despite being moderately refrigerated, which is manifest by a deterioration of response against bleaching clays. This occurs to some extent also in the case of prime oils. It is more pronounced in the case of the more active clays and is generally (but not always) absent in the case of A. O. C. S. Official earth. When it does occur in the case of A. O. C. S. earth the change of response is generally of smaller magnitude and often within the uncertainty of making Lovibond readings on the types of oils studied. (In a few isolated instances there appeared to be an improvement in bleaching response.) This behavior would mitigate against the use, in a standard bleach test, of any clay against which oils showed a marked deterioration of bleaching response, where the grading and evaluation of *refined* soybean oil is the primary concern, especially if the change referred to can be shown not to occur appreciably in the case of refined oil in bulk storage.

2. In the case of aging samples of crude soybean oil the change in bleaching response (R.B. color) is so slight as to be negligible in the strong dosage required, and hence the Committee believes that an activated or other active clay would be acceptable as the standard test bleach clay for the grading of crude oil.

3. Considering the extreme range of qualities which must be covered by a standard bleach test for grading crude soy oils, especially during seasons when crop damage is prevalent, we do not think that any test which properly grades the off-qualities of soybean oil can be considered an entirely satisfactory test for routine use by the industry in control and other than official grading work, especially during the majority of seasons when the crop is normal and prime oils predominate.

4. The present Official A. O. C. S. bleach test for soybean oil has been found by experience to be generally satisfactory in the routine testing and evaluation of soybean oils, and it would serve for the basis of grading crude soy oils in trading during all normal crop years. Moreover, it would serve also to a considerable extent as the basis for commercial grading even in years of crop damage, but might fail in the latter instance on an estimated 20 to 40% of the oil sold during a season of very heavy crop damage such as 1942-43. That, however, as last year's experience showed, is sufficient to rule it out for widespread use as the basis of trading.

5. Therefore, we believe that this committee should be continued and that further consideration be given to the question of a more powerful bleach test designed to grade all types of crude soy oil, specifically (1) to weigh the 4% activated clay test against an equivalent test using a much higher percentage of Official A. O. C. S. earth; (2) to check further on the magnitude of the change in bleaching response (R. B. Color) of soy oils stored as crude samples, and (3) to determine if possible whether refined soy oils in bulk storage undergo the same change in bleaching response shown in aging less than drum quantities.

Respectfully submitted,

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Stability Values of Fats by the Active Oxygen Method and by Storage in Glass Vials

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IT IS not unusual for large quantities of lard to be held in storage for periods in excess of six months. Whether or not a given lot of lard will be edible at the end of such storage periods depends upon its initial stability and the conditions of storage. Since it is generally thought that the natural stability or instability of fats and oils of equal degree of unsaturation is due chiefly to the presence or absence of inherent antioxidants, considerable interest has been stimulated in finding satisfactory antioxidants to add to edible fats. As an indication that some progress already has been made along this line, permission has been granted (1) to add small amounts of a number of antioxidants to lard.

Published work on the evaluation of antioxidants, however, has been limited almost entirely to rapid stability tests, with the result that little is known concerning the significance of results by these tests in terms of storage stability. Extensive work (2) has been reported on the storage stability of butter in relation to its rate of oxygen absorption at 105-107° C. The conclusions were that "the induction periods and the rates of oxidation vary so irregularly that there is no evidence of any relation of these to keeping quality." It has also been reported (3) that for lard containing added d-isoascorbyl palmitate and lecithin, the stability values determined by oxygen-absorption measurements in the Barcroft Warburg apparatus are more closely related to storage keeping quality than are stability values determined by the active oxygen method. In experiments on the evaluation of antioxidants in butterfat, a general relationship has been shown (4) between the protection factors determined by oxygen-absorption measurements at 100° and peroxide values in storage tests.

In an investigation on the improvement of lard, particularly by increasing its stability or resistance to rancidity through the addition of antioxidants, attempts are being made to compare stability values obtained by the more commonly used rapid methods with those determined by storage tests. The first storage experiments have been under way for 20 months; not all the test samples are rancid but the storage period has been long enough for practical requirements. In these experiments, stability values determined by storage in glass vials at 21° C. were compared with those determined by the active oxygen method.

General agreement was found in most instances but not a constant relationship between storage stability under these experimental conditions and stability determined by the active oxygen method, particularly

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when different antioxidants were added to the lard. In all cases where protection was shown by the active oxygen method, some protection was also shown in storage. The protection factors determined by the rapid method were greater in most instances than those determined by the storage test.

Experimental

Methods. The procedure described by King, Roschen, and Irwin (5) with minor modifications (6) was employed for determining stability values by the active oxygen method. A peroxide value of 15 millimols per kilogram of sample was taken as the end point of the induction period. This value seemed more closely correlated with incipient rancidity as determined organoleptically than the conventional end point of 10 millimols, particularly when antioxidants were added.

