of Dark Time)
560 foot candles	26 hrs.	26.7 hrs	3%
780	29	37	22
1,000 (Royce, 100° C.)	5	9	45

TABLE IIIb

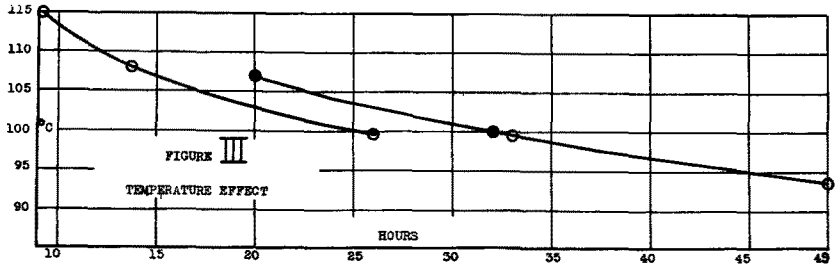
Error in Light-accelerated Test Due to Voltage Difference

Voltage	Illumination (foot candles)	Pct. of Dark Test Time	Hrs. in Light (on 45 hr. Dark Test)
110V	1,160 F.C.	30.5%	14 hrs.
107	1,060	43.0	19

Change of Peroxide Value in Tests Standing at Room Temperature

In connection with interruption of tests at the end of the day, King, Roschen, and Irwin state, "There is reason to believe that holding samples in this manner overnight gives a slightly lower keeping test than if the sample is carried on to rancidity without interruption." In the present work the tests run at the lower temperatures were interrupted at times, and no particular effect was noted, but there might have been a slight one, undetected. At times the "spreading" of the three tests through different time intervals was done some hours after the tests had run. That is, all three were started at the same time; then later two were removed, one for an hour, the other for two hours. When this was done on the high temperature runs, however, very erratic results obtained. An example is given.

As a check on this phenomenon, four samples were started and all



were removed at the rancid point and brought to room temperature. Peroxide values were made as follows:

In another experiment three tubes of the same fat were started simultaneously and all taken off at the end of thirteen hours at about the rancid point. They were chilled quickly to room temperature and the peroxide values determined. Then one of the tubes was again treated with air for an additional 30 minutes at the test temperature of 108° C.; another was treated with air but at room temperature; the third was held during the same period at 108° C., but was not aerated. Peroxide values were again determined, and still again after standing at room temperature for an hour.

In order to introduce the concept of equilibrium the reactions are

$$\text{Fat} + O_2 \rightleftarrows \text{Peroxides} \rightleftarrows \text{Aldehydes}$$

written as reversible, with the extent (or velocity) of the reverse reactions small. Assuming further that the first reverse reaction is negligible and remembering that the fat and O_2 concentrations may be regarded as constant, we may examine the effect of various influences on the peroxide - aldehyde equilibrium, which is to say, on the peroxide concentration of the system under different conditions. Applying the theorem of Le Chatalier, the removal of the aldehydes causes the reactions to proceed from left to right, and the velocity, other conditions being the same, will depend on the rate of removal of the aldehyde products; so that according to the law of mass action this rate (neglecting the other reaction) also determines the peroxide concentration. Therefore, when aeration of a test is stopped and the temperature lowered, removal of end products is interrupted and we may expect for a time an accumulation of both end and intermediate products. That the peroxide concentration increases under these conditions has been demonstrated by test. That the aldehydes also accumulate seems, in connection with the data of Table Va, to follow from a consideration of their role as catalysts for the reaction; for it would appear that the approximately fourfold increase of peroxide value for a test which had been interrupted over one that ran continuously, could only be explained by the assumption of a drastic catalytic action attributed to compounds formed during the time the test had been stopped. Moreover, an increase of this magnitude would hardly be expected to result from a 50% increase of peroxide concentration alone. This view of the effect of

TABLE Vc

Aerated 13 hrs. @ 108° C.—Regular Air Flow

Tube	1	2	3
Peroxide Value	100	100	134
	After Aerating 30 min. @ 108° C.	Holding 30 min. 108°, not aerated	Aerated 30 min. @ Room Temp.
	170	136	194
Increase	70	36	60
After 1 hr., 30° C.	170	140	194

TABLE Vd

Aerating Time, 15 hrs. at 115° C.

