# A Simple Method for the Improvement of the Keeping Quality of Oils and Fats

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As the keeping quality of oils and fats is of great importance in the manufacture and use of these products, it is very natural that quite a large number of oil chemists have been working to improve this property. As a consequence of the fundamental work of Moureu on antioxidants a large number of these were proposed, which for the greater part never came into practical use. The antioxidants in common use for edible oils and fats are the gallates and N.D.G.A. (nordihydroguaraietic acid), which are often combined with synergists, such as citric acid or tartaric acid.

The best way to judge the efficiency of antioxidants is, of course, by a practical keeping test under the usual storage conditions with repeated checks of taste and smell after a lapse of time. This however is a very lengthy procedure. To evaluate the antioxidants in a much speedier way, it has become common practice to accelerate the oxidation process by blowing air through the fats at elevated temperatures under standardized conditions and to estimate the increase in the peroxide value with the time (Swift test). This method however is only valid if one may assume that there exists a definite correlation between the keeping quality and the induction period of a fat.

It is quite probable that the oxidation of a fat starts with the formation of peroxides (or hydroperoxides) and that this formation is accelerated by a rise of temperature. The peroxides themselves however are not very stable products so that as soon as their formation has begun and their concentration has increased, their decomposition starts. This decomposition reaction has such a high temperature coefficient that if the temperature rises above a certain limit, the rate of decomposition may even exceed the speed of formation of the peroxides. For this reason it is advisable not to raise the temperature more than is absolutely necessary to speed up the oxidation to such an extent that the experiment may be ended in a reasonable time, and not to prolong the time beyond that needed to produce a rather low peroxide value. This means that for most oils and fats a temperature of 80°C. is quite sufficient and that a rise of peroxide value above about 6 to 7 Lea index is undesirable. Moreover a fat with a Lea index of 6 to 7 is already quite unpalatable, and the speed of oxidation at higher peroxide values is only of theoretical interest. For these reasons we do not use in our experiments the high temperature of the Swift test (about 99°C.), but a lower temperature (80°C.), and continue the oxidation no farther than to an average Lea index (L) of about 7 (1).

Working in this way, we have determined the rise in the Lea index (L) per hour at low L values after the induction period. We consider this value dL/dt, which

TABLE I

Values of dL/dt

| Kind of oil | Treatment | Value of dL/dt for oil containing | | | |
|---|---|---|---|---|---|
| | | No addition | S | Octyl gallate | Citric acid |
| Palmoil | | | | | |
| I.V. 52.0 | None | 0.55 | | | |
| Id. | None | 0.47 | | | |
| Id. | 0.10% S added | | 0.00 | | |
| Id. | 0.10% S added | | 0.05 | | |
| Id. | 0.05% S added | | 0.140 | | |
| Id. | 0.05% S added | | 0.095 | | |
| Id. | 0.05% S added | | 0.125 | | |
| Id. | Heated with 0.05% S 3 hours before steaming | | 0.33 | | |
| Id. | Id. | | 0.29 | | |
| Id. | Id. | | 0.39 | | |
| Id. | 0.02% octyl gallate added | | | 0.17 | |
| Id. | Id. | | | 0.06 | |
| Id. | Id. | | | 0.06 | |
| Hydrogenated soyabean oil | | | | | |
| I.V. 74.5 | None | 0.09 | | | |
| Id. | 0.05% S added | | 0.030 | | |
| Id. | 0.05% S added | | 0.035 | | |
| Id. | 0.02% octyl gallate added | | | 0.37 | |
| Cotton seed oil | | | | | |
| I.V. 100.6 | None | 2.86 | | | |
| Id. | 0.05% S added | | 1.46 | | |
| Id. | 0.05% S added | | 1.46 | | |
| Id. | 0.02% octyl gallate added | | | 0.56 | |
| Id. | Id. | | | 0.68 | |
| Soyabean oil I | | | | | |
| I.V. 127.6 | None | 1.25 | | | |
| Id. | 0.05% S added | | 0.89 | | |
| Id. | Heated with 0.05% S 3 hours before steaming | | 0.95 | | |
| Id. | 0.02% octyl gallate added | | | 0.95 | |
| Soyabean oil II | | | | | |
| I.V. 125.3 | None | 1.725 | | | |
| Id. | 0.05% S added | | 1.17 | | |
| Id. | 0.05% S added | | 1.17 | | |
| Id. | 0.05% S added (after 2 hours steaming) | | 1.57 | | |
| Id. | After 7 hours steaming | | 1.025 | | |
| Id. | 0.02% octyl gallate added | | | 0.85 | |
| Id. | 0.05% S added + 0.01% benzoylperoxide | | 0.95 | | |
| Id. | 0.01% citric acid | | | | 1.035 |
| Id. | 0.01% citric acid + 0.05% S | | | | 1.035 |
| Id. | Same repeated | | | | 0.94 |

