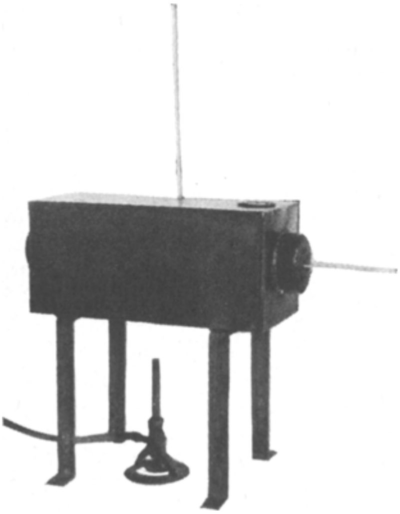
The Spontaneous Heating of Oils*

Describing a New Modification of the Mackey Testing Machine

BY NORMAN J. THOMPSON †

A PRELIMINARY consideration of this subject suggested the use of rapid chemical methods for determining the tendency of oils to oxidize at normal temperatures. It was realized that the iodine number does not indicate the extent or the rate of oxidation, except in a general way. Raw linseed oil, for example, has a higher number than boiled linseed oil; the latter, however, has a much greater tendency to oxidize under ordinary conditions. Furthermore, neat's-foot oil (Iodine Number 77), lard oil (Iodine Number 95), and olive oil (Iodine Number 91), will all show very much greater heating tendencies than castor oil or sperm oil whose iodine numbers are approximately 88. It has been thought in the past that an oil having an iodine number less than 100 was free from spontaneous heating. However, olive oil, with oxidation once begun, and showing a low iodine number (80 to 85), will have much greater tendency to heat spontaneously than would a pure corn oil (Iodine Number 125).



Apparatus for Testing Heating of Oils on Cotton

It was thought that an ideal way of indicating the spontaneous heating of oils would be to measure directly the oxygen absorbed during the heating, since the latter is essentially an oxidation reaction. Consequently, a bottle made of brass was designed to be used immersed in a bath of boiling water during tests. The bottle was closed by a rubber stopper in which were inserted sensitive thermometers and suitable connections for the determination of oxygen absorption by decrease in pressure. The apparatus was so designed that either air or oxygen could be admitted. When samples such as cottonseed oil, or oils of even greater heating tendencies were tested in this apparatus, it was found that the oxygen absorbed in a definite length of time was closely proportional to the heating rates as determined in other ways. However, when testing oils such as castor oil and mixtures of cottonseed and mineral oil, it was found that instead of a gas absorption there was an increase in pressure. This increase is due to the vapor pressure of the oil or its products of oxidation, and

---

* Presented at Second Fall Meeting, American Oil Chemists Society.

