proved quite convenient for testing a row of individual stacks rapidly. At 465°F. values of 41 seconds for new palm oil to 62 seconds for palm oil ready for carding were obtained with this tester. Values could be checked to plus or minus one second; the test was sensitive enough to detect small additions of fresh oil to the pot. Such a method of testing proves to be more rapid than the present Saybolt test now in use and also gives a meaningful indication of actual operating conditions in the tin pot.

Tinning Oil Screening Tests

1. *Petri Dish Test.* A layer of tin is melted in a petri dish and held a little above its melting point, about 465°F. Sufficient oil is added to cover the tin completely in a thin layer. Then a portion of the tin is exposed to the air by holding back a portion of the oil so that a layer of tin oxide may form. If the oil is active, the exposed portion of tin will not be covered again by the oil but instead will remain bright, with the oxide continually being pulled under the oil. The oil will not lie quiescent but will move around in the dish. The length of time the spot of tin remains bright and the oil remains in motion is a measure of the active life of the oil.

2. *Long Term Heating Test.* A two-liter beaker containing 1,500 grams of oil and 500 to 1,000 grams of tin is maintained at a temperature of 465°F. The beaker is weighed daily to record volatile losses. A specified amount of oil is removed daily to simulate dragout losses, and fresh oil added to restore the oil weight to 1,500 grams. To simulate mill practice the beaker is maintained at 300°F. with no replenishment each Saturday and Sunday. Daily viscosity readings are taken with the ARF viscosimeter, and the test is continued until an equilibrium viscosity is reached— the equilibrium viscosity being defined as that viscosity value which does not change on indefinitely prolonged heating.

An Improved Method for the Determination of Iodine Numbers [1]

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THE determination of the iodine number for measuring the degree of unsaturation in fats and oils is of such universal importance that a clarification of the various methods is needed. Many halogen absorption methods are available; the Wijs (18) and the Hanus (5) are the most widely used. The Wijs method is recommended by the American Oil Chemists' Society, and the Hanus by the Association of Official Agricultural Chemists.

The German Dispensatory uses a modification of Winkler's method, as described by Awe, Skroch, and Demelius (1). The Kaufmann method (9) has not been applied to any extent although Thayer and Glass (17) prefer it to the Hanus procedure. The Rosenmund-Kuhnhenn method (13, 14) has been used only occasionally, and then usually in biological work for substances like cholesterol (2). Yasuda (19) claims that the Hanus reagent may not be used for cholesterol and advocates the Rosenmund-Kuhnhenn method.

The various methods do not give identical iodine numbers, especially in highly unsaturated oils. In general, the Wijs method gives higher, and the Kaufmann and Rosenmund-Kuhnhenn methods lower, values in oils whose iodine numbers are greater than 100. This fact alone causes some confusion when comparisons are made and necessitates control methods using two procedures, usually the Wijs and the Hanus.

The Rosenmund-Kuhnhenn method has been used by Govindarajan (4) for linseed, sunflower, and croton oils. He notes the ease of preparation and stability of the reagent but finds results lower than those obtained by the Wijs method. Earle and Milner (3) confirm this and cite low results for many oils above 100.

All the methods specify long absorption times, 30 to 60 minutes and even 2 hours in the Kaufmann method. This time is too long for rapid control of continuous plant operation, and inconvenient at all times. Hübl (7), as long ago as 1884, suggested the use of mercuric chloride as a catalyst. This idea was not developed until 1938, when Scotti (16) used mercuric acetate in acetic acid to shorten absorption times. This has led to the adoption of the rapid Wijs method, described by Hoffmann and Green (6) and the rapid Hanus method, described by Norris and Buswell (12). The absorption time is hereby reduced to 3 minutes, and this procedure has been adopted in some laboratories. Satisfactory results are obtained with methylene-interrupted systems, but low and erratic results are obtained with conjugated double-bond systems. Rowe, Furnas, and Bliss (15) have tried to overcome this for tall oil by lengthening

absorption times to 16 hours, using the Rosenmund-Kuhnhenn method with catalyst. Such a long absorption time is not practical, and an investigation into the Rosenmund-Kuhnhenn procedure was undertaken to establish a rapid procedure suitable for all types of fats and oils.

The Rosenmund-Kuhnhenn reagent has been found satisfactory for the following reasons:

a) *Ease of Preparation.* Both the Wijs and the Hanus reagents are time-consuming to prepare, owing to the limited solubility of iodine in glacial acetic acid. This is especially true of the stronger types of Hanus, such as the Woburn solution used by Mikusch and Frazier (11).

In the Wijs reagent chlorine gas is passed into the iodine-acetic acid solution until the latter changes color to light brown. To avoid an excess of chlorine, which forms unstable ICl₃, some iodine is put back to ensure that there is no possibility of excess chlorine. There is an ambiguity here which is not conducive to regularity in this reagent when prepared by different individuals. It is now possible to buy iodine monochloride directly, which avoids this difficulty.

