A STUDY OF MECHANISM

AUTO

H. L. Roschen
Swift & Company

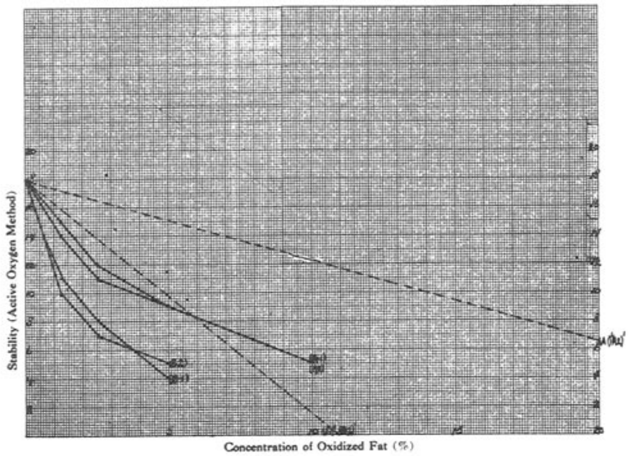

FIG. I
Effect of Oxidized Lard on Fresh Lard
(A1)—Rancid Lard P. V. 64.0
(A2)—Rancid Lard P. V. 62.0 Steam-blown 100° C.
(B1)—Rancid Lard P. V. 182
(B2)—Rancid Lard P. V. 182 Steam-blown 100° C.

The first definite attempt to explain the rancidification of fats as a *chemical* change is probably due to Scherer[1], who as early as 1795 took the position that fats obtained "sharp, burning and biting tastes" by contact with oxygen. By 1890 Ritsert[2] had established that rancidification was an oxidative change which required only the presence of oxygen and which could be accelerated by light. The first suggestion that rancid odors and tastes are due to aldehyde compounds is apparently due to Marx[3] in 1899. About this same time, Kreis[4] developed probably the first purely chemical test for rancidity. From the time he originally proposed his phloroglucinol test down to very recent years, investigations have to a large extent concerned themselves with explanations, refinements and modifications[5, 6, 7, 8, 9], of the Kreis reaction or with other color tests to replace it, such as that of Von Fellenberg[10].

More recently, oxygen absorption tests, measurements of the rate of volatile aldehyde formation[11], and measurements of the rate of methylene blue reduction[12, 13] have been proposed as means of studying the susceptibility of fats to oxidation. Wheeler[14] discusses these and other methods with adequate references in an article in which he proposes the measurement of peroxide formation as an index to the resistance of an oil to oxidative rancidity.

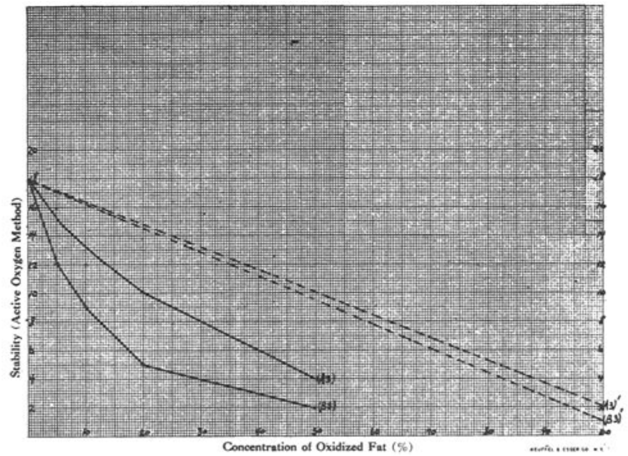

Fig. II
Effect of Oxidized Lard on Fresh Lard
(A3)—Rancid Lard—P. V. O.1—Steam-blown 200° C.
(B3)—Rancid Lard—P. V. 1.8—Steam-blown 200° C.

