Keeping Properties of Edible Oils—Part I. The Use of Accelerated Tests for Assessment of the Keeping Properties of Oils and the Value of Antioxidants

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Assessment of oil quality by two accelerated oxidation tests gave little or no correlation with organoleptic asessment during storage. Improvements in quality of oils refined in the factory, to which antioxidants had been added, are indicated by the accelerated tests but are not reproduced in normal storage. However a treatment of the oils with alumina, as a part of the refining process replacing earth bleaching, appears to remove antagonistic factors, and under these circumstances the addition of antioxidant has a pronounced effect.

THE MAJOR OUTLETS for edible refined oils and fats are in the production of margarine, shortenings, confectionery fats, and salad oils. These products have fairly well-defined shelf-life or keeping-time, based on organoleptic assessment. The keeping-time depends on the composition, and in particular the fat blend used, and also on the storage conditions and method of packaging. Moreover a correlation usually exists between the keeping-time of manufactured products such as margarine and the keeping-time of the component fats or oils. It is obviously desirable that some method should be available to assess the potential keeping-time of oils and fats, and the wide-spread use of various accelerated tests, both in commercial practice and also in laboratory investigations of the effects of antioxidants in oils, would seem to suggest that such assessment may be possible. However it is the authors' experience that such accelerated tests can be very misleading and give only a poor indication of the actual keeping quality of most fats and fatty products. It was the purpose of the present investigation to determine the degree of correlation between keeping-time and the prediction of keeping-time given by various accelerated tests. A further object was to determine the best means of assessing the efficiency of antioxidants, and to assess their effect on keeping properties of refined oils. Peanut oil was chosen as a substrate for most of this work.

Methods of Assessment

Organoleptic assessment was carried out by storage of 180 g. of the oil in loosely covered glass bottles kept in darkness at 10–20°C. The samples were tasted at weekly intervals and scores were allotted on the basis of a scale of 0 to 8: a bland oil of high quality would be rated 8, and an oil on the borderline between edible and inedible would be given a score of 3. Keeping time is defined as the time taken for an oil of initial good quality to deteriorate to a taste score of 3. Assessments by skilled tasters gave remarkably reproducible results. Peroxide values were determined weekly to find out whether any correlation existed with taste. This test is accelerated to some extent as the area of oil in contact with air may be greater than that encountered in practice. However a good correlation is obtained with larger samples.

The accelerated quality tests used were the Swift Test (1) and the measurement of oxygen absorption. These measurements were carried out as soon as possible following deodorization of the oil. In the Swift Test the sample is continuously aerated at 98.4°C., the time taken to acquire a specified peroxide value being used as a measure of quality. In the oxygen absorption test, oxygen uptake was measured for a sample of 10 g. shaken at a temperature of 140°C., the induction period, defined as the time taken before the commencement of rapid absorption of oxygen, being measured.

Correlation of Organoleptic Assessment with Accelerated Tests

A number of batches of peanut oil which had been freshly refined and deodorized in the factory were assessed by the three methods. Results are given in Table I.

It is clear that there is no correlation of practical value between the taste score and the results of the oxygen absorption test. Results for the Swift Test were less out of line, but no quantitative correlation existed with keeping time. Analysis of the data indicated that the error in prediction of the keeping time from the Swift Test could be as high as 65%. In a longer series of experiments the probable error might of course be lower, but the spread in the results would still be very high.

Similar, though less extensive, evidence of the error of prediction of flavor stability was found for other vegetable oils and fats including cottonseed oil and palm oil.

Effect of Antioxidants in Factory Peanut Oil

Various antioxidants were added to peanut oil at a level of 0.01% immediately following deodorization in the factory, and the quality of the oils was assessed (see Table II).

The accelerated tests indicate that B.H.A. has had no antioxidant effect whereas the other three antioxidants have conferred improved stability. By contrast, in the organoleptic test the samples containing

TABLE I

Sample	Keeping time (weeks)	Swift Test (hrs.)	Oxygen absorption test induction period (min.)
1	2	9.5	25
2	3	16	40
3	4½	17	45
4	5	....	48
5	3	....	55
6	2	14	56
7	2	....	66
8	7½	23	66

TABLE II

Antioxidant	Keeping time (weeks)	Peroxide value (Lea figure) at score 3	Swift Test (hrs.)	Oxygen absorption test, induction period (min.)
None	3	1.5	17	34
Nordihydroguaiaretic acid (N.D.G.A.)	3	2.3	29	50
Butylated hydroxyanisole (B.H.A.)	3	1.2	17	37
Butylated hydroxytoluene (B.H.T.)	3	1.3	25	44
Propyl gallate	3	1.7	28	47

