DECOMPOSITION OF PEROXIDES IN FATS WITH A PARTICULAR REFERENCE TO THOSE IN SAURY OIL

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The peroxide content of a fat is regarded as an index of the extent of oxidation which the fat has undergone in the early stage of its oxidation and also as a criterion for the rancidity in the fat. Also the rate of increase of peroxides is generally determined for the evaluation of the stability of fat. However, since the decomposition of peroxides takes place more or less concurrently with the formation of peroxides in fat oxidation, the existing amount of peroxides in fat does not afford the measure of the total amount of peroxides formed in fat oxidation unless the rate of peroxide formation to peroxide decomposition in the course of oxidation is known. Accordingly the peroxide value which gives the existing amount of peroxides in a fat can not be regarded as a correct measure of the extent of fat oxidation. Recent studies of Kaneda *et al.*[1),2)] and Matsuo[3)] confirmed that fat peroxides are highly toxic and the toxicity of autoxidized fat is markedly reduced when peroxides are decomposed or removed. Thus the problem of fat peroxide decomposition is also of practical importance in relation to the nutritive value of fat.

A vast number of reports have been published on the subject of fat peroxides, but there are not so many reports concerning the decomposition of fat peroxides. In 1937, Nakamura[4)] reported his extensive studies on the rate of thermal decomposition of peroxides in soybean and several other vegetable oils and also on the effect of driers such as manganese rosinate and lead soap of linseed oil fatty scids, antioxidants such as hydroquinone and naphthol, and finely divided solid materials such as acid clay, activated carbon and kieselguhr upon the rate of peroxide decomposition. Holman[5)] found the rate of decomposition of methyl linoleate peroxide at 80°C to be 1.6% per hr. The half-life for methyl linoleate peroxide at 80°C with an initial peroxide value of 1,222 was given as 28 hr. by Privett and Lundberg.[6)] According to Lundberg,[7)] the decomposition of methyl linoleate peroxide conforms to a first order reaction when the concentration of peroxides is low, but at a higher concentration it proceeds by a second order reaction. Privett and Quackenbush[8)] studied the effects of antioxidants and synergists upon the decomposition of lard peroxide at 100°C under vacuum with the results that α-tocopherol, NDGA and hydroquinone effected a marked acceleration on the peroxide decomposition while the synergists, citric and ascorbic acids, exerted by themselves no influence on the rate of peroxide decomposition although they suppressed more or less the accelerating effect of antioxidants. In a quite recent study by Cooney *et al.*[9)] the rate of peroxide decomposition in a soybean oil with a peroxide value of 98 was determined at 100°C, 150°C and 180°C, and the decomposition at 100°C was found to proceed linearly with time at a rate of about 6% per hr.

All previous studies on the peroxide decomposition cited above have been conducted with peroxides in vegetable oils and fatty acid esters of vegetable origin or in lard. No detailed studies on the decomposition of peroxides in marine animal oils have hitherto been available. Since dried fish products are one of the staple articles of daily diet in our country, it seems most desirable to study the peroxide decomposition in marine animal oils. Consequently the present study on the decomposition of fat peroxides has been undertaken with a particular reference to the decomposition of saury oil peroxides. First, peroxides in saury and several other oils were decomposed under the same conditions, and the degrees of peroxide decomposition were compared. Also effects of the addition of a highly unsaturated methyl ester upon the peroxide decomposition in several oxidized vegetable oils were investigated to ascertain the presumption, stated by Shimo-oka and Toyama[10] based on their finding that saury oil peroxides decompose much more readily than corn oil peroxides, that highly unsaturated acids favour the peroxide decomposition acting as an acceptor of oxygen from peroxides. Next, the rates of decomposition were determined for saury oil peroxides which were formed under several different conditions of oxidation. Finally, effects of the addition of pro-oxidants and anti-oxidants and the exposure to sunlight upon the rate of decomposition of saury oil peroxides were investigated.