Test	Previous Handling	Peroxide Value
A_1	As above cooled to 50° C. in air	70
A_2	Ditto A_1, plus 1 hr. @ 10° C.	60
A_3	Ditto A_2, plus 1 hr. @ 30° C.	60
B_1	Aerated 15 hrs.; cooled to 50° C.	110
B_2	Ditto B_1 10 min. later	112
B_3	Ditto B_1 20 min. later	132

TABLE Va

Effect on the Results of Removing Tests and Cooling
(Test—Temperature, 115° C.)

	Spread at Start			Spread During Last Half of Test		
Test	1	2	3	4	5	6
Start	noon	1 p.m.	2 p.m.	noon	noon	noon
End	8:30	8:30	8:30 p.m.	not interrupted	off 1 hr. (4 to 5 p.m.)	off 2 hrs. (4 to 6 p.m.)
			End	8:30	8:30	8:30
Time	8.5	7.5	6.5 hrs.	8.5	7.5	6.5
Peroxide No.	60	50	36	58	184	136

TABLE Vb

	Immediately	After 1 hr.	After 2 hrs.	After 2 hrs. but heated to 115° C. momentarily
Mille Equiv./kg.	86	122	124	140

The interpretation of these results is not readily apparent and takes us into the field of chemical kinetics. We may conclude from the data of Tables Vb, c, and d that, at least after the peroxide value has risen to a value not far below the rancid point, there is a tendency towards increase, even when the aeration is discontinued and the temperature lowered. This tendency is relatively slight at about 30° C. and negligible at 10° C., but at temperatures much above 30° C. it may be very pronounced. It undoubtedly depends largely on the magnitude of the peroxide value itself. The tendency is believed not to be appreciable in the case of tests aerated below 100° C.

The results of a third test follow:

These observations, however, do not explain the extreme peroxide values of tests 5 and 6, Table Va, where the two interrupted tests treated 6.5 and 7.5 hours show much higher values than the uninterrupted one treated 8.5 hours, and each, 3.75 times the peroxide value of the corresponding uninterrupted test. What reactions occur during the one and two hour periods of removal from the condition of high temperature and aeration, to a static condition at low temperature in the dark—reactions that result in an abnormally rapid formation of peroxides when the test is resumed?

We may consider that, in the main, three types of reactions or processes occur in the oil in the later stages of treatment with air: (1) The formation of peroxides; (2), the breakdown of peroxides into aldehyde compounds; (3), the removal of these compounds under the influence of heat and aeration. We may write this as follows:

the rate of removal of reaction products involves further consideration of the rate of gas flow through the fat. It has been shown that theoretically the results should be independent of this rate insofar as it concerns the oxygen concentration, and this has been shown to be true experimentally for a 100% change of flow rate. However, from the standpoint of the effect on the reaction equilibria this flow rate may be of some consequence, although any inert gas would have the same effect.

To throw additional light on this question a test was run on a sample in which the rate of flow was reduced to one-tenth the regular value. Instead of giving a longer keeping test, as might be expected from the ten-fold reduction of oxygen supply, the test was shorter, as follows:

			Percentage Change
Rate of Air Flow	98 cc/min	9.8 cc/min	1000%
Keeping Time	25 hours	19	24

This result is the same as that due to stopping the flow altogether for a time and is attributable to the same cause, as just discussed.

It is calculated that the total bubble surface area available per minute in the case of the 9.8 cc. rate is about the same as that due to the actual top surface of the fat in the tube, if sufficient agitation is provided to renew this surface about 35 times a minute. Since bubbling air is about as simple a form of agitation as could be found for this test, there is no need for considering any modification in this respect. These relations, however, suggest that by the use of petrie dishes or large beakers containing a relatively small quantity of fat keeping test results might be obtained in an air oven which ought to agree fairly closely with those of the Swift method. The principal disadvantages of this procedure would be: (1) large surfaces of glass apparatus requiring cleaning between tests, and (2) the increased liability to accidental contamination due to these large surfaces, (3) inconvenience in smelling the tests when testing for rancidity, (4) probability of errors resulting from temperature changes taking place when the oven is opened for inspection of the tests. The writer realizes that this oven method for stability testing has long been in use, and he mentions it here only to remark that conditions might be found under which it will yield the same values as the present test; so that it might be useful in laboratories not having the more elaborate stability test equipment, and not ordinarily needing it.