† *Factory Mutual Laboratories, Boston, Mass.*

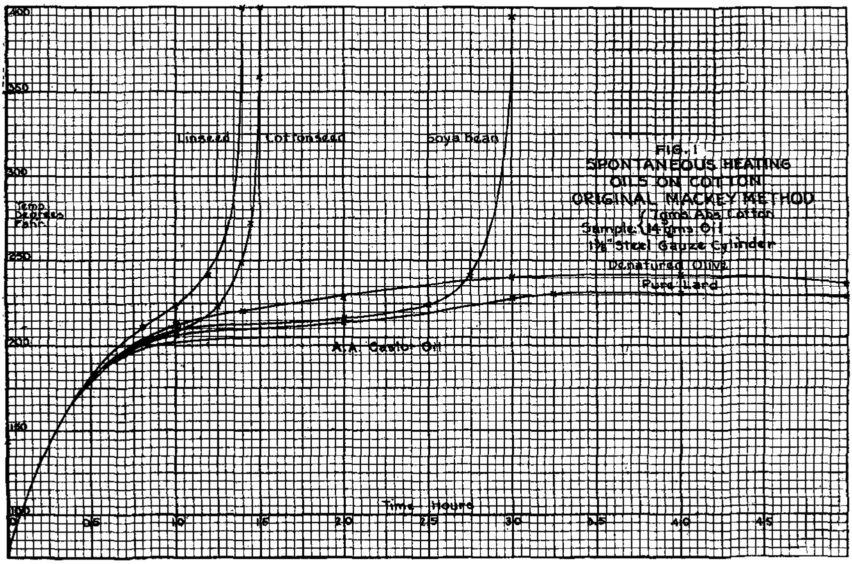


Fig. 1

is great enough at temperatures above 200°F. to make unreliable any figures obtained. Since we are most interested in the oils whose heating tendencies lie between that of castor oil and such oils as cottonseed, this oxygen absorption method proved to be quite disappointing.

Other Chemical Methods

Another chemical method which was tried made use of chromic acid as the oxidant. This acid was tried in aqueous solution alone and also with the addition of a small amount of chloroform, placing the chromic acid solution in a shallow dish of large diameter, such as a crystallizing dish, and then carefully pouring the oil to be tested over the aqueous solution. It was thought that with this arrangement where the surfaces in contact would be always the same and where temperature conditions could be carefully regulated, very consistent results could be obtained. Without the chloroform, however, the action of the chromic acid was very slow unless the solution was made quite hot, which resulted in considerable movement of the surfaces and consequent inconsistent results; and with chloroform added, the latter was oxidized to some extent as well as the oil being tested so that unreliable figures were again obtained.

Not being much encouraged by any chemical procedure, attention was given to methods of testing by actual measurement of temperature produced. The apparatus known as the "Ordway" consists entirely of a light steel tube about 4 in. in diameter in which were placed two 50-gram balls of cotton, one being oiled with an equal weight of the oil under test, and the other being left unoiled as a blank. The two balls of cotton were placed approximatly 12 in. apart and heated by an external air bath surrounding the 4 in. tube. Small holes in the ends of the air bath allowed a supply of fresh air to reach the sample. With the heating medium so arranged as to heat the balls of cotton equally, the blank was brought up to 212°F. and held there throughout the test. It has been customary to consider that a sample which heated to 300°F. within two or three hours would be dangerous under favorable conditions. It was extremely difficult to duplicate results with this apparatus and the operator must use more than ordinary care to prevent overheating the test sample.

The Mackey Apparatus

The apparatus which is in most general use today was devised by William Mackey, and is manufactured by Reynolds and Branson, Ltd., Leeds, England. This apparatus is essentially a jacketed cylinder 4 in. in diameter and 7 in. in height, closed at the top by a cover with a center hole to accommodate a thermometer, and having two draft tubes, each approximately 6 in. in length and ½ in. in diameter. One of these draft tubes extends down into the cylinder, and the other extends upwards from the cover. The procedure originally recommended for the Mackey apparatus calls for a sample consisting of seven grams of absorbent cotton carrying fourteen grams of the oil to be tested. The sample is placed in a wire gauze cylinder about 1⅜ in. in diameter and 6 in. long, the cylinder being held concentrically in the apparatus by a projection on the inside of the jacketed vessel. The customary procedure is to bring the water bath to boiling, insert the sample into the apparatus, and then take readings of the thermometer at frequent intervals. If the temperature does not exceed 100°C. within an hour, or 200°C. within two hours, the oil is considered safe as far as its tendency for spontaneous heating is concerned.

