tube with fresh solution from the appropriate pint reserve bottle.

5. Procedure:

Weigh out into a 250-ml. beaker 10 grams of the soap to be tested, using a rough balance (+ · 1 gram). Add about 100 ml. of distilled water and boil to dissolve. When thoroughly dissolved add successive portions of powdered lead subacetate and boil until the soap and salt are completely precipitated. A little experience will enable one to tell when the soap and salt are completely precipitated. Usually about 5 grams of dry powder will be sufficient. Boil until the precipitated soap is coagulated and the solution is clear. Decant into a 250-ml. beaker and wash out the original beaker once with about 10 ml. of hot water. Add 1 to 1 C. P. sulfuric acid until the excess lead is precipitated. This point has been reached when no further precipitate is formed on the addition of more H_2SO_4. Filter into a 400-ml. beaker, add 25 ml. of dichromate solution, 50 ml. of 1:1 sulfuric acid, and boil vigorously for at least two minutes.

Pour into a 500-ml. volumetric flask, cool under running tap water, and make up to the mark with distilled water. Mix well, and pour into a 5¼″ comparator tube, to the mark. Match against standard samples by looking through the length of the solutions at a frosted 75-watt light bulb fastened to a table. Estimate any glycerol colors falling between two standard sample colors.

Acknowledgments

We wish to acknowledge the help given by Mr. Daniel DeSande in trying out our theories on a practical scale.

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Progress Report of the Committee on Analysis of Commercial Fats and Oils

October, 1943

Thiocyanogen Numbers

A year ago this Committee recommended the adoption of revised constants for the calculations involved in the determination of thiocyanogen values. We now submit the formulae for these calculations based on the proposed constants.

The suggested constants were:

Acid	Pct.	Iodine Value	Thiocyanogen Value
Linolenic	X	273.7	167.1
Linoleic	Y	181.1	96.7
Oleic	Z	89.9	89.3
Saturated	S	0	0

When the iodine and the thiocyanogen values are determined on the fatty acids the calculations are as follows:

When no Linolenic acid is present:

$$181.1\,Y + 89.9\,Z = 100\text{ I.V.}$$
$$96.7\,Y + 89.3\,Z = 100\text{ T.V.}$$
$$S = 100 - (Y + Z)$$
$$Y = 1.194\text{ I.V.} - 1.202\text{ T.V.}$$
$$Z = 2.421\text{ T.V.} - 1.293\text{ I.V.}$$
$$S = 100 - (Y + Z)$$

When Linolenic acid is present:

$$273.7\,X + 181.1\,Y + 89.9\,Z = 100\text{ I.V.}$$
$$167.1\,X + 96.7\,Y + 89.3\,Z = 100\text{ T.V.}$$
$$X + Y + Z = 100 - S$$

$$X = 1.5902\text{ T.V.} - 0.1290\text{ I.V.} + 1.3040\,S - 130.40$$
$$Y = 1.3565\text{ I.V.} - 3.2048\text{ T.V.} - 1.6423\,S + 164.23$$
$$Z = 1.6146\text{ T.V.} - 1.2275\text{ I.V.} - 0.6617\,S + 66.17$$

When the iodine and thiocyanogen values are determined on the mixed triglycerides the calculations for the hypothetically pure triglycerides are as follows:

Glyceride	Pct.	Calculated from Fatty Acids	
		Iodine Value	Thiocyanogen Value
Linolenin	X	261.8	159.8
Linolein	Y	173.3	92.5
Olein	Z	86.0	85.5
Saturated and Unsaponifiable	S	0	0

When no Linolenin is present:

$$Y = 1.246\text{ I.V.} - 1.253\text{ T.V.}$$
$$Z = 2.525\text{ T.V.} - 1.348\text{ I.V.}$$
$$S = 100 - (Y + Z)$$

When Linolenin is present:

$$261.8\,X + 173.3\,Y + 86.0\,Z = 100\text{ I.V.}$$
$$159.8\,X + 92.5\,Y + 85.5\,Z = 100\text{ T.V.}$$
$$X + Y + Z = 100 - S$$
$$X = 1.6610\text{ T.V.} - 0.1332\text{ I.V.} + 1.3056\,S - 130.56$$
$$Y = 1.4137\text{ I.V.} - 3.3449\text{ T.V.} - 1.6441\,S + 164.41$$
$$Z = 1.6839\text{ T.V.} - 1.2805\text{ I.V.} - 0.6615\,S + 66.15$$

