A Study of Methods of Accelerating the Swift Stability Test*

V. C. MEHLENBACHER
Swift & Company, Chicago, Ill.

Probably the most satisfactory and certainly the most common method used to measure the antioxidative properties of fats and oils is that method which accelerates the development of rancidity by aeration at a temperature of 97.7° C. (208° F.) to certain predetermined peroxide levels. The peroxide concentration is then determined according to the method of Wheeler (1). The method of incubation along with all other details of the application to the determination of relative keeping quality was described in a paper by Messrs. King, Roschen and Irwin (2). Although in its original conception, the main idea was to devise a method by which it would be possible to measure the stability of lard, this procedure has since been applied to virtually all fat and oil products where keeping quality is significant. While the method has not found complete acceptance, it is the predominant one in the industry today.

In their original paper King, Roschen and Irwin said, "this method grew out of a need for a quick method for comparing the stability or keeping quality of lard samples." Over the period of time that has elapsed since then, two gradual but significant changes have been taking place which will now require a slight alteration in that statement. The method is no longer as quick as it was; at least, it should be quicker than it is. This is not because the procedure has changed but because changes have been taking place in the products that are being tested. Whereas the range in keeping quality used to be from 1 to 25 hours this has now been extended up to 200 hours. Furthermore, the pace of industry has and is continuing to quicken. If we are not to hold up plant operations, processes or products, it is necessary to rebuild or reshape our tools to do a quicker job.

In looking for a faster method, several ideas naturally came to mind and many have been mentioned in the literature from time to time by various workers. Of course, it might be possible to change to a completely different method but it does seem that our aim should be to try to find some way by which we might get the best correlation with the already existent data. Furthermore, since others might be interested in the same improvement that we are searching for, the easiest and simplest type of changeover would seem to be the most practical. Immediately, most of us would think of catalyzing the rate of reaction in one way or another.

The effect of metals in contact with the sample during incubation was reported on by King, Roschen and Irwin (3). One of the methods used by these workers to add the metal was in the form of stearate soaps dissolved in chloroform. The solvent being volatile was soon expelled at the incubation temperature, leaving the soap uniformly dispersed in the sample. Using a similar technique we studied the effect of several metals including aluminum, calcium, magnesium, and copper. Other metals including nickel and lead were studied at some length by the previous workers while we concentrated largely on the use of copper stearate because of its extreme effectiveness in lowering the induction period. Our results with copper can be summed up in the brief statement that they were not satisfactory. Our data would indicate that the effectiveness and consistency of results varied with different fats and were profoundly influenced by antioxidants. Some typical data obtained using copper stearate are shown in Table I. Figure 1 shows the effect of various concentrations of copper stearate and probably explains in part some of the inability to obtain consistent and reproducible results. At the low

TABLE I

Sample	Concentration of Copper Stearate in PPM	Keeping Quality		Ratio
		Regular	Accelerated	
Animal Fat	100	20	4	5
Animal Fat	5	19	2	9.5
Animal Fat	5	54	4	13.5
Animal Fat	100	20	2	10
Vegetable Fat	5	98	13	7.5
Vegetable Fat	5	45	14	3.2