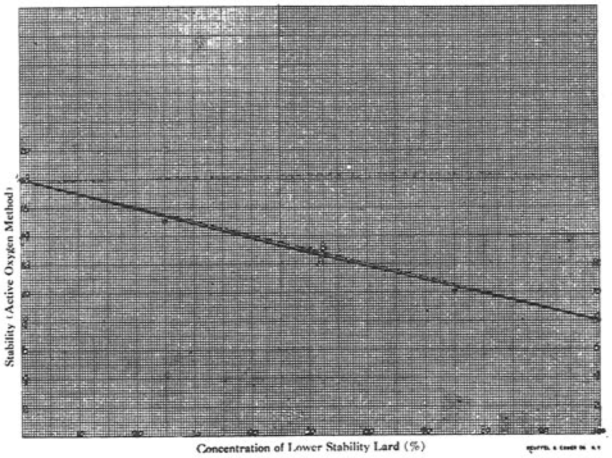

FIG. IIa
Stability Relationship of Non-Rancid Lard
A—Actual Curve
B—Calculated Curve

Considerable work has been done in recent years on the subject of pro- and negative catalysts of oxidation. Vibrans[15] has reviewed the field of negative catalysts in a recent address before the American Oil Chemists' Society. The study of positive catalysts has been confined largely to the effects of light and of metals and their salts.

The major attention of investigators in this field has been the detection and quantitative estimation of the end products of oxidation, and the measurement of induction period. Many decomposition products have been isolated and identified[6]. Although it has been long recognized that the oxidation of fats is autocatalytic, very little information is available on the effects of the accumulated end products on the oxidation itself. The question of whether heptaldehyde, for example, has any influence on the oxidation once it has accumulated in an oxidizing fat, has not been answered.

The work reported here represents an attempt to arrive at some general idea of the catalytic effects of the end products of oxidation. Rancid fat itself was used as a source of some of these end materials. It has been clearly appreciated in recent years that most fats possess a certain natural resistance to oxidation which is gradually overcome by continuous action of

OF OXIDATION

AND R. C. NEWTON
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oxidizing conditions, after which the oxidation proceeds most rapidly. There has been observed a wide difference in the extent of this induction period, depending among other things on the origin of the fat. Lard, for example, exerts a more forceful resistance to the uptake of peroxide oxygen than is the case of most refined vegetable oils. In this work, lard was chosen as the fat to be studied and the effect of various substances on the induction period has been measured. Just as the induction period of a fat is reduced when small amounts of metallic catalysts are added, so should the induction period of fresh fat be shortened by addition of rancid fat, provided positive catalysts are present. Rancid fats have been treated by distillation to remove some of the products of oxidation, after which the non-volatile products were compared with the untreated rancid fat in its effect on the induction period when added to fresh fat.

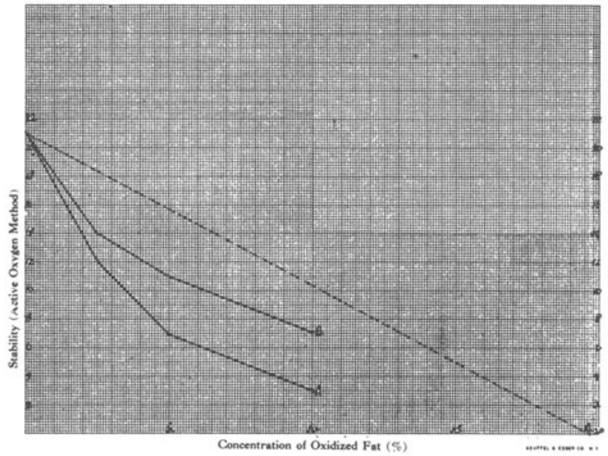

Fig. III
Effects of Oxidized Lard vs. Oxidized C. S. Oil
A—104 P. V. Lard
B—100 P. V. C. S. Oil
C—Calculated Curve

Yielded Six Samples

Two samples of about 1500 grams each of lard of excellent keeping quality were aerated at 80-90° C., one until it became slightly rancid, the other until it became highly rancid. Portions of these racid lards were then blown with steam at 100° C. and 3-5 mm. Hg. pressure for 3 hours. Samples were removed and the blowing continued at 200° C. for 3 hours. This treatment yielded six samples of oxidized lard with the following characteristics. (TableI.)

