

and saturated acids by using the following equations:

- (1)  $182.4 X + 89.9 y = 100$  (Iodine number by R. K. method)
- (2)  $91.2 X + 89.9 y = 100$  (Thiocyanogen value)
- (3)  $95.6 - (X + y + \text{unsaponifiable matter}) = \text{per cent of saturated acids}$   
 $X = \text{per cent of elaeostearic acid. } y = \text{per cent of oleic acid.}$

Inserting in equation (1) the iodine number of the Rosenmund-Kuhnenn method and in equation (2) the thiocyanogen value, the solution of the equations indicated that the oil contains 70.5 per cent of elaeostearic acid and 18.5 per cent of oleic acid. The third equation gave 6.03 per cent of saturated acids. It will be observed that

these calculated percentages for oleic and saturated acids are in good agreement with those by the Lapworth-Mottram (oleic acid 17.8 per cent) and Bertram (saturated acids 6.18 per cent) methods.

In view of this agreement, it seems that the above equations can also be applied to the determination of unsaturated acids in those oils of the genus *Aleurites* which contain elaeostearic acid, as we have been unable to detect the presence of either linoleic or linolenic acids in any of these oils.

From the percentages of elaeostearic acids, it was calculated that the true iodine number of the oil is 209.6.

#### SUMMARY

The chemical and physical char-

acteristics of Japanese tung oil have been determined. This investigation indicates that the oil contains 70.5 per cent of elaeostearic, 18.5 per cent of oleic, and about 6.2 per cent of saturated acids.

It has been shown that the Rosenmund-Kuhnenn method, together with the Kaufmann thiocyanogen method can be used in the determination of the unsaturated fatty acids in this and in other oils of the genus *Aleurites* which contain elaeostearic acid. It has also been shown that the Rosenmund and Kuhnenn procedure gives an iodine number with elaeostearic acid which indicates that two of the three double bonds present are reacting. This iodine number is independent of the weight of the sample taken for analysis.

## THE EFFECT OF VARIOUS ADSORPTIVE MEDIUMS UPON RANCIDITY AND THE KREIS TEST\*

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**I**N DISCUSSION involving the Kreis test, it may be well to start with a brief summary of the various theories which have been advanced, dealing with the causes of rancidity in oils and fats. Every one of the theories offered in regard to rancidity may be justified insofar as the field which it covers is concerned.

The most generally accepted theory occurring in the literature is that rancidity is brought about by the presence of oxygen. The changes for which oxygen is responsible appear to be very complex. In the spontaneous auto-oxidation of fats it has been suggested that peroxides are formed at the double bond linkages on the unsaturated portion of the glyceride. These organic peroxides are believed to form ethylene oxide derivatives plus hydrogen peroxide, which in turn may break down with the liberation of active oxygen to form odoriferous aldehydes and ketones.

As the concentration of these odoriferous compounds increases the fat reaches the point of organoleptic rancidity, or is rancid to the sense of smell. This is really the

ultimate test as to whether or not a fat is rancid, but it gives no indication as to when a fat is beginning to turn rancid nor is it dependable in determining the exact point of rancidity because there is a personal factor in a test of this sort under the most ideal conditions for running the test. In many cases the conditions of test are far from ideal because other odors natural to the fat or oil or which may develop during production may mask the rancid odor long after the point of organoleptic rancidity would have been passed had it not been masked by the other odor.

The work of King, Roschen and Irwin<sup>1</sup> in establishing the peroxide content of lard and other oils and fats at the point where organoleptic rancidity occurs is well known. They found this point to be approximately 20 milli-equivalents of peroxide per 1000 grams of lard. This value holds true only for the average pure lard. The peroxide content at the rancid point will vary for every type of fat or oil.

Experiments carried out by Coe and LeClerc<sup>2</sup> of the Bureau of Chemistry and Soils indicate that neither a color test such as the

Kreis test, nor the peroxide test may show conclusively that a fat is rancid. Their evidence supports the theory that organoleptic rancidity may not be due to the formation of peroxides, but possibly to an independent compound, the formation of which accompanies and is simultaneous with the formation of peroxides under certain conditions. This was supported by the fact that corn oil and cottonseed oil, oxidized in the absence of light, showed no organoleptic rancidity even though their peroxide values were much higher than those of the same oil which had been exposed to light until it was very definitely rancid.

This may indicate that rancidity, although closely allied with peroxide formation, is not entirely dependent upon it.

There has been little if any criticism of the method for peroxide determination developed in the Swift laboratories in connection with the accelerated rancidity tests, although there may have been some question as to whether the conditions of the test reproduce accurately, conditions which may be encountered in the actual handling and storage of

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these fats and oils commercially up to the time of their consumption.<sup>3</sup>

Certainly it appears that this is the best measure of stability which has been published up to this time, and that the results of these tests may be considered indicative of the probable life of the oil or fat tested before it becomes organoleptically rancid.