Experimental and Discussion

1. Comparison of the peroxide decomposition in several fatty oils and effects of the addition of highly unsaturated methyl ester upon the peroxide decomposition in vegetable oils

Seven samples of oxidized fatty oils were used in these experiments, among which oxidized saury, sardine, whale and linseed oils were prepared by aeration at 50°C while oxidized sesame, corn and camellia oils were those which had been oxidized by contact with air during the storage at room temperature in our laboratory. The highly unsaturated methyl ester used as an additive in these experiments was prepared from saury oil and had an iodine value of 373.8. Each 10 g. oxidized oil was placed in a 30-ml. test tube, and the latter was hold in an oil bath, the temperature of which was kept at 100°C, 90°C or 50°C. After a required period, the test tube was transferred into a cold water bath, and the peroxide value of oil was then determined. The percentage decomposition of peroxides was calculated from the peroxide values before and after the experiments. Also a series of parallel experiments were performed with the oxidized vegetable oils to which was added 10% of highly unsaturated methyl ester, and the percentage decomposition of the peroxides in oxidized vegetable oils was calculated after making corrections for the decomposition of the peroxides contained in a small proportion in the highly unsaturated methyl ester (peroxide value 15.5). In another series of experiments, each 20 g. oxidized oil was placed in a 25-ml. glass bottle, and air in the bottle was replaced by nitrogen. The bottle was tightly stoppered and sealed, and placed in a brown desiccator filled with nitrogen. After standing the desiccator for 140 days at room temperature, the peroxide value of each oil was determined and the percentage decomposition of peroxides during the storage was calculated. Peroxide values were determined by the Wheeler method with a modification of using 1 g. sample. The results are shown in Table 1.

TABLE 1. Comparison of the Peroxide Decomposition in Different Fatty Oils and Effects of the Addition of Highly Unsaturated Methyl Ester upon the Peroxide Decomposition in Vegetable Oils

Oil	Initial peroxide value	Decomposition of peroxides (%)			
		100°C	90°C	50°C	Room temp. (140 days)
Saury oil	280	67 (2 hr.)	46(1.75 hr.)	31 (4 hr.)	90
Sardine oil	184	56 (2 hr.)	45(1.75 hr.)	30 (4 hr.)	—
Whale oil	206	—	29(1.75 hr.)	16 (5 hr.)	71
Linseed oil	179	—	—	8.5(5 hr.)	—
〃 + 10% H.U.E.*	—	—	—	9.6(5 hr.)	—
Sesame oil	140	43 (3 hr.)	—	—	61
〃 + 10% H.U.E.	—	45 (3 hr.)	—	—	61
Corn oil	141	7.6(3 hr.)	—	—	5.7
〃 + 10% H.U.E.	—	18 (3 hr.)	—	—	9.2
Camellia oil	147	15 (3 hr.)	—	3.0(4 hr.)	36
〃 + 10% H.U.E.	—	19 (3 hr.)	—	3.0(4 hr.)	39

* H.U.E.=Highly unsaturated methyl ester.

Table 1 does not afford the data on the degree of peroxide decomposition after heating for the same period at the same temperature throughout all oils to permit a quantitative comparison of the degree of peroxide decomposition for each oil. However it is seen from Table 1 that peroxides in marine animal oils such as saury, sardine and whale oils show a higher degree of decomposition than peroxides in vegetable oils such as linseed, sesame, corn and camellia oils on the whole. The addition of highly unsaturated methyl ester to vegetable oils tends, in most cases, to increase the degree of peroxide decomposition. These results appear to affirm the postulation previously set forth by Shimo-oka and Toyama[10] that highly unsaturated acids are more reactive than less unsaturated acids as an oxygen acceptor in the decomposition of peroxides. However, as is seen from Table 1, effects of the addition of highly unsaturated methyl ester to vegetable oils upon the peroxide decomposition are not so large that the presence of highly unsaturated acid components in marine animal oils is considered to be the sole reason for the high degree of peroxide decomposition in marine animal oils. Some other factors may also be responsible for this. Comparing sesame, corn and camellia oils in Table 1, the degree of peroxide decomposition is highest for sesame oil followed by camellia oil and lowest for corn oil. Nakamura[4] found in his study on the thermal decomposition of peroxides in tung, linseed, camellia and castor oils that the peroxides in tung oil were most unstable and those in camellia oil most stable. Although many factors are considered as responsible for these differences in the thermal stability of peroxides in different vegetable oils, the following may be mentioned in the case of our experiments. Sesame, corn and camellia oils in Table 1 have inital peroxide values of an approximately same level, but they differ in the following respects. The sesame and camellia oils have been oxidized during the storage for more than ten years and have an increased viscosity and a decreased iodine value as compared with normal samples of respective oils, whereas the corn oil has been oxidized during the storage for about one year and its iodine value and viscosity do not differ noticeably from those of ordinary corn oil. Thus, these three oils, in spite of their peroxide values of a nearly same level, differ in the extent of oxidative polymerization which has occurred in them. These differ-