The use of only one halogen, namely bromine, in the Rosenmund-Kuhnhenn reagent, constitutes a simplification. In addition, as the original authors pointed out, it is less expensive.

b) *Stability.* The Hanus reagent is rather stable, but the Wijs is less so. Jamieson (8) has recommended discarding it after one month; others claim that it loses but 1% of its halogenating power per month. Many workers use it for long periods of time, re-standardizing each time. There is considerable doubt as to which procedure to follow; this indecisiveness is related in part to the vague method of preparation mentioned above. The Rosenmund-Kuhnhenn reagent is stable for more than a year in our experience under conditions wherein the volatility of bromine is not permitted to take effect.

c) *Versatility.* The increasing use and importance of systems containing conjugated double bonds renders the Wijs and Hanus reagents ineffective in giving a true measure of total unsaturation in these cases.

The Rosenmund-Kuhnhenn procedure, as modified for these systems by Klee and Benham (10), overcomes this difficulty. One easily prepared stable reagent may be used for all types of fats and oils.

Reagent. The reagent is made up as follows:

Place 40 ml. of C. P. glacial acetic acid in each of three pyrex erlenmeyer flasks. To the first flask, add slowly 28.4 ± .2 grams of C. P. pyridine, with cooling. To the second flask add slowly 35.5 ± .2 grams C. P. concentrated sulphuric acid, with cooling. When cool, add the contents of the second flask to the contents of the first flask, with further cooling.

To the third flask, add the contents of a 1-ounce bottle of C. P. bromine (28.35 grams). Add this solution to the mixture of the first two solutions and make up to one liter with C. P. glacial acetic acid. Mix thoroughly and transfer to a 4-liter amber bottle with a screw stopper. Add a further 2,500 ml. of C. P. glacial acetic acid, making a total of 3,500 ml. of reagent. In this way, the weighing or measuring of bromine is eliminated. The reagent is approximately 0.1N with respect to bromine.

The Relation of Amount of Catalyst to Iodine Number. The mercuric acetate was added after 50 ml. of the reagent had been added to the oil in carbon tetrachloride. The absorption time was fixed at one minute in diffused light and 125-150% excess reagent was used.

TABLE I
Relation of Amount of Catalyst to Iodine Number

Oil	Iodine Number—Milligrams of Catalyst			
	0	125	250	500
Coconut	10.3	10.4	10.6	10.6
Lard	61.1	62.2	64.8	65.0
Olive	82.2	83.3	84.8	84.6
Castor	83.0	83.6	85.3	85.3
Rapeseed	94.0	96.9	98.6	98.5
Almond	100.3	101.2	102.3	102.3
Cottonseed	104.2	109.2	111.7	111.8
Corn	120.2	122.8	124.9	124.9
Wheat Germ	120.3	122.2	126.1	126.3
Soybean	124.0	127.2	128.6	128.5

The results shown in Table I indicate that identical iodine numbers are obtained when either 250 or 500 mg. of catalyst are added. It is evident that maximum halogen absorption occurs under these conditions with 250 mg. of catalyst, which was therefore used in all subsequent studies. It is convenient to make up 2.5% mercuric acetate in glacial acetic acid, and take 10 ml. for a determination.

Effect of Excess Reagent on Iodine Number. Experiments were done on lard, castor oil, and corn oil using a fixed sample weight, 10 ml. 2.5% mercuric acetate solution, an absorption time of one minute, and varying amounts of reagent. The results tabulated in Table II show that for corn and castor oil, the iodine number increases with increasing percentage of excess reagent, becoming constant at values above 100%. In the case of lard 70% axcess reagent is sufficient. A constancy was obtained in all generally used fats and oils when not more than 150% excess reagent was used. When there is little unsaturation, 50% excess reagent is sufficient.

TABLE II
Effect of Excess Reagent on Iodine Number

Excess Reagent	Iodine Number		
	Lard	Castor Oil	Corn Oil
%			
15	63.2	83.3	122.5
30	64.2	83.5	123.0
45	64.7	83.8	123.4
70	65.0	84.3	124.1
100	65.0	84.9	124.8
150	65.0	85.3	124.9
200	65.0	85.3	124.9

Effect of Absorption Time on Iodine Numbers. A time study was made, using 125-150% excess reagent, both with and without catalyst.

TABLE III
Effect of Absorption Time on Iodine Numbers

Oil	Reaction Time—Minutes					
	With Catalyst			Without Catalyst		
	1	30	60	1	30	60
Coconut	10.6	10.5	10.9	10.3	10.4	10.5
Lard	65.0	65.0	65.0	61.1	64.8	64.9
Olive	84.8	84.8	85.3	82.2	84.0	84.2
Castor	84.8	85.6	86.1	83.0	84.3	84.2
Rapeseed	98.6	98.8	99.3	94.4	96.8	96.9
Almond	102.3	102.5	102.9	100.3	102.0	102.2
Cottonseed	111.8	112.3	112.6	114.2	109.1	109.4
Corn	124.9	125.2	125.7	120.2	122.0	122.3
Wheat Germ	126.3	127.1	127.3	120.3	123.4	123.7
Soybean	128.6	129.3	129.5	124.0	127.3	127.7
Linseed	177.5	177.6	178.0	170.2	177.0	177.5

It is apparent that the iodine numbers obtained in 1 minute with catalyst are slightly higher than those obtained after even 1 hour without catalyst. This is particularly evident in the more highly unsaturated oils. When the catalyst is used, there is no further absorption in 30 or even in 60 minutes over and above that obtained in 1 minute. This establishes the 1 minute values as being true values, for the oils in question. For all subsequent studies a 1 minute reaction time was used.