Should it appear that the writer has gone to unnecessary lengths in discussing some of the minor details of the stability test he may state that in undertaking this study, no factor, however apparently unimportant, was so regarded; and as the work progressed, one experiment led to another, and since the time and trouble was taken to make them, it has seemed desirable to report and record the results and their interpretation, as the writer sees it. Moreover, he perforce has become very conscious of the cost aspects of laboratory operation during the last few years, and since the manufactured stability equipment is rather expensive, partly because of its large size and partly because of the exact calibration of flow tubes, it has seemed especially in order to describe other designs, smaller and cheaper, and possessing certain advantages.

SUMMARY

The Swift stability test has been examined and most of the variables concerned in the results have been studied and their effects evaluated.

The rate of air flow has been shown to have practically no bearing on the results over a fairly wide range of variation, but a change of several hundred per cent may have some effect.

The temperature coefficient of the test keeping time has been shown to be of the same order of magnitude as the majority of organic chemical reactions; that is, the velocity is doubled for a 10° C. rise of temperature. This is suggested to be the most logical approach to the question of how to shorten the time of the test.

The effect of light on the test was investigated and the accelerating effects of different values of illumination from a common electric lamp have been evaluated. It has been shown that the use of strong light is not a practical means of producing a constant means of acceleration in the routine test.

Apparatus is described showing how the test may be conducted under various conditions of temperature and illumination.

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DISCUSSION

MR. R. H. FASH: Since the endeavor has been made to accelerate this test and reduce the time, have any tests been made using a copper tube instead of a glass tube to see if that will produce the results desired?

MR. IRWIN: We studied the accelerating effect of copper soaps on oils and fats and found that as little as .15 parts per million increased the rate of oxidation very rapidly. We also tried out copper strips suspended in the oil and again the accelerating effect was so great that it was not feasible to use this method of acceleration. I notice in the data submitted by Dr. Kilgore that he has not carried the samples to the point of rancidity. I should like to ask what he thinks would have happened had he carried his determinations further.

MR. KILGORE: Well, nine hours, as you will notice, is just on the edge of it. The point that you raise is very pertinent. I should have extended the data further, but when you go further, the points vary more in the chemical determination. In other words, when the peroxide value reaches a high value the errors in the chemical determination outweigh the errors which I am talking about.

I have the curves on data which show that the points along the curve, as it approaches a high millimol equivalent value, begin to scatter tremendously.

The second answer to your question is that it appears that if an oil starts out low, it stays low all the way through. The starting point during the first three hours, if they are plotted with five or six points,

will predict pretty accurately the top of the curve on the same oil under the same conditions. If an oil starts out with a peroxide value lagging behind its duplicate, it will lag behind all the way up. We felt the first nine hours were the most significant part of the determination, as concerns the rate at least.

MR. J. T. R. ANDREWS: I would like to offer a suggestion, as a reason perhaps why Mr. Freyer found no difference in the bubbling rates and the size of orifice. It might be due to the fact that the essential thing they are doing is keeping oil saturated with oxygen. That explains in my mind fairly adequately the reason for their unexpected results.

DR. NEWTON: In any accelerated stability test, the essential thing to determine is the inherent resistance of the fat, to rancidity. Since there are an infinite number of factors that may influence the rate at which it oxidizes and becomes rancid—I mean outside factors—the inherent resistance of a fat itself to rancidity probably depends upon several things. If we speculate a moment, we might say that the presence of certain natural anti-oxidants is one factor, and the presence of certain break-down products which are auto-catalytic. That is, their presence or absence is another factor, and perhaps the unsaturated value is at least one-third, the third very important factor.

Now, it is those factors, as I see it, that we are attempting to measure in any accelerated test, and not the factors that might come in from the outside, such as cooking temperatures, or other factors implied on the fat at the time they are used, because those vary with such a wide range that we could never get a test that would answer the question for all conditions.

It must be remembered that King, Roschen and Irwin did this work, attempting to make up a practical test out of the various data. They anticipated that the volatile break-down products from the fats would be auto - catalytic. For that reason and because there was not sufficient time, nor facilities available at the time to complete a study to show whether these volatile products were auto-catalytic, or whether they were not, or how much they were if they were, the air flow was considered a very important factor. This because the flow of air would carry off part of these volatile products, and if they were auto-catalytic, would change the results accordingly.