is easily reproducible, to be more closely correlated with the true keeping quality than the Swift test.

We have now found that a treatment with a very small amount of sulfur has a considerable effect on the speed of oxidation of fats, particularly if this treatment consists in simultaneous heating and steaming as in the usual deodorizing process.

We have obtained the figures shown in Table I with refined and freshly deodorized oils and fats. The steaming of the oils and fats was carried out for about 4 hours at 180°C. immediately after the addition of the sulfur. The iodine values were determined by the Hanus method.

For comparison we made similar experiments, using an addition of 0.02% octyl gallate (product of Chem. Fabr. Naarden, Holland) as antioxidant.

## Discussion

From these results we may draw the following conclusions:

1. The addition of 0.05% sulfur reduces the speed of oxidation considerably.

2. The addition of 0.02% of octyl gallate reduces the speed of oxidation considerably, as is well known.

3. The simultaneous heating and steaming with sulfur is much more effective than first heating with the sulfur and then steaming.

4. There is no direct apparent relation between the rate of oxidation and I.V., as might be expected, since this rate also depends upon the amount of positive catalysts (e.g., traces of Fe, Ni, Cu, etc.) and of negative catalysts originally present in the oils (e.g., tocopherols), and on the stereochemical configuration of the fatty acids (1).

5. Longer time of steaming with S reduces dL/dt still more. Taking the average values of dL/dt, we can calculate to what extent (as a percentage) the original oxidation velocity is reduced (Table II).

TABLE II

| Fat | I.V. | Reduction of original oxidation velocity to: | |
|---|---|---|---|
| | | With 0.05% S | With 0.02% octyl gallate |
| Palm oil | 52.0 | 23.5% | 19.5% |
| Hydr. soyabean oil | 74.5 | 37 % | 41 % |
| Cottonseed oil | 100.6 | 51 % | 21.5% |
| Soyabean oil II | 125.3 | 68 %–60% | 49.5% |
| Soyabean oil I | 127.6 | 71 % | ........ |

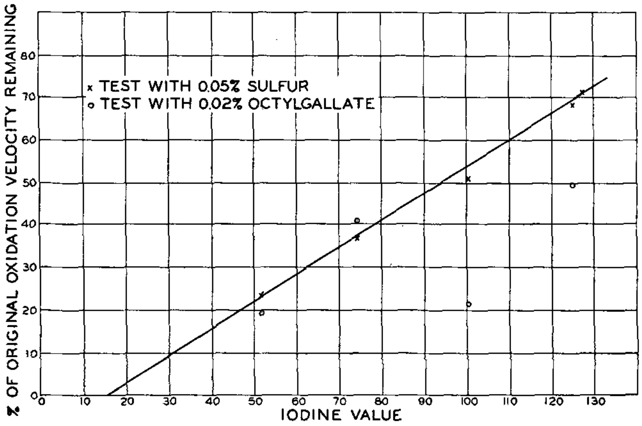

FIG. 1

TABLE IV

| S Contents in Parts per Million | |
|---|---|
| A. Ordinary deodorized oils and fats | |
| Rape oil I | 116 |
| Rape oil II | 160 |
| Rape oil III | 132 |
| Soybean oil I | 73 |
| Soybean oil II | 25 |
| Palm oil I | 101 |
| Palm oil II | 100 |
| Cottonseed oil | 75 |
| Hydr. soybean oil | 8 |
| B. Treated oils | |
| Palm oil | 160 |
| Palm oil | 180 |
| Palm oil | 243 |
| Hydr. soybean oil | 200 |
| Soybean oil | 295 |
| Soybean oil | 384 |
| Soybean oil | 320 |
| Cottonseed oil | 344 |
| Cottonseed oil | 211 |
| Cottonseed oil | 320 |

The graph shows the figures for the remaining speed of oxidation in % plotted against the I.V.

