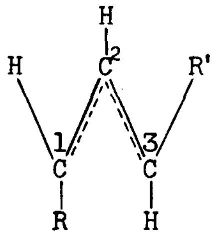
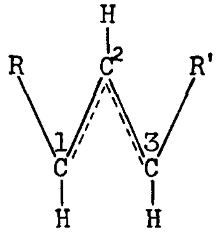
mechanism for the isomerization of olefins by the usual catalysts (3, 8, 23). Since double bonds shift during autoxidation, mixtures of cis and trans isomers in which the double bond is not in the original position should also be obtained.

c) The addition of oxygen to radicals III and IV may be reversible. While the oxygen is on carbon atom 3, free rotation would be possible about the 2,3 bond, and detachment of the oxygen would lead to two additional isomeric forms (VI and VII).



(VI)



(VII)

Reacquisition of a proton would then give a mixture of methyl oleate and elaidate as well as cis and trans methyl 8- and 10-octadecenoates. Attachment and detachment of oxygen to carbon atom 1 would not yield any isomers which have not already been discussed.

d) The radicals III and IV may be capable of some degree of rotation so that the isomerization takes place without the addition of oxygen to them. Subsequent addition of oxygen or reacquisition of a proton would give all of the hydroperoxides and octadecenoates mentioned previously.

It should be emphasized that autoxidative isomerization is only one of numerous reactions which are occurring during autoxidation.

Acknowledgment

The authors thank Jane R. Willis, T. D. Miles, R. E. Koos, and J. E. Coleman for analyses, determination of infrared spectra, and some of the calculations.

Summary

Methyl oleate irradiated with ultra-violet light has been autoxidized at 35° and the reaction has been followed by means of the infrared spectrophotometer. During the extremely early stages of autoxidation and continuing up to at least 700 hours, a cis-trans isomerization induced by oxygen is one of the reactions which occurs.

The data suggest that most, if not all, of the peroxides produced during the autoxidation of methyl oleate, at least up to 300 hours, are trans peroxides and not methyl oleate peroxides, as had been previously supposed. A mechanism for the formation of trans peroxides from allylic free radicals is proposed.

Mechanisms are also proposed for the formation of non-peroxidic trans materials during autoxidation. These could explain the formation of trans-9,10-epoxystearic acid and high melting 9,10-dihydroxystearic acid from autoxidizing oleic acid.

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Report of Cellulose Yield Committee, 1950-51

During the past year three sets of samples were sent out to 10 different laboratories for check analyses. Two second cut linters and one hull fiber were included in each set. The following table gives the analyses received from each laboratory and the overall average of all the results.

The check analyses on Samples A and B are very good. Sample No. C varies considerably. This is due to the fact that low yield samples, either linters or fiber, will at times plug the screen end of the washer and will not wash properly. It was mentioned in last year's report that this was being worked on. A number of tests were run on low yield linters and hull fiber and recommendations are made to improve, or at least clarify, certain steps of the procedure so that better checks can be obtained. When this procedure was first adopted, yields lower than 65% were not anticipated.

TABLE I

Laboratory No.	No. of Tests	Samples			Overall Average for the Year
		A Linter	B Linter	C Fiber	
1	3	75.1	70.1	66.1	70.5
2	3	74.4	69.9	67.0	70.5
3	3	74.6	69.5	66.8	70.3
4	3	74.7	69.9	66.1	70.2
5	3	75.1	70.0	67.0	70.6
6	3	75.2	69.8	64.7	69.9
7	3	75.0	69.3	63.6	69.3
8	3	74.7	69.4	65.9	70.0
9	3	74.7	69.3	67.4	70.4
10	3	75.2	70.1	67.7	71.0
Average		74.9	69.7	66.2	70.3

Six samples were sent out to each of the six laboratories which represent the Cellulose Yield Committee. Each laboratory ran at least three tests on each sample. The averages of these analyses were reported and are tabulated in Table II. Three hull fibers and three linters are included in the samples reported in the table below.

