Some Mackey Tests on Cottonseed Oil

*Test Believed to Have Possibility of Some Value as an Index of Keeping Qualities**

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THERE is comparatively little to be found in literature concerning the nature of the tri-glycerides in oils and fats in respect to their relation to the keeping quality of the oils and fats, especially when used in various food products. I thought, therefore, that some experiments to determine the tendency to oxidation carried out by means of the Mackey test might throw some additional light on this subject. The highly interesting articles as published by Norman J. Thompson[1] and Hans V. Nabell[2] throw quite some light on the spontaneous heating of various oils, fats and fatty acids, and distinctly prove the value of the Mackey test when used to determine the tendency of spontaneous combustion. Many factors, however, influence the results. Mr. Nabell in his article shows how to some extent the results for same fat or oil may vary due to catalytic action of metallic oxides and soaps, even if present in only minute quantities in the material to be tested, or in the instrument itself, and Mr. Thompson in his article has shown how entirely different results may be obtained by varying the quantities of oil and quantity of waste used in the test, and also by varying the relation between the quantities of oils and waste. Nothwithstanding, I believe, however, that the Mackey test for determining the keeping quality of oils and fats may eventually prove to be of some value.

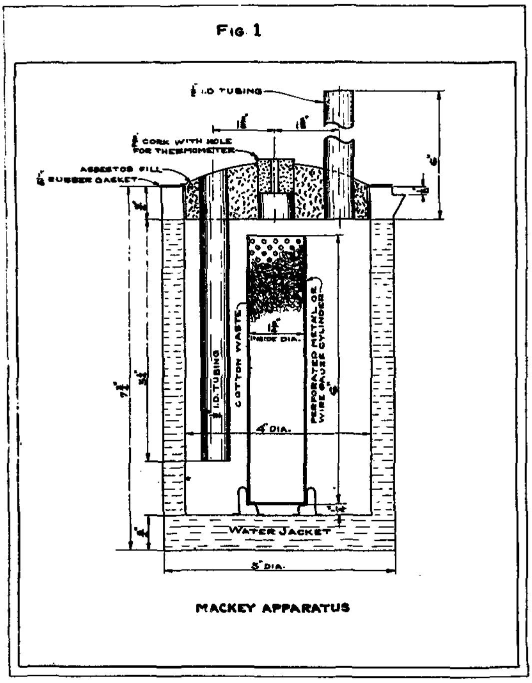

Fig. 1

I, therefore, arranged that in the laboratories of the Portsmouth Cotton Oil Refining Corp. under the supervision of our Chief Chemist, Mr. A. W. Putland, quite a few tests were made. The results of these tests have not led to any definite conclusion as to the value of the Mackey test. However, I believe that the publishing of some of the results will be of interest to other chemists working on similar problems, and I, therefore, believe it opportune at this time to give some information as to what we have done.

Description of Tester

The instrument (Figure 1) we are using is a water-jacketed copper pot, 4 inches inside diameter, 7 inches inside height; a perforated 6 inch high, 1⅜ inch diameter brass cylinder, with 48 3/32 inch holes per square inch, stands in the middle of the pot, with ¼ inch clearance from the bottom. The pot is covered with a top extending down ¾ inches. Through the top extends the thermometer for recording the temperature of the cotton waste, further a ½ inch tube extending down to 1¾ inches from the bottom, and on the opposite side of the cylinder a ½ inch tubing vent is located.

In all the tests made reference to, 15 grams of the oils or fats to be examined and 15 grams of cotton waste were used, the cotton waste being thoroughly teased in order to thoroughly distribute the oil, and

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[1]Industrial & Engineering Chemistry of March, 1927.
[2]Chemische Umschau Heft. 20 October, 1927.

packed in the upper half of the brass cylinder.

By using this instrument under uniform conditions, we were able to duplicate results fairly well, and a typical heating curve for refined cottonseed oil is shown on figure 2.

