

on the benzene nucleus as in *o*-dimethylaminoethyl-*p*-octylphenol. In most cases methylation of the phenolic group in an aminophenol caused a tremendous loss of activity.

Discussion

In general, it was found, in accordance with stabilization studies on gasoline (8) and paraffin wax (6) that alkyl substitution enhanced the activity of phenol. Furthermore this effect was more than additive. Substitution in the meta position was less effective than in either the ortho or para positions. In agreement with work on other substrates (6,8) maximum potency was obtained with the trisubstituted phenols when the substitution occurred in the highly reactive 2, 4, and 6 positions.

Although alkyl substitution was effective in enhancing the activity of phenol, catechol, and pyrogallol, it was not effective for hydroquinone. Thus addition of two butyl groups to hydroquinone reduced the activity to zero under our experimental conditions. This is contrary to results obtained in other substrates. For example, 2,5-ditertiary butyl hydroquinone was found to be an extremely effective antioxidant for carotene when added to alfalfa meal (9). The reason for the ineffectiveness of this compound in mineral oil solution is not immediately apparent. Golumbic (4) has also shown that the stabilizing action of hydroquinone was finally lost with progressive nuclear methylation.

Conversely, 2-*t*-butyl-4-methoxyphenol (butylated hydroxyanisole), which is a very effective antioxidant for carotene in mineral oil solution, is only slightly effective in alfalfa meal (9). In the same way ethyl gallate, which is one of the best antioxidants tested for carotene in mineral oil solution, is completely ineffective for carotene in alfalfa meal under our experimental conditions (9).

Work with 2,5-di(2',4'-dihydroxyphenyl) hydroquinone affords a further illustration of the difficulties involved in attempting to correlate the results obtained with antioxidants when employed in different substrates. Thus Lovern (5) has shown this compound, which he called diresorcinylquinol, to be an active inhibitor for carotene in ethyl acetate solution whereas the present studies show it to be completely ineffec-

tive under our experimental conditions (Table III). It should therefore be emphasized that generalizations which may be made regarding nuclear substitution of phenolic inhibitors and their stabilizing effect apply only under the conditions studied. That the generalizations do not always hold is shown by comparison with other work. They may or may not apply to other systems.

Summary

Relative values for the carotene-stabilizing effects in mineral oil solutions of a number of phenolic-type antioxidants were determined. Certain relationships between molecular structure and antioxidant activity were observed. Alkylation of the phenolic compounds in general enhanced activity. Hydroquinone was shown to be an exception in the system studied.

Several antioxidants which have been accepted for use in lard have been found to be effective antioxidants for carotene in mineral oil solution. These include nordihydroguaiaretic acid, 2-*t*-butyl-4-methoxyphenol, alpha tocopherol, and esters of gallic acid. In addition, certain bisphenols used as anthelmintics were effective antioxidants for carotene.

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The Flavor Problem of Soybean Oil. VII. Effect of Trace Metals¹

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IN any consideration of flavor stability of fats the importance of trace metals is fully recognized because of the pro-oxidant effects of such impurities. Enhanced oxidation soon lowers the flavor quality and reduces the stability of the product. Although the problem of metal contamination is quite generally appreciated, its rather insidious and stealthy

nature has kept it from being regarded at its full importance. Work on fat stability and the greatly increased activity in the entire field of antioxidants has developed a greater interest in metallic contamination. The lack of adequate methods for determining metal concentrations of less than 1 p.p.m. has been, no doubt, one of the most serious handicaps workers have faced in making a complete evaluation of the metal problem.

The detrimental influence of copper in developing fishiness and other oxidized flavors in butter is well-

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established. The dairy industry takes extreme care to avoid copper contamination. Butter containing only 0.7 p.p.m. of copper will develop an oxidized flavor in 10 to 20 days while at concentration of 2 p.p.m. copper causes tainted flavors to develop in only two to four days. About 25 p.p.m. of iron is said to be equally deleterious (1). Zeils and Schmidt (8) have shown that metallic contamination introduced during deodorization greatly reduced the stability of a cottonseed oil shortening. Iron and boiler plate showed up poorly in this study. In tests of a series of nickel alloys (2) it was found that each increment in the copper content of the different alloys resulted in a further marked decrease in the stability of the oil. Storage studies with various metals and alloys showed that copper and alloys containing copper were the most detrimental to the stability of cottonseed oil (6). King, *et al.* (3), from studies on the stability of lard, concluded that all metals are deleterious and that copper is the worst.

