

In Graph VII are plotted the complete curves for formation and disappearance of trans isomers during the hydrogenation of cottonseed oil and edible beef tallow. Again these oils were hardened at 200°C. and 30 PSI of hydrogen, with 0.2% by weight of reduced nickel catalyst.

It is obvious that the slope of the curve for tallow is unusually steep, considering its low initial iodine number and the short range through which it can be hardened. In Table IV are shown data on samples taken at the peaks in trans isomer content for the various hydrogenations described in this paper. The percentage of the total number of double bonds in the trans form was estimated for each sample on the basis of its iodine number.<sup>2</sup> The figure for tallow (74%) is considerably higher than that for any of the other fats.

TABLE IV  
Maximum Percentage of Trans Isomers Formed

Fat	Catalyst	No.	% Trans isomers	% Total double bonds in trans form
Linseed.....	Ni	91	68	64
Soybean.....	Ni	66	42	55
Soybean.....	Pd	65	53	65
Soybean.....	Pt	75	16	19
Cottonseed.....	Ni	58	36	53
Olive.....	Ni	58	36	54
Lard.....	Ni	42	26	53
Tallow.....	Ni	28	24	74

This observation is especially interesting in view of the published method of Swern *et al.* for the preparation of oleic acid from partially hydrogenated tallow (13, 14). Using the conditions described by Swern for the selective hydrogenation of tallow, we obtained a product which contained almost half of its double bonds in the trans form. Furthermore, after the glycerides had been split with water, the

resulting fatty acids were not readily separable into cis and trans forms by low temperature crystallization from acetone. In fact, with a change in the conditions of hydrogenation to favor the formation of trans isomers, preliminary experiments showed promise of providing a new method for the synthesis of elaidic acid.

### Summary

Conditions which favor the selective hydrogenation of glyceride oils also favor the development of trans isomers. Complete curves are presented showing the formation and disappearance of trans isomers during the hydrogenation of linseed oil, soybean oil, cottonseed oil, olive oil, lard, and edible tallow, as determined by the infrared spectrophotometric method. An unusually high percentage of trans linkages develops during the hydrogenation of tallow.

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## The Flavor Problem of Soybean Oil. XIII. Sulfur Coordination Compounds Effective in Edible Oil Stabilization<sup>1</sup>

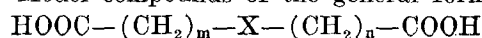
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SOYBEAN oil is subject to deterioration by the catalytic effects of pro-oxidant metals, such as iron and copper. The catalytic effect is destroyed by the formation of a metal chelate, and the efficiency of the chelate varies with the coordinating atom. A theoretical study has been made in which the coordinating atom of model compounds was varied and an order of effectiveness was established. The effectiveness of some nitrogen chelates was shown in a previous publication (22). A similar investigation of a number of sulfur compounds capable of metal chelation is presented in this communication.

The use of coordination compounds finds application in many industries where oxidation is promoted by trace metal contamination (4, 5, 15, 18, 25, 27). The

most common pro-oxidant metal encountered in soybean oil is iron, which occurs naturally in the oil in concentrations of about 0.8 part per million (10). Processing steps to which the oil is subjected may increase the iron concentration 4- to 8-fold. This increased iron content is associated with and is a cause for a greatly decreased flavor stability. Iron accumulated during processing has a much greater catalytic activity than iron native to the oil, and although improved processing conditions and the use of stainless and corrosion-resistant equipment offer a measure of control, damaging concentrations of iron still may persist. It is the role of the metal scavenger to inactivate the remaining traces of pro-oxidant metal.

Early work has emphasized that many acidic compounds capable of forming chelation complexes were effective stabilizers for edible oils (9, 22) and a systematized study with model compounds was undertaken. Model compounds of the general formula



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were prepared and evaluated. In this formula X can be sulfur, nitrogen, or oxygen, and m and n are 1 or 2. An alkyl or an aromatic group may be attached to the  $\alpha$ - or  $\beta$ -carbon atom.

