A Study of The Possible Catylytic Effect

Of some metal and alloys on the changes occurring in crude cottonseed oil during storage

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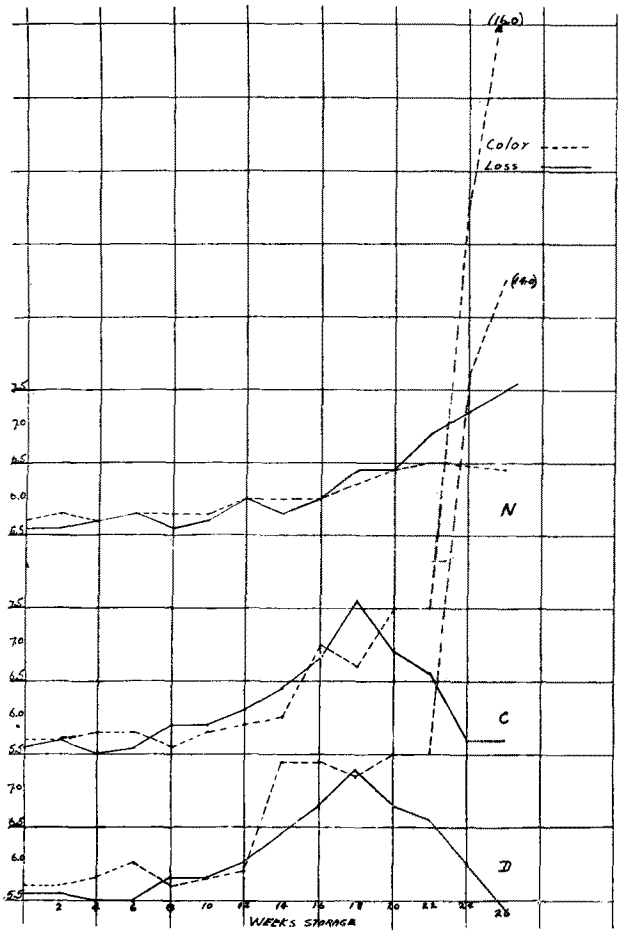
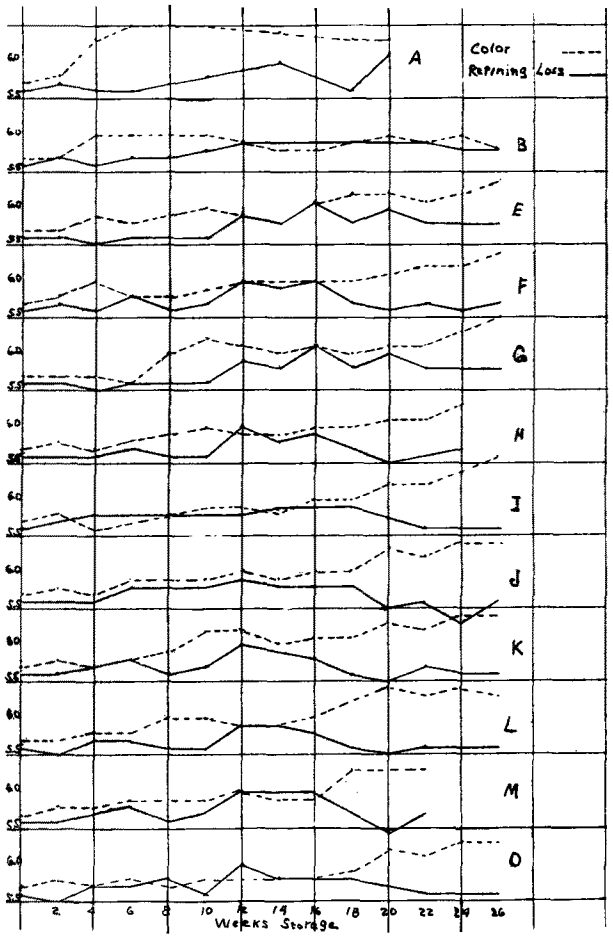
THE development of peroxides in lard due to the presence of various metallic soaps was presented before this society in a paper by King, Roschen and Irwin (1) two years ago. That certain metals or alloys containing certain metals have a decided influence on the keeping qualities of the lard as determined by the peroxide value is borne out by the results obtained both by using metallic soaps dissolved in the lard and by immersing strips of the metal in the heated fat. Although the authors declined to draw definite conclusions from the work done, they listed the metals in the order of activity when dissolved in the lard as soaps as follows: Copper, Iron, Zinc, Aluminum, Lead, Tin; when in contact with the sheet metal the order of activity is: Copper, Lead, Zinc, Tin, Iron and Aluminum.