TABLE I.—CHARACTERISTICS OF OXIDIZED LARDS
(Peroxide Values (milliequivalents/Kilo)

	A. Sl. Rancid	B. Highly Rancid
1. Rancid Lard	64.0	182
2. Rancid Lard blown with steam at 100° C................	62.0	182
3. Rancid Lard blown with steam at 200° C.................	0.1	1.8

The rancid lards, particularly the sample showing 182 Peroxide Value, possessed the characteristic disagreeable taste and smell. The samples blown with steam at 100° C. were odorless, bland-tasting, and entirely palatable. The treatment had removed by volatilization, all the decomposition products which give rise to the typical rancid odors and tastes, without materially reducing the peroxide content. The taste and odor of rancid lard cannot, therefore, be traced to the peroxides. The samples blown with steam at 200° C. were likewise odorless. Their flavor was somewhat flat but in no way suggestive of typical rancidity. The peroxides were almost completely destroyed by the treatment at 200° C. As the temperature during the blowing rose, a point was reached at about 140-160° C. where active distillation of some volatile materials occurred. This would seem to be the approximate decomposition temperature of the peroxides.

These six samples of treated lard were added in varying proportions to fresh lard. The stability as indicated by the induction period was then measured by the active oxygen or peroxide method proposed by King, Roschen and Irwin[16]. The stability in this

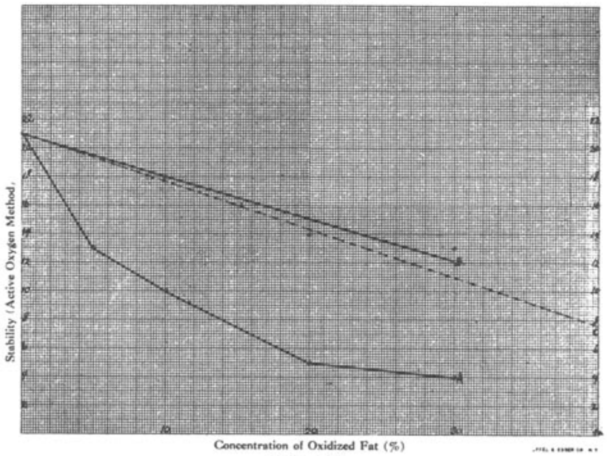

FIG. IV
A—31.8 P. V. Lard
B—30.6 P. V. C. S. Oil
C—Calculated Curve

TABLE II—STABILITY OF FRESH LARD TREATED WITH OXIDIZED LARD

Concentration of Oxidized Lard (%)	Rancid Lard 64 PV* (A1)	Rancid Lard 182 PV* (B1)	Rancid Lard Steam Blown at 100° C. 62 PV* (A2)	Rancid Lard Steam Blown at 100° C. 182 PV* (B2)	Rancid Lard Steam Blown at 200° C. 0.1 PV* (A3)	Rancid Lard Steam Blown at 200° C. 1.8 PV* (B3)
0.00	18	18	18	18	18	18
0.62	..	14	..	14	..	..
1.25	15	11	14	10	..	..
2.50	12	8	11	7	..	..
5.00	9	4	9	5	16	12
10.00	5	..	5	..	12	9
20.00	..	..	..	..	10	5
50.00	..	..	..	..	4	2

*Peroxide Value (milliequivalents/Kilo).

method is taken as the number of hours of aeration at 208° F. required to reach the first peroxide value greater than 20 milliequivalents/kilo of lard. Table II gives the results.

The results have been reproduced graphically in Figures I and II. Included with the experimental curves are sets of calculated curves drawn with broken lines. These curves are derived on the basis of the following considerations.

In the active oxygen test method, the stability of lard is defined as the number of hours required to reach a peroxide value of 20 milliequivalents per kilo of fat. If a fresh lard, which usually has a peroxide value under one, is mixed with a small amount of a rancid lard which has a peroxide value over 20, then the peroxide value of the mixture will be higher than that of the fresh lard, and proportionately less time will be needed to develop the required 20 milliequivalents per kilo. Furthermore, there will be a critical concentration of rancid lard at which the initial peroxide of a mixture with fresh lard will just equal 20.0 and the stability, by the above definition, will become zero. Referring to Fig. I, a mixture of Lard (B1), whose initial peroxide value is 182, containing 10.9% (B1) and 89.1% fresh lard (the initial peroxide of which in this case was 0.6) would have an initial peroxide of 20.0 and consequently a stability of zero. The curve (B1)^1 could be built up by a series of similar computations down to zero concentration of rancid lard, at which point the stability would be 18 hours. The curve (B1)^1 would therefore represent the expected or calculated stability due to initial peroxide in the mixtures. The catalytic action of any given lard is indicated by the deviation of the experimental curve from the calculated curve. The validity of the calculated curves is indicated by Fig. IIa which represents the stability relationships of two fresh lards. The experimental curve is identical with the calculated curve.