Thiodiacetic acid yields chelates with 5-membered rings whereas the next higher homologue,  $\beta, \beta'$ -thiodipropionic acid, yields chelates with 6-membered rings. Compounds such as  $\beta$ -carboxymethylmercapto butyric acid yields chelates containing both 5- and 6-membered rings. A series of patents have been issued to Gribbins *et al.* (12) on the use of thio acids, especially thiodipropionic acid and its esters, as stabilizers in organic materials, foods, feeds, fats, and oils. The utilization of thiodialiphatic acids as anticorrosive and rust-inhibiting agents has been patented by Zublin (29). Kleinholz (14) has shown the effectiveness of thioaliphatic acids as adducts to turbine and hydraulic oils in preventing rusting.

The literature does not present a systematic study of the relative effectiveness of 5- or 6-membered chelates, nor has any comparison been made with the corresponding oxygen, nitrogen, and sulfur analogs. Charles and Freiser (7), in studies on the stability of chelates of o-aminophenol and of o-aminobenzene-thiol, indicate that the strength of the bond of metal with sulfur is greater than that with oxygen because of the lower electronegativity of the sulfur and consequent increase in covalent character of the bond. That sulfur is more nucleophilic than oxygen is illustrated by Hine (13) in his experiments on the reaction of the thiophenoxide ion with sodium bromoacetate. He found that the thiophenoxide ion does react a thousand times more rapidly than the hydroxyl ion. Fyfe (11) presents evidence that the more negatively charged an electrogenative atom becomes, the greater the stability of its metal coordination compounds. This increased stability results from a smaller difference in electronegativity between the coordinating atoms and gives increased covalent bonding. In a review on sulfur bonds Tarbell and Harnish (26) explain the acidity of some sulfur derivatives on the premise that sulfur compounds can have an increased number of resonance forms because the valence shell of sulfur is expanded to 10 electrons. Phillips, Hunter, and Sutton (21) and Wells (28) discuss some possible resonance structures in articles on the coordinate bond. It is possible however that factors other than electronegativity and resonance may contribute to the stability of the coordinate bond. Bailar (1) has cited evidence that the lighter metals (such as sodium and lithium) coordinate more readily with oxygen while the heavier metals (such as iron and copper) appear to favor sulfur coordination. That ionic size is a determining factor of the coordination number has been demonstrated by Sidgwick (24). A comprehensive review on metal chelation is presented by Diehl (8), and a more recent review of the coordination theory is given by Burkin (6).

### Experimental

The following sulfur compounds were evaluated for their effectiveness in stabilizing soybean oil against oxidative and flavor deterioration: thiodiacetic acid,  $\beta, \beta'$ -thiodipropionic acid, carboxymethylmercapto succinic acid, carboxymethylmercapto butyric acid, carboxymethylmercapto phenyl propionic acid, monoethyl ester of carboxymethylmercapto succinic acid, mono-octadecyl ester of carboxymethylmercapto succinic

acid,  $\alpha, \alpha'$ -thio-di-n-caproic acid, p-toluene sulfonic acid, and sulfur dioxide. Also included are  $\beta, \beta'$ -oxidipropionic acid and  $\beta, \beta'$ -iminodipropionic acid for comparison with  $\beta, \beta'$ -thiodipropionic acid.

Thiodiacetic acid was prepared by the method described by Barkenbus and Landis (2).  $\beta, \beta'$ -Thiodipropionic acid was prepared by acid hydrolysis of the corresponding  $\beta, \beta'$ -thiodipropionitrile as described by MacGregor and Pugh (16). The carboxymethylmercapto succinic acid was a commercial sample and is being produced in limited quantity at the present time. Carboxymethylmercapto butyric acid and carboxymethylmercapto phenyl propionic acid were synthesized by the addition of thioglycolic acid to crotonic acid and cinnamic acid, respectively.<sup>3</sup>

Monoethyl ester of carboxymethylmercapto succinic acid was prepared by the addition of thioglycolic acid to ethyl potassium maleate and subsequent acidification and extraction with ether. The octadecyl ester was prepared in a similar manner. Details of these preparations and those of carboxymethylmercapto butyric acid, carboxymethylmercapto phenyl propionic acid, and  $\alpha, \alpha'$ -thio-di-n-caproic acid will be described in a separate publication.