The object of this paper is to give the results of refining tests on crude cottonseed oil stored in various metal containers over a period of six months, in an attempt to determine if a catalytic action may proceed on the oil in contact with the metals which may either inhibit or increase deterioration of the oil when stored under normal conditions.

We had hoped in the beginning to procure an oil in our work which had the tendency to go "off" in quality, but unfortunately from the results obtained the oil used reacted quite stable throughout the tests, making it impossible to draw any conclusions as to definite inhibitions.

In practice, ordinary tank steel is used for storage purposes, due probably to lower costs and ease of fabrication. However, we have included in our tests some metals which would be prohibitive in cost. We have done this purely from an experimental standpoint, believing that the results might not only prove of interest but may lead to a bet-





ter understanding in the selecting of materials for crude storage tank construction. Furthermore, it is our desire to extend these storage tests, while we have the containers, using refined cotton seed oil, noting any changes in free fatty acid, color, bleach and perhaps the peroxide value.

The metals used in this test are given in the following table:

TABLE I

Specimen	Metal	Composition
A	Hastelloy "A"	Mo 18-22%, Fe 18-22%, Ni balance
B	Everdur "A"	Tinned
C	Everdur "A"	Cu 96, Si 3, Mn 1
D	Deoxidized Copper	
E	Nickel	99-99.5%
F	Monel	Ni 65-70%, Cu 26-30%, Fe less than 3%
G	Inconel	Ni 80, Cr 14, Fe 6
H	Aluminum	High purity
I	Aluminum	Commercially pure
J	Armco	18-8 (Stainless)
K	Armco	17 (Stainless)
L	Armco	Ingot iron
M	Allegheny Metal	
N	Galvanized Iron	
O	Glass Bottle (Enameled black to exclude light)	

Although specimens H & I are quite similar in composition, it was suggested by the manufacturers that we compare the pure and commercially pure grades, believing that certain impurities may tend to vitiate the effect as produced by the pure metal.

Specimen B, the Everdur "A" (tinned), was submitted for use in the tests, but obviously the base metal did not enter into the tests since the oil was in contact only with the tin surface. Similarly in specimen N only the zinc coating would affect the oil since the coating was unbroken.

For control specimen a clean glass bottle of dimensions similar to the other containers was used, the outside of which was painted with black enamel to exclude light.

In order to maintain similar conditions throughout the test period all containers with but one exception were of same dimensions, namely, 10 inch diameter and 9 inch depth (three gallons in volume). By keeping the volume surface ratio constant all samples would be subjected to oxidation alike. Although all samples were loosely covered to keep out dirt and other contamination a dead rat was discovered in container "N" about the twelfth week, which fact probably accounts for the increase in free fatty acid and accompanying refining loss and color. All samples were well stirred with glass rods kept in each container throughout the tests. All refinings were made according to rules of the National Cottonseed Products Association, except that only one refining was made at each period.

With reference to the maximum loss curves, there is some question as to whether this is real. During this time the temperatures were lower and it is reasonable to suppose that less oil would drain off. However, there was a slight apparent change in the foots at this time. A small amount of oil was recovered after heating in several instances. This only occurred during the period showing the higher losses.

Since little change was expected in the bleaching quality of the refined oil only occasional bleach tests

TABLE II

Tests on Original Oil (Hydraulic); F.F.A—1.7; Loss—5.6; Color—55 Y, 5.7 R; Bleach—2.0 R.