Effect of Temperature. Owing to the fast reaction obtained under the conditions outlined above, it was not to be expected that temperature differences would have much effect. Experiments done at 20°C., 30°C., and 40°C. indicate identical values at 20°C. and at

30°C., and a mere 1% increase at 40°C. It is evident that room temperature differences between 20°C. and 30°C. have no bearing on results.

Absence of Secondary Reactions. It is important to establish that only halogen addition occurs. Samples after absorption were treated with water and the mixture extracted repeatedly with 30-ml. portions of chloroform until all the free bromine was removed, leaving any halogen acid in the aqueous layer. The separated aqueous solutions were acidified with nitric acid and the halogen precipitated with 10% silver nitrate, filtered, dried, and weighed. Blanks were run without the oil and the procedure repeated. There was no difference in the blank and the oil determinations, indicating the absence of secondary substitution reactions, substantiating the findings of Rowe, Furnas, and Bliss (15) in this respect.

The iodine numbers obtained by this modified Rosenmund-Kuhnhenn method were compared with those found by other methods in current use. The procedure of the American Oil Chemists' Society was followed for the Wijs method, and the Hanus method was carried out as adopted by the Association of Official Agricultural Chemists. The ordinary Rosenmund-Kuhnhenn method was carried out without catalyst and with an absorption time of half an hour.

TABLE IV

Comparison of Iodine Numbers Determined by Different Methods

Oil	Iodine Numbers Determined by			
	Modified	Hanus	Rosenmund-Kuhnhenn	Wijs
Coconut	10.6	10.5	10.4	10.4
Lard	65.0	65.1	64.8	65.0
Olive	84.8	84.7	84.0	85.0
Castor	84.8	84.6	84.3	85.7
Rapeseed	98.6	97.9	96.8	98.7
Almond	102.3	102.1	102.0	102.5
Cottonseed	111.8	113.0	109.1	116.0
Corn	124.9	124.3	122.0	126.0
Wheat Germ	126.3	126.1	123.4	128.6
Soybean	128.6	130.1	127.3	133.2
Linseed	177.5	178.7	177.0	184.3
Oleic Acid	89.4	88.8	89.4	89.6
Linoleic Acid	178.8	179.7	173.2	180.7
Linolenic Acid	268.5	267.9	261.2	272.5
Oiticica	195.4	195.2	139.4	144.8
Tung	229.4	216.3	156.7	162.4

The modified Rosenmund-Kuhnhenn method and the Hanus method agree very well except in the case of tung oil. The Wijs determinations also agree for oils of low iodine number but are slightly higher for oils having iodine numbers above 100. This is in agreement with the findings of Govindarajan (4). The standard Rosenmund-Kuhnhenn results and the Hanus results correspond well with those reported by Earle and Milner (3).

The presence of eleostearic and licanic glycerides in tung and oiticica oil is responsible for the erratic numbers obtained by the various methods. These oils are abnormal in that they contain large amounts of conjugated double bonds, and the methods in current use merely attempt to measure the halogen absorption required for saturating 2 of the 3 double bonds in a trienoic acid. This is shown in the case of the Wijs values for tung and oiticica oils. The high

iodine numbers for these two oils obtained by the modified 1-minute Rosenmund-Kuhnhenn procedure gave cause into the possibility that the true total unsaturation of these oils could be determined by increasing reaction time.

Summary of Procedure. The recommended rapid procedure, accurate for all non-conjugated systems, is as follows:

To a sample of the oil in 5 ml. carbon tetrachloride is added exactly 50 ml. of the Rosenmund-Kuhnhenn reagent. Ten ml. of 2.5% mercuric acetate in glacial acetic acid is added immediately. The bottle is allowed to stand for one minute at room temperature. Twenty ml. of 15% aqueous potassium iodide and 20 ml. of water are added. After one minute the liberated iodine is titrated in the usual way with standardized 0.1N sodium thiosulphate, using starch as indicator. Blanks containing everything except the oil are run simultaneously.

The iodine number is calculated as follows:

$$I.N. = [100 (A-B) C]/S$$

A = ml. of 0.1N sodium thiosulphate used for blank
B = ml. of 0.1N sodium thiosulphate used for sample
C = mg. of iodine equivalent to 1 ml. of 0.1N sodium thiosulphate solution
S = sample weight in mg.

The following sample weights are suggested for various oils, so that proper amount of excess reagents are present when 50 ml. of reagent are used:

Iodine number	Sample weight in milligrams
above 150	100-140
120-150	160-220
100-120	220-250
50-100	250-300
less than 50	500-1000

Summary

A modified Rosenmund-Kuhnhenn method has been described in which, with one easily prepared and stable reagent, consistent and repeatable iodine numbers are obtained in one minute with all ordinary non-conjugated fats and oils.

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