ening ability. Oxidation caused a slight increase in the Koettstorfer number of the fat. The greatest difference was found in the ease with which the fat saponified after it had been oxidized. It required about one-half hour of crutching to make soap from unoxidized beef tallow by the cold process, while with the highly oxidized beef tallow the saponification was complete almost as soon as the alkali had been added. This rapid saponification accounts for the greater ease with which an oxidized fat washed from a container with an alkaline washing powder. This greater ease of saponification was likewise noted in making soap by the graining process.

The color of the soap made from the oxidized stock was only slightly darker in color when fresh, but turned dark brown in a few days upon exposure to air. With the oxidized fat there appeared to be a considerable loss of soap in the spent lye as the nigre was almost black in color and set into a gel after the good soap had been grained out.

SUMMARY

The oxidation of fats for soap making greatly decreases the time required for saponification, but does not influence the cleaning properties of the soap. However, the color of the soap is impaired and the yield decreased.

APPLICABILITY OF THE STAMM REACTION FOR RANCIDTY

By H. L. ROSCHEN and W. J. LEHMANN

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IN 1925, J. Stamm[1-2-3-4] proposed a method of testing for rancidity which consisted of mixing an oil sample with a suspension of symmetrical diphenylcarbazid in paraffin oil. Upon heating for 3 minutes in boiling water, a red color appears. Stamm claims: (1) if the reaction is positive without accompanying rancid odor or taste that the sample will not keep much longer; (2) highly rancid condition is indicated by strong positive reaction; (3) no coloration or a very faint rose coloration indicates fresh fat.

In 1933 Istvan Korpaczy[5-6] proposed a modification of the Stamm reaction using, instead of the suspension of diphenyl-carbazid in parafin oil, a solution of this reagent in acetylene tetrachloride or tetrachlorethane ($CHCl_2.CHCl_2$). In addition, Korpaczy set up a series of color standards for purposes of measuring the intensity of the reaction. These standards consisted of aqueous solutions of the rose red dye Bordeaux S, shaded with the yellow dye Tartrazin, to compensate for the yellow color of fats. The intensity of the reaction was recorded as the number of milligrams of Bordeaux S contained in 100 c.c. of solution, the solution being matched in a suitable comparison device against the test sample.

The purpose of the work recorded in this paper was to survey the applicability of the Korpaczy modification of the Stamm reaction to oils and fats appearing on the American market.

Accordingly, reagent and color standards were prepared as follows:

Reagent: 0.5 gram of diphenylcarbazid (Eastman Kodak) were placed in a beaker; 100 c.c. of acetylene tetrachloride (C.P.) were added. The solution was heated to boiling and allowed to cool. Upon cooling, the reagent was filtered.

Color Standards: A series of Korpaczy standards was prepared using 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, 7.5, 10, 25, 50, 75, 100, 150, 200, 250 and 300 mgs. of Bordeaux S. These samples were dissolved in about 25 c.c. of distilled water and to each sample above 10 mgs. of Bordeaux S an amount of Tartrazin equal to 10 per cent the weight of Bordeaux S was added. In each sample below and including 10 mgs. of Bordeaux S, an amount of Tartrazin equal to 50 per cent the weight of Bordeaux S was used. The solutions were then diluted to 100 c.c. and shaken until completely dissolved. Portions of each solution were placed in small, flat-bottom, clear glass test tubes (12 mm. outside diameter, 10 mm. inside diameter, 10 cm. overall length), stoppered with a cork stopper and sealed with paraffin wax.

The method suggested by Korpaczy for carrying out this test was followed exactly. This method is as follows: X grams of melted and filtered fat are placed in a test tube with X cubic centimeters of the diphenylcarbazid reagent. The tube is placed in a boiling water bath for exactly 3 minutes, after which it is cooled very rapidly in a stream of cold water and immediately compared with the color standards.

Korpaczy claims the following for this test:

(1) A fat which shows a Stamm reaction of 0.5 or less is most probably fresh.

(2) A fat which shows a reaction from 1-2 is no longer fresh; its stability is limited and its early consumption is recommended.

(3) A fat which shows a reaction from 2-4 is in a state of incipient rancidity.

(4) A value of 5 or over indicates fat rancidified to the point of being inedible.