Since that time Roschen has published a paper in which he has shown that the volatile products are at most only infinitesimally effective as auto-catalytic agencies, and that the break-down products in the fat that produce the auto-catalytic effects are non-volatile. If that information had been available, it might possibly have changed the view.

I started to say at the outset that the important thing is to measure the inherent value of the resistance of the fat. To do this, you must control every possible factor.

There is one more point that I want to bring up. If you change the character of the apparatus from this set-up which has been suggested and is being used, you may change the rate of heat transfer to your tube. If, at the same time you change the rate of air flow over wide limits, you may change the actual temperature of the sample which is being tested.

MR. KILGORE: I might say that we covered some of those points. We tested the temperature of the fat. We used an electrically-heated bath so that we could regulate the temperature from 95 to 105 degrees, and hold it right there, plus or minus half a degree. The fat in the tube always maintained the bath temperature within any readable value. There is no variation in the temperature in the heat transfer between the bath and the sample. It does not make any difference if it is bubbling at two cc. or twelve cc. per second.

Another point that Dr. Newton raised was about the rate. We find that between two and four—preferably we use now three and four—we can get a smoother curve than at ten cc./sec. I do not know about eight, but the lower rate introduces less mechanical disturbance, in the case especially of an oil or fat that is liable to foam some. If you are shooting air through there at a high rate of speed, you get a certain splashing up and mechanical disturbance, and as a result of that we have been unable to get as close results as with the lower flow rate. For that reason, we have kept down to a lower flow rate.

Then there is this point about the factors which are not considered in the method influencing the determination of natural or added inhibitors. There are so many variations of that, that I do not believe any conclusion can be given. The matter which we want to discuss here is the maximum errors inherent in the method and whether or not the specified conditions should or should not be taken to such limits as to be wholly unreasonable with the accuracy of the method.

The reason we use flow meters on all our lines is that we can rely on them stronger than the capillary due to the fact that the air moisture occasionally condenses in a capillary, and the rate of flow varies somewhat. We use stopcocks in parallel, which are adjusted constantly to try to get the method as accurate as possible. But with all of that meticulous care, we find that five per cent is about as close as we can hope to get. Within that limit of five per cent, certainly the flow rate or the type of orifice would not make any difference. The important thing is the temperature. A half degree in temperature makes a tremendous difference. That is the reason we have been using an electrically-heated bath. That bath is one hundred degrees and if a half degree makes the error greater than five per cent, which I am not sure of at the present time, it seems to me that the temperature should be watched more carefully than the matter of air flow or jet.

MR. FREYER: Mr. Kilgore and myself have gone to great length to show that the air flow, within rather wide limits, has no effect on the test time. I have been concerned with the test time rather than any particular peroxide value. I did not quite get to this point in my paper, but I think it has such a bearing on the discussion that it is worth taking a couple of minutes to discuss.

When I varied the air flow rate two fold, and finally three fold, and got no effect, I was determined to see how much it could be varied without affecting the results. Finally I ran two tests in which the rate of air flow in one was 98 c.c.'s a minute, and in the other it was one-tenth of that value. We have in that case 98 c.c.'s and 9.8 c.c.'s a minute. The keeping time in the former case was twenty-five hours.

Now, we have often said that the more air put through there, the more concentrated the oxygen, the quicker the test will go out. But actually, cutting the air flow down to one-tenth the value, made the test go out in nineteen hours. In other words, just the reverse effect took place.

That is a wide variation of flow. It is a variation of one thousand per

cent. The percentage change in the result is twenty-four per cent, and it is in the reverse direction of what we would expect.

DR. NEWTON: May I ask if the temperature of the sample itself was measured in those two cases?

DR. FEYER: Yes, I measured the temperature with thermometers placed right in the glass oil tube. I did it a sufficient number of times to be convinced that that had no particular effect. I used rather thin wall, close-fitting copper sheaths. So, we will expect air flow, if varied beyond a certain limit, to have some effect.

MR. KILGORE: We have followed this same work and Mr. Freyer did also, only we ran probably thirty or forty samples like this. When we first began collecting this data that I have just given, I found in the case of the low flow rate, the curves tended to lie high all the time, and I thought there was actually a difference, that the low rate gave a higher value. But after running about one hundred of them, we found that they all stayed within about a five per cent limit.