In the light of these considerations, all six of the samples of oxidized lard appear as active catalysts or may be said to contain active catalytic material.

The Activity of Materials Volatile at 100° C.—Heptaldehyde

It will be noted from Fig. I that curves for rancid lard and lard blown at 100° C. are practically identical—that is, curves (A1) and (A2) correspond, as do (B1) and (B2). The materials volatile at 100° C., which include the materials responsible for rancid odor and taste, therefore appear to be inactive as catalysts. If these materials were active catalysts we should expect that lard which had been freed from them would produce smaller changes in induction period than lard which retained them, while as a matter of fact these lards show somewhat greater effects. The differences, however, are probably not significant.

This conclusion was unexpected as it seemed to be the general feeling that all the oxidative end products have some effect in promoting the oxidation. Additional experiments were undertaken to throw further light on this point by measuring the effect of the volatile constituents. A sample of rancid lard (PV104) was blown with nitrogen at 100° C. for 4 hours. Nitrogen was used to prevent further decomposition of the lard. The volatile oxidation products of the rancid lard, together with the nitrogen gas, were carried through fresh lard held at a temperature just sufficient to keep it melted (110° F.). The rancid lard from which some of the volatile materials had thus been removed was then compared with the original rancid lard in its effect on the induction period of fresh lard. The two lards again yielded identical graphs. The fresh lard which had absorbed the rancid vapors was tested for stability by the active oxygen method and gave results identical with a control sample which had been blown with nitrogen only. The untreated sample, the control sample, and the sample treated with rancid vapor all gave active oxygen method stabilities of 20 hours.

TABLE III—EFFECT OF MATERIALS VOLATILE AT 100° C. (70° C. INCUBATION)

Time (days)	Original Lard Peroxide Value	Original Lard Odor	Control. Orig. lard blown with Nitrogen only Peroxide Value	Control. Orig. lard blown with Nitrogen only Odor	Treated Sample. Orig. lard blown with Nitrogen + Rancid Vapor Peroxide Value	Treated Sample. Orig. lard blown with Nitrogen + Rancid Vapor Odor
1	1.1	Fresh	1.1	Fresh	1.4	Rancid
2	1.5	Fresh	1.6	Fresh	1.8	Sl. Rancid
5	6.3	Bland	6.1	Bland	6.1	Sl. Sharp
6	8.7	Sl. Sharp	9.0	Sl. Sharp	9.7	Sl. Sharp
7	19.2	Sl. Rancid	14.3	OK?	27.2	Sl. Rancid
8	35.9	Rancid	39.8	Rancid	50.0	Rancid

To guard against the possibility that the active oxygen method was not yielding reliable results in measuring the effects of volatile materials because of the ready escape of these materials in the aeration, incubation tests in tightly closed jars at 70° C. were conducted on the sample treated with rancid vapor. Table III shows that the oxidation of the treated sample under these conditions proceeds in a manner almost identical with the control samples, the induction period being just under 7 days for the treated sample and just over 7 days for the controls.

Heptaldehyde[17] has definitely established itself as one of the cleavage products of fatty oxidation. As an additional check, a sample of Eastman Kodak heptaldehyde was incorporated in lard. The oxidation of the heptaldehyde treated samples was followed in tightly closed jars at 70° C. and at room temperature, the test at room temperature being added to provide additional insurance against the escape of the volatile heptaldehyde. Table IV gives the results of this test.

The results show that heptaldehyde has no accelerating effect on the oxidation of lard under these conditions. The end of the induction period in the 70° C. tests was reached at the end of five days for all samples, control and treated alike. At room temperatures, all samples also oxidized equally although, of course, the induction period is longer at the low temperature.

The conclusion is, therefore, drawn that the materials volatile at 100° *C. are inactive as catalysts of oxidation. Included in these volatile end products are the products responsible for rancid odor and taste.*

The Activity of Peroxide

Figure II represents the effects on fresh lard of additions of oxidized lard which has been steam blown at 200° C. The peroxides of these steam blown lards have been practically completely decomposed, yet the lards show high catalytic activity. This would lead to the tentative conclusion that the peroxides

(*Continued on page* 236.)