The Kreis color test for incipient rancidity on the other hand, has been subject to a great deal of criticism in recent years, largely because a great number of compounds which may be present in oils or fats may react with phloroglucinol-hydrochloric acid to give a red color, which is indistinguishable from the color obtained with rancid fats.<sup>4</sup>

Although it may be questionable as to whether or not the Kreis test gives a sure indication of rancidity, there is no doubt that it does disclose the presence of materials in oils other than the pure glycerides. However it is well established that fat which is organoleptically rancid always gives a positive Kreis reaction.

From the commercial angle, the Kreis test is still being used quite extensively by the mayonnaise industry and by some other buyers of oils in judging the acceptability of the oils which they purchase, therefore it seemed desirable to study the effect of the various adsorptive mediums commonly used in the decolorizing and purification of oils and fats upon the bodies which govern the development of a positive Kreis reaction in oils and fats.

Activated carbons seemed especially to be indicated in this case because of their unusually adsorptive action, and so they were most largely employed in making this study.

Since activated carbons are notoriously selective in their action, we employed as many of the well known and commonly used brands of activated carbon as could be secured. For obvious reasons these carbons are coded in listing our results.

We first investigated the effect of treating prime summer yellow bleachable cottonseed oil, which showed a negative Kreis test with six per cent of several activated carbons and with fullers earth, and, to our surprise, we found that, while after treatment with some of the carbons, the oil still showed a negative Kreis test, other carbons and the fullers earth caused the development of bodies in the oil which

reacted positively when making the Kreis test. The most natural supposition is that some form of oxidation is promoted by these latter adsorptive mediums in the positive reaction, whereas there appears to be no such oxidation in case of other carbons.

The results follow:

TREATMENT OF P. S. Y. BLEACHABLE COTTONSEED OIL HAVING A NEGATIVE KREIS TEST

(6% Adsorptive Agent used in each case)	
Carbon	Kreis Test
A	Negative
B	Negative
C	Negative
D	Positive 3
E	Positive 5
F (fullers earth mixed with Carbon E)	Positive 7
G (fullers earth alone)	Positive 1

The method used in testing the effect of the above adsorptive materials consisted of agitating the oil and adsorptive agent together for five minutes at a temperature of 95° to 100° C. Agitation was carried out in porcelain cups, using glass stirrers, since it was found in our earlier studies that metallic equipment (especially copper) had a strong effect towards inducing a positive Kreis test. The numerals following the positive Kreis test denote the approximate color of the test in terms of Lovibond red when viewed through the side of a Lovibond block comparator having an inside diameter of 22 mm. Therefore these figures are intended to give some indication of the degree of positiveness.

A sample of cottonseed oil having a Kreis test of positive 1 was then treated with 5 per cent of a number of activated carbons, with the following results:

Carbon	Kreis Test
A	Negative
B	Negative
C	Negative
D	Positive 2
E	Positive 6
H	Positive 7
I	Positive 4
J	Positive 5
K	Positive 8

It will be noted that the same three carbons, A, B and C, which failed to change the negative Kreis test oil to positive in the previous experiment, this time actually removed the bodies which had caused the development of a positive reaction, whereas all of the other carbons used caused the Kreis test to develop with increased intensity, ranging from an indicated 2 to 8 as measured by our readings.

A sample of cottonseed oil having a positive Kreis test of 8 was then treated with various doses of different activated carbons in order to determine the effect of various types of activation upon a carbon's

ability to remove compounds responsible for a more strongly positive test.

ORIGINAL OIL—POSITIVE 8

Carbon	Per Cent Carbon Used		
	2%	5% Kreis Test	7% 7% 9%
A	6	4	2
B	6	5	2
C	5	4	1
D	12	7	4
E	13	16	Very dark red
H	Very dark red	Too dark to read	

It will be noted that carbons A, B and C again completely removed the compounds which were responsible for the development of a strongly positive Kreis test in this oil which shows that it is possible to remove the compounds responsible for a positive Kreis reaction by applying certain activated carbons. Exclusive of carbons A, B and C, none of the carbons tested showed removal sufficient to produce a negative Kreis test, when using as high as 9 per cent of carbon, although Carbon D did show a diminishing color intensity in the higher dosages of carbon.

The above work was then extended to cover corn oil, and the results obtained were very similar to those obtained on cottonseed oil, which are cited above.

It must be remembered that all of the above results were obtained when working upon a laboratory scale and therefore the doses required are only comparative within themselves to show that a difference does exist between carbons which have been prepared from different raw materials and activated under various conditions. In translating these results into plant operations there would be other factors to consider such as the type of equipment used, the nature of the metal from which the equipment is fabricated and the various conditions of handling and storing the oil.