Recent work in our laboratory has indicated that iron may be more detrimental than copper in the concentrations which occur in refined soybean oil. Studies with a trained taste panel to make the evaluations have shown that copper is detrimental to soybean oil when added in concentrations of only 1 part in 100 million, and iron is detrimental when present in concentrations of about 1 part in 10 million. Analytical methods with this degree of sensitivity were not available, and one of our first problems was to develop a method capable of determining iron and copper in these extremely low concentrations.

Experimental Procedure

Samples of soybean oil obtained at various times over the past four years from eight different soybean oil processors have been analyzed for their copper and iron content. These oils were received a) as salad oils or b) as refined, bleached, but undeodorized oils. Quantities ranged from 1 to 55 gallons. The laboratory-refined oils were produced from commercially extracted crudes and refined in small lots in the laboratory. Since all oils were for taste panel work, only edible grade oils of first quality were requested.

Cottonseed, peanut, and corn oil were received as salad oils. The less important oils listed were obtained from various sources as crudes and then laboratory refined. The particular mustard oil listed is a laboratory-extracted and refined oil obtained from seeds of known history and variety.

A high quality soybean oil which fortunately was very low in both iron and copper was used for the studies on the effects of added trace metals. Metals were added to the oil just prior to deodorization as a weak aqueous or alcoholic solution of the chloride salt. Preliminary work with iron at concentration levels of 3 p.p.m. showed no difference in activity whether the iron was added as iron stearate or as ferric chloride. The chloride salt was used in all cases except that of lead, in which the acetate was employed because of its solubility in alcohol. Highest grade chemicals were used throughout the study, but no spectrographic analysis was made on the purity of the salts. Addition of salts was made on the basis of metal content.

Metals occurring naturally in refined oils were determined by a spectrographic method, with beryllium as an added standard reference element. A descrip-

tion of the spectrochemical method employed for metal analysis in this work was recently presented (4). The Northern Regional Research Laboratory processing technique is set up to handle four samples at a time, with one of these always a control sample for the series (7). Organoleptic evaluation is made by the paired sample technique described previously by Moser, *et al.* (5).

Results

Copper and iron contents determined spectroscopically in refined soybean oils are shown in Tables I and II. Also tabulated are the peroxide values developed by the oils when held under A.O.M. conditions for eight hours, and the organoleptic flavor scores obtained immediately after deodorization and also after storage at 60°C. for three days. The copper content showed a variation from 0.3 parts per 100 million to 4.5 parts per 100 million; roughly, there was a ten-fold variation in all the oils examined. The range of copper in cottonseed oil did not appear different from that of soybean oil, nor was any difference observed between laboratory and commercial refining. Values for copper are in the range where deterioration can readily be detected organoleptically, i.e., when copper is catalytically present in concentrations of more than 1 part in 100 million.

TABLE I
Comparison of Metal Content and Stability Evaluations
of Soybean Oil

Sample No.	Metal Content		A.O.M.†		
	Fe PPM.	Cu PPM.	8 Hours-- 100°C.	0 Days	3 Days 60°C.
Commercial, Salad					
1	2.30	0.017	26	7.0	5.3
2	.25	.015	60	7.4	3.6
3	.085	.014	41	6.0	5.4
4	2.50	.045	35	8.4	6.3
5	1.70	.013	75	6.3	4.8
6	1.45	.025	5	8.0	7.2
7	.25	.014	61	5.6
8	.20	.013	67	3.5
9	.17	.013	26	6.6	5.3*
10	.054	.003	286	3.4	2.1*
Commercial, Undeodorized					
1	.19	.011	49	6.3	5.2
2	.042	.003	17	8.6	7.0*
3	.52	.022	44	6.7	3.7*
4	.08	.020	47	6.3	5.3*
5	.25	.006	16	8.0	5.5*
6	.21	.010	26	8.4	6.1*
7	.21	.006	18	8.8	6.5*
8	.093	.007	35	7.1	5.1*
9	.08	.011	58	6.7	4.6*
10	.14	.025	29	7.4	4.9*
Laboratory Refined and Deodorized					
1	.08	.016	6	8.2	6.2**
2	.19	.017	7	8.2	6.5**
3	.09	.010	18	8.4	5.6**
4	.08	.016	6	8.5	6.4*
5	.17	.005	11	8.8	6.3**
6	.03	.035	15	8.7	6.6*
7	.035	.014	5	8.1	7.3*
8	.12	.017	20	8.8	7.2*
9	.058	.004	15	8.3	6.3*
10	.18	.023	5	8.3	7.1*

† Peroxide values under A.O.M. conditions.