TABLE IV—EFFECT OF EASTMAN KODAK HEPTALDEHYDE

Time (days)	Control Peroxide Value	Control Odor	0.01% Heptaldehyde Peroxide Value	0.01% Heptaldehyde Odor	0.10% Heptaldehyde Peroxide Value	0.10% Heptaldehyde Odor
			70°C.			
1	5.3	OK	6.2	Heptaldehyde	5.1	Strong Heptal.
2	10.3	OK	10.6	Heptaldehyde	10.8	Strong Heptal.
3	16.0	?	17.0	Sl. Heptaldehyde	16.7	Strong Heptal.
5	26.0	SR	27.9	Sl. Heptaldehyde	25.8	Strong Heptal.
9	41.5	R+	41.5	Rancid+	39.6	Heptal.-Rancid
			Room Temperature (80-85° F.)			
5	4.0	OK	4.0	Heptald.	4.0	Strong Heptal.
8	4.6	OK	4.7	Heptald.	4.7	Strong Heptal.
11	4.7	OK	4.7	Heptald.	5.0	Strong Heptal.

REPORT OF THE OLIVE OIL COMMITTEE FOR 1933-1934

By M. F. Lauro, Chairman

The Committee has had under advisement the drafting of specifications for OLIVE OIL and for OLIVE OIL FOOTS otherwise known as sulphur oil.

Values for these oils are today not satisfactorily defined either in the literature or by any authority. Since there is a need for their proper limitation in the case of olive oil and a growing demand by the trade in the case of sulphur oil for a closer control on quality and freedom from foreign material, it was felt that this committee could perform this meritorious and necessary function in the interest of the Society and for the benefit of the industries involved. The American Society for the Testing of Materials has accomplished such a service in the case of oils like linseed, soya bean and perilla. Our purpose is to establish an A. O. C. S. set of standards or specifications as a guide for those of the trade that care to avail themselves of a superior classification than heretofore exists.

Obviously, we must proceed with considerable thought and caution, and plenty of time must be allowed to insure fair and proper results. We must avoid any hasty conclusions which may be regretted later. A tentative schedule of values may be published in the journal and allowed to stand for some time, inviting criticism by all and their suggestions for further improvement.

It was in August, 1933, that the chairman suggested to the committee the task of setting up "standards" for these two products and the response was very favorable to an undertaking wider in scope that had originally been proposed. All thought it an excellent idea for the Society to go into this phase of activity, with the proper safeguards, of course. The majority of the membership felt it incumbent on the committee to study oils from other localities than Italy and Spain, taking in those oils that differ in some respects, such as from Algeria, Tunis and Dalmatia.

Replies were received from time to time from the various members, into which it is unnecessary to go in detail, offering valuable suggestions, modifying some of the values and adding others. It is a pleasure to note that a large part of the data subsequently submitted rests on the actual analysis over a period of years of samples of oil and foots dealt with in the trade with the larger users of these products. This gives us figures representing the fair and usual values for our basis for the normal limits.

It would appear from the various comments and figures submitted that as a whole there is substantial agreement, but one view would widen the scope to take in all pure oils regardless of how large a difference this would make in the range of value from minimum to maximum and the other view would narrow this range to cover only such values as represent the fair and usual oils appearing on the market. I have purposely drawn this distinction more sharply than the replies on their face would warrant, because when studied it will be seen that these two views are inconsistent and antagonistic to each other.

However, a good start has been made and it is hoped that with the publication of these results, the necessary interest will be aroused to bring forth the criticism required to build up a durable structure. Comment is therefore invited from all quarters, from the olive oil trade as well as from the chemists.

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U. S. Obtains Larger Share of China's Chemical Imports

The participation of both the United States and Japan in China's chemical import trade was greater in the first half of the current year than in the corresponding period of 1933, while the share of Germany in this trade declined, according to C. C. Concannon, chief of the Commerce Department's chemical division. China's imports of chemicals and allied products were valued at $16,500,000 during the first six months of 1934, a decline of 14 per cent compared with the corresponding period last year. Germany continued the largest source of supply, accounting for 30 per cent of the total compared with 34 per cent last year, while the United States increased its share from 14 to 16 per cent and that of Japan increased from 11 to 15 per cent, it was stated. Substantial reductions in receipts of industrial chemicals, especially sulphuric acid, ammonium sulphate, bleaching powder, potassium chloride, soda ash, nitrates were largely responsible for China's reduced imports. China with its large textile interests, Concannon points out, is an important market for dyes and takes more American dyes than any other foreign country. Exports of chemicals and allied products from China are limited, the largest item being tung oil, a commodity used extensively as a raw material in the paint and varnish industry. Exports of tung oil during the first half of the year declined 6 per cent in value to $6,600,000 compared with the corresponding period last year. The United States is China's largest export market for this product.