In order to find out how the changes in cottonseed oil during hydrogenation would influence the Mackey test, quite a few determinations were made on successive samples taken during the process of hydrogenation. Figures 3, 4 and 5 shows the results of the Mackey test on 10 samples taken April 17th, 1928, during the hydrogenation process of cottonseed oil with iodine number of 107

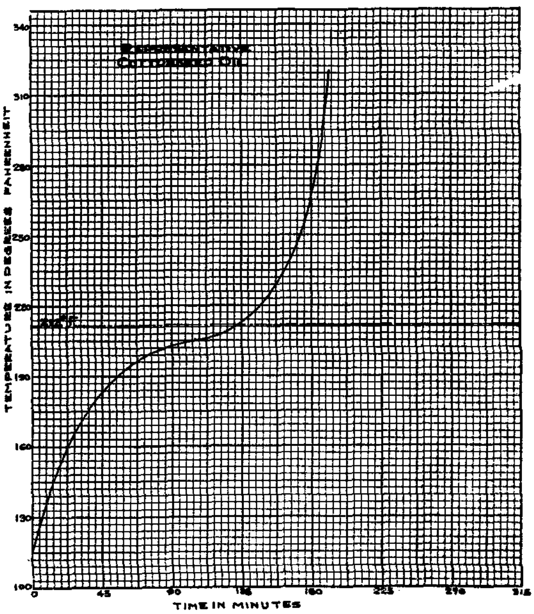

Fig. 2

when hydrogenated to iodine number 64.6. The table gives analyses of the various samples, showing iodine number and percentage of saturated, isooleic, oleic and linoleic acids. It will be noticed that the heating curves gradually flatten out and the tendency to heat in the Mackey test had nearly disappeared when the hydrogenation process had advanced so far as to reduce the linoleic acid content to 16 per cent and with linoleic acid practically disappeared, but 83 per cent still of isoleic and oleic acid, the fat did not show any tendency whatever to spontaneous heating during the Mackey test.

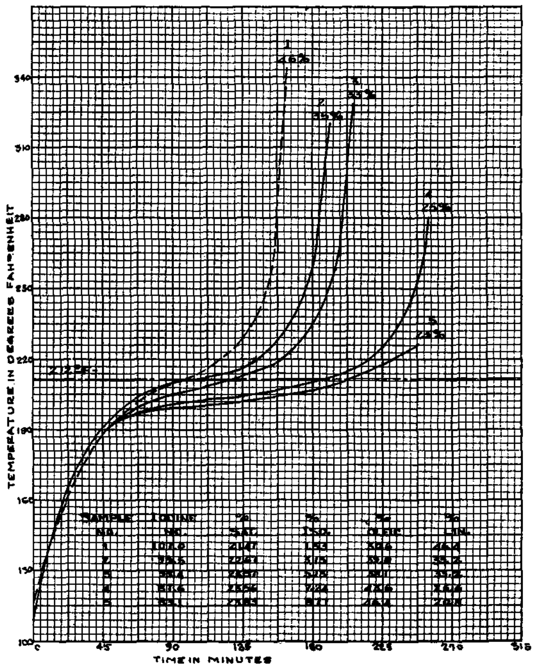

Fig. 3

Effects of Linoleic Acid

It was thought that possibly the Mackey test would show some difference between the linoleic acid present in the original oil