ences may be conceivable as a reason for the different stability of peroxides in these oils.

2. The rate of decomposition of the saury oil peroxides formed under different oxidation conditions

It appears from the foregoing remarks in the case of vegetable oils that peroxides in oil samples which have undergone oxidative polymerization to extremely different extents show different rate of decomposition. A series of comparative experiments have been made to examine whether saury oil peroxides formed under several different conditions of oxidation show different rates of decomposition. The sample of saury oil used in these experiments had d_4^{30} 0.9137, n_D^{30} 1.4705, acid value 5.0, saponification value 186.9, iodine value 156.9 and peroxide value 7.0. This oil sample was oxidized in the following way.

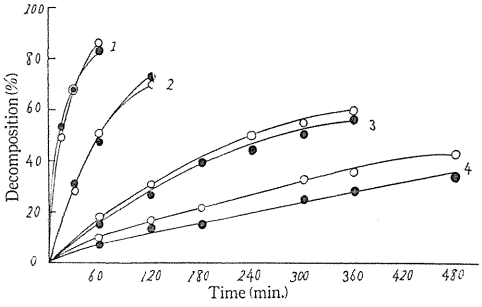
(i) The oil sample (150 g.) was placed in a flat bottomed glass dish of 12 cm. diameter, and the dish was loosely covered with a polyethylene film and stored in the dark for 8 to 17 days to give two samples of oxidized oil with peroxide values of 50 and 150 levels, respectively.

(ii) The dish containing the oil sample was exposed to direct sunlight for a definite period. By exposure to direct sunlight for 2 to 8 hr. during the storage for 1 to 2 days, two samples of oxidized oil with peroxide values of 50 and 150 levels, respectively, were obtained.

(iii) The oil sample was aerated at 100°C for 1 to 3 hr. to give two samples of oxidized oil with peroxide values of 50 and 150 levels, respectively.

Each oxidized sample (20 g.) obtained above was placed in a test tube and the latter was hold in an oil bath which was kept at 125°C, 100°C, 75°C or 50°C. A current of nitrogen was passed into the test tube during the experiments. After a required period, a portion of oil sample was taken out from the test tube, and the peroxide value of oil sample was determined. The percentage decomposition of peroxides was calculated from the initial peroxide value and the peroxide value after heating. The results are illustrated in Figs. 1-A, 1-B and 1-C.