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Elected to A.N.A.I.

The Norwich Pharmacal Company, drug manufacturers of Norwich, New York, has been elected to membership in the Association of National Advertisers, Inc. Dr. W. M. Stofer, Vice-President in Charge of Advertising, will represent his company in the A. N. A.

AUTO OXIDATION

(*Continued from page 228.*)

may also be inactive in the oxidation. The following tests were made in an attempt to verify this conclusion.

It has been known for some time that lard develops the typical odor of aldehyde rancidity at relatively low peroxide values (about 20.0 milliequivalents/Kilo), while some vegetable oils do not develop aldehyde rancidity odors until a peroxide value above 100 has been reached. It follows that a lard with a peroxide value 100 would presumably contain relatively large amounts of other decomposition products, while vegetable oil with 100 peroxide would contain at most only relatively small quantities. Similarly a lard of 30.0 peroxide would contain some other oxidation products while the vegetable oil of equal peroxide would presumably contain only extremely small amounts. It was thought that a comparison of lard and cottonseed oil at equal peroxide values would yield, by difference, some information on the effect of peroxides.

Samples of lard and cottonseed oil of the following peroxide values were prepared by aeration at 80-90° C.

1. Lard—Peroxide Value...... 104
2. C. S. Oil—Peroxide Value.. 100
3. Lard—Peroxide Value....... 31.8
4. C. S. Oil—Peroxide Value.. 30.6

It is difficult to control the aeration to get identical peroxide values, but these values were considered sufficiently close for the purpose of this study.

The oxidized products were then incorporated in fresh lard and the stability of the resulting mixtures was measured by the active oxygen method. Table V gives the results.

The results have been plotted in Figures III and IV, Figure III representing results for 100 PV fats, Figure IV for 30 PV fats.

In both cases the activity of lard exceeds that of cottonseed oil, the lard curves lying substantially below the curves for cottonseed oil, indicating that the active factor is something besides the peroxide. The interesting curve is the one shown in Figure IV where the lard of P. V. 31.8 shows definite catalysis, while the cottonseed oil of *equal* peroxide shows *no* catalytic action, in fact, seems to stablize the mixture beyond the ex-

TABLE V
EFFECT OF OXIDIZED LARD VS. OXIDIZED COTTONSEED OIL
Stability (Active Oxygen Method)

Concentration of Oxidized Fat (%)	Lard P. V. 104	C. S. Oil P. V. 100	Lard P. V. 31.8	C. S. Oil P. V. 30.6
0.0	21	21	21	21
2.5	12	14	..	..
5.0	7	11	13	21
10.0	3	7	10	18
20.0	..	..	5	14
30.0	..	..	4	13

pected stability. This, however, may be due somewhat to change in oxidation characteristics of lard when cottonseed oil is added.

The conclusion that the peroxides are inactive as catalysts would, therefore, appear to be justified.

With the peroxides and volatile end products inactive and lard which has been freed from volatile materials and peroxides by steam distillation at 200° C. still showing strong catalytic action, the inference that the active catalytic material is some substance of high molecular weight not readily volatile at 200° C. and 3-5 mm. Hg pressure seems logical. Figure VI represents a possible mechanism of oxidation, starting with a triglyceride of stearic and oleic acids, passing through the peroxide stage, and ending with glycerol alpha beta distearin, gamma azelaic semi-aldehyde and pelargonic aldehyde. The peroxide and pelargonic aldehyde would presumably be inactive on the basis of evidence presented above, leaving as the active material an aldehyde of high molecular weight. Figure VII represents the oxidation of oleic acid according to Powick[6]. Applied to the triglyceride represented in Figure VI, the end products would be heptaldehyde, epihydrin aldehyde and glycerol alpha beta distearin, gamma pimelenic semi aldehyde, the latter compound being the active material.