From this we may see that:

a) there is no visible relation between I.V. and the remaining speed of oxidation in % in the tests made with gallate.

b) there is a linear relation between I.V. and the remaining speed of oxidation in % in the tests made with 0.05% S. (With remaining speed we mean the percentage of oxidation velocity remaining after treatment with respect to the original oxidation velocity of the untreated oil.) The reduction of the velocity is inversely proportional to the iodine value. At an iodine value of about 15 we may expect a remaining velocity of about 0%; and at an I.V. of about 175 there probably will be no reduction of the original speed of oxidation.

In our opinion this behavior points to quite a different behavior of the S as compared with gallate as an antioxidation catalyst. So we may expect that the combination of the sulfur treatment followed by addition of gallate will yield a remarkable improvement. We proved this in the following tests:

TABLE III

| | dL/dt | Reduction of oxidation velocity to: |
|---|---|---|
| 1. Soyabean oil II | 1.725 | ........ |
| 2. Soyabean oil II + 0.02% octyl gallate | 0.85 | 49.5% |
| 3. Soyabean oil II + 0.05% S and steaming | 1.17 | 68 % |
| 4. Soyabean oil II + 0.05% S + 0.02% octyl gallate added afterward | 0.63 | 36.5% |

The effects of the gallate and the sulfur seem to be additive. Now what is the practical use of addition of 0.05% S during the deodorization process of fat and oils?

1. The oxidation velocity is diminished to 25-70% (depending on the I.V.) of the original speed, which probably means that the keeping time will be from 4-1.4 times longer.
2. If combined with a subsequent addition of 0.02% gallate, the keeping time will be considerably longer still as the effects of the gallate and the sulfur will be combined.

The treatment with 0.05% S causes no or a very slight change in color and taste of the treated oils and fats. The treatment costs no extra time or heat during the usual deodorizing process. Sulfur is cheap so there are practically no extra costs. In laboratory tests the addition of sulfur produced no attack on iron. The absolute residual amount of sulfur left in the oils and fats after deodorization is very small and only slightly higher than that present in ordinary deodorized oils and fats (chosen at random) as the following Table IV shows. The presence of sulfur in ordinary oils shows that there can be no objection against it.

### Summary

The efficiency of antioxidants is judged by means of a modified Swift test. Addition of 0.05% sulfur during the deodorizing process yields a 4-1.4 times prolonged keeping time of oils and fats.

There is a linear relation between iodine value and the remaining speed of oxidation in % in the tests made with sulfur. The reduction of the velocity is inversely proportional to the iodine value. The effects of gallate and the sulfur seem to be additive. The residual amount of sulfur left in the oils and fats after deodorization is very small and only slightly higher than that present in ordinary deodorized oils and fats.

REFERENCE

1. Bertram, S. H., J. Am. Oil Chem. Soc., *26*, 83-85 (1949).

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# The Fatty Acids of Cottonmouth Moccasin Depot Fat[1,2]

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SNAKE oil, as used in this article, refers to the lipids obtained from the fat lobes of the cottonmouth moccasin, *Agkistrodon piscivorus*. Well-fed snakes in good physical condition have fat lobes deposited along both sides of the intestines in the area between the stomach and vent. At its maximum this fat depositation involves about one-fourth of the total length of the snake; at the end of the hibernation period the fat deposit may have disappeared completely.

## Experimental and Discussion

The cold-pressing method extraction was employed for all samples since it helps to eliminate changes in the lipids by heat or oxidation. From 10 to 30 snakes were butchered soon after capture, and the lobes were pooled. The fat lobes were dried on filter paper, and all connective tissue and blood vessels were carefully removed. The supply of fat was wrapped in filter cloth before it was pressed. The expressed oil was centrifuged at 1,400 r.p.m., and clear samples were siphoned off for analyses.

Results of preliminary analyses were: $D_4^{25}$, 0.9268; $n_D^{25}$, 1.4690; Saponification Number, 192.6; Iodine Number (Hanus), 104.4; Thiocyanogen Value, 77.2; Soluble Acids, 0.13; Hehner Number, 94.85; Reichert Meissl Value, 0.07; Polenske Value, 0.04; Saturated Acids, 22.7; Unsaturated Acids, 72.7; Free Fatty Acids, 0.52; Acetyl Value, 4.1; and Unsaponifiable Residue, 0.46.