TABLE II

Sample No.	Laboratory No.	Standard A.O.C.S.	Proposal No. 1	Proposal No. 2
1—Linters	1	47.9	47.5	45.9
	2	....	47.7	45.8
	3	48.8	48.1	46.7
	4	46.8	47.0	45.4
	5	50.5	47.1	45.0
	6	46.1	47.1	45.4
	Avg.	48.0	47.4	45.7
2—Linters	1	53.2	52.3	52.3
	2	....	50.9	51.5
	3	52.8	52.1	52.0
	4	51.6	52.2	50.7
	5	55.6	52.1	50.5
	6	51.6	51.8	50.1
	Avg.	53.0	51.9	51.2
3—Linters	1	63.5	62.3	61.5
	2	....	63.1	60.6
	3	62.7	62.1	62.0
	4	61.8	62.0	59.8
	5	63.4	62.5	60.3
	6	62.1	61.9	60.5
	Avg.	62.7	62.3	60.8
4—Hull fiber	1	51.2	49.7	48.9
	2	....	49.7	48.7
	3	53.4	50.0	50.7
	4	50.6	49.8	48.8
	5	55.4	50.3	48.6
	6	49.1	49.2	48.0
	Avg.	51.9	49.8	48.9
5—Hull fiber	1	58.4	57.4	56.8
	2	....	57.6	55.4
	3	57.4	57.7	57.2
	4	57.5	58.2	56.0
	5	58.7	58.4	55.3
	6	58.0	57.7	57.1
	Avg.	58.0	57.8	56.3
6—Hull fiber	1	62.3	61.9	59.6
	2	....	61.8	60.3
	3	63.3	62.2	61.9
	4	63.6	62.8	60.2
	5	64.5	63.8	60.8
	6	61.3	61.2	59.9
	Avg.	63.0	62.3	60.5

Proposal No. 1 is a modification or a clarification of Part 6 in the Cellulose Yield Procedure. The method as written is not too clear as to what to do if the screen end is plugged by lint, as happened with low yield cellulose. It has been found that it is necessary completely to drain the digesting liquors from low yield cellulose; otherwise the screen end will plug. There are several ways to do this, and some laboratories have been using these procedures, which accounts for some laboratories obtaining good results—apparently by the standard procedure—while for other laboratories the screen will plug. The exact procedure used in Proposal No. 1 is given in recommendations for change at the bottom of this report. In Proposal No. 2 the standard A.O.C.S. method is followed with the exception that during the washing the cylinder is stopped twice, once after 15 seconds of washing and again after 45 seconds of washing. The top of the cylinder is removed and the pulp hand-squeezed and returned to the washer in both cases. Other than this change, the procedure is the same as the normal A.O.C.S. procedure.

It is noted that Laboratory No. 2 did not report any analyses for the standard A.O.C.S. procedure as it was claimed that the screen plugged in a number of instances which rendered the values useless.

An analysis of the above table showed the following: a) The overall averages of the different methods are significantly different:

Standard A.O.C.S.	56.1
Proposal No. 1	55.3
No. 2	53.9

b) An analysis of each method separately shows:

	Laboratory No.	Average Yields
A. Standard A.O.C.S.	1	56.1
	2	......
	3	56.4
	4	55.3
	5	58.0
	6	54.7
Conclusion: No agreement between any laboratories.		
B. Proposal No. 1	1	55.2
	2	55.1
	3	55.4
	4	55.3
	5	55.7
	6	54.8
Conclusion: Good agreement.		
C. Proposal No. 2	1	54.2
	2	53.7
	3	55.1
	4	53.5
	5	53.4
	6	53.5
Conclusion: Four agree, two differ.		

Since we can expect to obtain some low yield linters and hull fiber in the future, the committee recommends that Part 6 of the Cellulose Yield Procedure be rewritten to include the method used in Proposal No. 1. The following paragraph is therefore recommended to be included as Part 6 of the Cellulose Yield Washing Procedure.

Remove the sample from the autoclave and add sufficient water to fill the digester container. Pour the mixture directly into the lower half of the lint washer. Rinse the sample container with enough water to insure a complete transfer of all fiber and pour into the washer. Fill lower half of washer with water, approximately 2,300 cc. Attach the upper portion of the cylinder, and turn by hand the screened end of washer down and allow the water to drain. After draining, the position of the washing cylinder is reversed and the closed cylinder is then filled with water through the perforated tube. The cylinder is then reversed and water allowed to drain through the sieve end. Start washer after last draining and open water valve. Observe the time at which the water turned on. Maintain the water pressure constant at 22 pounds per square inch and at a rate of 3.9 to 4.0 gallons per minute. Wash for 5 minutes.