Several tests were made with the Mackey apparatus according to di-

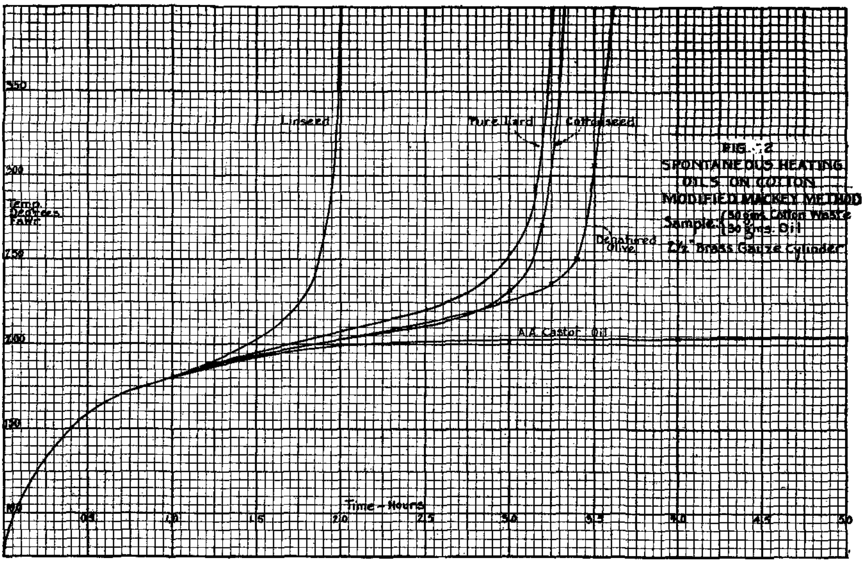


Fig. 2

rections. It was found that oils such as linseed, cottonseed, and the fish oils would heat, but other oils also known to be dangerous such as corn, oil, soya bean oil, denatured olive oil, red oil, and pure lard oil did not exceed 100°C. within two hours. Samples of these same oils tested under favorable conditions were found to heat quite readily.

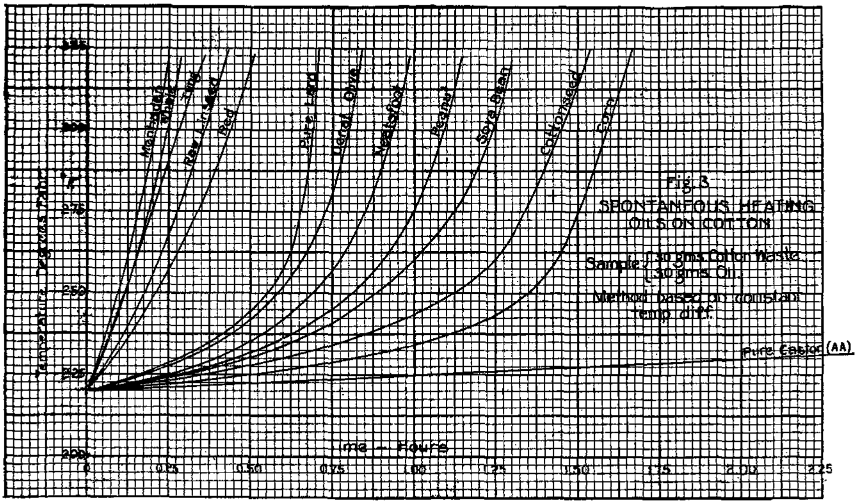


Fig. 3

A few test results obtained by the original Mackey method are shown in Fig. 1. It will be noted that according to this method there appears to be little difference in the heating of linseed and cottonseed oil; also that cottonseed oil is widely separated from denatured olive oil and pure lard oil. No such characteristics as these are evidenced by practical experience. Therefore, an attempt was made to modify this method so as to duplicate in greater measure conditions which might exist in practice where it is usually necessary to consider the heat-insulating effect of a large mass of material. Consequently, a larger sample was chosen, using thirty grams of clean cotton waste, into which had been worked an equal weight of oil under test. By increasing the sample size, the heat loss to the surroundings is not appreciably changed, but the heat available for raising the temperature of the sample itself is considerably increased. Of course, with a larger sample a longer time is required to heat it artificially to the test temperature; and also it requires a little more time for oxygen to penetrate into the center of the sample. The curves in Fig. 2 show some results obtained by this modified Mackey method. It will be noted that cottonseed oil, denatured olive oil, and pure lard oil are now grouped closely together, but that these three oils are all widely separated from raw linseed oil. Another point of interest is the fact that pure lard oil evidences a greater heating tendency than cottonseed, although in the original Mackey method these results were reversed. A theoretical explanation for this peculiar reversal of results is that lard oil has a greater initial rate of oxidation, but the oxidation of cottonseed oil is increased more on account of the catalytic action of the products of its oxidation.

