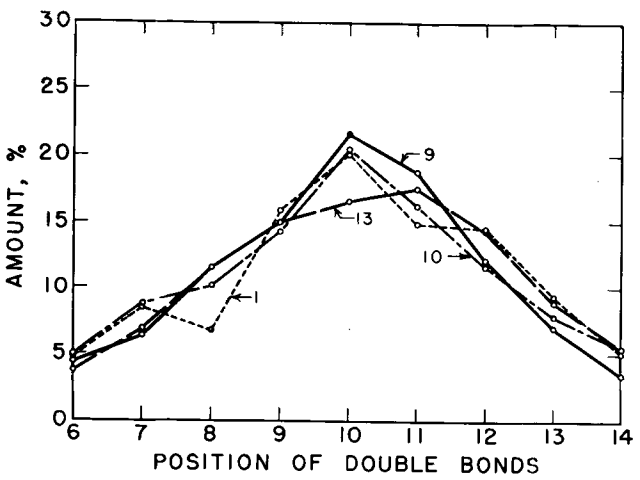

FIG. 6. Distribution of double bonds produced by different hydrogenation catalysts: nickel, 1; sulfur-poisoned nickel, 9; palladium, 10; and platinum, 13. Curve numbers refer to run numbers in Table I.

Summary

Methyl linoleate was hydrogenated to an iodine value of about 80 under various operating conditions. The temperature, rate of hydrogen dispersion, catalyst concentration, and type of catalyst were varied. The several hydrogenation products were analyzed for content of *trans* isomers and the positions of the residual double bonds.

The pattern of distribution of the double bonds was similar in most of the hydrogenations. The greatest concentration of double bonds was found in the 10 position, and the concentrations in the other positions decreased as the distance from the 10 position increased. The distribution curve tended to be symmetrical, that is, approximately the same number of double bonds was found on each side of the 10 position. Operating conditions which normally tend to increase selectivity and the formation of *trans* isomers also tended to increase the concentration of double bonds at the 10 position.

Greatly lowering the temperature of hydrogenation produced a different pattern of distribution of the double bonds. With nickel catalyst at 110°C. the greatest concentrations of residual double bonds were found at the 9 and 12 positions. More than 50% of the total double bonds were in these positions.

The several hydrogenation catalysts (nickel, sulfur-poisoned nickel, platinum, and palladium) produced the same pattern of distribution of double bonds when used under identical conditions. Also the platinum and palladium produced much higher proportions of *trans* isomers than did the nickel.

Acknowledgment

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Evaluating Refined Cottonseed Oils in Storage

LEWIS A. BAUMANN, Market Organization and Costs Branch, Agricultural Marketing Service, U. S. Department of Agriculture, Washington, D. C.

THIS PROJECT is of value to the vegetable oils industry and to the Government in any marketing operation involving the storage of large quantities of fats and oils, particularly cottonseed oil. It can indicate economies in the type and grade of oil best suited for storage and in the methods used as to size and condition of tanks and their location. Improvements can be indicated in the management of tank farm operations and of fats and oils inventories.

Industry rarely stores oil for its own use beyond the season's requirements in view of the lack of knowledge as to possible deterioration. During the early 1950's however the Government stored cottonseed oil up to two years. Experience with these stocks showed deterioration, with a corresponding decrease in market value when stored in commercial field tanks available at that time.

If oils can be stored for longer periods than is now practiced in industry without change of quality or value, a more orderly and efficient marketing operation would be possible. Furthermore a better knowledge as to the storage of oils will contribute much to the production of oils of better quality and value.

Little information on the subject is available from industry, and the judgment of the members of industry does not agree well on the basis of problems which have been presented. This has required that a controlled storage experiment be set up to obtain the data needed to arrive at the economic considerations involved.

The cost and impracticability of using commercial field tanks for the work suggested the use of 50–55

[1] Presented at annual meeting, American Oil Chemists' Society, Memphis, Tenn., April 22, 1958.