It was our object to synthesize a compound of similar structure and to test its action on lard. Dr. Young, of our Research Staff, has synthesized a product which apparently is alpha gamma dilaurin beta glyoxalin (Figure VI). The yields, however, were so small that both tests for catalytic activity and a derivative to determine structure could not be made. The material showed a high catalytic activity, a lard of 18 hour AOM stability being reduced to 12, 8 and 4 hours by respectively 0.087%, 0.175% and 0.35% of material. Silver oxide was used in the preparation of this substance. It is possible that the catalytic action is due to remaining traces of silver. In view of the possible effects of this metal, and the small yields which made it impossible to check the structure, this synthesis will need to be repeated.

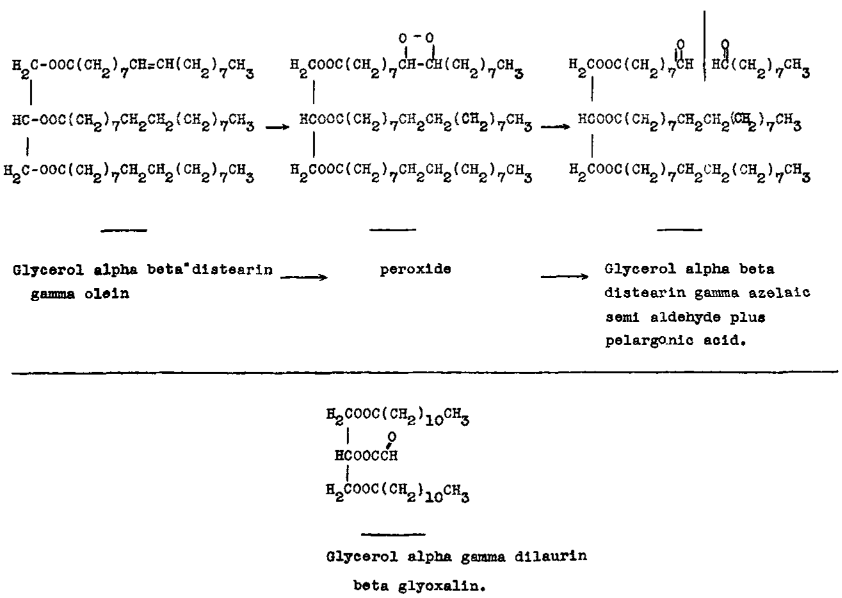

FIGURE VI
Oxidation Mechanism for a Triglyceride

Summary

Evidence has been presented:

(1) That materials volatile from ran-

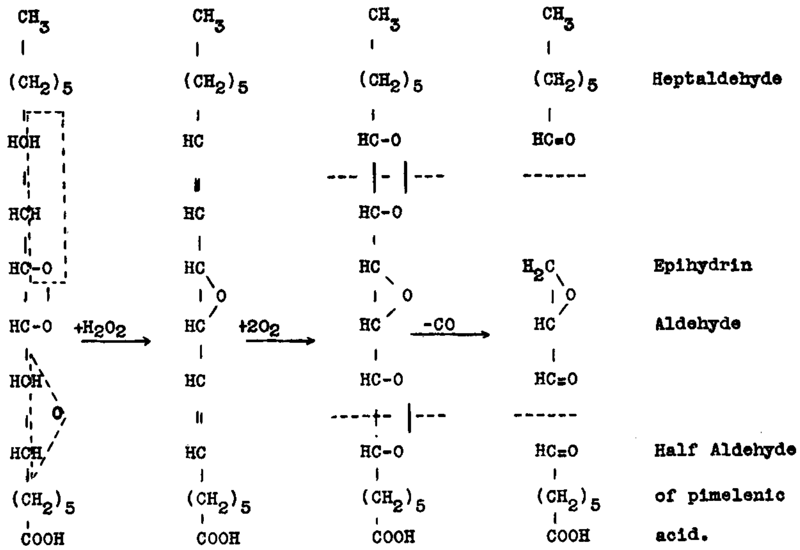

FIGURE VII

Oxidation of Oleic Acid According to Powick

cid lard at 100° C. and 3-5 mm. Hg pressure are inactive as catalysts of oxidation. These materials include the substances which are responsible for rancid odor and taste.

(2) That the peroxides are inactive as catalysts of oxidation.