Modification of the Tester

In an endeavor to stimulate as closely as possible practical conditions where large quantities of material may be stored, an apparatus was designed so that the surroundings of the sample under test could be made to follow it in temperature by any desired lag. This apparatus consisted of a steel tube 2½ inches inside diameter and 12 inches in length, the tube being jacketed by an oil bath, except for an inch on either end. The apparatus was designed so that the tube could be placed horizontally and caps were provided for each end of the tube, in which were drilled nine 3/16 in. holes. In this apparatus, by the use of the oil bath, almost any desired temperature can be maintained quite easily by the use of a Bunsen flame. Furthermore, the air supply is entirely adequate for any oxidation requirements of a sample of oiled cotton up to thirty grams. The method followed in using this apparatus was to heat the oil bath to the test temperature, then insert the sample in the center of the steel tube, allowing the sample to come up rapidly to the temperature of the bath. A thermometer was, of course, placed in the center of the sample. In giving results, time was reckoned from the moment the sample reached the test temperature.

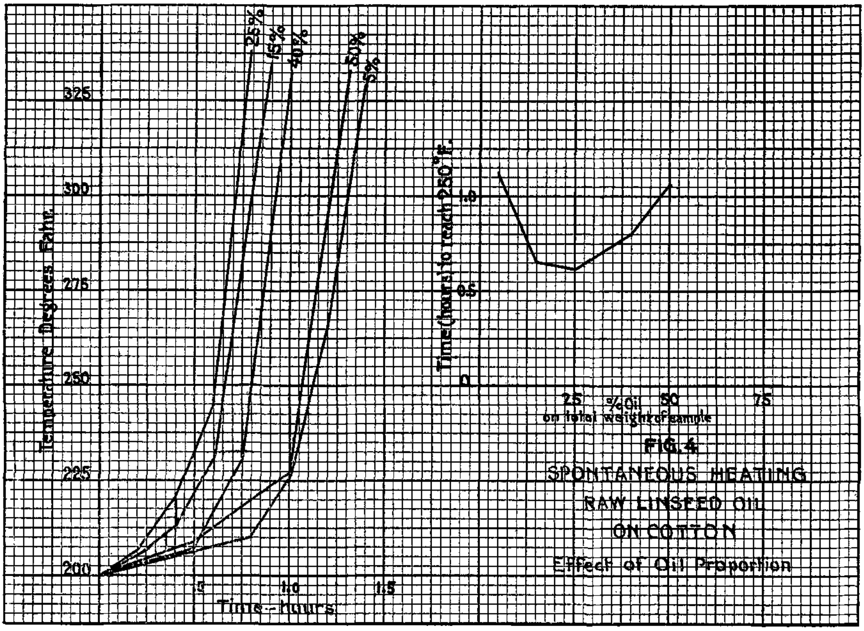


Fig. 4

Testing Procedure

For most work, the test temperature chosen was 220°F. It was thought that the apparatus might later be used in general test work and, as samples might sometimes contain water, it was desired to have relative figures for comparison at bath temperatures which would allow rapid evaporation of moisture. In operating the apparatus, a sample was placed in the tube after the bath had reached the test temperature, this bath temperature then being maintained constant until the temperature of the sample exceeded it by 3°F. From this time on, the bath temperature was kept 3°F. below that of the sample until the latter began to heat much more rapidly, when this difference could be increased gradually to a maximum of about 12°F. for a heating rate approximating 5°F. per minute.

Fig. 3 shows test results of several commercial oils of high purity when tested according to this experimental method. It will be noted on consideration of the curves that pure lard oil and denatured olive oil both heat more rapidly than cottonseed oil. It is also interesting to note that pure castor oil will heat spontaneously in this apparatus, although there is no evidence of any increase in its rate of oxidation during the test period shown.