The evaluation of metal-deactivators consisted in determining their effect on the oxidative stability of the oil. If these tests proved satisfactory, a series of organoleptic evaluations were made according to the procedure of Moser *et al.* (19). The first evaluation of a compound for stabilizing activity was its performance in a screening test in which 0.01% concentration of the compound was added to soybean oil just prior to deodorization. In general, three treated samples and a control oil sample were deodorized simultaneously in an all-glass apparatus at 210°C. for 3 hours under a vacuum of 1 mm. or less (23). Effectiveness of each compound was measured by the peroxide development in the test sample in comparison with the control sample after 8 hours under A.O.M. conditions. Oils of poor stability, presumably high in iron and copper, were used in these tests so that the degree of effectiveness between compounds might be ascertained more readily.

The index of efficiency was obtained by dividing the peroxide value of the control sample by the peroxide value of the treated sample. Thus an index of 5 means that the compound was effective in holding the peroxide value to one-fifth that of the control for an 8-hour test under A.O.M. conditions. Compounds showing high activity may have an index between 3 and 10 in regular refined oils, but in the presence of added metals the index may rise as high as 80. After the activity has been established, the effect of concentration is determined both in the presence and absence of added iron and copper. Metallic ions were added to the oil prior to deodorization as an aqueous solution of the chloride salt.

### Results

Table I lists the oxidative stabilities of soybean oils treated with  $\beta, \beta'$ -oxidipropionic acid,  $\beta, \beta'$ -iminodipropionic acid, and  $\beta, \beta'$ -thiodipropionic acid. All these compounds are tridentate and give 6-membered rings with metals; the compounds differ only in the nature of the coordination atom. From the data of

<sup>3</sup>The addition of thioglycolic acid to a conjugate system is expected to take place as a 1-4 addition with rearrangements to give the  $\beta$ -carboxymethylmercapto derivative.

Table I it appears with  $\beta,\beta'$ -dipropionic acids that the order of effectiveness is  $S > N > O$ . This order is that of increasing electronegativity and suggests a decrease in the covalent character of the bond.

Oxidative data obtained with thiodiacetic acid and  $\beta,\beta'$ -thiodipropionic acid, both in the presence and absence of added metals, are listed in Table I. Both compounds are heat-stable and are effective when added on either the upgrade or the downgrade side of the deodorization. Although there is little evidence in the table in favor of a 5-membered chelate ring, it is generally agreed that the chelates which form 5-membered rings are more stable than those giving 6-membered rings. Indications were obtained in favor of the greater stability of the 5-membered ring system with the model compounds in which nitrogen and oxygen were the coordination atoms.

Table II gives the organoleptic evaluation of soybean oil stabilized by thiodiacetic acid, both in the presence and absence of added copper and iron. The oil samples to which copper or iron are added always show low flavor scores. On the other hand, higher flavor scores were obtained from the sample which had thiodiacetic acid added in addition to the metals, and the scores were of the same order of magnitude as that found for the control sample. In the latter experiment the metals were added before deodorization and the thiodiacetic acid added on the downgrade.

The results obtained with carboxymethylmercapto succinic acid are given in Table I. This acid is not heat-stable, and its use is limited to additions on the downgrade side of the deodorization. When added under these milder conditions, this compound is very effective against either iron or copper. This material may find wide application in edible products since it is reported to be non-toxic. A separate publication will present additional data obtained from both laboratory and pilot-plant experiments with carboxymethylmercapto succinic acid.

Table I lists the oxidative data with carboxymethylmercapto butyric acid and carboxymethylmercapto phenyl propionic acid. Both of these acids improved the oxidative stability, but the initial flavors of the oils were very undesirable.

To achieve oil solubility and still maintain the essential structure for effective complexing, two esters of carboxymethylmercapto succinic acid were investigated. The results with the monoethyl and monoctadecyl ester are listed in Table I. Although good oxidative stability and oil solubility were obtained, the ethyl ester imparted an objectionable flavor to the oil sample. However the octadecyl ester did not impart an objectionable flavor since a significant difference in flavor scores was not found when compared with the control sample. Neither the ethyl ester or the octadecyl ester are heat-stable, and their addition is limited to the downgrade side of the deodorization.