TABLE I

Quality Test Observations Initially and at End of 10-Month Storage of Refined Cottonseed Oils[a]

		Types of storage[b]				From different sources		
Drum number		1	2	4	3[c]	6	7	8
Test for	Observation	Breather—inside at room temperature	No breather	Breather—filled only one-half	Breather—solvent	Breather—screw-press extracted	Breather—screw-press extracted	Breather—prepress solvent extracted
		percentage	*percentage*	*percentage*	*percentage*	*percentage*	*percentage*	*percentage*
Moisture and volatile matter	Initial	0.05	0.07	0.07	0.05	0.20	0.08	0.12
	Final	.10	.10	.08	.07	.07	.07	.09
Free fatty acid	Initial	.04	.03	.03	.04	.04	.07	.05
	Final	.02	.05	.03	.03	.03	.03	.04
		A.O.C.S.[d]	*A.O.C.S.*[d]	*A.O.C.S.*[d]	*A.O.C.S.*[d]	*A.O.C.S.*[d]	*A.O.C.S.*[d]	*A.O.C.S.*[d]
Refined color	Initial	3.8	3.8	3.8	4.0	5.5	5.0	6.2
	Final	4.0	4.0	4.0	4.0	5.4	4.6	6.5
Bleached color	Initial	1.2	1.3	1.2	1.2	1.5	1.2	2.0
	Final	1.1	1.1	1.1	1.1	1.7	1.4	2.9
		me./kg.	*me./kg.*	*me./kg.*	*me./kg.*	*me./kg.*	*me./kg.*	*me./kg.*
Peroxide value	Initial	10	11	19	12	3	5	2
	Final	10	13	56	25	26	24	30
		hours[e]	*hours*[e]	*hours*[e]	*hours*[e]	*hours*[e]	*hours*[e]	*hours*[e]
AOM fat stability	Initial	13	13	13	13	19	19	15
	Final	10	12	9	10	10	9	11

[a] Drums painted aluminum, all exposed to outside atmospheric conditions (except Drum 1), at Beltsville, Md. No data at 10-month period on Drum 5, sealed for 28-month period.
[b] Oil was solvent-extracted and refined in miscella.
[c] The oil in Drum 3 is from the same source as in Drums 1, 2, and 4 and also under a different type of storage. It also is under the same type of storage as Drums 6, 7, and 8 and is from a different source.
[d] A measure of red color according to Methods of the American Oil Chemists' Society.
[e] Samples were rancid one hour later than reported.

gal. steel drums. More than 70 drums of cottonseed oil are in the experiment, most of which are stored at Beltsville, Md. Twenty-four drums of refined oil and two drums of crude oil have been in storage since June 1955 (four of these drums containing refined oil are stored at New Orleans). Twenty-eight drums of refined oil and 24 drums of crude oil were added in December 1956. Eight of these drums containing refined oil are stored at New Orleans, and eight are stored at Albany, Calif. Drums of identical oils were placed under various conditions to simulate field tank operations, and oil from several areas and processed by the different methods were placed under similar storage conditions. Work on the project includes comparisons of drums to a field tank under commercial conditions.

The present report covers only the history of eight drums of refined cottonseed oil, five drums having been stored 28 months and three drums 10 months. Oils from four sources are included, one of which has been subjected to various types of storage environment. The eight drums of oil were chosen as representative of wide differences in keeping quality as has been indicated so far in the project from some of the tests used to determine fat stability.

All of the eight drums (painted aluminum) are stored outside at Beltsville, Md., and are freely exposed to atmospheric conditions except No. 1, which is stored under room temperature inside a building. The seven drums (not including No. 1) are tilted at an angle with asphalt roofing on the top end to permit water drainage.

Five of the drums, 1 through 5, contain the same original oil, which was solvent-extracted and refined in miscella. These five differ in the type of storage in that No. 1 has a breather, No. 2 has no breather, No. 3 has a breather, No. 4 has a breather but is only half filled, and No. 5 has been sealed during the entire storage period. All of these drums had been stored for 28 months as of October 1957.

The other three drums of oil were stored under the same conditions as No. 3, but the oils were processed by two different methods, *i.e.*, No. 6 and No. 7 were screw-press extracted, and No. 8 was extracted by prepress solvent. These had been in storage 10 months as of October 1957.

All samples are taken by glass pipette at the center of the oil, through the top bung.

Only the possible decrease in value of the oils as of October 1957 is considered at this time. Other economic aspects, such as transportation, storage costs, costs of different methods of storage, market value changes, etc., are not included but will be reported at the completion of the controlled storage tests.