These constants are based on the assumptions that the addition of thiocyanogen to the fatty acids and the triglycerides is on a strictly stoichometrical basis. This relationship has not been definitely proved. Several samples were analyzed during the past year in an attempt to show whether or not this relationship would hold true. The results are shown in the following tabulation:

IODINE NO.—FATTY ACIDS

	1	2	3	4	5	6	Average
Cottonseed—A	112.4	112.8	112.7	114.3	112.3	112.5	112.8
Cottonseed—B	112.3	112.8	113.1	113.5	112.0	112.1	112.8
Soybean	134.2	133.5	134.0	134.2	133.0	135.2	134.0
Peanut	99.4	98.7	99.5	99.5	99.7	100.1	99.6
Corn	125.6	132.1	132.2	131.9	133.0	131.7	131.1

IODINE NO.—GLYCERIDES

Cottonseed—A	107.0	106.9	108.5	108.5	108.0	108.0	107.8
Cottonseed—B	108.8	107.9	109.8	109.0	109.5	109.3	108.9
Soybean	129.2	129.7	129.7	129.7	130.0	129.8	129.6
Peanut	95.7	94.8	98.0	95.5	97.7	96.3	96.4
Corn	126.9	127.1	127.9	127.5	128.5	127.2	127.0

Son. No.—Fatty Acids

Cottonseed—A	71.5	67.9	69.1	69.0	69.8	71.3 69.6	69.8
Cottonseed—B	70.5	69.6	70.2	69.8	69.6	71.2 71.4	70.4
Soybean	85.9	85.6	84.4	84.9	83.7	84.7 85.2	84.8
Peanut	71.8	70.5	71.6	70.9	70.8	72.7 71.2	71.2
Corn	84.0	80.4	80.6	81.3	81.6	81.3 82.9	81.8

Scn. No.—Glycerides

Cottonseed—A	70.2	68.4	67.1	69.5	68.6	69.5 69.7	68.9
Cottonseed—B	71.1	68.5	67.5	71.0	67.6	68.2 69.8	68.9
Soybean	85.2	81.5	82.4	84.6	82.1	84.6 84.8	83.6
Peanut	71.6	67.4	68.6	70.4	68.9	70.9 71.1	69.8
Corn	82.5	80.7	81.5	83.4	80.0	82.5 82.3	81.8

Oleic Acid—Fatty Acids

Cottonseed—A	27.6	18.3	21.3	19.1	23.8	27.2 23.1	22.9
Cottonseed—B	25.3	22.7	23.4	22.0	23.7	27.5 28.0	24.6
Soybean	34.5	34.5	30.0	32.2	30.7	30.3 31.5	31.9
Peanut	45.3	43.0	44.5	43.1	42.5	46.7 43.0	44.0
Corn	31.8	32.6	24.0	26.5	25.6	26.6 30.5	26.9

Oleic Acid—Glycerides

Cottonseed—A	31.8	28.5	22.9	29.3	27.7	30.0 30.5	28.7
Cottonseed—B	32.9	27.1	22.2	32.4	23.1	24.9 29.0	27.3
Soybean	37.8	30.6	33.2	38.8	32.1	38.8 39.3	35.8
Peanut	51.1	42.2	40.9	49.1	42.4	49.3 49.8	46.4
Corn	37.4	32.2	33.3	38.8	28.8	37.0 36.4	34.8

Linoleic Acid—Fatty Acids

Cottonseed—A	48.3	53.0	51.5	53.6	50.2	48.6 50.6	50.8
Cottonseed—B	49.4	51.0	50.7	51.5	50.1	48.2 48.0	49.8
Soybean	56.9	56.5	59.5	58.2	58.2	59.6 59.0	58.2
Peanut	32.3	33.1	32.7	33.5	33.9	32.1 33.9	33.1
Corn	57.4	60.9	61.0	59.8	60.7	59.5 57.6	59.5