I have in my room a table showing a spread between the lower and highest rates. In all cases, the low rate tends to run high. In other words, the low rate will give a shorter keeping time than a high rate, but it is within about five per cent. When we began collecting data for this paper, we thought that we had discovered something in that the low rate apparently does not remove the peroxide as fast as the high one does, or something of that sort. But when we worked over a large number of samples, instead of using one or two, we found that all came within this five per cent average range. Therefore, in doing work of this kind, by this method, it seems to me that at least duplicates should be run, and that the total number of samples should be very sizable in order to make a generalization. Although you might get a smooth curve in one run, if you do it over half a dozen times, you will find that a nice smooth curve is not a true picture.

BAGILUMBANG OR SOFT LUMBANG (ALEURITES TRISPERMA) OIL*

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CONTRIBUTION FROM THE OIL, FAT AND WAX LABORATORY, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE

THE bagilumbang, also known as the banucalag, soft lumbang and by other native names in the Philippines, where it is indigenous, is related to the lumbang or candle nut tree, Aleurites moluccana, the Chinese tung trees A. fordii and A. montana, and the Japanese A. cordata. It is being cultivated in Malaya and the Philippines on a small scale, and a few scattered trees are to be found in southern Florida. It can be propagated from both seeds and cuttings and is a rapid grower. At maturity the tree in favorable localities reaches a height of about 45 feet. Like the lumbang tree and in contrast to the tung trees, it appears to thrive in calcareous soils. The somewhat rounded, angled fruit, which is from 5 to 7 centimeters in diameter, usually has three cells, each of which contains a single seed or nut. The oval, smooth seeds, which are about 3 cm. long and nearly as broad, have hard, thin brittle shells, 0.25 to 0.5 mm. thick. The fleshy, white, oily kernel is enclosed in a thin white paper-like membrane. Unlike the candle nuts, the kernel with this membrane shrinks slightly from the seed coat or shell as the seed dries after maturity is reached, thus making it the shells. The kernels have a pleasant nutty flavor, but leave a burning sensation in the mouth and easy to separate the kernels from within a few hours cause an extremely violent purging. This is also a characteristic of the kernels of other species of Aleurites. Although the oil is not prepared on a commercial scale, the Philippine natives in localities where the tree grows have used it for many years to paint their boats.

The present investigation is concerned with fruits and seeds collected and sent to us by H. S. Wolfe, Horticulturist in charge of the Florida Semi-Tropical Experiment Station, from a tree growing in the vicinity of Homestead. The fruits ranged in weight from 23 to 39 grams, and the seeds or nuts consisted of 63.3 per cent of kernels and 36.7 per cent of shells. The kernels, which ranged in weight from 4 to 5.3 grams, contained 59.94 per cent of oil and 3.95 per cent of moisture. Richmond and del Rosario (Phil. J. Sci. 2, p. 439, 1907), who examined the seeds, reported that they consisted of 64.3 per cent of kernels and 35.7 per cent of shells. Those grown in Malaya (G. D. V. Georgia, Malayan Agric. J. 14, p. 290, 1926) had 56.4 per cent of kernels and 43.6 per cent of shells. The kernels contained 50.9 per cent of oil.

On account of the small quantity of kernels available, the oil was extracted with ether. During the removal of the last part of the solvent an atmosphere of carbon dioxide was maintained to protect the oil from oxidation. The oil was a pale yellow limpid liquid. A portion of the oil was mixed with an equal volume of a 10 per cent chloroform solution of antimony trichloride, according to M. T. Francois (Comp. rend. 198, p. 1046, 1934). In about two hours the solution had solidified. Tung oil similarly treated solified in one-half hour, although Francois stated that it should gel immediately. Oiticica oil was also found to require two hours for solidification. On the other hand, linseed, perilla and lumbang oils treated with the antimony trichloride solution remained liquid even after standing for 24 hours. The test clearly indicated that bagilumbang oil is not similar in composition to lumbang oil, as claimed several times in the literature.

When this oil was heated to 280°, 300° and 310° no gelation took place. R. G. Aguilar (loc cit) could not solidify the oil by heating it.

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