Methods Used in Evaluating the Oils

Tests Used in Grading Refined Cottonseed Oils. The tests as given in the Trading Rules of the National Cottonseed Products Association (hereafter referred to as the "Rules") are used in the project. The Rules list 10 different grades of refined cottonseed oils; however only a few of these grades are of concern in the report. Most of the oils in storage were initially in the top grade of prime bleachable summer yellow, with none less than choice summer yellow.

The Rules include the following four analytical tests (in accordance with the methods of the American Oil Chemists' Society), which were used in the project and can determine the grade:

1. Moisture and volatile matter, by A.O.C.S.—Ca 2d-25.
2. Free fatty acid, by A.O.C.S.—Ca 5a-40.
3. Refined color, by A.O.C.S.—Cc 13b-45.
4. Bleached color (in some grades only), by A.O.C.S.—Cd 8-53 and Cc 13b-45.

In addition, several additional tests which depend only on observation are as follows: clarity at temperatures at which stearine is melted, freedom from visible foreign matter, flavor and odor. Several of the grades are distinguished only by "flavor and odor," which can be "sweet in flavor and odor," "sweet in flavor and odor other than an earthy odor," or "off in flavor and odor."

Based on tests of some of the refined oils during the first year of the project, it was anticipated that the Rule which would finally determine the grade of the oil would be the one concerning "flavor and odor," and, in view of the subjective nature of such a test, the problem was presented as to what value could be placed on an oil even if there was general agreement that it was "off in flavor and odor." It was believed that the opinions of only a few observers, such as laboratory technicians, would not be representative of buyers of oil in the market in determining an "off flavor and odor" and more especially of placing a value on an oil which was graded as "off in flavor and odor." Accordingly samples of the eight drums of oil reported at this time have been graded and, in some cases, evaluated by workers in those organizations in industry which have supplied all the oils for the project.

Tests to Indicate Deterioration of the Oils. It is well known in industry that there are many factors which can affect the capacity of an edible fat or oil to resist deterioration, both as an intermediate product, such as in the crude or refined state, but, more important, in the end-product to the consumer. This capacity of the fat to resist change in flavor determines the shelf life of the end-product. Many tests have been devised to determine this "stability" of the fat or oil, but as yet no reliable, objective test or group of tests can predetermine the length of time required for a refined cottonseed oil to reach a point of having an "off flavor and odor," recognizable by most observers, due solely to deterioration under commercial storage conditions.

In addition to all the tests as required under the Rules to grade the oils, several other tests are being used which could possibly indicate any decrease in fat stability because of deterioration in storage. All of these tests, although not a part of the Rules, are in use by industry to aid in predetermining the shelf life of end-products made from edible fats and oils.

Although it is possible for an oil to deteriorate in storage, producing "off flavors and odors" (which did not exist in the oil originally), without the presence of air, or more fundamentally oxygen, deterioration to rancidity is generally assumed to be an oxidative reaction. Based on this assumption, the Peroxide Value test (PV) is used in the project on all refined oils and, as well, in those instances where several of the refined oils are bleached and deodorized just prior to other tests. The A.O.C.S. has accepted this test tentatively but does state, "this method determines all substances . . . which oxidize potassium iodide under conditions of the test. These are generally assumed to be peroxides or other similar products of fat oxidation." The test is given by A.O.C.S. under Cd-8-53.

The Active Oxygen Method for Fat Stability test (A.O.M.) is also used on all refined oils in the project as well as on a number of specified samples of refined oils which have been bleached and deodorized. This test accelerates the fat decomposition by using high temperatures with air under pressure in the oil. The method with some modifications and further standardization has been adopted by A.O.C.S. as tentative under Cd-12-57. It is suggested that the end-point be determined objectively by using a specified Peroxide Value for the product under test. The end-point of the test as used in this project has not been determined in accordance with A.O.C.S. End-points for the test in the project have been reported as one hour less than rancidity as determined by the "break" in peroxide value during this last hour, during which higher rates of increase of peroxide value occurred over previous hours.

The Schall oven test is also used here but only on all samples of refined oils which had been bleached and deodorized. A forced draft oven at 140°F. was used with 100 cc. of sample. Inspections were made every 24 hrs. End-point was determined by the rate of change of peroxide value from the previous 24 hrs. and by organoleptic observation.