An inspection of Figs. 1-A, 1-B and 1-C shows that the rates of peroxide decomposition for a pair of oxidized samples with peroxide values of 50 and 150 levels do not differ markedly from each other, except that the rate of peroxide decomposition at 50°C is a little higher for the sample with a peroxide value of 50 level than for the sample with a peroxide value of 150 level. Also the difference in the oxidation conditions described above appears not to affect noticeably the rate of peroxide decomposition in oxidized samples, though the rates of peroxide decomposition are not quite same for all oxidized samples. On the other hand, however, the results of another series of experiments illustrated in Fig. 1-D show that the rate of peroxide decomposition in a somewhat viscous sample of oxidized saury oil of a peroxide value of 393, obtained by storage at room temperature, is higher than the rate of peroxide decomposition in a sample of oxidized saury oil of a peroxide value of 138 obtained by aeration at 100°C. This is related to the finding in the preceding experiments given in Table 1 that the rate of peroxide decomposition was markedly high for viscous samples of oxidized sesame and camellia oils obtained by a very long term storage at room temperature. It is rather striking to find that the rates of peroxide decomposition for oxidized saury oil are remarkably high in every case of our experiments as compared with those reported by previous investigators for oxidized methyl linoleate,[5),6)] lard[8)] and soybean oil.[9)]

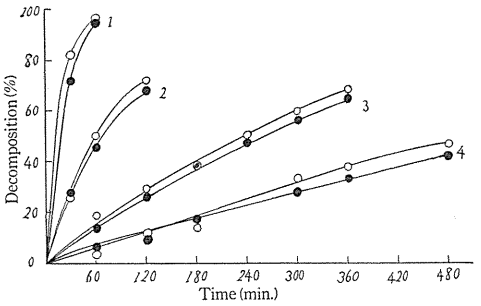


1. Decomposition at 125°C
2. Decomposition at 100°C
3. Decomposition at 75°C
4. Decomposition at 50°C

○ Oxidized saury oil with peroxide value of 50 level

● Oxidized saury oil with peroxide value of 150 level

FIG. 1-A. The rate of peroxide decomposition in oxidized saury oil prepared by storage in the dark.

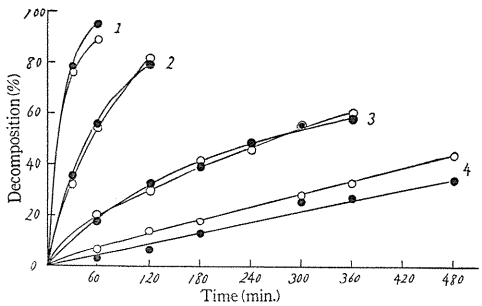


1. Decomposition at 125°C
2. Decomposition at 100°C
3. Decomposition at 75°C
4. Decomposition at 50°C

○ Oxidized saury oil with peroxide value of 50 level

● Oxidized saury oil with peroxide value of 150 level

FIG. 1-B. The rate of peroxide decomposition in oxidized saury oil prepared under exposure to direct sunlight.

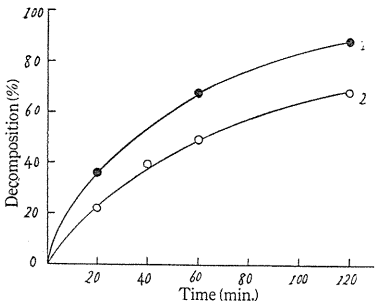


1. Decomposition at 125°C
2. Decomposition at 100°C
3. Decomposition at 75°C
4. Decomposition at 50°C

○ Oxidized saury oil with peroxide value of 50 level

● Oxidized saury oil with peroxide value of 150 level

FIG. 1-C. The rate of peroxide decomposition in oxidized saury oil prepared by aeration at 100°C.



○ Oxidized saury oil of peroxide value 138

● Oxidized saury oil of peroxide value 393

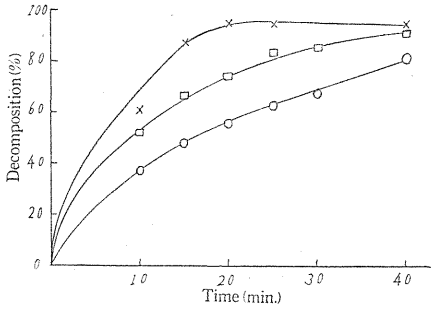
FIG. 1-D. Comparison of the rate of peroxide decomposition at 100°C for an oxidized saury oil of peroxide value 138 and an oxidized saury oil of peroxide value 393.