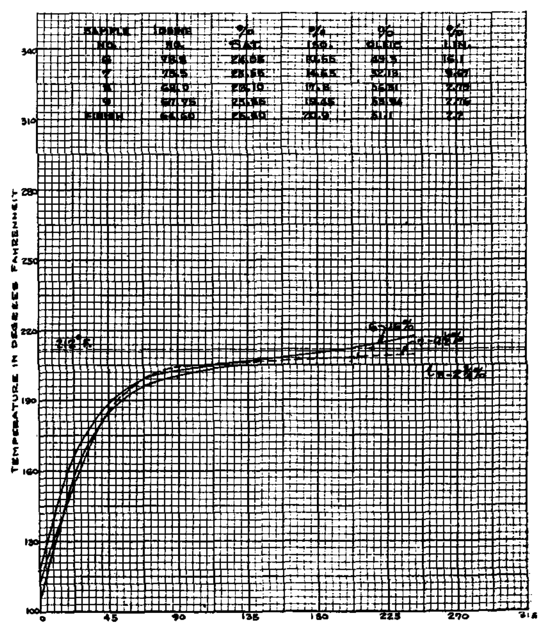

Fig. 4

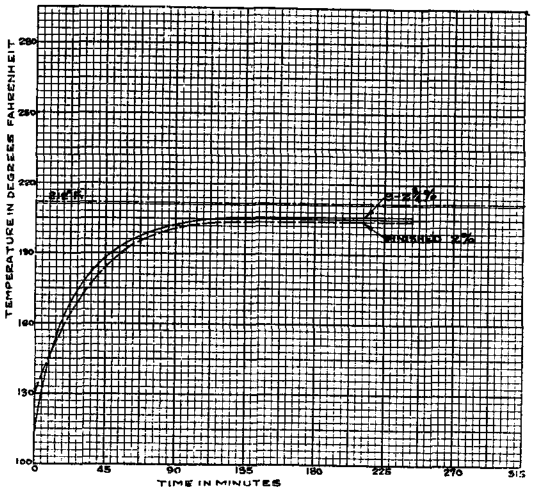

Fig. 5

and the linoleic acid during the latter part of the hydrogenation process, in the tendency to heat, and therefore oils from sample 1 and sample 8 were mixed in various proportions to produce a mixture of 33, 24, 16, 12 and 8 per cent linoleic acid content. Fig. 6 shows the results of the Mackey test of those samples. Comparing this chart with

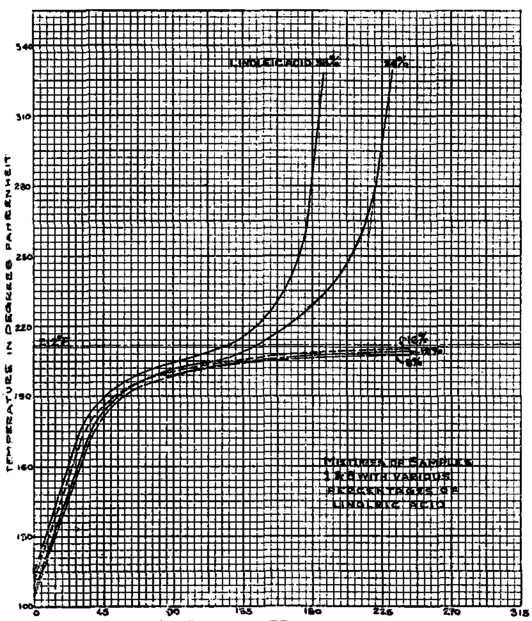

Fig. 6

chart in figures 2, 3 and 4 it would appear as if the same percentage of glycerides of linoleic acid which have not been exposed to the hydrogenation process would have a tendency to develop a steeper heat curve than that same percentage of glycerides of linoleic acid which have been exposed to the hydrogenation process.