The Flavor and Odor of Refined Oils. The three tests, AOM, PV, and Schall, are directly concerned with the capacity of an oil to resist deterioration from oxidation in the presence of air, and their use in the

TABLE II

Quality Test Observations Initially and at End of 28-Month Storage of Refined Cottonseed Oil Under Different Types of Storage[a]

Test for	Observation	Drum number				
		1	2	3	4	5
		Breather—inside at room temperature	No breather	Breather	Breather—filled only one-half	Sealed entire period
		percentage	*percentage*	*percentage*	*percentage*	*percentage*
Moisture and volatile matter	Initial	0.05	0.07	0.05	0.07	0.06
	Final	.09	.07	.07	.09	.07
Free fatty acid	Initial	.04	.03	.04	.03	.03
	Final	.03	.02	.02	.03	.04
		A.O.C.S.[b]	*A.O.C.S.*[b]	*A.O.C.S.*[b]	*A.O.C.S.*[b]	*A.O.C.S.*[b]
Refined color	Initial	3.8	3.8	4.0	3.8	3.8
	Final	3.1	3.0	3.1	3.0	3.1
Bleached color	Initial	1.2	1.3	1.2	1.2	1.3
	Final	1.2	1.3	1.4	1.3	1.6
		me./kg.	*me./kg.*	*me./kg.*	*me./kg.*	*me./kg.*
Peroxide value	Initial	10	12	12	19	9
	Final	41	30	76	172	76
		hours[c]	*hours*[c]	*hours*[c]	*hours*[c]	*hours*[c]
AOM fat stability	Initial	13	13	13	13	13
	Final	9	10	6	0	2

[a] Drums painted aluminum, and all exposed to outside atmospheric conditions (except Drum 1), at Beltsville, Md. Oil was solvent-extracted and refined in miscella.

[b] A measure of red color according to Methods of the American Oil Chemists' Society.

[c] Samples were rancid one hour later than reported.

project is based on the assumption that storage of the oils decreases the resistance of the oils to such deterioration. Not only can "off flavors and odors" develop in the oils during storage without oxidation but can be present in the freshly refined oil. Storage of the oils may or may not intensify these flavors and odors without oxidation. There are no objective tests to distinguish flavors and odors that might develop due solely to storage other than those due to possible fat decomposition and, in view of the lack of experienced graders judging the flavor of refined oils which have been stored over long periods, a problem is presented in determining the value of the oils stored over such long periods. The solution becomes a major objective of this project.

Effects of 10 Months' Storage on the Oils

The more important tests that have been made on seven of the drums of oil at the beginning and end of the first 10-month period of storage are shown in Table I. One drum (number 5, sealed for a 28-month period) was not sampled at the end of 10 months. All samples were clear and free from visible foreign material.

At the end of the 10-month period all the oils were under the moisture and volatile matter content requirement of the Rules for all grades of refined cottonseed oils: however Drums 6 and 8 were above .10% initially. It was indicated that some moisture had settled out from these oils during the storage. Although it was indicated that the oils with the lower moisture and volatile matter content originally showed a tendency to increase during the storage period, changes have not been enough to decrease their market value.

Free fatty acid content of all the oils was considerably under requirements of the Rules for the best grades, both initially and at the end of the period. There were no significant changes during this period of storage.

Changes in refined color of all the oils during the first 10 months of storage were not significant from a market-value standpoint. At the beginning and end of this time each oil could readily qualify for top grade in refined color and was also under the limitation of 7.6 A.O.C.S. units according to the Rules.

Only one of the oils (number 8) has changed significantly in bleached color during this time, and this oil had a higher bleached color than the other oils on entering storage. All of the oils initially were PBSY. The oil in number 8 drum was no longer bleachable at the end of the 10-month storage period. This is the only instance of a decrease in market value, based on analytical tests as required in the Rules. The specifications as given for flavor and odor in the Rules are discussed later.

Although not a part of the Rules, tests for peroxide value and AOM fat stability have been made on the oils, which also are shown in Table I. The use of these tests in the project may give some indication of a relationship to the subjective tests under the Rules pertaining to flavor and odor, with particular reference to "off flavors and odors" due to deterioration in storage from oxidation of the oils.