Using the new test method based on the constant temperature difference between the sample and its surroundings, a series of tests were made to determine the effects of factors which are apt to vary considerably in practice, such as oil proportion, moisture content, temperature, age or condition of the oil, presence of metallic oxides, dilution by mineral oils, and the addition of negative catalysts.

The next figure (No. 4) shows what happened when the ratio of weight of oil to weight of cotton was varied. In these tests, the heating rate increased up to 25% of oil and then decreased up to

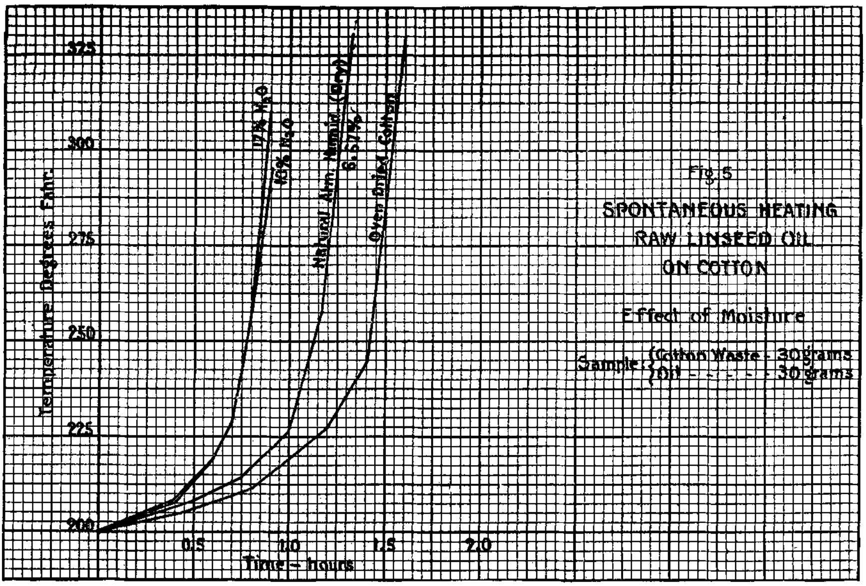


Fig. 5

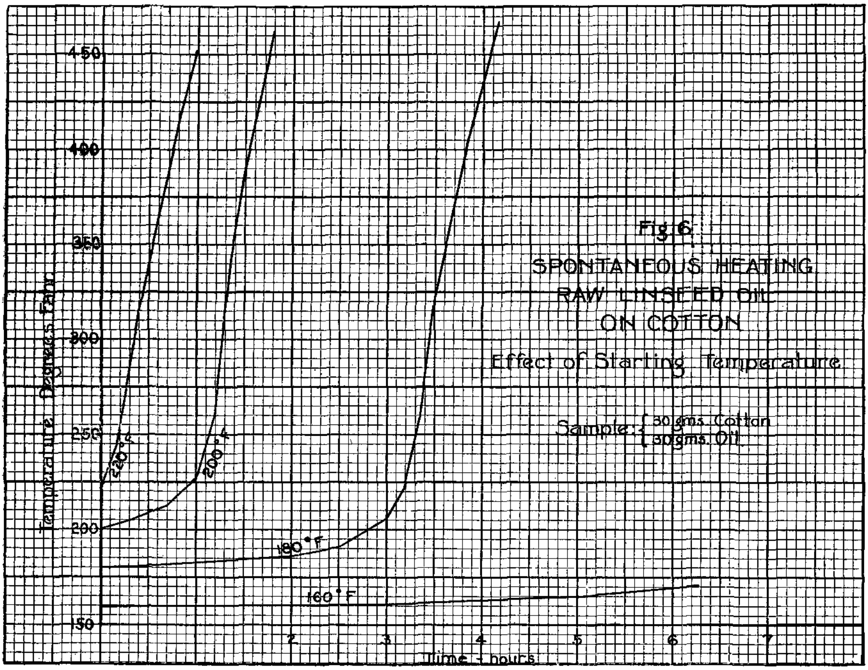


Fig. 6

50%. As the percentage of oil is increased the balance of heat losses by conduction and convection is changed and an increasing quantity of the heat evolved is required to bring about a given temperature rise in the sample itself. Furthermore, we found at very low oil percentages uneven distribution of the oil on the fibre with many individual fibres or sections thereof which were not entirely covered by an oil film,—and at high oil percentages oil films were formed so heavy that the ratio of surface exposed to weight of oil was less than the proportion most favorable for oxidation. From the data obtained, it seems reasonable to assume that the most rapid heating will be secured when the fibres are coated by the thinnest film of oil which can completely cover all their surface.