	Time—2 Wks. Oil Temp. 19° C.			Time—4 Wks. Oil Temp. 19° C.			Time—6 Wks. Oil Temp. 19° C.			Time—8 Wks. Oil Temp. 19.5° C.			Time—10 Wks. Oil Temp. 25° C.			
	FFA	Loss	Color	FFA	Loss	Color	FFA	Loss	Color	FFA	Loss	Color	FFA	Loss	Color	Bleach
A	1.7	5.7	5.8	1.7	5.6	6.3	1.7	5.6	6.5	..	..	..	1.7	5.8	6.5	2.1
B	1.7	5.7	5.7	1.7	5.6	6.0	1.7	5.7	6.0	1.7	5.7	6.0	1.7	5.8	6.0	2.0
C	1.7	5.7	5.7	1.7	5.5	5.8	1.6	5.6	5.8	1.7	5.9	5.6	1.6	5.9	5.8	..
D	1.7	5.6	5.7	1.7	5.5	5.8	1.7	5.5	6.0	1.6	5.8	5.7	1.7	5.8	5.8	..
E	1.7	5.6	5.7	1.7	5.5	5.9	1.6	5.6	5.8	1.6	5.6	5.9	1.7	5.6	6.0	..
F	1.7	5.7	5.8	1.7	5.6	6.0	1.7	5.8	5.8	1.6	5.6	5.8	1.7	5.7	5.9	..
G	1.7	5.6	5.7	1.7	5.6	5.7	1.6	5.5	5.6	1.6	5.6	6.0	1.7	5.6	6.2	..
H	1.7	5.6	5.8	1.6	5.6	5.7	1.7	5.7	5.8	1.7	5.6	5.9	1.7	5.6	6.0	..
I	1.7	5.7	5.8	1.6	5.8	5.6	1.7	5.8	5.7	1.6	5.8	5.8	1.7	5.8	5.9	..
J	1.7	5.6	5.8	1.6	5.6	5.7	1.7	5.8	5.9	1.7	5.8	5.9	1.7	5.8	5.9	..
K	1.7	5.6	5.8	1.6	5.7	5.7	1.7	5.8	5.8	1.7	5.6	5.9	1.7	5.7	6.2	..
L	1.7	5.5	5.7	1.7	5.7	5.8	1.7	5.7	5.8	1.7	5.6	6.0	1.7	5.6	6.0	..
M	1.7	5.6	5.8	1.7	5.7	5.8	1.7	5.8	5.9	1.7	5.8	5.9	1.7	5.7	5.9	..
N	1.7	5.6	5.8	1.7	5.7	5.7	1.7	5.8	5.8	1.7	5.6	5.8	1.7	5.7	5.8	..
O	1.7	5.5	5.8	1.7	5.7	5.7	1.7	5.7	5.8	1.7	5.8	5.7	1.7	5.6	5.8	..

	Time—12 Wks. Oil Temp. 19° C.				Time—14 Wks. Oil Temp. 19° C.				Time—16 Wks. Oil Temp. 16° C.				Time—18 Wks. Oil Temp. 24° C.			
	FFA	Loss	Color	Bleach	FFA	Loss	Color	Bleach	FFA	Loss	Color	Bleach	FFA	Loss	Color	Bleach
A	..	..	..	..	1.7	6.0	6.4	..	..	..	..	..	1.7	5.6	6.3	2.1
B	1.7	5.9	5.9	2.0	1.7	5.9	5.8	..	1.7	5.9	5.8	..	1.7	5.9	5.9	2.1
C	1.6	6.1	5.9	2.1	1.6	6.4	6.0	..	1.6	6.8	7.0	..	1.6	7.6	6.7	2.8
D	1.7	6.0	5.9	2.1	1.6	6.4	7.4	..	1.6	6.8	7.4	..	1.6	7.3	7.2	3.0
E	1.7	5.9	5.9	2.0	1.6	5.8	5.8	..	1.7	6.1	6.1	..	1.7	5.8	6.2	2.1
F	1.7	6.0	6.0	2.0	1.7	5.9	6.0	..	1.7	6.0	6.0	..	1.7	5.7	6.0	..
G	1.7	5.9	6.1	..	1.6	5.7	6.0	2.1	1.7	6.0	6.1	..	1.7	5.6	6.0	..
H	1.7	6.0	5.9	..	1.7	5.8	5.9	2.0	1.7	5.9	6.0	..	1.7	5.7	6.0	..
I	1.7	5.8	5.9	..	1.6	5.9	5.8	2.0	1.7	5.9	6.0	..	1.7	5.8	6.0	..
J	1.7	5.9	6.0	..	1.7	5.8	5.9	2.1	1.7	5.8	6.0	..	1.7	5.8	6.0	..
K	1.7	6.0	6.2	..	1.6	5.9	6.0	..	1.7	5.8	6.1	2.1	1.7	5.6	6.1	..
L	1.7	5.9	5.9	..	1.6	5.9	5.9	..	1.7	5.8	6.0	2.0	1.7	5.6	6.2	..
M	1.7	6.0	6.0	..	1.6	6.0	5.9	..	1.7	6.0	5.9	2.0	1.7	5.7	6.2	..
N	1.7	6.0	6.0	..	1.7	5.8	6.0	XX	1.8	6.0	6.0	2.1	1.9	6.4	6.2	..
O	1.7	6.0	5.8	..	1.7	5.8	5.8	..	1.7	5.8	5.8	2.0	1.7	5.8	5.9	..