The storage tests were carried out as follows: Glass screw-neck specimen vials, 21 mm. in outside diameter and 70 mm. high in a series of 10 for each sample to be tested were filled to a depth of 33 mm. with the melted fat. The weights of the samples ranged from 7.0 to 7.5 gm. The vials were fitted tightly with bakelite screw caps and placed in a refrigerator so that the samples would congeal quickly. After cooling overnight, they were then placed in a partitioned cardboard box and stored in a room maintained at 70° F. (21.1° C.) and 65 percent relative humidity, where the samples were protected from light. After a few hours' conditioning in this constant temperature room, the screw caps were loosened about a half turn to allow some diffusion of air into the vials. Periodically, a sample from each series was examined for peroxide content, odor, and flavor. After the first tube of a series of ten was examined, it was put back in storage and re-examined at about monthly intervals until a significant change in analyses was observed. Then the second tube of this series was analyzed, the results being recorded for the second storage period. In this way it was possible to use one tube as a guide to tell when to examine the next. The storage stability was recorded as the time in months required for the sample to attain a peroxide level of 15 millimols per kilogram. In a few instances the samples showed no significant change at this peroxide level for several months. The end point in these instances was decided by organoleptic tests.

Qualitative Kreis tests also were carried out at the various storage periods. The intensity of color, as judged by visual comparisons, seemed to be roughly proportional to the peroxide values.

The protection factors reported are merely the ratio of the stability of the sample containing the antioxidant to the stability of the control.

Results and Discussions

THE results in Table 1 show the stability values obtained by the active oxygen method and by storage tests. The steam-rendered lard used in these experiments was commercial lard made from the usual proportions of killing fat and cutting fat. The refined lard was prepared commercially from the same steam-rendered lard (Lard A) by the common practice of bleaching 20 percent with Fuller's earth and then mixing it with the remaining 80 percent. The refined-and-deodorized lard was also prepared commercially by deodorizing a portion of this same refined lard.

From inspection of the data given in Table 1, it is evident that under these experimental conditions, there was no constant relationship between the stability values by the active oxygen and storage methods, particularly when different antioxidants were added and compared by calculated protection factors. In all cases where an increase in stability was shown by the active oxygen method, however, an increase in storage stability was also shown.

The storage samples containing the ternary combination of antioxidants—tocopherol, lecithin, and d-isoascorbyl palmitate—did not become rancid in 20 months. At the end of this period, the peroxide values were 2.8, 9.9 and 1.6, expressed as millimols, for the steam-rendered, refined, and refined-and-deodorized lards, respectively. Color developed in these particular samples during storage to an extent that probably would make them unacceptable to the trade. There was considerably less color in the refined and refined-and -deodorized samples, however, suggesting that it might have been caused by some minor constituent of the lard reacting with the antioxidant, and that more complete refining may overcome this difficulty. The stability was greater when the ternary combination was added to deodorized lard. Similar observations were reported in a previous publication (1).

Further comparisons of stability values determined by these methods with various antioxidants are given in Table 2.

TABLE I

Active Oxygen and Storage Stability Values of Lard Stabilized with Tocopherol, Lecithin, and d-Isoascorbyl Palmitate.
[Storage in Glass Vials at 21° C. (70° F.)]

Antioxidants added percent	Steam-rendered lard—A				Refined lard—A				Refined and deodorized lard—A			
	Stability		Protection factor		Stability		Protection factor		Stability		Protection factor	
	A. O. M. 98.5° C.	Storage 21° C.	A. O. M. 98.5° C.	Storage 21° C.	A. O. M. 98.5° C.	Storage 21° C.	A. O. M 98.5° C.	Storage 21° C.	A O. M 98.5° C.	Storage 21° C.	A. O. M 98.5° C	Storage 21° C.
	hrs.	*mos.*			*hrs.*	*mos.*			*hrs.*	*mos.*		
Control	2.5	4.5	1	1	1.5	3	1	1	0.8	1	1	1
+.06 d-IP[1]	1.3	4	0.5	0.9	1.0	3	0.7	1	0.5	1	0 6	1
+.06 lec[2]	5	8	2 0	1.8	3.5	6	2 3	2	3	3	3.8	3
+.01 toc[3]	13	11	5.2	2 5	11.	10	7.3	3 3	3.5	8	4.4	8
+.01 alpha tocopherol	9	9.5	3.6	2.1	....	....	....	....	....	....	....	....
+.01 toc +.06 lec	27	12	10.8	2.7	24	13	16	4.3	28	12	35	12
+.01 toc +.06 d-IP	24	18	9.6	4.0	21	19.5	14	6.5	23	15	28.8	15
+.01 toc +.06 lec +.06 d-IP*	62	>20	24.8	>4.5	44	>20	29.3	>6 7	85	>20	106	>20
+.06 lec +.06 d-IP*	10	11	4.0	2.4	4.5	8	3.0	2.7	16	14	20	14

[1] d-Isoascorbyl palmitate.
[2] Commercial soy lecithin.
[3] Tocopherol concentrate (30%) in vegetable oil.
* Samples containing these levels of lecithin and d-isoascorbyl palmitate darkened during storage.

TABLE II

Active Oxygen and Storage Stability Values Obtained with Various Antioxidants. [Storage in Glass Vials at 21° C. (70° F.)]