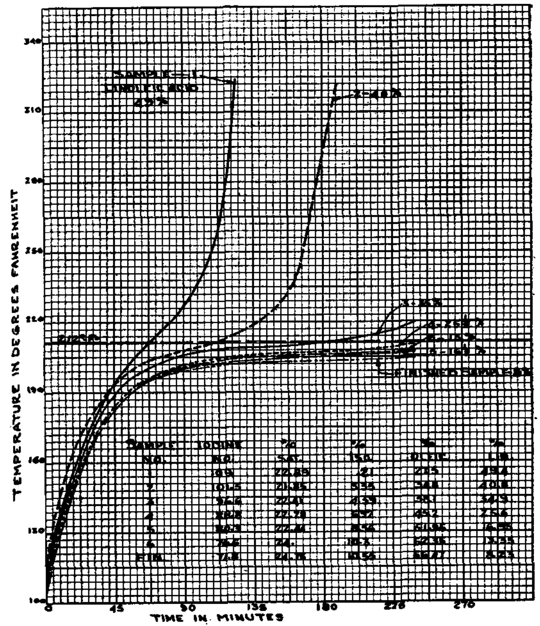

Fig. 7

Figure 7 shows the heating curves of 6 samples of cottonseed oil taken during hydrogenation June 14th, 1928, varying in percentage of linoleic acid from 49.4 to 8.23 per cent.

It will be noticed when comparing the results of the test made from the oil hydrogenated April 17th and June 14th that especially the samples with a percentage of linoleic acid of about 25 and 35 per cent show greatly different results in the two tests, however, the test in figure 8 also shows distinctly that oils with 16 per cent

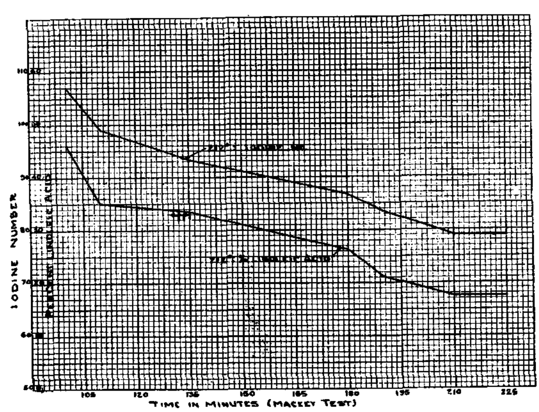

Fig. 8

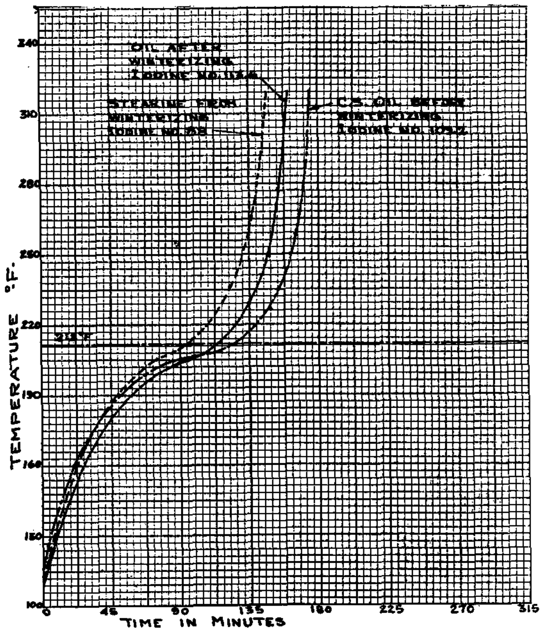

Fig. 9

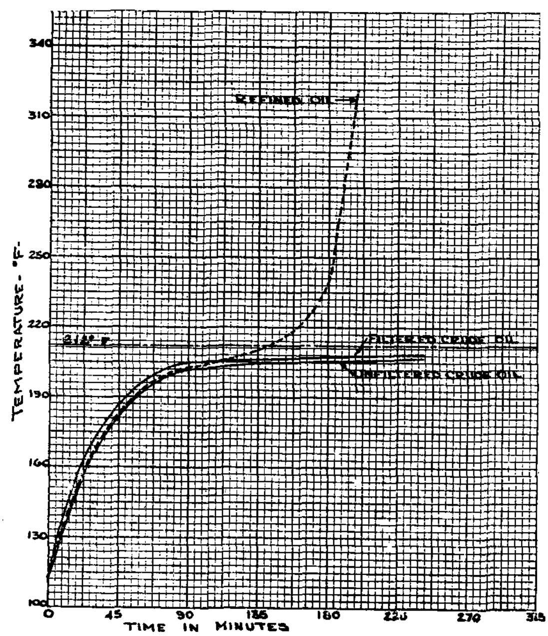

Fig. 11

or less linoleic acid content have very little, if any, tendency to heat.