XX Rat Discovered.

	Time—20 Wks. Oil Temp. 26° C.				Time—22 Wks. Oil Temp. 23° C.				Time—24 Wks. Oil Temp. 26° C.				Time—26 Wks. Oil Temp.			
	FFA	Loss	Color	Bleach	FFA	Loss	Color	Bleach	FFA	Loss	Color	Bleach	FFA	Loss	Color	Bleach
A	1.7	6.1	6.3	X	..	..	..	..	..	..	..	..	..	..	..	..
B	1.7	5.9	6.0	..	1.7	5.9	6.0	..	1.7	5.8	6.0	2.1	1.7	5.8	5.9	2.1
C	1.5	6.9	7.5	X	1.5	6.6	7.5	..	1.4	5.7	13.0	4.4	1.4	5.7	16.0	6.1
D	1.7	6.8	7.5	X	1.5	6.6	7.5	..	1.4	6.0	12.7	4.3	1.4	5.4	14.0	6.0
E	1.7	6.0	6.2	..	1.7	5.8	6.1	..	1.7	5.8	6.2	2.2	1.7	5.8	6.4	2.2
F	1.7	5.6	6.1	..	1.7	5.7	6.2	2.3	1.7	5.6	6.2	..	1.7	5.7	6.4	2.2X
G	1.7	5.6	6.1	..	1.7	5.7	6.1	2.2	1.7	5.6	6.3	..	1.7	5.8	6.5	2.2
H	1.7	5.5	6.1	..	1.7	5.6	6.1	2.2	1.7	5.7	6.3	..	..	..	..	..
I	1.7	5.5	6.2	..	1.7	5.6	6.2	2.2	1.7	5.6	6.4	..	1.7	5.6	6.6	2.2
J	1.7	5.5	6.3	..	1.7	5.6	6.2	2.2	1.7	5.3	6.4	..	1.7	5.6	6.4	2.2
K	1.7	5.5	6.3	..	1.7	5.7	6.2	2.2	1.7	5.6	6.4	..	1.7	5.6	6.4	2.2
L	1.7	5.5	6.4	..	1.7	5.6	6.3	2.2	1.7	5.6	6.4	..	1.7	5.6	6.3	2.2
M	..	..	..	..	1.7	5.7	6.2	2.2	..	..	..	..	..	..	..	..
N	2.0	6.4	6.4	..	2.0	6.9	6.5	2.4	..	..	..	..	2.2	7.6	6.4	2.4
O	1.7	5.7	6.2	..	1.7	5.6	6.1	2.2	1.7	5.6	6.3	..	1.7	5.6	6.3	2.2

X Flavor rancid.

were run as indicated in Table II. The flavor of all samples was "Prime" except where noted.