* Aged 4 days.

** Aged 6 days.

Iron was found present in quantities about 100 times greater than those of copper. The variation however from high to low value in these samples is about hundred-fold. If the five cottonseed oils can be accepted as typical, their content of iron is more uniform and equal to the lower values of the commercial edible soybean oils. Undeodorized commer-

TABLE II
Comparison of Metal Content and Stability Evaluations
of Refined Oils

Sample No.	Metal Content		A.O.M.†	Flavor Score		
	Fe PPM.	Cu PPM.	8 Hours—100°C.	0 Days	4 Days 60°C.	
Butter	11.4	0.72	
	13.6	.38	
Corn	.24	.008	7	4.5	5.3	
	.10	.015	
Cottonseed	0.75	0.017	24	7.9	4.7	
	.16	.016	14	7.1	5.2	
	.22	.023	40	8.5	4.0	
	.16	.014	30	8.0	6.4	
	.09	.012	30	7.4	6.1	
Mustard*	.083	.005	10	8.7	5.1	
	.045	.006	18	8.5	4.5	
Peanut	1.45	.012	
	.31	.009	10	8.7	6.7	
Rapeseed	1.47	.13	244	3.6	1.7	
Safflower*	.095	.003	97	8.0	5.1	
	.042	.011	46	9.4	5.8	
Sesame	.33	.021	28	7.5	4.3	
Sorghum	1.55	.041	54	5.0	3.9	
Sunflower	.35	.006	41	7.6	5.7	
	2*	.07	.004	31	7.4	3.9
	3*	4.20	.023	243	5.5	4.0

† Peroxide values under A.O.M. conditions.

* Laboratory refined oils.

cial oils and laboratory-refined soybean oils are more uniform and lower in iron content and equal to or lower in iron than the cottonseed oils. The iron and copper contents of soybean oil, presented in Tables I and II are plotted in Figure 1 to show more graphically the range in values of the two metals. The heavy concentration of points in the range of iron below 0.5 p.p.m. would indicate soybean oil of relatively low iron content can be obtained. The values for iron above that figure may lead one to suspect that the samples were from contaminated or improperly handled oils.

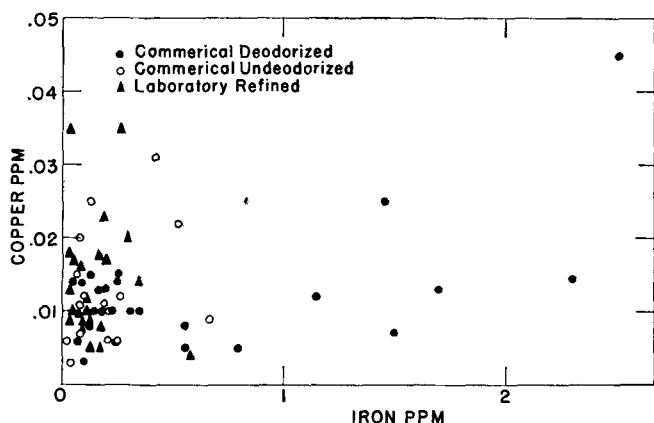


Fig. 1

It is readily seen from the data in Tables I and II that a very poor correlation would result between the oxidative or flavor stability values and the metal contents of the oils. Laboratory-refined samples have been consistently low in metal content, low in A.O.M. peroxide values, and high in flavor score. Commercial samples have been extremely variable in both their

metal contents and stability values. Numerous reasons can be given for these variable results, but the most important in reducing the expected correlation between metal content and stability of the commercial samples can be attributed to the fact that some of the processors use metal deactivators. If a high correlation were to be obtained between the iron or copper contents and the stability values for these oils, the high correlation would then mean that the metal scavengers were very inefficient. That a number of the oils contained added metal scavengers is definitely known, and since many metal scavengers are very efficient in reducing the A.O.M. peroxide values and increasing the stability of soybean oil, it must be concluded that any high correlation would be impossible. Other unpublished data obtained in the evaluation of several commercial deodorizers substantiate the effectiveness of metal deactivators in soybean oil.