3. Effects of pro-oxidants and antioxidants upon the rate of decomposition of saury oil peroxides

In order to examine effects of the addition of pro-oxidants, such as copper and iron soaps, and antioxidants, such as NDGA, BHA and PG, upon the rate of decomposition of saury oil peroxides, a series of comparative experiments were performed on oxidized saury oil samples with or without the addition of these substances. The oxidized saury oil samples were prepared by aeration of saury oil at 100°C and had peroxide values ranging from 80 to 100. For the preparation of copper and iron soaps, a solution of ammonium soap of saury oil fatty acids was added with solutions of copper sulphate and ferric chloride, respectively. Precipitates of metallic soaps formed were thoroughly washed with water and then taken up with a relatively large quantity of ether. On distilling off ether from the solution, the metallic soaps were obtained. Since it was difficult to dissolve antioxidants promptly in an oxidized saury oil without applying heat to avoid a partial decomposition of peroxides, antioxidants were dissolved first in an unoxidized saury oil (peroxide value less than 1) by using ether. Distillation of ether from the ether solution gave a concentrated solution of antioxidants in the unoxidized saury oil. A definite quantity of this concentrated solution of antioxidants was then added to the oxidized saury oil to be used in the experiments so as to make a required concentration of antioxidants in the oxidized saury oil. In this case, the control sample was composed of the oxidized saury oil added with the unoxidized saury oil containing no antioxidants in the same proportion as in the case of the oxidized saury oil containing antioxidants. Figs. 2-A, 2-B, 2-C, 3-A, 3-B and 4 illustrate the results of these experiments.

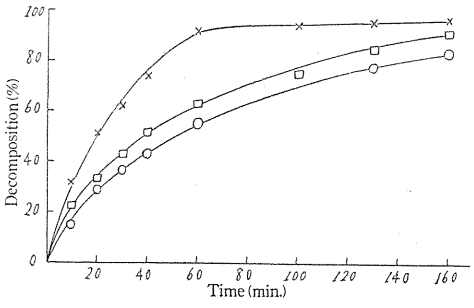
An inspection of Figs. 2-A, 2-B and 2-C shows that the addition of 0.2% of copper soap or iron soap accelerates the peroxide decomposition in oxidized saury oil; copper soap being more effective than iron soap. Effects of antioxidants are not clear, suggesting that these are very small as compared with effects of pro-oxidants, though the addition of 0.01% PG appears to retard slightly the peroxide decomposition at 125°C (Fig. 3-A). In the case of the addition of a combination of pro-oxidants and antioxidants (Fig. 4), the accelerating effect of pro-oxidants upon the peroxide decomposition is little suppressed by the presence of antioxidants. When phenolic antioxidants, such as NDGA and PG, and metallic soaps were simultaneously used, a dark color developed indicating that some reactions occurred between both substances. However, the accelerating effect of metallic soaps upon the peroxide decomposition appeared not to be affected noticeably by these reactions.

When the velocity constants of peroxide decomposition reaction at 125°C, 100°C, 75°C and 50°C were calculated from the data obtained in each run of our experiments, the values for each run obtained by taking the reaction as a first order type showed a smaller variance than the values obtained by taking the reaction as a second order type. However, even the former showed an unallowable variance in most cases; nearly uniform values were obtained only in a few cases. A few examples of the normal equation derived from our data showing the relation between the rate of peroxide decomposition (R, %) and the heating time (t, min.) are given below.



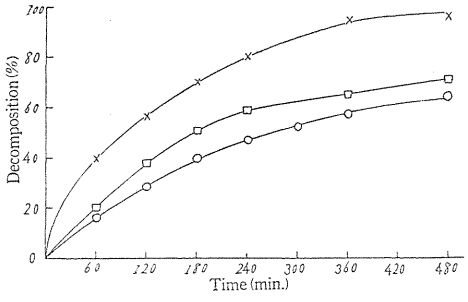
× Added with 0.2% copper soap
□ Added with 0.2% iron soap
○ No additives

FIG. 2-A. Effects of pro-oxidants upon the rate of decomposition of saury oil peroxides (at 125°C).