Another type of compound prepared to achieve oil solubility and effective metal deactivation was  $\alpha,\alpha'$ -thio-di-n-caproic acid. The results obtained with this compound are listed in Table I. While the results show good oxidative protection, the compound imparts a poor initial flavor. The  $\alpha,\alpha'$ -thio-di-n-caproic acid is oil soluble, and if the flavor problem can be solved, it should be a good metal deactivator for edible oils.

The data of Table III show that p-toluene sulfonic acid is an excellent metal deactivator for some com-

TABLE I  
Oxidative Evaluations of Soybean Oils Treated With Chelating Agents

Compound (0.01% concentration)	Initial flavor score	Peroxide values <sup>a</sup>	In- dex
Control oil A.....	8.6	41	
$\beta,\beta'$ -Oxidipropionic acid.....	8.9	27	1.5
0.3 p.p.m. Fe.....	4.9	97	
$\beta,\beta'$ -Oxidipropionic acid+0.3 p.p.m. Fe.....	8.7	38	2.6
Control oil B.....	....	47	
$\beta,\beta'$ -Iminodipropionic acid.....	....	21	2.2
0.3 p.p.m. Fe.....	....	240	
$\beta,\beta'$ -Iminodipropionic acid+0.3 p.p.m. Fe.....	....	31	7.5
Control oil D.....	8.5	32	
$\beta,\beta'$ -Thiodipropionic acid.....	8.9	6.4	5.0
0.3 p.p.m. Fe.....	5.4	150	
$\beta,\beta'$ -Thiodipropionic acid+0.3 p.p.m. Fe.....	8.3	22	7.0
Control oil C.....	8.7	28	
Thiodiacetic acid.....	8.5	5.4	5.1
0.1 p.p.m. Cu.....	6.8	74	
Thiodiacetic acid+0.1 p.p.m. Cu.....	8.3	18	4.0
Control oil B.....	7.6	57	
Thiodiacetic acid.....	8.2	11	5.1
0.3 p.p.m. Fe.....	4.6	240	
Thiodiacetic acid+0.3 p.p.m. Fe.....	8.4	14	17.0
Control oil E.....	8.2	57	
$\beta,\beta'$ -Thiodipropionic acid.....	8.0	4.1	14.0
0.1 p.p.m. Cu.....	5.8	190	
$\beta,\beta'$ -Thiodipropionic acid+0.1 p.p.m. Cu.....	7.7	59	3.1
Control oil A.....	8.9	45	
Carboxymethylmercapto succinic acid.....	8.9	1.7	26.0
0.3 p.p.m. Fe.....	3.5	120	
Carboxymethylmercapto succinic acid +0.3 p.p.m. Fe.....	7.7	2.3	52.0
Control oil A.....	7.9	56	
Carboxymethylmercapto succinic acid.....	8.9	1.8	31.0
0.1 p.p.m. Cu.....	3.4	180	
Carboxymethylmercapto succinic acid +0.1 p.p.m. Cu.....	8.7	2.2	82.0
Control oil B.....	8.0	61	
Carboxymethylmercapto butyric acid.....	5.0	7.4	8.2
0.3 p.p.m. Fe.....	5.6	240	
Carboxymethylmercapto butyric acid +0.3 p.p.m. Fe.....	3.4	19	13.0
Control oil B.....	8.2	47	
Carboxymethylmercapto phenyl pro- pionic acid.....	3.6	11	4.4
0.3 p.p.m. Fe.....	5.7	250	
Carboxymethylmercapto phenyl pro- pionic acid+0.3 p.p.m. Fe.....	3.8	38	6.6
Control oil B.....	....	40	
Monoethyl ester of C.M.S.A. <sup>b</sup> .....	....	4.6	8.6
0.1 p.p.m. Cu.....	....	84	
Monoethyl ester+0.1 p.p.m. Cu.....	....	25	3.4
Control oil B.....	7.9	38	
Monoethyl ester of C.M.S.A.....	6.2	4.6	8.3
0.3 p.p.m. Fe.....	3.9	250	
Monoethyl ester+0.3 p.p.m. Fe.....	5.1	8.4	30.0
Control oil E.....	8.9	51	
Monoctadecyl ester of C.M.S.A. (0.005%).....	8.6	3.0	17.0
0.3 p.p.m. Fe.....	5.3	110	
Monoctadecyl ester (0.005%)+ 0.3 p.p.m. Fe.....	5.4	30	3.8
Control oil B.....	....	55	
Monoctadecyl ester of C.M.S.A.....	....	7.3	7.6
0.1 p.p.m. Cu.....	....	79	
Monoctadecyl ester+0.1 p.p.m. Cu.....	....	18	4.4
Control oil C.....	8.0	22	
$\alpha,\alpha'$ -Thio-di-n-caproic acid.....	4.0	3.8	5.9
0.3 p.p.m. Fe.....	5.2	64	
$\alpha,\alpha'$ -Thio-di-n-caproic acid +0.3 p.p.m. Fe.....	3.0	22	2.9
Control oil C.....	....	30	
$\alpha,\alpha'$ -Thio-di-n-caproic acid.....	....	6.9	4.4
0.1 p.p.m. Cu.....	....	73	
$\alpha,\alpha'$ -Thio-di-n-caproic acid +0.1 p.p.m. Cu.....	....	27	2.7