It should also be stated that the development of a positive Kreis test in oils when they are treated with certain carbons and earths may not have any connection with the development of incipient rancidity, although it appears to be indicative evidence. The importance of the Kreis test from the commercial angle is well illustrated by a recent occurrence. An oil refinery had a shipment of oil rejected because it showed a positive Kreis test, although the oil showed a negative test at time of loading. This oil was returned to the refinery and given a polishing with a dose of 1.0 per cent of carbon A listed above.

After treatment, the oil showed a negative Kreis test and was returned to the original customer, who commented favorably upon the quality of this oil, and requested that future shipments be so selected to represent equal quality.

#### REFERENCES

1. Oil & Soap, Vol. 10, No. 6, June, 1933, pp. 195.
2. Industrial and Engineering Chemistry, 26, 3, pp. 245.
3. Oil & Soap, Vol. 13, No. 8, pp. 203 (Committee Report).
4. Journal Agri. Research, 26, 323 (1923).

## METHOD REVISIONS

The 1936 revisions of the American Oil Chemists' Society official analytical methods are now available for distribution. The price per set of these revisions is 50c. Complete sets of methods revised to 1936 are available at \$3.00 per copy with binder and \$2.00 per copy without binder.

The Society maintains a list of members who desire to have revisions sent them each year. The Secretary advises that less than half of the membership is carried on this list. This is an extremely low figure in view of the fact that revisions are made annually, and in view of the rapid addition of new methods. *All members should keep up to date on their methods.* We therefore urge that all members not now on the Secretary's list for receipt of revisions each year, have themselves placed on the list immediately. Address correspondence to Mr. J. C. P. Helm, Secretary, 509 Tchoupitoulas Street, New Orleans.

## SOAPS AND DETERGENTS

Committee D-12, Soaps and Detergents, of the American Society for Testing Materials, held an all day meeting and luncheon in the

Hotel New Yorker, New York City, December 3, at which 46 were present.

The organization of the various subcommittees and sections was completed, and a program of work outlined. Plans were made for a spring meeting, at which all committees will report and all specifications on which work will have been completed by that time will be considered by the whole committee for adoption by letter ballot. Such specifications will then be submitted to the American Society for Testing Materials at their annual meeting for their consideration and action.

A number of the American Oil Chemists' Society members are active on this new committee and Mr. M. L. Sheely has been designated as our official representative. The methods of analysis of the American Oil Chemists' Society Soap Committee were considered by Committee D-12 and approved for submission for adoption by letter ballot.

# USE OF MERCURATED FATTY COMPOUNDS AS WEED KILLERS\*

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**I**N A PREVIOUS paper presented before this Society the importance of finding new inedible uses for fatty acid derivatives was stressed. The object of this paper is to discuss the preparation of a series of mercury derivatives of fatty acids or their esters and the use of these compounds for the control of various weed pests.

The problem of weed control is one of considerable magnitude and large sums of money are expended annually for the killing of weeds along railroads and public rights of way. The usual methods employed by railroads are either to spray the weeds with a killing solution, such as a tar distillate, or else to actually burn the weeds by means of specially designed flame throwers. The principal objection to either of these methods is that the weeds are not permanently killed, due to the fact that the root system is left essentially unaffected and the weeds are quite apt to regrow.

Another interesting problem in this connection is the control of

weeds such as dandelions, plantain weeds and other common weeds in lawns, public parks, golf courses, etc. These are a constant source of trouble and the maintenance of the average lawn requires continual work to keep them under control. Here the problem is complicated by the fact that any proposed treatment must not have a destructive effect upon the grass and it is obvious that measures such as those employed by railroads cannot be used for the treatment of weeds occurring in lawns because such methods would kill the grass. The means of controlling weeds in lawns is essentially limited to various ingenious mechanical devices which have been developed, or to treating each individual root system with acidic substances, such as solutions of sulfuric acid.

From the above it appears that there is a very definite need for substances which will kill weeds by drying up the root system so that the weed cannot regenerate and is, therefore, permanently re-

moved. It is also evident that if substances can be found which will preferentially kill weeds and not grass they can be employed for the control of weeds in lawns.

Realizing this need, a series of mercury derivatives of fatty acids was investigated for this purpose and it was found that very effective weed killers could be synthesized by the action of mercuric salts such as the acetate, chloride, nitrate, or iodide upon esters of unsaturated fatty acids. One of these compounds, methyl-9-acetoxy mercuri 10-methoxy stearate, has been extensively tested for this purpose. The method of preparation of this compound is as follows:

We start with 500 parts by weight of ethyl oleate dissolved in 500 parts by weight of methyl alcohol and to this we add 543 parts by weight of mercuric acetate. The reactants are placed in a flask equipped with a motor stirrer and reflux condenser and the flask is heated by means of a water bath to the refluxing temperature of the

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