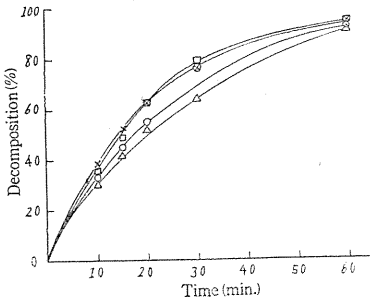
× Added with 0.2% copper soap
□ Added with 0.2% iron soap
○ No additives

FIG. 2-B. Effects of pro-oxidants upon the rate of decomposition of saury oil peroxides (at 100°C).



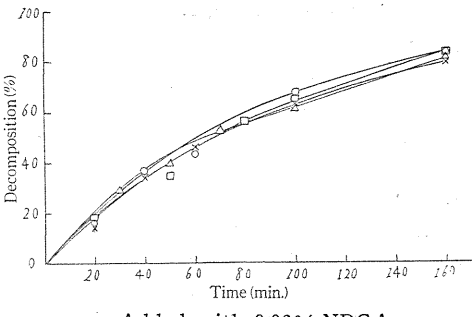
× Added with 0.2% copper soap
□ Added with 0.2% iron soap
○ No additives

FIG. 2-C. Effects of pro-oxidants upon the rate of decomposition of saury oil peroxides (at 75°C).



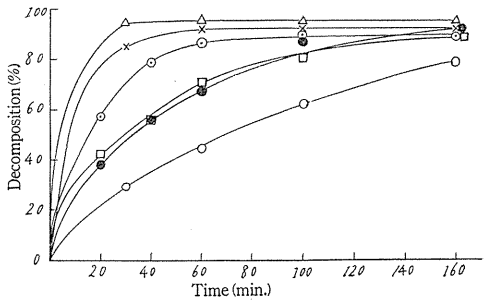
× Added with 0.01% NDGA
□ Added with 0.01% BHA
△ Added with 0.01% PG
○ No additives

FIG. 3-A. Effects of antioxidants upon the rate of decomposition of saury oil peroxides (at 125°C).



× Added with 0.06% NDGA
□ Added with 0.05% BHA
△ Added with 0.04% PG
○ No additives

FIG. 3-B. Effects of antioxidants upon the rate of decomposition of saury oil peroxides (at 100°C).



△ Added with 0.2% copper soap and 0.05% BHA
● Added with 0.2% iron soap and 0.06% BHA
⊙ Added with 0.2% iron soap and 0.07% PG
× Added with 0.2% copper soap
□ Added with 0.2% iron soap
○ No additives

FIG. 4. Effects of a combination of pro-oxidants and antioxidants upon the rate of decomposition of saury oil peroxides.

At 125°C:

Added with 0.2% copper soap,

$$\log R = (2.1 \pm 0.38) - (2.61 \pm 0.022)/t$$

Added with 0.2% iron soap,

$$\log R = (2.1 \pm 0.06) - (3.46 \pm 0.004)/t$$

No additives,

$$\log R = (2.0 \pm 0.27) - (3.86 \pm 0.024)/t$$

At 100°C:

Added with 0.2% copper soap,

$$\log R = (2.0 \pm 0.23) - (5.46 \pm 0.010)/t$$

Added with 0.2% iron soap,

$$\log R = (1.9 \pm 0.46) - (6.36 \pm 0.062)/t$$

No additives,

$$\log R = (1.9 \pm 0.48) - (7.46 \pm 0.020)/t$$

4. Effects of sunlight upon the peroxide decomposition in oxidized saury and soybean oils

While it is well known that sunlight accelerates the fat oxidation, Shimo-oka *et al.*[11] compared the properties of oxidized saury oils with peroxide values of the same level, one prepared under exposure to direct sunlight and the other prepared by aeration, and found that the former had undergone deterioration to a larger extent than the latter. This appears to suggest that the direct sunlight accelerates the decomposition of peroxides as well as their formation. In an attempt to examine effects of sunlight on the peroxide decomposition, the rates of peroxide decomposition under exposure to sunlight and under protection from sunlight were compared for oxidized saury and soybean oils. The oxidized oil samples used in these experiments were prepared by aeration at 100°C. Each 2 g. sample was placed in 5-ml. bottles, pairs of clear glass bottle and brown glass bottle, and air in bottles was replaced by nitrogen. The bottles were tightly stoppered and sealed, and stored in our laboratory. During the storage, the bottles were exposed to direct sunlight for some periods. Samples in pairs of bottles were taken out