From the above data it would appear that the content of low molecular weight fatty acids is slight. Only negligible quantities of high molecular weight alcohols and waxes are indicated by the unsaponifiable residue.

Although an "apparent" acetyl value of 4.1 was determined in the preliminary analyses, the corrected acetyl value was so low that it may be concluded that little, if any, hydroxy acids are present in moccasin snake oil.

Percentage-content of fatty acids was determined primarily by distillation, through a Lecky-Ewell column at pressure of 1.0 mm.; and by spectrophotometric studies.

*Distillation of Methyl Ester Fractions.* A sample of moccasin snake oil was separated into two portions by the lead salt-ether method (1). Each portion was converted to its methyl ester and was distilled. Data produced by these fractional distillations are presented in Tables I and II. The unsaturated acid fraction was 71.0% and the saturated acid fraction, 24.4% of the original moccasin snake oil based on weights.

TABLE I

Physical and Analytical Data on 13 Fractions of Methyl Ester of Liquid Acids[a] from Cottonmouth Moccasin Fat Lobes

| Fraction | Temperature (°C.) | Weight of Fraction (in g.) | $n_D^{25}$ | Saponification Equivalent | Iodine Value (Hanus) |
|---|---|---|---|---|---|
| 1 | 107-117 | 0.2 | 1.4452 | ........ | 56.3 |
| 2 | 117-128 | 0.7 | 1.4445 | 230.0 | 50.8 |
| 3 | 128-132 | 1.0 | 1.4449 | 250.0 | 63.6 |
| 4 | 133-138 | 1.7 | 1.4460 | 263.5 | 70.3 |
| 5 | 138-148 | 3.7 | 1.4483 | 280.0 | 80.1 |
| 6 | 149-153 | 13.2 | 1.4520 | 298.2 | 102.9 |
| 7 | 153-157 | 8.1 | 1.4532 | 302.1 | 104.9 |
| 8 | 158-162 | 4.2 | 1.4542 | 293.5 | 104.9 |
| 9 | 162-165 | 1.2 | 1.4598 | 296.8 | 87.4 |
| 10 | 165-168 | 0.9 | 1.4679 | 290.0 | 120.3 |
| 11 | 168-169 | 1.9 | 1.4679 | 276.0 | 109.3 |
| 12 | 170-200 | 4.3 | 1.4805 | 313.3 | 212.0 |
| 13 | Residue | 4.2 | ........ | ........ | ........ |

[a] "Liquid" acids were produced by lead salt-ether method. Fractions were obtained by distillation at 1 mm. of 45.3 g. of the methyl esters of these "liquid" acids.

TABLE II

Physical and Analytical Data on Nine Fractions of Methyl Ester of Solid Acids[a] from Cottonmouth Moccasin Fat Lobes

| Fraction | Temperature (°C.) | Weight of Fraction (in g.) | $n_D^{25}$ | Saponification Equivalent | Iodine Number (Hanus) |
|---|---|---|---|---|---|
| 1 | 121-124 | 0.2 | 1.4358 | ........ | 3.2 |
| 2 | 125-128 | 0.3 | 1.4365 | ........ | 0.7 |
| 3 | 129-139 | 4.1 | Solid | 270.9 | 1.7 |
| 4 | 140-143 | 4.5 | Solid | 275.3 | 0.3 |
| 5 | 144 | 3.3 | Solid | 280.2 | 0.0 |
| 6 | 145-150 | 1.2 | 1.4398 | 277.0 | 6.5 |
| 7 | 150-154 | 1.0 | Solid | 281.9 | 11.7 |
| 8 | 154-164 | 3.9 | Solid | 299.5 | 8.4 |
| 9 | Residue | 0.7 | Solid | 292.5 | 9.3 |

[a] "Solid" acids were produced by Lead Salt-Ether Method. Fractions were obtained by distillation at 1 mm. of 20.0 of the methyl ester of these "solid" acids.

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[1] This paper is abstracted from a portion of a dissertation submitted by Joseph McLaughlin Jr., to the Graduate Council of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Presented at the 43rd meeting of the American Oil Chemists' Society, Houston, Tex., April, 1952.

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