Conclusion

The conclusion has been drawn that the active catalytic materials are of high molecular weight and not readily volatile at 200° C. and 3-5 mm. Hg pressure. This conclusion has been *tentatively* checked by the use of a synthetic product.

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REPORT OF SULPHONATED OIL COMMITTEE

(*Continued from page* 230.)

that part of the condenser tube should reach within 0.25 inch of the surface of the liquid.

C. P. Long. It is very desirable that the F. A. C. hot-plate method, which is one of the official methods of the A. O. C. S., be standardized much better than it is now. We believe that the size of the sample, the dish used, and the hot plate itself, and its temperature should be specified. We have set a limit of 130° C. as the maximum temperature to which the oil should be heated.

It has been our sad experience that calcium chloride will give up moisture to dry samples long before its physical appearance will give any indication of its condition. For this reason the committee should place some limit on the use of desiccating agents to be used in the desiccator.

H. H. Mosher. We have compared the hot-plate and distillation methods with ten samples of different oils and obtained practically check results when the time factor and the temperature of the hot plate was accurately controlled. We have found, however, that there is a small progressive deterioration of oil by the hot-plate method with a gradual loss in weight, so that some care and intelligence must be exercised in determining the end point. We have usually estimated this at the point at which the loss of weight flattens out.

R. H. Pingree. In order to eliminate the difficulty and expense of replacing parts of the distillation apparatus, I would recommend that both ground joints be "Standard Taper and Interchangeable Joints" and would suggest for this purpose Standard Joint No. 25 (Bureau of Standards, Commercial Standard CS21-30).

W. H. Tiffany. After making a number of tests with rapid evaporation methods, it would appear that the results are unreliable and subject to variations due to the speed of the determination, superheating at walls of vessel, or other unknown factors. However, after running a number of analyses according to the specifications of the hot-plate method as modified by the committee, I find that the results check well and are in good agreement with those by the distillation method.

Ralph Wechsler. Concerning the distillation apparatus, I fully agree with Mr. Lauro that the lower end of the condenser tube should not dip into the liquid of the trap, but should extend only to about 0.25 inch above the surface, in order to prevent the liquid from shooting up into the tube.

Summary

The committee finds that both the A. A. T. C. C. distillation method and the modified hot-plate method are satisfactory for the determination of moisture in commercial sulfonated oils that are free from other volatile matter. The agreement among different analysts was about the same for both methods, with an average variation of about 0.3%, which may also be considered as the probable precision or reliability of each method. Hence, the committee recommends the A. A. T. C. C. distillation method as a standard method and the modified hot-plate method as an alternative method. In the proposed procedures, the A. A. T. C. C. moisture apparatus has been modified so that the end of the condenser tube is raised above the level of the liquid in the trap, and the specifications for the ground joints have been changed to correspond to Interchangeable Ground-Glass Joint 25 of Commercial Standard CS21-30. The F. A. C. hot-plate method has been modified to include a short thermometer (for the control of temperature and to serve as a stirring rod), heating in an air-oven before weighing, and the addition of oleic acid to keep the sample homogeneous and liquid.

Proposed Standard Method of Test for Water in Sulfonated (Sulfated) Oils

A. O. C. S. Distillation Method

1. *Scope.* This method of test determines water existing in a sample of sulfonated (sulfated) oil by distilling the sample with a volatile solvent. It applies only to sulfonated oils that do not contain the following: mineral acids, free sulfonic acids, or free sulfuric acid ester; or alcohol, glycerol, diethylene glycol, acetone, or other water-miscible volatile compounds.

Apparatus

2. *General.* The apparatus shall consist of a glass flask, heated by suitable means and provided with a reflux condenser, discharging into a trap and connected to the flask. The connections between the trap and condenser and flask shall be ground joints. The trap serves to collect and measure the condensed water and to return the solvent to the flask.

Before use, the condenser and the receiving tube shall be thoroughly cleaned with soap and warm water, rinsed well, then treated with hot cleaning solution (a mixture of 10 ml. of saturated potassium bichromate and 990 ml. of concentrated sulfuric acid), and finally thoroughly washed and dried.

3. *Flask.* The glass flask (Fig. 1A) shall be of the short-neck, round-bottom type, made of well-annealed glass, having an approximate capacity of 500 ml.

4. *Heat Source.* An oil bath (stearic acid, paraffin wax, etc.) or an electric