When comparing the same original oil held under different types of storage, *i.e.*, Drums 1, 2, 4, and 3, there are differences in the rate of increase of the peroxide value during the 10-month period of storage. Increase in peroxide value of the four drums of oil from different sources are more uniform over this period, *i.e.*, Drums 3, 6, 7, and 8.

All of the oils decreased in the value of AOM fat stability by the end of 10 months in storage. The change was greatest for the two oils having the highest AOM values originally, *i.e.*, Drums 6 and 7. At the end of the period all of the oils were in the range of 9–12 hrs. AOM.

The importance of the changes in both the peroxide value and the AOM fat stability tests on the oils during the periods of storage can be determined only when organoleptic observations are made for the detection of "off flavors and odors" resulting from oxidation of the oils because of storage. As of the end of the 10-month period, it is however indicated that no such "off flavors and odors" were likely present in the oils.

Effects of 28 Months' Storage on the Oil Held Under Different Storage Conditions

Information on the five drums of oil, originally all from the same source but each held under a different type of storage environment, is shown in Table II. Changes in tests for the entire 28-month period are shown.

All of these drums of oil were under .10% moisture and volatile matter at the end of 28 months even though two of the drums had reached .10% at the end of 10 months.

Free fatty acid content was not significantly different at the end of this longer period than at 10 months.

There have been definite decreasess however in refined color. In view of the fact that refined color on the oils was well under the limits of 7.6 of the Rules, this decrease over the storage period is not significant from a market-value standpoint.

All of these oils had original low bleached color, and even though some increase in bleached color was indicated at the end of 28 months, all of these oils were still PBSY, with no decrease in market value from tests in the Rules.

There have been decided differences in the increase of peroxide value for the original oil held under the five different types of storage, as of the end of 28 months.

There also have been decided differences in the decrease of AOM fat stability for the five different types of storage. The drum half-filled (number 4) has reached an AOM values which, according to the methods of the test, should be close to the point of rancidity. At the other extreme of AOM value, the drums numbered 1 and 2 have decreased only a few hours in test from the original oil put in storage 28 months previously.

Relationship of the AOM Fat Stability of Refined Oils and the Same Oils Deodorized

Bleaching and deodorizing a refined cottonseed oil should, if the oil is not already in a rancid state, rid the oil of any "off" flavors that may be present from its original processing or taken up or intensified during storage. Peroxide value will be greatly reduced. Such a second AOM determination on the oil could prove to be a better indicator of fat deterioration from oxidation than an AOM test on the refined oil alone.

TABLE III

Summary of Cooperators' Reports in Grading Refined Cottonseed Oils from Storage for "Off" Flavors[a]

Drum number	Type of storage	Method of extraction	Time in storage	Cooperators reporting "off" flavors			
				All graders[b]		"Qualified" graders[c]	
			months	*number*	*percentage*	*number*	*percentage*
2	No breather	Solvent	28	5	11	4	13
3	Breather	Solvent	28	7	15	6	19
1	Breather–inside	Solvent	28	12	26	8	26
6	Breather	Screw press	10	14	30	7	23
5	Sealed	Solvent	28	16	35	11	35
4	Breather–filled one-half	Solvent	28	17	37	11	35
7	Breather	Screw press	10	20	43	11	35
8	Breather	Prepress solvent	10	30	65	12	39

[a] Twelve mills or refineries have supplied oil for the project, and two laboratories have made tests. Workers in these organizations have cooperated in grading and evaluating the oils.
[b] A total of 46 reports were received.
[c] Thirty-one of the 46 reports were called "qualified" graders on the basis that these graders had more experience than the others in the organoleptic observation of refined cottonseed oils.

A number of the refined oils in the project have been bleached and deodorized. A second AOM determination was then made on each of the oils. In all cases the PV was reduced to less than 1.0 by these operations. The AOM value on the deodorized oil was different from the AOM value on the refined oil. There was a good degree of relationship between the two AOM values on each oil for all the oils so processed. These data are not shown in this report. Refined oils with AOM's over 8 hrs. showed lesser AOM values after deodorization whereas those under 8 hrs. showed higher AOM values after deodorization. The refined oil in drum number 4, having an AOM of 0 hr., showed an AOM of 5 hrs. after deodorization.