Tests (see Fig. 5) were made on four 30-gram samples of cotton waste, each carrying an equal weight of linseed oil:—one was thoroughly dried in the electric oven; another carried 6.7% water; another 10% water; and the fourth one 17% of water. When tested at 200°F., the time in hours to reach 225°F. were respectively,—1.13, 0.97, 0.66, and 0.65, The conclusion from these tests is that spontaneous heating is favored by increasing the humidity up to the point where the cotton is carrying approximately 10% water. The tests conducted on the oven-dried sample of cotton cannot be assumed to have run under conditions of absolute dryness because the air supply to the testing apparatus was of atmospheric humidity (around 50% relative). What would have hap-

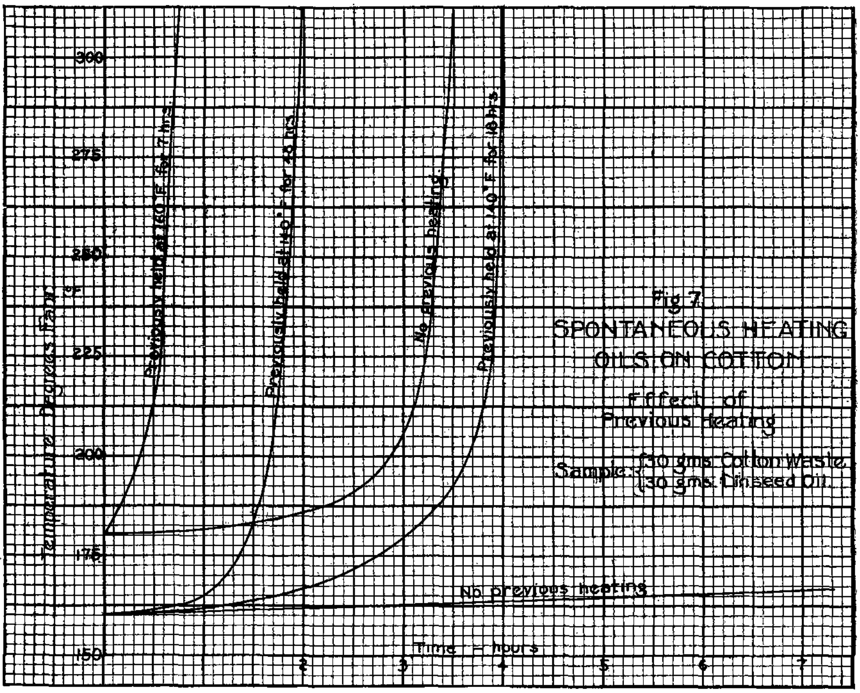


Fig 7
SPONTANEOUS HEATING
OILS ON COTTON
Effect of
Previous Heating
Sample {30 gms Cotton Waste
{30 gms. Linseed Oil.
Temperature Degrees Fahr.
°F
300
275
250
225
200
175
150
Previously held at 160° F for 7 hrs.
Previously held at 140° F for 48 hrs.
No previous heating.
Previously held at 140° F for 18 hrs.
No previous heating
Time — hours
2
3
4
5
6
7