<sup>a</sup> After 8 hours under A.O.M. conditions.

<sup>b</sup> Carboxymethylmercapto succinic acid.

mercial soybean oil samples, but it is unsatisfactory for edible products because of the noticeable taste developed at concentrations of only 0.002%. With some soybean oil samples a marked antioxidant effect was observed, and an increasing concentration of the acid gave a corresponding increase in antioxidant

TABLE II

Organoleptic Evaluations of Soybean Oil Treated With Thiodiacetic Acid in the Presence and Absence of Metals

Thiodiacetic acid	0.1 p.p.m. Cu	Thiodiacetic acid + 0.1 p.p.m. Cu	Soybean oil control	Significant difference*
Initial Flavor Score				
8.5	6.8	8.3	8.7	1**2*3†4 2**4†1†3
After 4 days' storage at 60°C.				
6.3	2.6	....	....	**
5.6	....	....	6.8	†
....	2.8	6.2	....	**
6.1	....	5.4	....	†
....	2.2	....	5.6	**
....	....	5.4	6.9	†
	0.3 p.p.m. Fe	Thiodiacetic acid + 0.3 p.p.m. Fe		
Initial Flavor Score				
8.2	4.6	8.4	7.6	1**2**3*4 2**4†1†3
After 4 days' storage at 60°C.				
5.9	2.6	....	....	**
5.7	....	....	4.4	**
....	3.0	5.4	....	†
5.5	....	5.7	....	†
....	3.5	....	4.8	*
....	....	5.7	3.7	**

\* † No significant difference.

\* Significant difference (5% level).

\*\* Highly significant difference (1% level).

effect. With cottonseed oil samples both inactivating and pro-oxidation effects were observed. With one sample an extreme pro-oxidant effect was obtained. A sample of mixed alkane sulfonic acids was found to be effective while the higher alkyl and other aromatic sulfonic acids were found to be ineffective.

Results of tests with sulfur dioxide are given in Table IV. The mechanism by which sulfur dioxide increases the oxidative stability is not known. It may be one of catalyst poisoning similar to that discussed by Maxted (17). The oxidative tests show that as low as 3 p.p.m. sulfur dioxide is effective in stabilizing soybean oil; however this concentration and even smaller concentrations are readily detectable by the taste panel. When the amount of sulfur dioxide is decreased to a value undetectable by the panel, effective oxidative stability is lost. The addition of small amounts of sulfur dioxide before deodorization was only slightly effective and the addition of large amounts resulted in oils with low initial flavor scores. Sulfur dioxide and a number of other sulfur compounds tested are not satisfactory for the edible oil industry because they impart undesirable flavors, but they may find application in the manufacture of soap, petroleum, or other non-edible products.