While Korpaczy does not indicate to which types of fat this test was applied, his work apparently was confined to rancid goose fat and lard, or to animal fats.

The tests reported here were made in tubes of the same size as were used in preparation of the color standards, taking in all cases 3 grams of fat and 3 c.c. of reagent. The color comparisons were made in ordinary daylight using a small wooden block provided with three slots to hold the sample tube and two color standards. It was felt that the color graduations between each standard were sufficiently large to make the use of a colorimeter unnecessary.

A number of animal, vegetable and marine oils were examined using this method. Methods of oxidizing some of these fats were applied and the Stamm reactions on the oxidized samples recorded. Since the peroxide value is generally accepted as a good index to the state of rancidity, these values were also determined, using the method of Wheeler[7] modified with respect to the manner of expressing the results. The Kreis test, which is no longer used extensively as a measure of the state of oxidation of fats, was also recorded in some cases as a matter of interest. This was not done in a quantitative way, the results being recorded simply as negative, slightly positive, positive and very positive. The failure of a color to develop is taken as a negative Kreis test, the development of a slight red color as a slightly positive test, a distinct red color as a positive test, and a dark red color as a very positive test.

The table gives the results on the samples examined:

CONCLUSIONS:

The first and immediately obvious conclusion from these results is that the Stamm reaction is apparently very limited in application. It does not yield satisfactory results with any fats or oils other than those of animal origin. Regardless of method or degree of oxidation, in the case of oils other than animal the Stamm reaction never reached a value over 3.0 except in three cases. One of these was cottonseed oil blown with air at 230° F., where a value of 100 was obtained. The other two cases were samples of unoxidized crude whale and herring oil. Here the Stamm reaction even reverses when the samples are oxidized.

In the case of hog fat and beef fat, fresh samples gave very slight or negative Stamm reactions while positive reactions were generally obtained with the oxidized samples, indicating that this test will probably give a good idea of the condition of the sample. Furthermore, in the case of lard the Stamm values correlate quite well with the peroxide