The AOM values of the several oils, after deodorization, are discussed further in the grading of the oils for "off flavors and odors" by members of industry.

Grading the Refined Oils for "Off Flavor and Odor"

"Flavor and odor" appear in the grading of all refined cottonseed oils, according to the Rules. An "off flavor and odor" alone can degrade the oil and possibly its market value.

Industry does not have many occasions to grade refined oils for this requirement of the Rules, because of the limited number of refined oils changing ownership and the short storage period of such oils. This requirement of the Rules however becomes important in the present project, in view not only of "off flavors and odors" present in the refined oils when produced but as well of those developing during storage either with or without incipient oxidation. It was believed that in order to grade the refined oils for "flavor and odor" only a consensus from a number of those in industry having some experience could be relied on and particularly to place a market value on any oil "off in flavor and odor."

The eight oils were submitted to all those organizations in industry who have supplied all the oils for the project and to those laboratories having a direct interest. Table III summarizes the replies to the questionnaires concerning the grading of the oils. Fifteen out of the 46 persons submitting reports stated that they had had limited experience in grading refined cottonseed oils for flavor and felt that their opinions were not reliable. Accordingly the replies were divided so as to exclude these "inexperienced graders" from the group classed as "qualified graders." The percentages of the number of graders grading each of the oils "off" were not significantly different between all the graders and the "qualified" graders.

Table IV shows the relationship of the number of "qualified" graders, declaring each oil to be "off" in flavor, to the PV and AOM tests (both the latter, on the refined and the deodorized oils). The PV indicates little as related to the number of times each oil is graded "off." The AOM value on the refined oil also bears little relationship to the number of times each oil was graded "off." There is some relationship however between the number of times the oil is graded "off" to the AOM value (after deodorization) in the cases of the same oil held under various types of storage, *i.e.*, numbers 2, 3, 1, 4, and 5. This is not true of the four oils, *i.e.*, numbers 3, 6, 7, and 8, from different sources held under the same type of storage. As an example, oil in Drum 8 with the highest AOM value both before and after deodorization was judged "off" more times (39%) than any of the other oils.

Various descriptions of the flavors of the oils were given by the graders not only when the oils were graded "off" but also when not so graded. There were no relations between oils called "oxidized" or "rancid" to the AOM values of the oils. As many graders called some oils "oxidized" and/or "rancid" that had high AOM tests as had low AOM tests. It is evident that "off flavors and odors," according to the graders, were present in the oils which could have been present originally or had developed or intensified with storage, which had little relation to flavors from incipient oxidation.

Evaluating the Refined Oils Graded "Off in Flavor and Odor"

Although the "qualified" graders (some of these were the only ones who would place a market value on the "off" oils) stated that oils were "off" varying from 13% in one oil to 39% in the extreme case, a few stated that a discount should be applied and the discount when applied usually was quite low. This summary is shown in Table V.

On an average, this discount was not significant. These average discounts vary from 0.01¢ to 0.07¢ on a 14¢ oil and bear no relationships to the number of times oils were graded "off" in flavor.

The most usual discount used when the oil was graded "off" was 0.2 of a cent per pound, which is about 1.5% of the base price. This amounts to $120 on a 60,000-pound tankcar, but only about 5% of the graders would apply a discount. On this basis it can be concluded that any of the oils, regardless of

TABLE IV

Relationship of Refined Cottonseed Oils from Storage, Graded "Off" in Flavor, to Specified Laboratory Tests[a]

Drum number	Type of storage	Method of extraction	Time in storage	"Qualified" graders[b] reporting "off" in flavor		Laboratory tests		
						Peroxide value	AOM fat stability	
							Refined oil	After deodorization
			months	*number*	*percentage*	*me./kg.*	*hours*[c]	*hours*
2	No breather	Solvent	28	4	13	30	10	9
3	Breather	Solvent	28	6	19	76	6	7
6	Breather	Screw press	10	7	23	26	10	9
1	Breather–inside	Solvent	28	8	26	41	9	8
4	Breather–filled one-half	Solvent	28	11	35	172	0	5
5	Sealed	Solvent	28	11	35	76	2	6
7	Breather	Screw press	10	11	35	24	9	8
8	Breather	Prepress solvent	10	12	39	30	11	9

[a] Twelve mills or refineries have supplied oil for the project, and two lasis that these graders had more experience than the others in the organolep- in grading and evaluating the oils.