Fig. 7

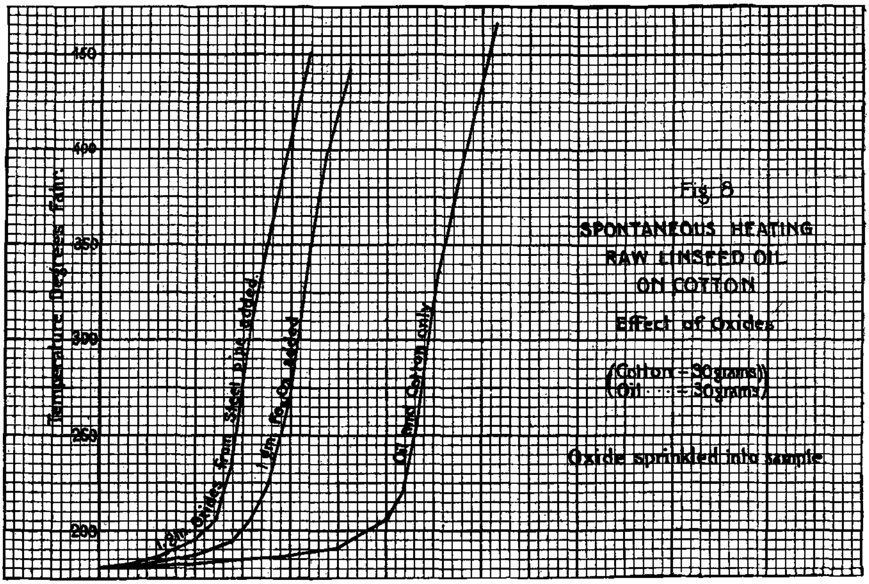


Fig 8
SPONTANEOUS HEATING
RAW LINSEED OIL
ON COTTON
Effect of Oxides
(Cotton - 30grams)
(Oil - - - 30grams)
Oxide sprinkled into sample
Temperature Degrees Fahr.
450
400
350
300
250
200
1 gm. Oxides from Steel pipe added
1 gm. Fe₂O₃ added
Oil and Cotton only

Fig. 8

pened if the test had been run in the absence of any moisture whatever is not indicated by these results and could not be determined without a change in the apparatus.

The next figure (No. 6) shows the effect of temperature on samples of cotton weighing thirty grams, each oiled with an equal weight of raw linseed oil. These samples were tested at 160, 180, 200, and 220°F. The heating rates in degrees Fahrenheit per hour for the first 5°F. rise were respectively 1.0, 2.8, 16.7 and 125. The results are expressed in this way because the tendency of any material to heat spontaneously at a given temperature is considered to be proportional to the rate of heating at or near the temperature in question.

Progressive Heating

It was observed that samples showed a greater heat evolution the longer they were maintained at or near any definite temperature (see Fig. 7). Accordingly, a sample of oiled cotton was held at 160°F. for seven hours, than cooled off and allowed to remain at room temperature over night. In the morning this sample was tested at 180°F., showing a much greater initial heating rate than a fresh sample would have at this same temperature. The rates in degrees per hour from 180 to 185°F. for the previously heated and fresh samples were 50.0 and 2.8, respectively. In a second set of tests, one sample was held at about 140°F. for forty-eight hours and another at approximately the same temperature for eighteen hours. When these were tested in comparison with a fresh sample at 16°F., the rates observed for the first 5°F. rise were as follows:—

48 hrs. at 140°F. Sample—
Rate—10.0°F. per hour

18 hrs. at 140°F. Sample—
Rate—3.1°F. per hour

Fresh Sample
Rate—1.0°F. per hour

In order to find out whether any of this difference was due to a more complete absorption of oil by the individual fibres, a sample of cotton was oiled and allowed to re-