Figure 8 shows the reaction of percentage of linoleic acid and iodine number to time required to reach 212 deg. F., the curves plotted from figures 3, 4 and 5.

Figure 9 shows some Mackey test curves of a cottonseed oil of iodine number 109.2 before and after having gone through the winterizing process; also shows the Mackey heating curves of the winter oil stearine separated in the process. It is remarkable that the winter oil stearine with the iodine number of 88 showed more tendency to heat than the original oil, which shows that the iodine number even when testing the same kind of oils cannot be taken as a guide for what the oil is going to develop during the Mackey test.

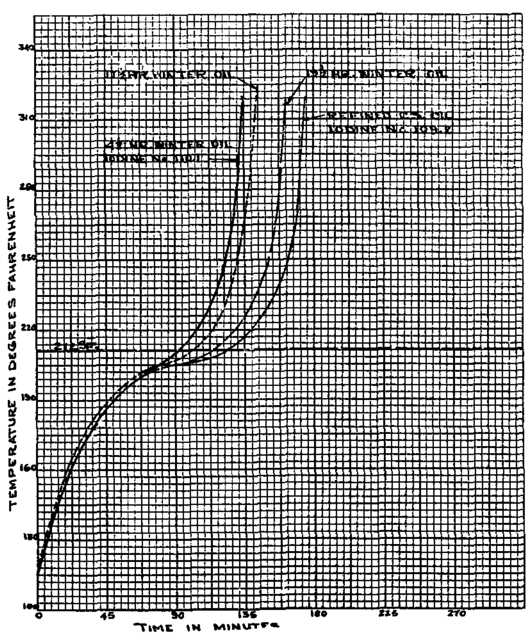

Fig. 10

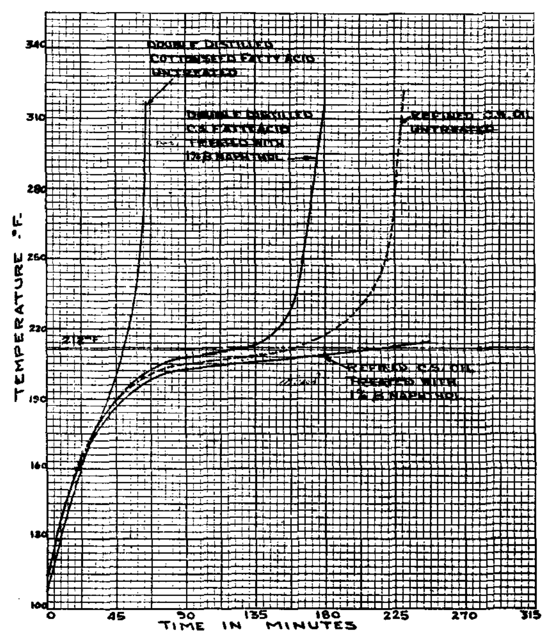

Fig. 12

Figure 10 shows the heating curve of some undeodorized winter oils of various length of winter oil test standing qualities. Also in this chart is included a heating curve of an undeodorized cottonseed oil of iodine number 109.2. However, the iodine numbers of the winter oils were not determined. The heating curves of the winter oils show the steepest curve for the weakest winter oil and the flattest curve for the strongest winter oil, which again is quite contrary to what may be expected.

I have not found in literature any specific information as to how the individual oil molecule is changed during the hydrogenation process. Except for the recent very interesting research published by G. Collin and T. P. Hilditch,[3] there is not much information to be found in literature as to how the individual molecules in the cottonseed oils and other vegetable oils are built, and if more was known about these matters we might find some answer to some of the seemingly confusing results from oils and fats in the Mackey test.