Linoleic Acid—Glycerides

Cottonseed—A	45.9	47.4	51.1	48.2	48.6	47.4 47.2	47.8
Cottonseed—B	46.4	48.3	52.2	46.9	51.7	50.7 48.7	49.3
Soybean	54.2	59.6	58.3	55.8	59.1	55.6 55.4	56.9
Peanut	29.9	33.5	36.1	30.8	35.3	31.1 30.8	32.5
Corn	54.4	56.9	57.2	54.5	59.8	55.0 55.3	56.2

Saturated Acids—Fatty Acids

Cottonseed—A	24.1	28.7	27.2	27.3	26.0	24.2 26.3	26.3
Cottonseed—B	25.3	26.3	25.9	26.5	26.2	24.3 24.0	25.5
Soybean	8.6	9.0	10.5	9.6	11.1	10.1 9.5	9.9
Peanut	22.4	23.9	22.8	23.4	23.6	21.2 23.1	22.9
Corn	10.8	15.5	15.0	12.7	13.7	13.9 11.9	13.4

Saturated Acids—Glycerides

Cottonseed—A	22.3	22.3	26.0	22.5	23.7	22.6 22.8	23.1
Cottonseed—B	20.7	24.6	25.6	20.7	25.2	24.4 22.3	23.3
Soybean	8.0	9.8	8.5	5.4	8.8	5.6 5.3	7.3
Peanut	19.0	24.3	23.0	20.1	22.3	19.6	21.1
Corn	8.2	10.9	9.5	6.1	11.4	8.0 8.3	9.1

Unfortunately the agreement between Laboratories on identical samples was so poor that we could not expect the results to prove or disprove what we set out to do. Further work is anticipated in this method to see if we can obtain more concordant results and perhaps locate the cause or causes for disagreement.

Halphen Test

Rule 149 of the National Cottonseed Products Association specifies that peanut oil shall not contain more than ½ of 1% cottonseed oil as indicated by the Halphen Test. We were requested to make an investigation to see if this test was sufficiently quantitative for this purpose. Apparently many difficulties have arisen between buyers and sellers on this score.

Several samples were prepared of known amounts of cottonseed and peanut oil and submitted to various members of our Committee. The results are shown in the following tabulation:

COTTONSEED OIL IN PEANUT OIL

Samples Contained	0.30%	0.70%	0.50%
Laboratory			
1	Trace	About 0.5	0.25-0.50
2	Below 0.5	Below 0.5	Below 0.5
3	Below 0.5	Above 0.5	Below 0.5
4	Over 0.5	Over 0.5	Over 0.5
5	Less than 0.5	0.50-0.75	About 0.5
6	Less than 0.25	0.5-1.0	0.25-0.5
7	0.2	0.6	0.8
Samples Contained	0.25%	0.50%	0.75%
Laboratory			
1	Less than 0.25	0.25-0.5	0.75-1.0
2	Over 0.75	Over 0.75	Over 0.75
3	Less than 0.5	0.5	0.5-0.7
4	0.4	0.4	0.6
5	0.5	0.5-0.75	About ¾
6	1.3	1.5	1.5+
7	0.3	0.75	0.75-1.0

These data serve to confirm the general opinion of the Halphen Test and the method as it is printed in the Official Methods of the American Oil Chemists Society which states, "the depth of color is to a certain extent proportional to the amount of oil present." Consideration of some of the factors which are known to influence the depth of color obtained in the Halphen Test such as the effect of heat treatment of the oil, hydrogenation, and the variation in oils from one lot to another leads us to conclude that the method is principally qualitative, only roughly quantitative and that no further work is warranted at the present time.

Swift Stability Test

This Committee has been asked to re-open the problem of standardizing the Swift Stability Test with the view of adoption as a method of this Society. A sample of shortening was sent to several Committee members as well as to other Laboratories. The keeping quality as determined and reported by these Laboratories is shown in the following tabulation:

Results obtained by Committee members:

Laboratory	Stability Test
1	30 hrs.
2	29 hrs.
3	26 hrs. (1st analyst)
3	27 hrs. (2nd analyst)
4	28½ hrs.
5	30 hrs.
6	23 hrs.
7	26 hrs.
Average	27 hrs.