TABLE

Fat or Oil	Remarks	Odor	Stamm Reaction	Peroxide Value (Mill-equivalents Per Kilo)	Kreis Test
Hog Fat					
Steam rendered lard	Fresh	Fresh	Less than 0.5	0.4	Positive
Steam rendered lard	Fresh	Fresh	Less than 0.5	0.2	Negative
Steam rendered lard	Fresh	Fresh	Less than 0.5	1.1	....
Steam rendered lard	Fresh	Fresh	Less than 0.5	1.0	....
Open K. R. lard	Fresh	Fresh	Less than 0.5	3.4	Sl. Pos.
Open K. R. lard	Fresh	Fresh	0.0	2.0	Negative
Steam rendered lard [2]	Oxidized[1]	Questionable	3.0	15.0	....
Steam rendered lard	Oxidized[1]	Questionable	3.0	18.2	....
Steam rendered lard	Oxidized[1]	Rancid	10.0	42.0	....
Steam rendered lard	Oxidized[1]	Very rancid	25.0	76.0	....
Steam rendered lard	Oxidized[1]	Very rancid	50.0	136.0	....
Beef Fat					
Oleo oil [2]	Fresh	Fresh	Less than 0.5	0.6	Negative
Oleo oil [2]	Oxidized[1]	Rancid	50.0	346.0	Very Pos.
Cottonseed Oil					
C. S. oil	Refined and deod.	Sl. off but not rancid	3.0	30.4	Positive
C. S. oil	Winterized	Fresh	0.5	10.2	Positive
C. S. oil [2]	Winterized	Fresh	Less than 0.5	4.6	....
C. S. oil	Oxidized[1]	Not rancid	1.0	35.8	....
C. S. oil	Oxidized[1]	Not rancid	2.0	35.0	....
C. S. oil	Oxidized[1]	Not rancid	1.0	82.0	Very Pos.
C. S. oil	Oxidized[1]	Sl. rancid	1.0	134.0	Very Pos.
C. S. oil	Oxidized[1]	Very rancid	3.0	370.0	Very Pos.
C. S. oil	Oxidized[3]	Very rancid	100.0	44.0	....
C. S. oil—C. S. stearine shortening	Old sample[4]	Very rancid	3.0	101.0	....
Same as above	Old sample[4]	Rancid	3.0	44.1	....
C. S. oil (hydrogenated)	Fresh	None	0.0	0.1	Negative
Same as above	Fresh	None	0.0	0.1	Negative
Other Vegetable Oils					
Raisin seed[5]	Refined	Not rancid	1.0	21.0	Positive
Babassu [2]	Refined and deod.	Not rancid	Less than 0.5	5.0	Negative
Babassu	Oxidized[1]	Rancid	Less than 0.5	42.0	Very Pos.
Babassu	Oxidized[6]	Very rancid	Less than 0.5	167.0	Very Pos.
Cocoanut oil [2]	Refined	Not rancid	Less than 0.5	8.0	Positive
Cocoanut oil	Oxidized[1]	Very rancid	1.0	264.0	Very Pos.
Cocoanut oil	Oxidized[6]	Rancid	Less than 0.5	181.0	Very Pos.
Hempseed oil [2]	Refined, bleached and deod.	Not rancid	Less than 0.5	17.2	Positive
Hempseed oil	Oxidized[1]	Very rancid	Less than 0.5	526.0	Very Pos.
Hempseed oil	Oxidized[6]	Sl. rancid	Less than 0.5	36.0	Very Pos.
Peanut oil [2]	Refined and deod.	Not rancid	1.0	35.0	Sl. Pos.
Peanut oil	Oxidized[1]	Very rancid	Less than 0.5	670.0	Very Pos.
Peanut oil	Oxidized[6]	Rancid	Less than 0.5	181.0	Very Pos.
Perrilla oil [2]	Refined	Linseed	Less than 0.5	35.0	Positive
Perrilla oil	Oxidized[1]	Linseed	Less than 0.5	378.0	Very Pos.
Perrilla oil	Oxidized[6]	Linseed	0.5	91.0	Very Pos.
Teaseed oil [2]	Refined and deod.	Not rancid	Less than 0.5	12.2	Sl. Pos.
Teaseed oil	Oxidized[1]	Rancid	Less than 0.5	338.0	Very Pos.
Teaseed oil	Oxidized[6]	Rancid	Less than 0.5	144.0	Very Pos.
Marine Oils[7]					
Whale oil [2]	Refined and bleached	Fishy	Less than 0.5	23.4	Positive.
Whale oil	Oxidized[1]	Fishy	Less than 0.5	175.0	Very Pos.[8]
Whale oil	Oxidized[6]	Fishy	Less than 0.5	144.0	Very Pos.[8]
Whale oil	Crude	Fishy	25.0	4.0	Positive
Whale oil	Oxidized[1]	Fishy	Less than 0.5	78.0	Very Pos.[8]
Whale oil	Oxidized[6]	Fishy	10.0	43.0	Very Pos.[8]
Herring oil [2]	Crude	Fishy	10.0	4.0	Positive
Herring oil	Oxidized[1]	Fishy	Less than 0.5	94.0	Very Pos.[8]
Herring oil	Oxidized[6]	Fishy	Less than 0.5	93.0	Very Pos.[8]
Sardine oil [2]	Crude	Fishy	Less than 0.5	5.0	Positive
Sardine oil	Oxidized[1]	Fishy	Less than 0.5	142.0	Very Pos.[8]
Sardine oil	Oxidized[6]	Fishy	3.0	7.0	Very Pos.[8]

[1] Oxidized by the active oxygen method at 210° F. in the dark by blowing with air at rate of 2.3 c.c. per second per 20 c.c. sample.

[2] Samples in brackets represent portions of the same sample in various stages of oxidation.

[3] Blown with air at 230° F.

[4] Samples stored in closed metal pails at room temperature until rancid.

[5] Random sample of unknown history.

[6] After 95 days in diffuse daylight on laboratory shelves, clear glass containers.

[7] Laboratory samples which had been stored for some time at room temperature in brown glass bottles.

[8] All samples of oxidized fish oil gave Kreis colors of deep red brown, not the characteristic red of other fats.

value, the two values rising together and confirming, at least for lard, the suggestion of Korpaczy that a Stamm value of 5 defines the boundary between rancid and nonrancid products.

Speaking of oils and fats as a whole, the Kreis test shows better correlation with peroxide value and rancid condition than the Stamm reaction. While this may not be the case with hog fat, it is quite clear in the case of all the vegetable, seed and marine oils examined. An oxidized or rancid sample gave an intense Kreis reaction and a high peroxide value, but not necessarily a high Stamm value.