This lack of correlation applies only to the commercial samples for which we did not have a complete history. Laboratory-refined oils, to which known amounts of iron were added, have shown high correlation between the iron content and the stability values of the oil. A similar correlation resulted when iron was added to commercially refined oils which are known to contain no added metal scavengers.

The effects of trace quantities of added iron on the oxidation and flavor stability of soybean oil are shown in Table III. The table also presents a typical organoleptic evaluation of four oils, one of which is a control or a standard for the series. The increasing deleterious effect with each increment of added iron is illustrated by a) the decreasing flavor score, b) the increasing peroxide value at the time of each testing, and c) the increasing peroxide values developed in 8 hours under A.O.M. conditions. Each of the three sets of data shows excellent correlation between iron content and the decrease in stability of the oil. Other pertinent data shown in this table illustrate how destructive iron contamination can be to soybean oil in only three hours at elevated deodorization temperatures of 210°C. "Zero time" organoleptic evaluations, performed within a few hours after deodorization, have shown that 0.3 p.p.m. of added iron are very detrimental if present during deodorization. This amount of iron so affects the oil during deodorization that the taste panel invariably detects

TABLE III
Effect of Trace Quantities of Iron on the Stability
of Soybean Oil

1 1.0 PPM. Fe	2 0.3 PPM. Fe	3 0.03 PPM. Fe	4 Control	Sig. Diff. ¹
0 Time				
4.6(0.35) ²	6.1(0.40)	8.5(0.31)	8.1(0.20)	1+2**3+4 3**1**4**2
4 Days—60°C.				
3.1(4.60)	6.4(4.33)		6.9(1.15)	**
3.3(4.65)				**
	5.3(4.32)	6.5(2.33)		*
		6.5(2.28)		**
4.0(4.80)	6.0(4.62)		7.4(1.31)	**
		6.4(2.33)	7.1(1.16)	+
Peroxide Values (A.O.M. Conditions—8Hrs.)				
144	60	32	13

¹+ No significant difference.

* Significant difference (5% level).

** Highly significant differences (1% level).

²Peroxide value at time of organoleptic evaluation, shown in parentheses.

its effect in samples fresh from the deodorizer. In this particular example the high quality oil used has been reduced in quality to a score that is barely acceptable while the addition of 1 p.p.m. of iron has reduced the quality below acceptable standards. The addition of only .03 p.p.m. of iron had an effect on the oxidative stability of this oil, as shown by both sets of peroxide data. Organoleptically however the taste panel could detect no difference between this oil and the control at either the zero time evaluation or after storage. The control oil used in these experiments had a natural content of .015 p.p.m. of iron, an amount insufficient to affect the result of any of the samples containing added iron.

The effects of iron contamination on soybean and cottonseed oils held in storage at 60°C. for extended periods are shown in Table IV. When 0.3 p.p.m. of

TABLE IV
Effect of Iron on the Stability of Cottonseed and Soybean Oils

1 Cottonseed +0.3 PPM. Fe	2 Cottonseed	3 Soybean +0.3 PPM. Fe	4 Soybean	Significant Difference ¹
0 Time				
8.4(0.25)	8.4(0.35)	6.0(0.50)	7.8(0.40)	1+2**3**4 3**1+4+2
5 Days—60°C.				
4.9(21.9)	5.1(26.3)	3.4(13.1)	5.1(5.9)	1+2**3**4 3**1**4+2
8 Days—60°C.				
5.1(34.1)	5.7(38.3)	3.9(19.1)	5.3(10.1)	1+2+3**4 3+1+4+2
10 Days—60°C.				
4.0(54.9)	4.8(41.9)	3.2(19.3)	4.0(14.8)	1+2*3+4 3+1+4+2
Peroxide Values (A.O.M. Conditions—8 Hrs.)				
29	17	44	14

¹+ No significant difference.

* Significant difference (5% level).