TABLE III

Sample	A.O.C.S. Standard	Proposed Procedure
First Cut Linters		
1	78.7	78.4
2	80.1	80.4
3	82.0	82.6
4	81.4	81.3
5	82.0	81.7
6	82.5	81.6
Average	81.1	81.0
Second Cut Linters		
1	69.8	69.8
2	70.3	69.8
3	70.3	71.4
4	68.9	68.6
5	68.6	68.9
6	69.5	69.5
7	70.1	69.8
8	72.3	72.6
9	72.0	72.6
10	71.2	71.2
11	67.2	66.6
12	68.6	68.6
13	69.5	69.5
14	69.5	69.2
15	69.3	69.9
Average	69.8	69.9

In order to be sure that this clarification of the procedure does not alter the values obtained with high yield linters, the following table shows the yield results obtained with the standard A.O.C.S. method and with the recommended procedure.

No differences were found between the two procedures with the high yield linters, but the proposed procedure can be used for both high and low yield linters and hull fiber whereas the Standard A.O.C.S. procedure, as now written, cannot be used without some clarification on the low yield celluloses.

Recommendations

We recommend that the proposed procedure, as outlined above, be adopted this year so that it can be used as soon as possible to clear up the discrepancies which are obtained at times by some laboratories on the low yield materials.

E. C. AINSLIE   E. H. TENENT
C. H. COX   P. A. WILLIAMS
W. S. HUDE   L. N. ROGERS, Chairman

Sieve Analysis of Ground Soybeans and Soy Flour[1]

IRMA J. BOLAM and F. R. EARLE, Northern Regional Research Laboratory,[2]
Peoria, Illinois

THE strong tendency to agglomerate, exhibited by soy flour, particularly those samples finely ground or containing oil, has prevented the satisfactory use of mechanical sieving to determine the particle size distribution.

Methods used in the past, when it has been necessary to get at least an approximate measure of the particle size, have included brushing the sample through sieves with a soft brush, washing the sample through with a liquid, usually carbon tetrachloride, and combinations of these two techniques. If an operator carefully standardizes his procedure, he can obtain consistent results on the coarser screens. As an example of the difficulties encountered in attempts to use finer screens however, three replicates of soy flour brushed through a 200-mesh sieve showed 18.8, 14.5, and 13.4% retained on the sieve. Other replicates of the same flour treated by a combination of washing and brushing showed 19.2, 12.9, and 15.0% retained. These data are in agreement with the statement of the Subcommittee on Soy Flour Sieving Methods that "the commonly-used brushing or shaking methods are not satisfactory" (1).

During testing of washing methods a procedure was developed which has given acceptable, though not perfect, results. The apparatus (Figure 1) consisted of an aluminum sprinkler, such as is commonly used in the home laundry, connected by Tygon tubing to a 4-liter aspirator bottle in which air pressure was controlled by a finger placed over a vent in a compressed air line. The sprinkler was mounted above a 10-inch glass funnel which collected the used liquid and discharged it into a container. The operation should be carried out in a hood or in a well-ventilated place.

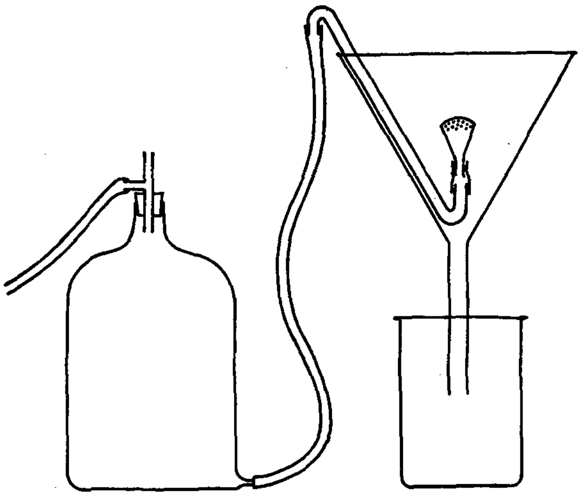

FIG. 1. Sieve-washing apparatus.

For the determination, two-gram samples of the ground soybeans or flour were suspended in 50 ml. of carbon tetrachloride and, unless low in fat, were allowed to stand 30 minutes. Lumps were broken with a stirring rod, and the sample transferred with additional liquid to a standard three-inch sieve. The sieve was held over the sprinkler and the sample was washed by directing a spray of carbon tetrachloride against the bottom of the screen with enough force to cause the liquid to penetrate the screen but not enough to cause splashing over the top of the sieve. After having been washed with from two to four liters, the residue was transferred to a Selas XFF crucible, dried at 100°C. for one-half hour, cooled, and weighed. (The Selas crucible was used because it can be cleaned by ignition.)

Data obtained in comparing two laboratory mills are presented in Table I to illustrate the results produced by the method. The hammermill was one de-

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[1] Presented at the San Francisco fall meeting, American Oil Chemists' Society, Sept. 26-28, 1950.

[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.