[b] Thirty-one of the 46 reports were called "qualified" graders on the baboratories have made tests. Workers in these organizations have cooperated tic observation of refined cottonseed oils.

[c] Samples were rancid one hour later than reported.

the effects of storage or the source of the oil prior to storage, has only a small chance of being discounted.

Further storage could change the value of these oils, particularly in view of possible rancidity developing which should then be more generally recognized as an "off" flavor and could prompt discounts more often among graders. At the present stage of the project it can be concluded that the market value of all the oils has not decreased significantly because of the presence of "off flavors and odors."

Discussion

All of the oils were under 0.10% moisture and volatile matter content at the end of the two storage periods; however two of the drums (held for 28 months) had reached 0.10% moisture and volatile matter at 10 months. Two of the drums, held for 10 months' storage only, had moisture and volatile matter content above 0.10% at the beginning but had decreased below 0.10% at the end of the 10 months.

There were no significant changes in free fatty acid content, either in the oils held for 10 months or in those drums held for 28 months. Free fatty acid was low in all the oils at all times in storage. Only one oil reached above 0.05% in one sample (0.07%).

Changes in refined color of all the oils during the first 10 months of storage were not significant. There were however definite decreases in refined color between 10 and 28 months' storage for the same oil held under different types of storage. In view of the fact that these drums of oil entered storage well under the limit of 7.6 A.O.C.S. units of the Rules of the N.C.P.A., these decreases were not significant from a market-value standpoint.

With the exception of one of the oils having a bleached color of 2.0 A.O.C.S. units at the beginning of the 10-month storage period which increased to 2.9 A.O.C.S. units at the end of this period, all bleached colors were low at all times during storage.

Peroxide value increased in all the drums of oil during storage. There was not much difference in the rate of increase in the three drums of oil from different sources held for 10 months and as compared to the drum of oil (another source) at the end of 10 months of the 28-month storage period. All these four drums were held under the same type of storage. There were however distinct differences in the rate of increase in peroxide value of the same oil held under different types of storage, both at the end of 10 months and, even more so, at the end of 28 months.

Fat stability by the Active Oxygen Method, using peroxide value "break" as an end-point, was run on all the oils. Although two of the oils had an AOM value of 19 hrs. on entering storage, the AOM values on all the oils ranged from 9 to 12 hrs. at the end of 10 months in storage. There were however far greater differences in the decrease of AOM value by the end of 28 months for the same oil held under different types of storage. The AOM values on these oils at the end of 28 months range from 0 to 10 hrs. (Rancidity is reported as occurring 1 hr. later.)

An AOM fat stability test made after bleaching and

TABLE V

Summary of Cooperators' Reports in Evaluating Refined Cottonseed Oils from Storage, Graded "Off" in Flavor[a]

Drum number	Type of storage	Method of extraction	Time in storage	"Qualified" graders[b]				Average estimated value of oil	
				Reporting "off" flavor		Who would discount value		Discounting only[c]	All graders[d]
			months	*number*	*percentage*	*number*	*percentage*	*cents*	*cents*
2	No breather	Solvent	28	4	13	1	3	13.8	13.99
3	Breather	Solvent	28	6	19	2	6	13.7	13.98
6	Breather	Screw press	10	7	23	2	6	13.7	13.98
1	Breather–inside	Solvent	28	8	26	1	3	13.8	13.99
4	Breather–filled one-half	Solvent	28	11	35	2	6	12.9	13.93
5	Sealed	Solvent	28	11	35	5	16	13.6	13.93
7	Breather	Screw press	10	11	35	2	6	13.8	13.99
8	Breather	Prepress solvent	10	12	39	4	13	13.7	13.97

[a] Twelve mills or refineries have supplied oil for the project, and two laboratories have made tests. Workers in these organizations have cooperated in grading and evaluating the oils.

[b] Thirty-one of the 46 reports were called "qualified" graders on the basis that these graders had more experience than the others in the organoleptic observation of refined cottonseed oils.

[c] Average value of oil in cents per pound based only on graders who would discount.