** Highly significant difference (1% level).

²Peroxide value at time of organoleptic evaluation, shown in parentheses.

iron has been added to both a cottonseed oil and a soybean oil, a blank of each oil completes the series of four, for a unit deodorization. Again the destructive nature of iron to soybean oil during deodorization is observed while no such destructive effects are noticed for cottonseed oil. No difference is observed in any comparison made between the stored cottonseed oil and the stored cottonseed oil containing 0.3 p.p.m. of added iron. It may be concluded from this

experiment that iron in concentrations of 0.3 p.p.m. is not destructive to cottonseed oil under these storage conditions. The A.O.M. peroxide value for the sample of cottonseed oil containing iron is somewhat greater, but the storage peroxides do not show any great variation. The effect of iron on soybean oil is considerably different. Deodorization in the presence of iron shows a highly significant difference between the control and the sample containing added iron. This difference between samples becomes more pronounced as the storage time is lengthened to five and eight days. Finally both samples become so bad that after 10 days no difference is discernible. The oxidative results likewise are considerably different from those for cottonseed oil. The sample containing iron had peroxide levels at about twice those of the control. The A.O.M. peroxide values of the sample containing iron was about three times that of the control.

Flavor descriptions and the taste response have not been presented for any of the previous experiments, but in storage experiments with soybean oil containing added iron the taste responses were so informative and descriptive that a summation of them is presented in Table V. The intensity levels of the tasters' responses, whether weak, moderate, or strong, are not being considered in this discussion.

The undesirable off-flavors developed in aged soybean oil are generally characterized as painty, grassy, fishy, etc., as against the development of a typical oxidative type of rancidity normally associated with lard or cottonseed oil and simply described as rancid. The development of rancid responses in soybean oil follows a normal expected development. After five days of storage the sample of soybean oil without added iron is typically rancid with no off-flavors and with a flavor score identical to cottonseed oil. The flavor descriptions for the iron-containing soybean oil after five days show a high number of rancid responses, but the soybean off-flavor responses are rapidly developing. It is not until the eighth day that painty responses develop in the control sample while the number of rancid responses remain about the same. The eight-day sample containing iron has almost as many painty responses as rancid responses. After 10 days of storage the sample containing iron has 12 painty responses to six rancid. At this stage of deterioration the painty responses are so strong that they mask the milder rancid taste. After 10 days the blank is still predominantly rancid but with increasing off-flavor development. The painty, grassy, and fishy responses are summarized and tabulated as off-flavors at the bottom of Table V. With an adjacent tabulation of rancid responses, the trend of the

TABLE V
Flavor Descriptions of Soybean Oil After Storage With and Without Added Iron

Taste Panel Flavor Responses	0 Time		5 Days—60°C.		8 Days—60°C.		10 Days—60°C.	
	Blank	0.3 PPM. Fe	Blank	0.3 PPM. Fe	Blank	0.3 PPM. Fe	Blank	0.3 PPM. Fe
Bland.....	2	0	0	0	0	0	0	0
Buttery.....	2	1	2	1	2	0	0	0
Beany.....	8	9	3	3	2	2	2	4
Rancid.....	1	3	10	8	8	11	9	6
Painty.....	2	5	3	8	4	9
Grassy.....	3	1	1	0	1	1
Fishy.....	1	1	1	1	2
Metallic.....	1	4	1	1	1	1	0
Burned.....	5	5	2	2	3	1
Rancid.....	1	3	10	8	8	11	9	6
Off-Flavors.....	0	6	0	7	4	9	6	12
Flavor Score.....	7.8	6.0	5.1	3.4	5.3	3.9	4.0	3.2
Peroxide Value.....	0.40	0.50	5.9	13.1	10.1	19.1	14.8	19.3

development of off-flavors as a result of iron contamination is readily seen.

Flavor response can be compared at equal peroxide levels by comparing zero time evaluations of the two samples, or by comparing a five-day storage soybean oil containing iron with the control which has been stored for 10 days. The first of these two comparisons show a high preponderance of off-flavors in the sample containing iron while the second comparison shows about equal rancidity and off-flavor responses. Flavor evaluation of oils on the basis of equal peroxide levels is also open to question, and a much more fundamental basis would be at equal oxygen absorption values. Iron appears to catalyze the formation of high peroxide levels while other metallic oxidation catalysts such as cobalt, chromium, and zinc do not produce high peroxide values in soybean oil. These last three catalysts, when used as driers in typical paint oils, do not produce high peroxide levels.