periodically and their peroxide values were determined. The results are shown in Table 2. Comparing the degrees of peroxide decomposition in the same period, it is seen from Table 2 that sunlight accelerates markedly the peroxide decomposition, since peroxides in the samples in clear bottles show a greater degree of decomposition than peroxides in the corresponding samples protected from sunlight by storing in brown bottles.

TABLE 2. Effects of Sunlight upon the Peroxide Decomposition

Duration of storage (day)	Exposure to sunlight during storage (hr.)	Degree of peroxide decomposition					
		Saury oil No. 1		Saury oil No. 2		Soybean oil	
		In clear bottle	In brown bottle	In clear bottle	In brown bottle	In clear bottle	In brown bottle
1	5	19.8	10.5	17.5	2.3	—	—
3	10	—	—	—	—	16.3	<1
4	15	36.2	18.9	33.4	16.6	—	—
7	30	52.3	26.4	46.8	21.5	24.1	6.2
10	40	62.6	28.9	52.2	25.7	30.7	8.2
20	60	75.1	31.8	67.3	36.1	31.7	10.5

Notes: Initial peroxide values of saury oils, No. 1 and No. 2, and soybean oil are 140, 236 and 83.5, respectively. The experiments are performed parallel for each oil sample, not for all samples.

Summary

1. Degrees of the peroxide decomposition on heating at 100°C, 90°C and 50°C and during storage at room temperature have been compared for oxidized samples of saury, sardine, whale, linseed, sesame, corn and camellia oils. Peroxides in oxidized marine animal oils are decomposed more readily than peroxides in oxidized vegetable oils. Decomposition of peroxides in vegetable oils does not proceed alike for all oil samples. Comparing vegetable oils with peroxide values of the same level, peroxides in a vegetable oil which has undergone oxidative polymerization to a marked degree and become viscous appear to decompose more rapidly than peroxides in a vegetable oil which has been deteriorated to a lesser extent. The addition of 10% of a highly unsaturated methyl ester prepared from unoxidized saury oil to oxidized vegetable oils tends, in most cases, to accelerate somewhat the decomposition of peroxides.

2. Rates of peroxide decomposition at 125°C, 100°C, 75°C and 50°C have been compared for oxidized saury oils with peroxide values of 50 and 150 levels prepared in three different ways—by storage in the dark, under exposure to sunlight and by aeration at 100°C. Rates of peroxide decomposition do not differ markedly for all oxidized samples. However, as compared with these oxidized samples, the rate of peroxide decomposition in an oxidized saury oil with a peroxide value of 393 and an increased viscosity, prepared by storage at room temperature, is remarkably high.

3. The addition of 0.2% pro-oxidants such as copper and iron soaps to oxidized saury oil accelerates markedly the peroxide decomposition. The addition of 0.01–0.06% antioxidants such as NDGA, BHA and PG to oxidized saury oil does not affect noticeably the peroxide decomposition. When a combination of pro-oxidants

and antioxidants is added to oxidized saury oil, the accelerating effect of pro-oxidants upon the peroxide decomposition is not suppressed noticeably.

4. Within the limits of our experiments, the overall reaction of peroxide decomposition in oxidized saury oil is allied to a first order type rather than a second order type. However, a fairly good accordance with the first order reaction is observed only in a few cases.

5. Exposure to sunlight accelerates the peroxide decomposition in oxidized saury and soybean oils.

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