TABLE III

Antioxidant	Keeping time (weeks)	Peroxide value (Lea fig. ure) at score 3	Oxygen absorption test, induction period (min.)
None (Control)	4	2.4	34
B.H.A.	4	2.8	42
Propyl gallate	4	2.4	65
None (Control)	7	2.2	50
B.H.T.	7	2.4	70
N.D.G.A.	6	2.6	88

TABLE IV

Antioxidant	Keeping time (weeks)	Peroxide value (Lea figure) at 6 weeks	Swift Test (hrs.)	Oxygen absorption test, induction period (min.)
None (Control)	9	3.7	2	4
0.01% N.D.G.A.	8	1.0	65	87
0.01% Propyl gallate	>12	0.8	49	52
0.01% B.H.T.	>12	1.3	24	35
0.01% B.H.A.	>12	1.6	17	30

antioxidant showed no advantage over the control. It appears therefore that no correlation exists between the accelerated tests and the normal storage test, and therefore only the normal storage test gives a true assessment of the value of an antioxidant for most uses of edible oils. It is also apparent that, at the point at which the oils just become inedible, the degree of oxidation is very low and is not affected by the addition of antioxidant.

Other results showing the lack of effect of added antioxidants and also the noncorrelation between the organoleptic test and an accelerated test are shown in Table III for two other samples of peanut oil.

Again, we are forced to conclude that the flavor deterioration in peanut oil refined and deodorized in the factory arises through a factor or the interaction of factors whose development is not significantly affected by the presence of added antioxidants.

Effect of Antioxidants in Laboratory Processed Oils

During the refining operations in the factory iron vessels are used which may lead to contamination of the oil with traces of metals. Moreover slight oxidation may occur between the various refining stages. It was of interest therefore to examine the effect of antioxidants in oils refined in the laboratory using methods which eliminate these factors. It was found that, in peanut oil carefully refined in the laboratory in glass apparatus, antioxidants had in some cases a slight advantageous effect. This finding leads one to suggest the presence in oils refined in the factory of factors which are antagonistic to antioxidants. In order to obtain an oil as free as possible from such factors a sample of peanut oil was neutralized and then dissolved in petroleum ether (boiling point 40–60°C.), the solution passed through a column of activated alumina, and the solvent removed from the eluate. It was unnecessary to bleach the resulting oil but it was deodorized in the normal way. The bulk of the more polar impurities were removed from the oil in this manner, including the whole of the natural antioxidant. Table IV records the extent of flavor deterioration of a sample of peanut oil treated with alumina in this way, both with and without the subsequent addition of antioxidants.

Accelerated tests indicate that the control should have a very low stability on storage, but in fact this control was by no means inferior on a taste basis to normally processed peanut oil, which on the basis of accelerated tests (see Table I) should have had the greater storage stability.

With regard to the effect of the addition of antioxidant, the most striking feature is that B.H.A., B.H.T., and propyl gallate greatly lengthen the keeping time of the oils. However the remarkable stability of the samples containing antioxidant is not indicated by the results of the accelerated tests. This appears to confirm the fact that factors antagonistic to the added antioxidant are removed on the alumina. The surprisingly low keeping time of the sample containing N.D.G.A. is due to the development of an unusual flavor thought to be derived from the antioxidant rather than the oil.

Effect of Antioxidants in Margarine

Although antioxidants had been shown to have little influence on the keeping properties of many of the component oils of fats used in margarine production, it was thought desirable that the effect of the addition of antioxidants to margarine should be tested experimentally. A margarine was used of which the main components of the fat blend were peanut oil and hardened palm oil. The fat formed about 80% of the margarine, the remainder consisting of 16% water, 2.25% milk solids, and 1.75% salt. The pH of the aqueous phase was between 5.5 and 5.7. The addition to the fat blend of 0.005% of 3:7:8:2′5′-pentahydroxy flavone, which is claimed to be a very powerful antioxidant (3), had no significant effect on the storage properties of the finished product. A similar result was found by adding butylated hydroxytoluene to margarine.

Discussion

The results presented show that the two accelerated tests used in this work can give little or no information on the initial deterioration in taste which occurs on storage of peanut oil and other vegetable oils. A similar view has also been stated by Tollenaar and Vos (2). Animal fats have not been examined in the present work but it has been stated elsewhere that accelerated tests are rather more effective in this case in predicting their storage properties *(ibid.)*. The accelerated tests also indicate a marked improvement in quality of vegetable oils refined in the factory by the addition of antioxidants whereas no advantage was found in practice. A similar lack of effect of antioxidants has also been shown in the case of margarine. The addition of antioxidants to fatty products with a more pronounced flavor has not been investigated; and it is possible they might be more effective in baked goods, potato chips, etc.