Results obtained by another group of Laboratories on the same sample:

Laboratory	Stability Test
8	33 hrs.
9	24 hrs.
10	34 hrs.
11	24 hrs.
12	24 hrs.
13	28 hrs.
14	30 hrs.
15	34 hrs.
16	28 hrs.
17	32 hrs.
18	30 hrs.
19	30 hrs.
20	30 hrs.
21	28 hrs.
22	33 hrs.
23	29 hrs.
Average	29 hrs.

Results obtained by an Independent Laboratory: 12 hrs.

The foregoing results were obtained by using the method as it was originally published by King, Roschen, and Irwin in *Oil and Soap*, *10*, 105 (1933). Further work is necessary and will be carried on during the next year.

Other Methods

Work on methods other than those mentioned above is on our program but there is no progress to report at this time.

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A Report on Ester Interchange

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Ester interchange may be defined broadly as a reaction between an ester and an alcohol. Another name for this effect is alcoholysis, meaning a decomposition involving alcohol. A typical example is the reaction between methanol and a triglyceride to give glycerine and methyl fatty acid esters. Another example well known to the industry is the treatment of triglycerides with glycerine to give mono- and di-glycerides. Alkaline catalysts are ordinarily used, although in some cases acids are preferred.

Ester interchange between glycerides or other fatty acid esters and various alcohols has been the subject of research by this laboratory. Types of ester interchange reactions of these materials to be dealt with here include reactions of monohydric alcohols with esters of polyhydric alcohols, monohydric alcohols with esters of monohydric alcohols, polyhydric alcohols with esters of polyhydric alcohols and polyhydric alcohols with esters of monohydric alcohols.

Ester interchange between monohydric alcohols and glycerides can be effected in the presence of small amounts of alkalies or acids. The glyceride is thereby converted almost entirely into free glycerine and fatty acid esters of the monohydric alcohol used. The lower alcohols, methyl and ethyl, react rapidly and smoothly with glycerides in the presence of sodium hydroxide (2, 7). A typical reaction would require 1.6 equivalents of anhydrous methyl or ethyl alcohol per equivalent of a neutral glyceride with 0.5% sodium hydroxide, on the basis of the oil, as catalyst, dissolved in the alcohol. The alcoholic sodium hydroxide solution is merely mixed with the glyceride until homogeneous. This reaction may be carried out at room temperature or at higher temperatures, if necessary to keep the glyceride more fluid. Within thirty minutes glycerine starts to separate as a lower layer and in from one to two hours has separated almost completely. The glycerine layer is withdrawn, the ester layer acidified to break up any soap formed and washed free of unsettled glycerine, unreacted alcohol and salt.

For best results, the materials used should meet certain qualifications. When ethyl alcohol is used and the acid number of the glyceride is below about one, the reaction takes place as described previously. If the acid number is somewhat greater than this it may be at least partly compensated by adding sodium hydroxide in excess of catalytic amounts to neutralize free acids. However, because of the resulting soap formation the reaction mixture tends to become viscous or to gel. The reaction mixture must then be acidified after a standing period to permit separation of the alcohol-glycerine and the fatty acid-ester layers. Gels or viscous reaction mixtures may sometimes be prevented by using a larger excess of alcohol, but in these cases the glycerine will be held in solution. Acidification of the reaction mixture is necessary here also to promote separation of layers.

Another prerequisite for effectively carrying out the reaction is that the materials be substantially anhydrous. Presence of water causes soap formation, with consequent loss of alkalinity. For example, when 30 parts ethyl alcohol, 0.5 part sodium hydroxide and 100 parts cottonseed oil are used, as little as 0.3% water in the reaction mixture appreciably lowers the glycerine yield and causes the reaction mixture to become viscous, preventing separation of glycerine. Sodium hydroxide in excess of catalytic amounts and/or excess alcohol may be used to compensate in some measure for the presence of water. In these cases the reaction mixtures usually must be acidified to cause separation of the glycerine and ester layers. The specific effects of water on the reaction using cottonseed oil with ethyl alcohol are given in Table I.