The results obtained with sulfur, sulfuric acid, and hydrogen sulfide are given in Table III. Neither sulfur nor sulfuric acid appeared to increase the oxidative stability, but hydrogen sulfide did show a slight effect, especially to the sample containing added iron. Bertram (3) reports that the addition of 0.05% (500 p.p.m.) sulfur added before deodorization prolongs the keeping time of fats and oils, and he believes that the stabilizing action of sulfur is different from that of propyl gallate. It is also stated that the addition of this amount of sulfur produced little or no change in color or taste of the oil. Our findings however show that a significant taste difference occurs at levels below 200 p.p.m. of added sulfur.

The activity of hydrogen sulfide could be through the formation of sulfides or polysulfides in which the

TABLE III

Oxidative and Organoleptic Evaluations of Oils Treated With Sulfonic Acids, Hydrogen Sulfide, Sulfuric Acid, and Sulfur

Compound (0.01% concentration)	Initial flavor score	Peroxide values*	Index
Soybean Oil			
Control oil H.....	8.2	9.2	
p-Toluene sulfonic acid.....	4.3	2.5	3.7
0.3 p.p.m. Fe.....	7.5	22.0	
p-Toluene sulfonic acid+0.3 p.p.m. Fe.....	4.4	2.4	9.2
Control oil F.....			
p-Toluene sulfonic acid.....	....	28.0	
0.1 p.p.m. Cu.....	....	4.0	9.5
p-Toluene sulfonic acid+0.1 p.p.m. Cu.....	....	95.0	
....	....	5.5	17.0
Control oil F.....			
p-Toluene sulfonic acid (0.1%).....	6.8	39.0	
p-Toluene sulfonic acid (0.01%).....	....	1.9	21.0
p-Toluene sulfonic acid (0.01%).....	....	2.6	15.0
p-Toluene sulfonic acid (0.001%).....	6.6	39.0	1.0
Control oil G.....			
p-Toluene sulfonic acid (0.008%).....	8.3	45.0	
p-Toluene sulfonic acid (0.005%).....	2.9	93.0	0.48
p-Toluene sulfonic acid (0.005%).....	3.7	70.0	0.64
p-Toluene sulfonic acid (0.002%).....	6.1	52.0	0.87
Control oil B.....			
Hydrogen sulfide.....	....	65.0	
0.3 p.p.m. Fe.....	....	55.0	1.2
Hydrogen sulfide+0.3 p.p.m. Fe.....	....	250.0	
....	....	140.0	1.8
Control oil H.....			
200 p.p.m. sulfuric acid.....	8.4	11.0	....
20 p.p.m. sulfuric acid.....	5.1	43.0	....
20 p.p.m. sulfuric acid.....	8.0	9.1	....
5 p.p.m. sulfuric acid.....	8.2	9.0	....
Control oil E.....			
200 p.p.m. sulfur.....	8.8	56.0	....
20 p.p.m. sulfur.....	7.2	54.0	....
5 p.p.m. sulfur.....	8.3	58.0	....
5 p.p.m. sulfur.....	8.5	57.0	....
Cottonseed oil			
Control oil J.....	....	38.0	
p-Toluene sulfonic acid.....	....	290.0	0.13
Control oil K.....			
p-Toluene sulfonic acid.....	....	21.0	
....	....	21.0	1.0
Control oil L.....			
p-Toluene sulfonic acid.....	7.9	37.0	
Sorbitol (0.01%).....	....	21.0	1.8
....	7.8	31.0	1.2

\*After 8 hours under A.O.M. conditions.

metal is coordinated by the sulfur, or perhaps the ferric ion is reduced to the ferrous state and in that state iron does not exert as great a pro-oxidant effect. It is well known that the metals which are more stable to oxidation such as aluminum, nickel, and tin, are the least detrimental to the stability and flavor of edible oils. The effects of a reducing agent or a reducing atmosphere on the stability of edible oils have not been fully investigated. Positive results have been obtained from the addition of minute amounts of sulfur dioxide, carbon monoxide, and hydrogen sulfide, all of which are reducing agents. These compounds are however also capable of coordination according to the unshared electron theory.