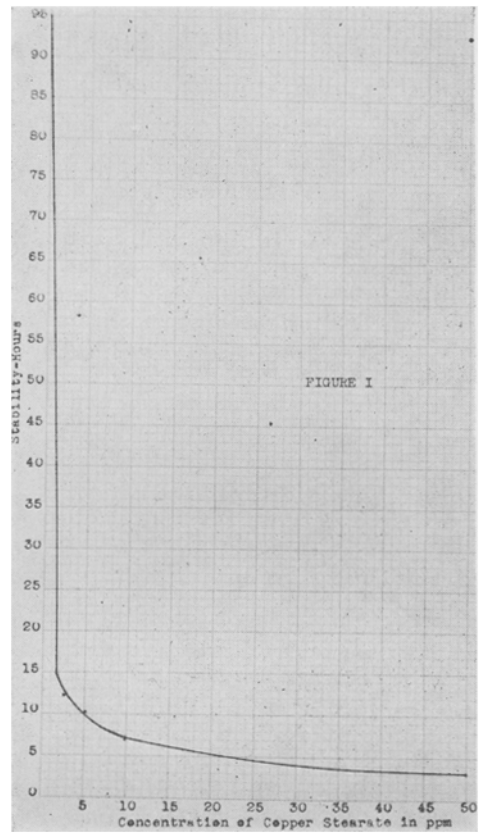


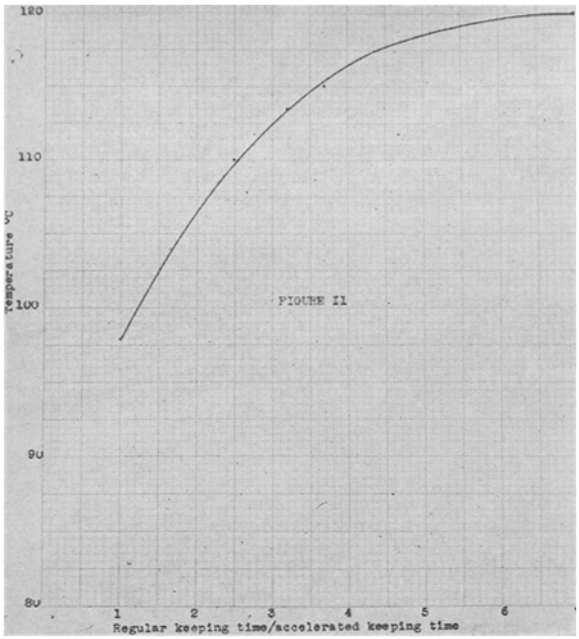
FIGURE I

* Presented before the American Oil Chemists' Society, Houston, Texas, May 1, 1942.

range of concentration where it is practical to operate for the purpose of the test the rate of change of keeping quality varies considerably with small changes in concentration of the catalyzer.

Temperature as a means of speeding up reactions needs no introduction. Freyer suggested the possible advantages which might accrue from the use of a higher temperature and presented some data (4). However, it has not been known whether an elevation of temperature would result in a simple, regular and uniform increase in the rate of reaction. It seemed conceivable that other things might happen such as splitting, rearranging or even the formation of peroxides different from those formed at 208° F.

The first thing we did was to try to get some idea of the rate of development of rancidity at various temperatures. At the same time we determined what degree of correlation might be expected at each of these temperatures. In Figure 2 is shown the curve we



obtained by running a series of samples at various temperatures. The samples were representative of animal fat, vegetable fat and combinations of the two. These samples also had a considerable range in keeping quality.

In Table II is shown a summary of the type of cor-

TABLE II

Temperature °C	Average Ratio Regular Time / Accelerated Time	Deviation from Average Ratio	
		Maximum	Average
120	7.0	3.0	1.8
115	3.7	0.8	0.2
110	2.5	0.2	0.1

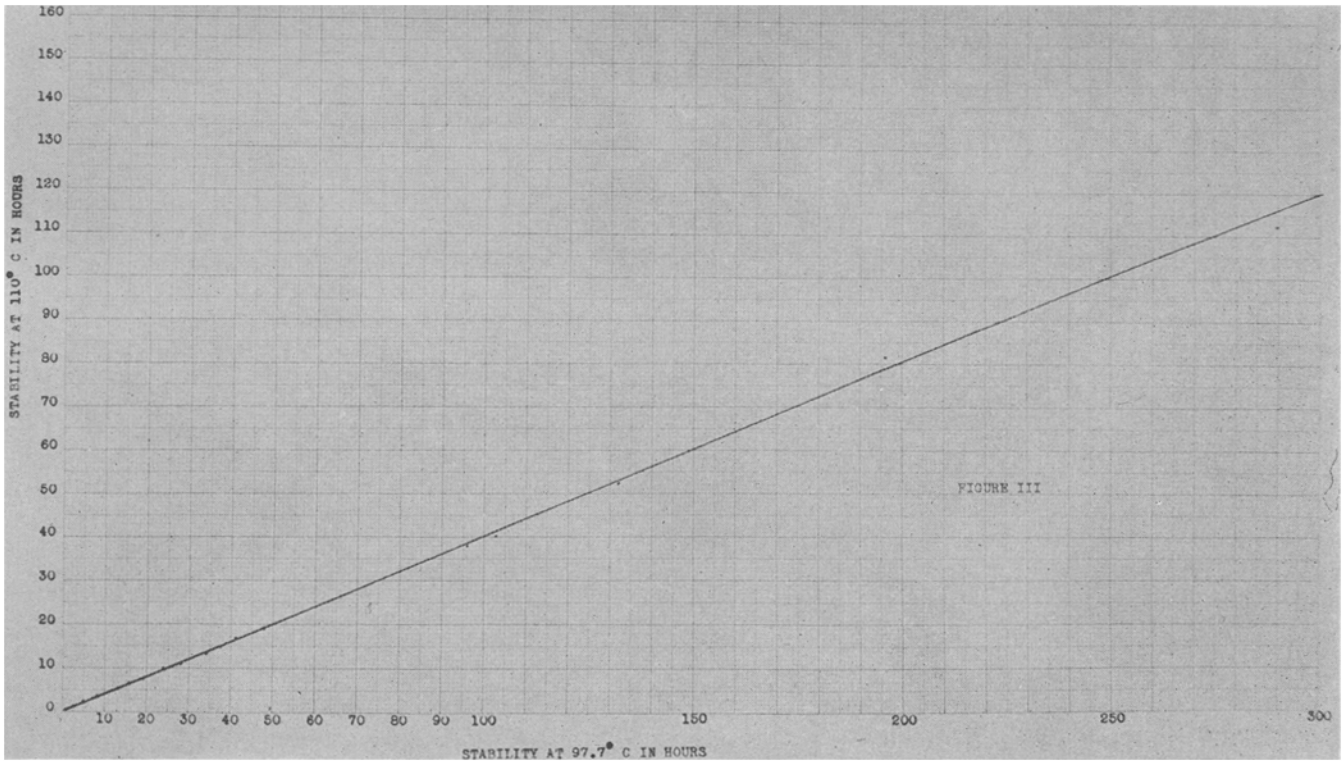
relation we got over the range of temperatures worked at. It may be observed that at a temperature of 120° C. the correlation was poor. This may be accounted for by the report of Taffel and Revis to the effect that when rancidity is developed at temperatures such as 120° C. or higher some of the peroxides formed are not easily reduced by hydriodic acid (5). It appeared to us that a temperature of 110° C. would combine a good correlation with an appreciable decrease in the time required to complete the test.