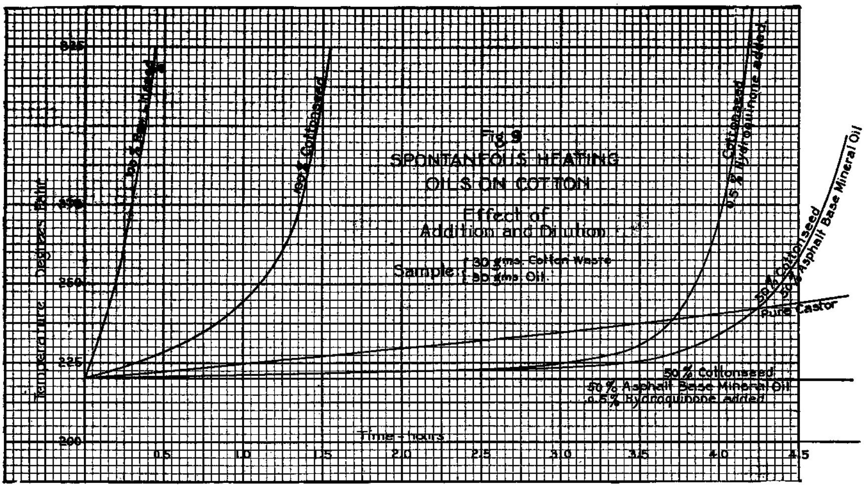


Fig. 9

main at room temperature in an air-tight container for two weeks. When tested, however, it behaved like a fresh sample. The foregoing shows in a striking manner how spontaneous heating is accelerated by the products formed during the oxidation.

The next figure (No. 8) shows the effect of the presence of oxides, such as ordinary iron rust. Three samples were prepared, all of thirty grams of raw linseed oil on the same weight of cotton waste. One gram of powdered rouge was thoroughly worked into one of the samples. To another sample was added one gram of oxide artificially prepared by solution of a small piece of steel in dilute nitric acid with subsequent precipitation and drying. The third sample was untreated. Tests were all made at 180°F. The initial heating rates were, for oil and cotton only, 3°F. per hour; with rouge added, 5°F. per hour; and with the oxide prepared from steel added, 6°F. per hour. These results clearly show the increase in fire hazard when oily waste is used for wiping of rusty machinery or tools, or when allowed to come in contact with rusty steam pipes.

The next and last figure (No. 9) shows the effect of dilution of vegetable oil by the more inert mineral oil, and also the effect of an anti-catalyst.

The curves show that when cottonseed oil is diluted by an equal amount of the mineral oil, there is practically no oxidation evidenced for three or four hours, but that after this time the rate is almost as great as the straight cottonsed oil. Results somewhat similar are obtained by the addition of one-half of one per cent of hydroquinone. This addition serves merely to postpone the heating. At ordinary atmospheric temperature, however, either one of these additions might serve to slow down the oxidation of cottonseed oil so that no heating would ever be apparent. If we dilute cottonseed oil with an equal weight of mineral oil and then add to the mixture an anti-catalyst, no increase in temperature whatever can be observed from 220°F. even during the test extending over eight hours.

Conclusions Drawn

Going back again to the consideration of what represents the most desirable testing equipment, it is felt that the method which gives the most significant results is the one involving the maintenance of the small temperature difference between the sample and its surroundings. However, it is expensive to maintain this difference automatically; and if the regulation is secured manually, the method is somewhat laborious. The original Mackey method is not suitable for indication, except to show the hazard of very dangerous oils. By increasing the size of the sample to thirty grams, using clean cotton waste carrying an equal weight of oil, we were able to obtain more significant results with no more attention, even though the test time may be longer.

When testing oils for their tendency to heat spontaneously, it is necessary in every case to take into account the practical conditions under which the oil may be used. Even a pure castor oil will heat spontaneously to ignition temperatures under favorable conditions. When testing unknown samples, the spontaneous heating test should always be made in conjunction with a chemical analysis to determine the presence of agents which serve only to delay oxidation but which may not affect the final result.