A Study Of The Possible Catalytic Effect Of Some Metals And Alloys On The Changes Occurring In Refined Cotton Seed Oil During Storage*

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LAST year the authors were privileged to report on "A Study of the Possible Catalytic Effect of Some Metals and Alloys on the Changes Occurring in Crude Cotton Seed Oil During Storage." This year a similar study is being reported, using refined cotton seed oil to complete the study of possible catalysis of the more common metals and alloys on this type of vegetable oil. The same containers used in the first series were used in the refined oil test.

In reviewing the previous paper, it was found that copper and copper bearing metals influenced both the color and flavor of the crude oil and produced toward the end of the storage period (5 months) a gelatinous substance, the iodine value of which indicated a polymerized body. The Hastelloy Metal (a molybdenun-iron-nickel alloy) also produced an undesirable effect, causing an early rancidity which became very pronounced with age. Of the remaining metals included in the experiment, no single specimen could be selected as being outstanding in quality based on the color and loss tests obtained.

The metals used in the present series of tests are shown in Table I with their approximate compositions.

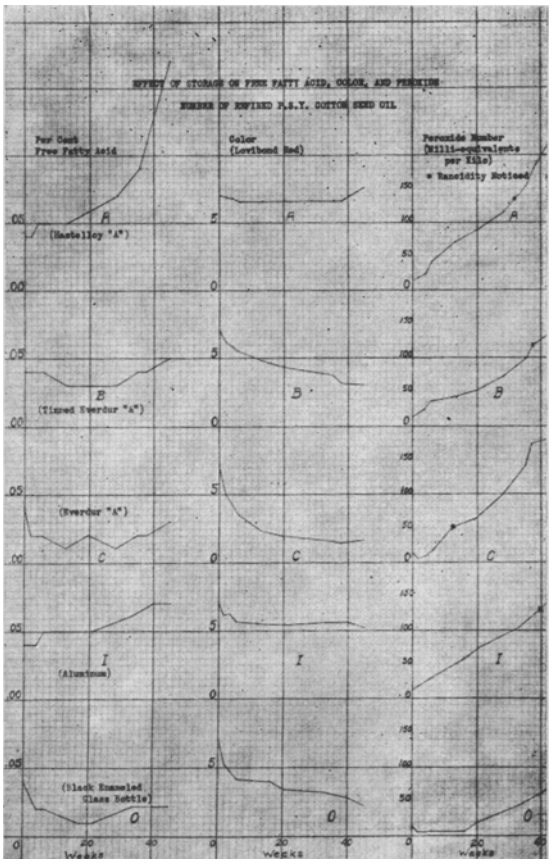

TABLE I

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).	

One of the tests included in this study was the determination of the peroxide value which was run according to the method described by King, Roschen and Irwin, OIL & SOAP, Vol. 10, p. 107. Any pronounced difference in the samples regarding this test should be attributed directly to the effect of the metal itself since all other factors affecting this test were the same for all samples. The containers were practically identical in size and shape, thus possessing the same ratio of exposed surface to volume. The temperature and light were also the same for all containers which were kept loosely covered for free access to the air with but one exception, namely, the glass bottle used for control. Thoughtlessly this sample was kept stoppered for the first seventeen weeks when it was noticed that there was no change in peroxide value excepting a lowering at the beginning. However, on substituting a plug of absorbent cotton for the stopper, a gradual rise immediately took place, continuing throughout the subsequent tests. Whether this apparent stability in peroxide content was actually due to the bottle being stoppered was not proved, but it would seem that it should not affect the oxidation since the bottle was only two-thirds full.

As in the case of the glass bottle, a considerable reduction in peroxide value was also noted in the Everdur "A" and the Deoxidized Copper containers during the first two weeks of storage, their values dropping from 12.8 to 4.5. Although no explanation is advanced for this reduction, an attending improvement in flavor was detected during this same period in these three samples. A similar improvement in flavor was also noted in the tinned container despite the fact there was a gradual increase in the peroxide test from the very beginning. This improved flavor was still noticeable in both the tinned and glass specimens for approximately three months, but the cop-

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TABLE II.

Tests on Original Oil (Hydraulic): Color—7.0 Red; Flavor—Prime; Bleach—2.5 Red F.F.A.—0.04; Peroxide Number—12.8.

Time—2 Weeks; Oil Temp. 35° C.