In order then to definitely establish the reliability of results at a temperature of 110° C. a very extensive series of determinations were made at this temperature and at the regular temperature. The keeping quality range of products tested varied from 1 hour to about 300 hours on the old basis. The products represented were selected so as to include just about every type of fat or oil commonly used or encountered. Several different antioxidants were included in the study. Hydrogenated and compound type shortenings were investigated. We also included a series of samples about which we knew neither the history nor the composition. A number of these results are shown in Table III and Figure 3.

TABLE III

Sample	Keeping Quality @ 97.7° C	Keeping Quality @ 110° C	Ratio 97.7° C/110° C
1	15	6	2.5
2	15	6	2.5
3	13	5	2.6
4	16	6	2.7
5	8	3	2.7
6	13	5½	2.4
7	24	9½	2.5
8	3	1¼	2.4
9	18	8	2.3
10	26	10½	2.5
11	36	13½	2.7
12	6	2½	2.4
13	290	112	2.6
14	100	43	2.3
15	32	13	2.5
16	38	15½	2.5
17	41	16½	2.5
18	31	12	2.6
19	11	4½	2.5
20	10	4	2.5
21	35	14	2.5
22	2½	1	2.5
23	92	37	2.5
24	38	15	2.5
25	48	19	2.5
26	19	7½	2.5
27	28	11	2.5
28	96	38	2.5
29	132	52	2.5
30	5	2	2.5
31	12	5	2.4
32	12	5	2.4
33	10	4	2.5
34	34	13½	2.5
35	34	13	2.6
36	103	40	2.6
37	38	14	2.7
38	4	1¾	2.4
39	7	3	2.3
40	11	4¾	2.3
41	8	3½	2.3
42	6	2½	2.4
43	13	5	2.6
44	15	6	2.5
45	15	6	2.5
46	15	6	2.5
47	15	6½	2.3

It has been our observation that the ratio of the time required at 97.7° C. to the time required at 110° C. is 2.5. The maximum deviation from this that we obtained was 0.2, that is, 2.3 to 2.7. The average difference calculated by taking the sum of all the deviations from 2.5 and dividing by the total number of determinations was 0.1 which amounts to 6 minutes per hour. This ratio of 2.5 is in agreement with previous workers who have said that the rate of accumulation of peroxides between 100° C. and 115° C. is about doubled for a rise of 10° C. (6) (7). As a matter of fact, this work has indicated that perhaps this ratio might be expressed with less deviation than we have shown if we had some continuous indicator method



by which we could tell within narrow limits just when a definite peroxide level had been reached. It is customary in our laboratories and we presume in most other laboratories to examine samples while they are incubating at certain stated intervals. This interval will vary with the range of stability of the product and may be one hour or more. Convenience enters the picture here because if a chemist is running many samples at a time it is difficult to keep track of them if the interval is too short. We reduced this period correspondingly as we reduced the time but nevertheless this interval is sufficient to account for a deviation of 0.1 or 0.2.

A point which must not be overlooked, especially when working at elevated temperatures is the necessity for close temperature control of the incubation bath. Figure 4 shows how results on the same sample will run at different temperatures. It is quite apparent from this that a variation of 1° C. is sufficient to change the final result appreciably. Finally, if it is desirable to continue to report results on the old basis then it is only necessary to multiply the hours obtained at 110° C. by 2.5 to obtain the hours which would have resulted at 97.7° C.

Summary

An investigation of possible methods of accelerating the Swift Stability Test has been made.

A comprehensive study has been made of the effect of temperatures and a considerable amount of data have been accumulated. These point to the fact that satisfactory correlation with existent data can be obtained at 110° C. with a saving of 60 per cent of the time previously required to complete the test. The ratio of the time required on the old to the accelerated basis is 2.5. This figure is an average of all results obtained.

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