[d] Oils not discounted were valued at 14 cents per pound.

deodorization may prove to be a better indicator of fat deterioration than an AOM test made on the same oil as refined. Refined oils with AOM values over 8 hrs. showed lesser AOM values after deodorization and refined oils with AOM values under 8 hrs. showed higher AOM values after deodorization. A refined oil of zero AOM value had an AOM value of 5 hrs. after deodorization.

Conclusions

There have been insignificant decreases in market value of seven out of eight drums of refined cottonseed oil held in storage for longer periods than are generally used in industry. Five drums containing oil from the same source (solvent-extracted and refined in miscella) had been held for 28 months under different types of storage. Three drums containing oil from different sources (screw-press and prepress-solvent extractions) had been held for 10 months under the same type of storage.

All of the oils entered storage as prime bleachable summer yellow, but one drum of oil became unbleachable after the first 10 months of storage. This oil however had a bleached color of 2.0 A.O.C.S. units originally, which was much higher than on the other oils.

There had been insignificant changes in free fatty acid, moisture and volatile matter, and refined color on all the oils.

Peroxide values have increased appreciably in some of the oils, and values of fat stability by the Active Oxygen Method have decreased appreciably, especially on some of those oils stored for 28 months. However laboratory tests at the end of the storage periods do not indicate that a point of rancidity has been reached on any of the oils.

Although the flavor of all the oils was criticized quite extensively by most of the 46 members of industry who have cooperated in grading the oils, only about a quarter to a third of the graders would call the oils "off in flavor and odor" in accordance with Rules of the National Cottonseed Products Association. Furthermore only a few of these graders (from one to five in the cases of the several oils) would actually decrease the market value of the oil for being "off" in flavor, and this discount on the average was insignificant.

There were no relationships between the graders' judgments of the oils for "off flavor and odor" and the tests for peroxide value and AOM fat stability. Industry generally regards these tests as reliable indicators of quality. On the basis of these tests the oil in the drum only half-filled has shown the greatest deterioration at the end of the 28-month period whereas the oil in the drum having no breather has shown the least deterioration.

It must be emphasized that the information in this paper has been drawn from a small sample. Results from the larger number of test drums of oil now in storage may necessitate modifications in the conclusions reported.

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Reaction of Ethylene Oxide or Propylene Oxide with Long-Chain Fatty Acids. Mono- and Diester Formation[1]

A. N. WRIGLEY, F. D. SMITH, and A. J. STIRTON, Eastern Regional Research Laboratory,[2] Philadelphia, Pennsylvania

INEXPENSIVE fat-based nonionic detergents and surface-active agents are readily made by the reaction of ethylene oxide with long chain fatty acids, such as lauric or stearic acid, under the influence of an alkaline catalyst.

The reaction, as generally understood,

$$RCO_2H + n\underset{\diagdown\,O\,\diagup}{CH_2CH_2} \xrightarrow[\text{catalyst}]{\text{alkaline}} RCO(OC_2H_4)_nOH$$

where RCO_2H is the parent fatty acid and n is the average number of ethenoxy groups, would lead only to the formation of monoesters (14). From this point of view the reaction with ethylene oxide would be preferred to the esterification reaction,

$$RCO_2H + H(OC_2H_4)_nOH \longrightarrow RCO(OC_2H_4)_nOH + H_2O$$

where the possible formation of diesters

$RCO(OC_2H_4)_nO_2CR$ is more apparent.

There has been evidence in the case of acetic or benzoic acid (1, 15) that the reaction with ethylene oxide is more complex than is represented by the first equation. With respect to the higher fatty acids, transesterification (6) or alcoholysis may occur under the reaction conditions, according to the equation:

$$RCO_2(C_2H_4O)_nH + RCO(OC_2H_4)_nOH \xrightarrow[\text{alkaline catalyst}]{\text{high temperature}} RCO(OC_2H_4)_nO_2CR + H(OC_2H_4)_nOH$$

Furthermore a recently published method of analysis (7) has shown that water-soluble nonionic surface-active agents of the ester type, from the reaction of ethylene oxide with the higher fatty acids, are in reality composed of comparable amounts of glycols, monoesters, and diesters.

The monoester may be expected to be a more valuable detergent and surface-active agent than the diester, or than a mixture of monoester, diester, and polyethylene glycol. In any event the properties of a reasonably pure monoester preparation would be of interest. As an initial phase in understanding the

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[2] Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.