Antioxidants added percent	Stability		Protection factors	
	A. O. M. 98.5° C.	Storage 21° C.	A. O. M. 98.5° C.	Storage 21° C.
	hrs.	*mos.*		
Control (steam-rendered lard—A)	2.5	4.5	1	1
+1.0 crude corn oil	8	13	3.2	2.9
+1.0 refined corn oil	3.5	8	1.2	1.8
+5.0 crude corn oil	18	20	7 2	4.5
+5.0 crude corn oil +.06 d-IP[1]	26	>20*	10.4	>4.5
+5.0 refined corn oil	9	15.5	3.6	3.4
+5.0 refined corn oil +.06 d-IP	15	>20	6.0	>4.5
Control (refined corn oil)	10	7	1	1
+.06 d-IP	30	>20	3	>2.9
Control (steam-rendered lard—B)	1.5	4	1	1
+.05 ethyl phosphoric acid	4	8	2.7	2.0
+.05 butyl tyrosine	2	6	1.3	1.5
+.1 galacturonic acid	4	7	2.7	1.8
+.05 gum guaiac	7	17	4.7	4.3
+.01 hydroquinone	10	>20	6.7	>5
+.05 NDGA[2]	40	>20*	27	>5
+.05 B,B′-thiodipropionic acid	95	>20	63	>5
+.14 lauryl thiodipropionate	52	>20	35	>5

$>$ means greater than; test still under way.
[1] d-Isoascorbyl palmitate.
[2] Nordihydroguaiaretic acid.
* Became discolored to an objectionable extent.

THE difference in the protection factors by the active oxygen method and by the storage test is not so great as in the results given in Table 1. The data indicate that the addition to lard of about 5 percent of a tocopherol-bearing oil, such as corn oil, may provide a practical means of imparting sufficient protection for most storage requirements. There is good reason to think that even greater storage stability would be gained by adding similar amounts of partially-hydrogenated corn oil, soybean oil, or similar tocopherol-bearing oil (7).

The most effective antioxidants of the series given in Table 2, as indicated by the active oxygen method, are still in the storage test. The samples containing NDGA and those containing both crude corn oil and d-isoascorbyl palmitate have developed an off-color to an objectionable extent.

Some "off" odors and flavors in all the samples were detected during the latter part of the storage period before they were classified as rancid. Probably in some instances, these would be called "reverted" odors and flavors; in other instances they seemed to be characteristic of the antioxidant used.

It should be borne in mind that these storage data, obtained on small samples in glass, may not be comparable with results on large samples in commercial packages. But at least, they give a rough indication of the relative significance of rapid stability tests by the active oxygen method in terms of storage and point out the need for further comparisons with other rapid stability tests. Further experiments of this sort, including stability tests on stabilized lard stored in commercial packages, are in progress.

Summary

The stability of lards containing various antioxidants was determined by the active oxygen method and by storage in glass vials at 21° C. In many instances there was general agreement in the results, but no constant relationship was found. The difference between the results of the rapid test and those of the storage tests seemed to be greatest when tocopherol concentrate and lecithin were added to lard. In most instances where antioxidants were used, the protection indicated by the rapid stability test was higher than that found in the storage test.

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Abstracts

Oils and Fats

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PROCESSING SOYBEANS. W. H. Goss. *Soybean Digest 5*, No. 1, 6-9 (1944).

DETERMINATION OF CRUDE LIPID IN VEGETABLE MATTER. J. P. Nielsen and G. S. Bohart. *Ind. Eng. Chem., Anal. Ed., 16,* 701-3 (1944). This quick method of detg. fat in moist material is based on extn. with acetone, evapn. and extg. the residue with petr. ether.

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THE OXIDATION OF THIO-ETHERS BY UNSATURATED FATTY ACIDS. W. v. B. Robertson, J. L. Hartwell and S. Kornberg. *J. Am. Chem. Soc. 66,* 1894-7 (1944). It was observed that β,β-dichloroethyl sulfide was oxidized at room temp. to the sulfoxide by unsatd. oils in the presence of O_2. All the unsatd. acids and their esters which were examd. were found to mediate the oxidation, with the following exceptions: *a*-eleostearic (in which the double bonds are conjugated), Δ^{10}-undecylenic, ricinoleic and the acetylenic acids tariric and stearolic. The agents found to be responsible for the oxidation of the thio-ethers were the peroxides of the unsatd. fatty acids or esters. One mol. of peroxide oxygen was consumed for each mol, of thio-ether oxidized. In addn., carotene and *p*-dimethylaminoazobenzene were decolorized and biotin was found to be inactivated by peroxidized oils.

FORMATION OF ISOMERIC HYDROXY ACIDS BY SULFATION OF OLEIC ACID. B. B. Schaeffer, E. T. Roe, J. A. Dixon and W. C. Ault. *J. Am. Chem. Soc. 66,* 1924-5 (1944). Hydroxy acids resulting from the sulfation and subsequent hydrolysis of oleic acid were oxidized with nitric acid. Esters of dibasic acids having more than 10 C atoms were found by fractionation of the Me esters of the steam-non-volatile, water-insol. portion. The dimethyl ester of 1,14-tetradecanedicarboxylic acid was isolated and identified. Esters of