A peculiar condition arose in the last two refinings for specimens C & D. A gelatinous mass having a darker red color than the oil formed in the refined oil which disappeared upon warming. The warmed oil was passed through a single filter paper, but the resulting oil appeared so cloudy in the color tube that a true reading could not be obtained. Upon filtering the oil at room temperature through two papers the gel was retained, whereupon the clear filtrate was read at 35 Yellow, 7.8 Red. The iodine number of the gel thus obtained was 107.0 as compared to 110.0 of the filtered oil. From the appearance of the gel and its lower iodine number we believe it to be a polymerized body probably resulting from a catalytic action of the copper on the oil. The gelatinous mass, however, did not appear in the filtered bleached oil, which of course was filtered hot. Whether this material was rendered more fluid again or whether the earth prevented its passing through the filter, we could not determine.

The interior of both containers C & D was well coated with a dark green copper soap insoluble in the crude but readily soluble in both chloroform and gasoline. This, no doubt, explains the reduction of the free fatty acid in these two samples. From the work of King, Roschen and Irwin (1) we attribute the early development of rancidity of both these oils to their contact with the copper. A decided rancidity was later found in the sample stored in container "F" which is composed of about 30 per cent copper. The only other case of rancidity was in the oil stored in container "A," although this alloy is supposedly free of copper. The remainder of the samples, while not quite as sweet as at the beginning, still in our opinion would be classed as "Prime" under the refining rules. Examination of the containers after the tests revealed no corrosive action except in containers C & D.

From the series of tests run no definite conclusions can be drawn except that in the case of copper and copper bearing alloys, neither should be used in contact with crude cotton seed oil.

In the use of Hastelloy "A" a slight increase of color over the control was noted with an attending increase in rancidity, but no decided increase in refining loss was detected.

Catalysis is suspected in the formation of a gel in the use of Deoxidized copper and Everdur "A" metals, the gel having the appearance and test of a polymerized oil.

In conclusion we express our sincere appreciation to the following manufacturers who have made possible these tests by furnishing and fabricating the necessary containers:

The Allegheny Steel Co., Brackenridge, Pa.

The Aluminum Cooking Utensil Co., New Kensington, Pa.

The American Brass Co., Waterbury, Conn.

The American Rolling Mill Co., Middletown, Ohio.

Haynes Stellite Co., Kokomo, Ind.

The International Nickel Co., Inc., New York, N. Y.

Wilson & Bennett Mfg. Co., Chicago, Ill.

Wyatt Metal & Boiler Works, Houston, Texas.

References:

(1) "The Accelerating Effect of Metals on the Development of Peroxides in Oils & Fats," by A. E. King, H. L. Roschen and W. H. Irwin; Oil & Soap, Vol. X, No. 11, p. 204.

REPORT OF

THE REFINING COMMITTEE

FOR THE SEASON OF 1934-1935

THE Refining Committee for the season 1934-1935 begs to submit the following report:

Tentative procedures for refining Peanut, Cocoanut and Corn Oil have been outlined and in use for a number of years. Your Committee recommends that the methods for refining these oils be now adopted as official methods of this Society. The methods are now designated as "Tentative" and are printed as part of our official methods.

There is a correction to be made in the printed method for Cocoanut Oil. In line with the results obtained and reported by Mr. Cluff on some fifty samples of crude cocoanut oil the amount of salt to be used shall be 0.1% for each 1.0% F.F.A. and the amount of lye reduced from 1.25 times the F.F.A. to 1.10 times the F.F.A. Temperature conditions have also been changed

The attention of the Committee has been directed to the variation in the characteristics of different lots of crude soya bean oil, some of which do not refine satisfactorily by the proposed method. We recommend that the work on methods for refining crude soya bean oil be continued next year.

There was a suggestion made a few years ago that on some cold pressed cottonseed oils better results were obtained with 22° Be. lye than with 20° Be. The Committee has been unable to obtain more than one sample of this type and we, therefore, recommend that since such types of cold pressed oil are so rare, they do not warrant an investigation by the Refining Committee.

Your Committee has not tested any additional brands of filter papers during the past season, but still believes that development of specifications for a suitable paper which will make it unnecessary to mention manufacturers' names or brands in the official methods is desirable.

Your Committee recommended to President Hutchins that the investigation pending of a method for determining traces of soap in refined cocoanut oil should be broadened to include all refined oils and a special committee be appointed to undertake this investigation. President Hutchins acted favorably on this suggestion and we believe a report on this subject will be submitted to