SUMMARY:

The Korpaczy modification of the Stamm reaction for detecting rancidity in fats has been applied to a variety of fats and oils, including hog and beet fat, cottonseed oil, a number of other vegetable and seed oils, and a group of marine oils. This reaction has been shown to be generally inapplicable to vegetable, seed and marine oils but applicable to lard and beef fat.

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REPORT OF THE SOAP ANALYSIS COMMITTEE 1936

M. L. SHEELY, Chairman

AT THE Fall Meeting of the Society held in Cincinnati October, 1935, the Soap Committee met and made the following recommendations:

1. That the standard methods for soap analysis adopted October, 1933, be made official.
2. That a new method for Volatile Hydrocarbons be adopted as a tentative method.
3. That a method for screen analysis be adopted including both a hand screening and a Ro-Tap procedure as an alternative, both methods to be tentative.

The above recommendations were approved by the Uniform Methods Committee and were officially adopted by the Society at the same meeting. The changes and new procedures are now being printed and will shortly be sent out for incorporation in the Lefax Method book.

During the past year the Committee has not conducted any further cooperative test work. Several discussions have been carried out by letter involving the following tests.

1. Water insoluble in built soaps.
2. Free alkali determination.
3. Moisture in paste soaps containing glycerine.

The discussions on these tests, while not accompanied by collaborative studies, developed some important facts and are consequently recorded in this report as a matter of general interest. In connection with Points No. 2 and No. 3 above, namely, free alkali and moisture determination in paste soaps containing glycerine, the Committee has voted to make minor changes in the present official methods as will be noted later in this report.

Water Insoluble in Built Soaps

One of the Committee members called attention to the fact that the amount of water insoluble in soaps containing high percentages of silicate of soda as determined by the present official method gives higher results than when determined by dissolving the soap directly in hot water. This difference was still greater if the alcohol insoluble, after filtration, is dried at 105° C. and then water insoluble determined thereon. As a confirmation of the above facts one member reported the following data:

TABLE I—PER CENT OF WATER INSOLUBLE

Sample	Soap Dissolved in 95% Alcohol (Standard Method)	Soap Dissolved Directly in Hot Water
1. Built Flakes (10-30 days old).............	0.52%	0.14%
2. Built Flakes (10-30 days old).............	0.48%	0.22%
3. Built Flakes (10-30 days old).............	0.76%	0.30%
4. Built Flakes (10-30 days old).............	0.18%	0.02%
5. Built Flakes (Very old sample)..........	15.40%	12.20%
6. Built Flakes (One day old)................	0.18%	0.00%
7. Built Flakes (One day old)................	0.00%	0.00%
8. Built Flakes (One day old)................	0.00%	0.00%
9. Built Flakes (One day old)................	0.00%	0.00%
10. Built Flakes (One day old)................	0.00%	0.00%
	Standard Method Not drying Alc. Insoluble	Standard Method Drying Alc. Ins. 16 hrs.—105° C.
11. Built Flakes (One day old)................	0.00%	3.00%
12. Built Flakes (Similar to No. 11)..........	0.00%	1.34%

The above data indicate definitely that with the exception of very fresh soaps, the standard procedure gives higher results than the direct water method. Suggestions were made to revise the method to use a separate sample of soap and the direct hot water method, but our studies to date indicate that the method is impractical, since the rate of filtration is exceedingly slow. A fritted gooch filter was also suggested to replace the paper filter, but this does not apparently overcome the difficulty.

Another interesting fact was pointed out by one of our Committee, namely, that the concentration of soap in the soap solution being filtered influenced results, higher results being obtained with increasing concentrations of soap used. The following data was submitted to substantiate this

TABLE II

Per cent Soap Concentration	Water Insoluble (Soap dissolved direct in the hot water)
1%	2.67%
2½%	4.71%
5%	5.12%

The sample was an old silicated flake soap showing 5.68 per cent by the Standard Method.

It is evident from the above summarized discussion that various factors must be considered and studied further before any changes can be recommended in the present procedure. Consequently, no action has been taken by the Committee on this test.

Free Alkali Determination

In the cooperative work on this test last year it was found and reported that the present official