	Color	Flavor	Bleach	F.F.A.	Peroxide No.
A	6.8	Prime	2.5	0.04	17.9
B	6.2	Prime	2.4	0.04	19.1
C	5.0	Prime	2.2	0.02	4.5
D	5.0	Prime	2.2	0.02	4.5
E	6.4	Prime	2.4	0.04	17.8
F	6.2	Prime	2.4	0.04	19.3
G	6.4	Prime	2.5	0.04	16.7
H	6.3	Prime	2.4	0.04	19.0
I	6.1	Prime	2.4	0.04	17.0
J	6.1	Prime	2.4	0.04	19.6
K	6.1	Prime	2.4	0.04	19.0
L	6.2	Prime	2.4	0.04	19.6
M	6.0	Prime	2.4	0.04	19.3
N	6.0	Prime	2.4	0.04	19.9
O	5.2	Prime	2.4	0.02	2.1

Time—4 Weeks; Oil Temp. 34° C.

	Color	Flavor	Bleach	F.F.A.	Peroxide No.
	6.7	Prime	2.4	0.05	23.2
	5.9	Prime	2.3	0.04	22.6
	4.3	Prime	1.9	0.02	7.4
	4.0	Prime	1.9	0.01	9.6
	5.9	Prime	2.3	0.04	21.1
	5.9	Prime	2.3	0.04	21.6
	5.9	Prime	2.4	0.04	22.8
	5.9	Prime	2.4	0.04	28.0
	6.2	Prime	2.4	0.04	22.8
	6.2	Prime	2.4	0.04	25.1
	6.3	Prime	2.3	0.04	24.3
	6.3	Prime	2.3	0.04	25.6
	6.2	Prime	2.4	0.04	24.2
	6.0	Prime	2.3	0.04	23.9
	4.6	Prime	2.2	0.02	1.6

Time—6 Weeks; Oil Temp. 24° C.

	Color	Flavor	Bleach	F.F.A.	Peroxide No.
A	6.5	Prime	2.5	0.05	40.4
B	5.5	Prime	2.4	0.04	34.9
C	3.6	Prime	2.0	0.02	14.9
D	3.4	Prime	2.0	0.01	19.1
E	5.7	Prime	2.4	0.05	37.1
F	5.6	Prime	2.4	0.05	30.6
G	5.6	Prime	2.4	0.05	33.3
H	5.3	Prime	2.4	0.05	33.1
I	5.6	Prime	2.4	0.05	28.8
J	5.6	Prime	2.4	0.05	34.2
K	5.6	Prime	2.4	0.05	31.6
L	5.6	Prime	2.4	0 05	34.0
M	5.5	Prime	2.4	0.05	33.6
N	5.6	Prime	2.3	0.05	35.9
O	4.1	Prime	2.1	0.02	3.2

*Slightly rancid.

Time—16 Weeks; Oil Temp. 27° C.

	Color	Flavor	Bleach	F.F.A.	Peroxide No.
	6.5	Prime	2.5	0.05	69.1
	4.8	Prime	2.2	0.03	40.2
	2.3	*S. R.	1.8	0.01	49.2
	2.3	Prime	1.8	0.01	42.0
	5.8	Prime	2.4	0.05	52.0
	5.3	Prime	2.4	0.05	57.8
	5.6	Prime	2.4	0.05	54.8
	5.4	Prime	2.4	0.05	64.2
	5.4	Prime	2.4	0.05	57.9
	5.6	Prime	2.3	0.05	65.6
	5.6	Prime	2.3	0.05	63.5
	5.4	Prime	2.3	0.05	64.5
	5.4	Prime	2.3	0.05	69.4
	5.4	Prime	2.3	0.05	68.2
	3.9	Prime	2.1	0.01	2.7

Time—20 Weeks; Oil Temp. 19° C.

	Color	Flavor	Bleach	F.F.A.	Peroxide No.
A	6.5	Prime	2.5	0.06	87.3
B	4.3	Prime	2.2	0.03	50.5
C	1.9	*S. R.	1.7	0.02	62.6
D	1.9	*S. R.	1.7	0.01	52.8
E	5.8	Prime	2.4	0.06	60.5
F	5.2	Prime	2.3	0.05	60.1
G	5.6	Prime	2.3	0.05	58.6
H	5.4	Prime	2.3	0.05	69.8
I	5.4	Prime	2.3	0.05	70.3
J	5.7	Prime	2.3	0.05	75.4
K	5.8	Prime	2.3	0.05	74.2
L	5.4	Prime	2.3	0.05	75.6
M	5.6	Prime	2.3	0.05	81.3
N	5.4	Prime	2.3	0.05	82.1
O	3.3	Prime	1.9	0.01	17.0

*Slightly rancid.

Time—32 Weeks; Oil Temp. 20° C.