TABLE VI
Concentration Effects of Highly Injurious Metals on Soybean Oil

Metal	Metal Content, PPM.	A.O.M.†		
		8 Hours—100°C.	0 Days	4 Days 60°C.
Iron	3.0	200
	1.0	144	4.6	3.5
	.3	60	6.1	5.9
	.03	32	8.5	6.5
Copper	.3	205	4.2	1.8
	.03	30	8.2	5.2
	.003	24	9.0	6.9
Cobalt	3.0	98	7.6	3.0
	.3	21	9.1	7.1
	.03	20	9.1	7.0
Chromium	3.0	18	6.0	4.3
	.3	13	8.3	6.2
	.03	14	8.5	6.5
Control Oil No. 176	0.0	13	8.6	7.3

† Peroxide values under A.O.M. conditions.

The effects of the more injurious metals which we have investigated are shown in Table VI. The complete data presented in Table III for iron have been summarized in this table. Similar data have been obtained for copper, cobalt, chromium, and other metals. The results are summarized in Tables VI and VIII.

TABLE VII
Effect of Trace Quantities of Copper on the Stability of Soybean Oil

1 0.3 PPM. Cu	2 0.03 PPM. Cu	3 0.003 PPM. Cu	4 Control	Sig. Diff. ¹
0 Time				
6.5(0.37)	7.8(0.40)	8.8(0.40)	8.6(0.31)	1 * 2 * 3+4 3**1**4+2
4 Days—60°C.				
2.3(4.03) 2.0(3.93)	5.6(5.79)		6.9(1.23)	**
	4.5(5.68)	6.9(1.81)		**
2.4(4.39)		7.1(1.91)	7.3(1.45)	**
	5.2(5.90)		6.7(1.20)	**
		6.5(1.36)		+
Peroxide Values (A.O.M. Conditions—8 Hrs.)				
102	24	9	10

¹+ No significant difference.

* Significant difference (5% level).

** Highly significant difference (1% level).

Copper is extremely deleterious to the stability of soybean oil. Its effect is at least 10 to perhaps 100 times more detrimental than that of iron. Concentrations of copper at levels of 0.003 p.p.m. did not damage the oil to the extent that it could be detected by the taste panel at either zero time or after four days of storage at 60°C. The organoleptic evaluation of soybean oil containing added copper is shown in Table VII.

Cobalt, widely used as an excellent oxidation catalyst, was unexpectedly mild in its effects at concentrations below 0.3 p.p.m. under the conditions of these tests. A surprising thing about cobalt was the flavor response obtained from the sample containing 3 p.p.m. Almost all of the taste panel marked this sample extremely painty. This high agreement in panel responses further indicates that the off-flavor development is the result of a particular series of oxidation reactions catalyzed to a greater extent by metals than is the oxidation reaction resulting in rancid products.

The effects of chromium on the flavor and the stability of soybean oil are also given in Table VI. The effects are detrimental but to a less extent than with the other metals listed. The detrimental effect of metals as they occur naturally in soybean oil is probably in the same order as they are arranged in the table. Copper, of course, in equal concentrations would be much worse than iron. Until further experimentation shows that cobalt and chromium are found to occur naturally in detrimental concentrations in soybean oil, extensive organoleptic evaluations like those made for iron would not be profitable.

Metals with less effect on the stability of soybean oil are shown in Table VIII. This table shows that

TABLE VIII
Concentration Effects of the Less Injurious Metals on Soybean Oil

Metal	Metal Content PPM.	A.O.M.†		
		8 Hours—100°C.	0 Days	4 Days 60°C.
Aluminum	30	*55	6.2	4.3
Nickel	30	*49	6.6	4.5
Tin	30	*47	6.9	7.4
Ammonium	30	*59	6.5	4.6
Zinc	30	*196	2.4	2.5
	3	32	8.7	5.3
Lead	30	147	7.7	4.1
	3	*55	5.7	4.6
Calcium	30	82	7.5	4.7
	3	22	8.8	6.7
Magnesium	30	69	6.4	5.3
	3	57	8.3	5.4
Sodium	30	17	8.4	6.0
Control Oil No. 176	0	17	8.6	7.3
*Control Oil No. 168	0	49	6.3	5.2

† Peroxide values under A.O.M. conditions.

aluminum, nickel, and tin have the least effect on the quality and stability of the oil, substantiating the high regard of the food processing industry for these metals as the best materials available for equipment used for processing relatively unstable foods and food products.