TABLE IV

Oxidative and Organoleptic Evaluation of Sulfur Dioxide Treated Soybean Oil

SO <sub>2</sub> p.p.m.	Time of addition	Initial flavor score	Peroxide values*	Index
29.0.....	After deod.	4.5	4.1	5.2
15.0.....	After deod.	5.2	3.9	5.5
2.9.....	After deod.	6.3	3.4	6.3
Control oil H.....	After deod.	8.8	21.0	
116.....	Before deod.	4.1	57.0	0.57
11.6.....	Before deod.	8.1	24.0	1.3
Control oil H.....	Before deod.	8.4	32.0	
29.0.....	After deod.	....	5.7	14.0
23.0.....	After deod.	....	5.9	14.0
17.0.....	After deod.	....	6.7	12.0
12.0.....	After deod.	....	31.0	2.8
5.8.....	After deod.	....	60.0	1.4
2.9.....	After deod.	....	70.0	1.2
Control oil I.....	After deod.	....	84.0	

\*After 8 hours under A.O.M. conditions.

### Summary

Sulfur compounds of the tridentate class having at least 2 carboxy groups in  $\alpha$  or  $\beta$  position to the coordinating atom have been found to be effective in the stabilization of soybean oil. Comparing model compounds with different coordinating atoms, the order of effectiveness appears to be  $S > N > O$ . This order of effectiveness follows an order of increasing electronegativity.

Carboxymethylmercapto butyric acid, carboxymethylmercapto phenyl propionic acid, the monoethyl ester of carboxymethylmercapto succinic acid, p-toluene sulfonic acid,  $\alpha, \alpha'$ -thio-di-n-caproic acid, and sulfur dioxide all improved the oxidative stability but gave undesirable flavors.

Thiodiacetic acid,  $\beta, \beta'$ -thiodipropionic acid, carboxymethylmercapto succinic acid, and the monooctadecyl ester of carboxymethylmercapto succinic acid were found to be excellent stabilizers. The first two may be added either on the upgrade or the downgrade of deodorization, but the heat instability of the latter two limits their addition to the downgrade. All these compounds improved the flavor stability as well as the oxidative stability. The monooctadecyl ester has the added advantage in that it is oil soluble.

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## A Halogenation Method for the Determination of the Total Unsaturation of Tung Oils and of Eleostearic Acids<sup>1</sup>

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THE value of various halogen absorption methods for the determination of unsaturation in tung oil and other oils containing conjugated double bond systems has recently been reviewed by Benham and Klee (1, 3). These authors proposed use of the Rosenmund-Kuhnnehn reagent (pyridine-sulfuric acid-bromine-acetic acid) and mercuric acetate as a catalyst for the determination of the iodine value of such oils. The original Rosenmund-Kuhnnehn method with no mercuric acetate catalyst results in iodine values of about 160 for tung oil. Klee and Benham (3) obtained an iodine value of 156.7 for a sample of fresh tung oil, using the Rosenmund-Kuhnnehn method without mercuric acetate and 250.6 for the same oil when mercuric acetate was added. An iodine value of 250 for tung oil is higher than would be expected on the basis of the generally accepted composition of tung oil (2). This fact was evidently recognized by Klee and Benham, but their efforts to determine whether substitution reactions might be the cause for the high iodine value resulted only in some evidence for the absence of any secondary substitution reaction.

Recently a method for the determination of total

unsaturation of tung oil by quantitative catalytic hydrogenation was published (4). Using this method, iodine values of 225-241 for various tung oils were obtained. These values are in good agreement with those to be expected for such oils. Application of the method proposed by Klee and Benham to a tung oil with a hydrogen-iodine value of about 230 in this laboratory at first gave very erratic and generally high values. Klee and Benham reported that "during preliminary tests it was noted that the presence of light during absorption affected the results to a slight degree." On investigation it was found that exposure to light had a very marked effect both upon the blanks and on the solutions containing the oil samples. A series of determinations on samples of a tung oil run in the same way, except that the samples and their accompanying blanks were stored for the 2-hour reaction period under different conditions of illumination, gave iodine values ranging from 250 when the solutions were stored in a dark cabinet to 56 when they were exposed to bright sunlight. Even a few minutes' difference in exposure to light in a partially darkened laboratory (illumination less than 0.5 foot-candle as measured by a lightmeter) resulted in distinctly different iodine values.

Consistent and reproducible results could however be obtained by taking suitable precautions against exposure to light. The iodine values for tung oil

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