Results on Crude Oil

Figure 11 shows the heating curves of a crude cottonseed oil before filtration through filter paper and after filtration, as well as the curve for the refined oil obtained through the regular laboratory refining process. The refined oil was filtered through filter paper.

It is quite interesting to notice that the crude cottonseed oil apparently had no tendency thus far to oxidation,[4] and that the refined oil shows a somewhat flatter curve than ordinarily is the case with refined cottonseed oil. What caused the crude cottonseed oil to show practically no tendency towards heating during the Mackey test I do not know. Possibly some of the impurities in cottonseed oil may have a retarding catalytic influence. In this connection it may be mentioned that Bag and Novikow have found that B-Naphthol even if present in only a very small quantity in fatty acids has the power of very considerably retarding the oxidation of fatty acids, in other words acts as a negative catalyzer, and in figure 12 is shown a test made at our laboratory giving the heating curve during Mackey test of double distilled cottonseed oil fatty acids with and without B-Naphthol.

The fact that B-Naphthol seemingly acts as a negative catalyzer and further that crude cottonseed oil shows practically very little disposition to oxidize or heat in the Mackey test, would indicate that possibly several chemicals may be found which have the power to retard oxidation and act as negative catalyzers when present in vegetable oils. Possibly such chemicals or organic compounds may prove to be of considerable use not only in fatty acids for the textile industry, but also in the vegetable oil industry for preventing such rancidity which is caused by oxidation. Interesting experiments have been published by William J. Husa and Lydia M. Husa.[5]

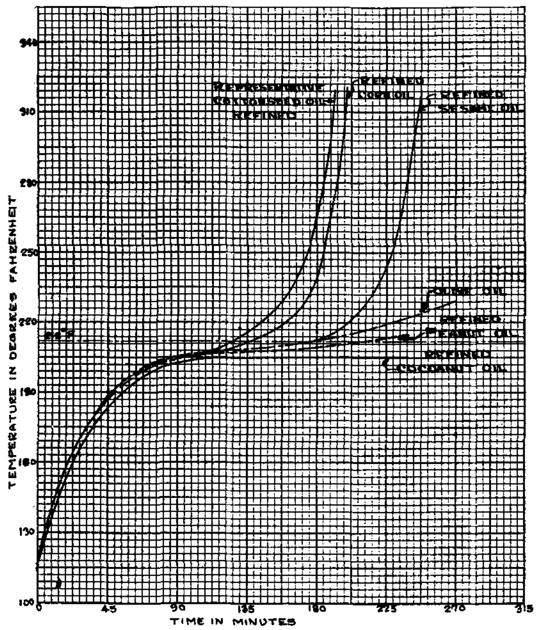

Fig. 13

Figure 13 shows some heating curves of refined cottonseed oil, corn oil, sesame oil, olive, peanut and cocoanut oil. These curves indicate that with decreased percentage of linoleic acid the Mackey test heating curves flatten, and evidently the Mackey curves are principally affected by the percentage of linoleic acid, and to a very much less extent by the percentage of oleic acid. In this connection it may be well, however, to refer to experiments made by Geo. E. Holm, Geo. R. Greenbank, and E. F. Deysher,[6] which show that in oxidation of cottonseed oil, compounds which give a tallowy odor are not found to any great extent, and further, that of the unsaturated acids in vegetable oils, oleic acid is mainly concerned in the products of tallowy odors and flavors.

[3]Journal of the Society of Chemical Industry, Sept. 21, 1928.

[4]See Geo. F. Holm, Geo. R. Greenbank and E. F. Deysher. Industrial & Eng. Chemistry, Vol. 19, No. 1, Jan., 1927.

[5]Journal of the American Pharmaceutical Association, March, 1928.

[6]Industrial & Eng. Chemistry, Vol. 19, No. 1, Jan., 1927; Vol. 16, No. 5, May, 1924; Vol. 15, No. 10, Oct., 1923.