However nickel added as a finely divided metal (as in the form of hydrogenation catalyst) to soybean oil just prior to deodorization of the oil has shown greater detrimental effects on oxidative stability of the liquid oil than has the addition of an equivalent amount of nickel in the form of its chloride salt. The effect of surface area on catalytic activity is well known and a similar effect on the rate of oxidation could logically be expected.

Both zinc and lead are detrimental, but it is doubtful if they are likely to occur in concentrations which would produce effects that could be detected organoleptically. Concentration effects that can be detected organoleptically are probably near the toxic level and for this reason further care is warranted in avoiding contamination. It has been stated that zinc is not detrimental to butter (2); however this does not hold true for soybean oil.

The effects of the alkaline-earth metals offer another problem primarily connected with refining and removal of soaps. Such metals are detrimental, and although investigation of their influence was not extensive, it is believed the effects are sufficiently important to warrant further studies.

Summary

The concentration of iron as determined spectroscopically in commercial soybean oils showed almost a hundred-fold variation. Values from 0.003 p.p.m. to a high of 2.50 p.p.m. of iron were obtained. The average for 12 edible oils was 0.90 p.p.m. of iron. Commercial undeodorized oils had an average iron content of only 0.19 p.p.m., and laboratory-refined samples had an average iron content of 0.12 p.p.m.

No correlation was found between the metal content and the stability of commercial edible soybean oil. This lack of correlation is attributed to the use of metal deactivators by some processors. A high correlation between stability and metal content has been shown in studies on both laboratory-refined soybean oils and oils containing added iron and other metals.

Iron added to soybean oil in concentrations of 0.3 p.p.m. was very detrimental to the oxidative and flavor stability. A.O.M. values for the sample containing 0.03 p.p.m. of added iron were higher than the control. Organoleptically however no difference between the two samples was discernible after three days of storage at 60°C. Taste panel flavor responses

showed that soybean oil containing added iron developed off-flavor responses very quickly while the oil containing no added iron first became predominantly rancid and later developed the off-flavors so typical of aged soybean oil.

Iron is a high temperature catalyst and at deodorization temperatures is very detrimental to soybean oil. Iron contamination also promotes the development of high peroxide values, in contrast to chromium, cobalt, and zinc. These last metals when present in relatively low concentrations do not produce high peroxide levels but promoted the formation of off-flavors.

Under similar conditions the effects of iron contamination on cottonseed and soybean oil showed that little change was produced in the cottonseed oil sample containing 0.3 p.p.m. of added iron, but very drastic changes, such as high peroxide values and low flavor scores, were produced in the soybean oil containing added iron.

Different concentrations of copper in soybean oil showed copper to be at least 10 times, but probably less than 100 times, more detrimental than iron. In soybean salad oil iron was more detrimental than copper when evaluated on the basis of actual amount of metal present in the oil. This was especially true for the oils containing the higher amounts of iron. The copper content was rather consistent in all oils examined regardless of the source or method of processing. This indicated little contamination from copper-containing equipment, and perhaps the amount of copper present was native to the bean and the oil.

All metal contamination is probably detrimental to the stability and quality of soybean oil and the less the contamination, the better the oil. Since oil must be processed in metallic equipment, the amount of contamination that cannot be avoided can be counteracted by the judicious use of metal deactivators.

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Improved Procedure for Cleaning Glassware Used in Determining the Stability of Fats and Oils by the Active Oxygen Method

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EXPERIENCE with the active oxygen method or accelerated stability test of King, Roschen, and Irwin (1) for determining the keeping quality or stability of fats and oils led various workers to the realization that rigid cleanliness of the glassware used in the test, and particularly the aeration and

sample tubes, was essential in obtaining reproducible results with replicated samples. In recognition of this fact the Committee on Analysis of Commercial Fats and Oils (2), in preparing for the Quartermaster Corps a standard method for determining the stability of fats and oils "incorporating the best technique known at the time," included specific directions for the preparation of a cleaning solution and

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