	Color	Flavor	Bleach	F.F.A.	Peroxide No.
	6.5	Prime	2.5	0.07	113.0
	4.0	Prime	2.1	0.03	71.7
	1.7	*S. R.	1.5	0.01	97.6
	1.6	*S. R.	1.4	0.01	84.2
	5.8	Prime	2.3	0.06	78.6
	5.3	Prime	2.3	0.06	86.5
	5.7	Prime	2.3	0.06	83.8
	5.4	Prime	2.3	0.06	99.6
	5.5	Prime	2.3	0.06	101.5
	5.7	Prime	2.3	0.06	110.0
	5.8	Prime	2.4	0.06	106.8
	5.5	Prime	2.4	0.06	110.2
	5.6	Prime	2.3	0.06	124.5
	5.5	Prime	2.3	0.06	116.0
	3.0	Prime	1.9	0.02	40.5

Time—39 Weeks; Oil Temp. 27° C.

	Color	Flavor	Bleach	F.F.A.	Peroxide No.
A	6.5	Rancid	2.5	0.09	175.0
B	3.1	*S. R.	2.2	0.04	118.0
C	1.4	Rancid	1.3	0.02	172.0
D	1.4	Rancid	1.3	0.02	131.0
E	5.6	*S. R.	2.3	0.07	114.0
F	5.3	Rancid	2.4	0.07	117.0
G	5.6	Prime	2.3	0.07	111.0
H	5.5	*S. R.	2.3	0.07	131.0
I	5.5	*S. R.	2.3	0.07	129.0
J	5.6	*S. R.	2.3	0.07	142.0
K	5.8	Prime	2.4	0.07	127.0
L	5.6	*S. R.	2.4	0.07	132.0
M	5.6	*S. R.	2.3	0.07	144.0
N	5.3	*S. R.	2.3	0.07	136.0
O	2.6	Prime	1.8	0.02	59.0

*Slightly rancid.

Time—45 Weeks; Oil Temp. 28° C.

	Color	Flavor	Bleach	F.F.A.	Peroxide No.
	7.6	Rancid	2.7	0.17	237.0
	3.0	Rancid	2.1	0.05	141.0
	1.7	Rancid	1.5	0.03	182.0
	1.4	Rancid	1.4	0.02	143.0
	5.3	*S. R.	2.3	0.07	130.0
	4.9	*S. R.	2.3	0.07	129.0
	5.3	*S. R.	2.3	0.07	130.0
	5.3	*S. R.	2.3	0.07	165.0
	5.2	*S. R.	2.3	0.07	152.0
	5.2	*S. R.	2.3	0.07	181.0
	5.3	*S. R.	2.3	0.07	175.0
	5.3	*S. R.	2.3	0.07	159.0
	5.4	*S. R.	2.3	0.07	182.0
	5.0	*S. R.	2.3	0.07	172.0
	2.3	Rancid	1.8	0.02	80.0

per container soon lost the sweet flavor, developing rancidity as early as sixteen weeks' storage.

As to the relation of the peroxide value to the development of rancidity, this seems to be fairly close with most of the metals, rancidity developing in the peroxide range of 114 to 140. Exceptions are Everdur and the Deoxidized Copper samples which became rancid at the values of 49.0 and 84.0, respectively, and the sample stored in glass which turned rancid between the values of 59 and 80.

The color in these two samples during the first sixteen weeks of storage was reduced from 7.0 red to 2.3, which was less red than the original bleached sample, and at forty-five weeks was reduced to 1.4 red. The average color of all other samples excepting that stored in the glass container was 5.4 red in forty-five weeks. During the same period the oil stored in glass had reduced to 2.3 red which compares quite favorably with the copper vessels.

With reference to the action of the copper on the fatty acids, attention is directed to the curves in the accompanying diagram showing the relative drop during the first four weeks from 0.04% to 0.02% for the Everdur and to 0.01% for the Deoxidized Copper. Both samples reached their minimum in thirty-two weeks, after which both samples started an upward trend. Again the glass container appears to retain its desirable effect in regard to the free fatty acid change the latter dropping consistently to a low of .01% in twenty weeks.

All the other metals and alloys which include the stainless steels, pure iron, pure nickel, nickel alloys, aluminum and zinc, react so nearly alike on the oil that there is little choice in selecting one over another from the standpoint of possessing properties inhibiting the deterioration of refined cotton seed oil, unless the improvement in color as in the case of the tinned coating would warrant the added expense of applying this metal to the lining of storage tanks to accomplish this end. For a graphical representation of this group the commercially pure aluminum was chosen and is shown in the diagram.

From the results of the tests conducted in this experiment the grouping of the metals and glass according to the best results obtained for each test at the end of thirty-nine weeks storage is shown in Table III.

TABLE III

Thirty-nine Weeks' Period.

Color	F. F. A.	Peroxide No.	Flavor
D	O	O	G
C	D	G	K
O	C	E	O
B	B	F	B
F	E	B	E
N	F	K	H
I	G	I	I
H	H	D	J
E	I	H	L
G	J	L	M
J	K	N	N
L	L	J	A
M	M	M	C
K	N	C	D
A	A	A	F