In considering the reasons for the failure of antioxidants to retard the formation of off-flavors it is necessary to consider the nature of the off-flavors which are produced. A number of aldehydes have been isolated from autoxidized oils, and decadienal,

hexanal, and octenal have recently been isolated from an oxidized emulsion of ammonium linoleate (4). However the off-flavor material present in a sample of oil which has barely become inedible on an organoleptic scale has never been investigated. A sample of peanut oil of such an organoleptic quality was therefore examined. The volatile components responsible for the off-flavor were removed by de-gassing (5), and were found to consist almost entirely of aldehydes. These were investigated by gas chromatography, and also as their dinitrophenyl-hydrazone derivatives by paper chromatography, and shown to consist very largely of a mixture of hexanal and the two isomeric *trans-trans-* and *cis-trans-*decadienals. The latter two compounds were also isolated from oxidized peanut oil by Hoffmann (6). Hexanal and decadienal have been isolated many times from autoxidized oils and it therefore appears that the aldehydes formed in the initial stages of oxidation, and which constitute the off-flavors, are similar to those produced during gross oxidation. A similar mechanism of decomposition of hydroperoxides would therefore appear to operate in the two cases.

It is therefore surprising at first sight that the present work shows that antioxidants can suppress gross oxidation but cannot prevent the development of sufficient of the off-flavor aldehydes to render the oil inedible. However it must be remembered that very small amounts of aldehydes are sufficient to give a very strong off-flavor (7). Moreover the advantageous behavior of antioxidants in peanut oil purified on alumina suggests the presence of factors antagonistic to antioxidants, and it seems probable therefore that the suppresion of oxidation in a normally processed vegetable oil involves a number of factors of which the action of the antioxidants is only one.

The surprising improvement of quality of oils by treatment with alumina during the refining process will be the subject of a further communication.

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Keeping Properties of Edible Oils. Part II. Refining by Treatment with Alumina[1]

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A new refining technique is described in which the normal earth-bleaching process is replaced by a treatment of the neutral oil, in light petroleum solution, on a column of activated alumina. The products are generally of somewhat improved color and have considerably longer keeping times compared with conventional oils. The application of the process on the semi-large scale is described.

IN THE REFINING of edible oils the bleaching process plays an important part in removing not only the color, but also the soap remaining from neutralization, flavored impurities, various off-flavor precursors, and other trace components. Oils for edible use are bleached almost exclusively by diatomaceous earth, or in a few cases with activated carbon. In a previous paper (1) it was shown that the addition of antioxidants to an oil conventionally processed in the factory led to no improvement in quality. However when the bleaching process was replaced by a treatment of the oil in petrol on a column of activated alumina, the addition of antioxidant led to an oil with a considerably longer keeping time. An investigation has been made of this process of treating oils on alumina in order to determine whether the quality improvement is of general application to various oils, particularly groundnut and soybean oils, and also whether the process would be suitable for application in the factory.

Refining Methods

Neutralization. The neutralization process used varied according to the type of oil, and generally followed that normally employed for the particular oil in the factory. In general caustic soda was used in a batch process, the oil being water-washed and dried prior to bleaching. Frequently oils already neutralized in the factory were employed for further refining purposes.

Bleaching. Samples of neutralized oil were divided and the separate parts treated either by the bleaching process usually employed in the factory, or by the alumina column method. For simulation of factory bleaching conditions the oils were stirred with 2% of activated diatomaceous earth for 30 min. under nitrogen at 110C. The oil was then rapidly filtered and deodorized similarly to the other sample of oil, which had been treated on the alumina column (see below).

Treatment on Alumina. A number of methods of alumina treatment have been used but that given below, the so-called "standard method," has been used in most of the laboratory work and has been shown to give satisfactory results. Unless statements are made to the contrary, alumina treatment in this text will imply treatment by this standard method. Rather large quantities of solvents and alumina are used in this method but later work has shown that economies can be effected.

The alumina column was prepared by pouring the alumina, previously activated by heating at 400C, into a glass tube of the required length. Neutralized and dried oil (250 g.) was dissolved in light petroleum, boiling point 40–60C (750 ml.), and the solution passed through a column of 500 g. of alumina, the length of the column being approximately 45 cm. After elution of the solution of oil in petroleum the column was finally washed with light petroleum, boiling point 40–60C (1,500 ml.), and the washings combined with the main solution of treated oil. The

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