

Removal of Copper From Hydrogenated Soybean Oil¹

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Abstract

Hydrogenation with a copper-chromite catalyst at 170 C, 30 psi, increased the copper content of a refined, bleached soybean oil from 0.02 to as much as 3.8 ppm. Removing residual copper from soybean oil is essential to the successful use of copper catalysts for selective hydrogenation. Various methods were examined to remove this copper, including alkali refining, bleaching, acid washing, citric acid treatment and cation-exchange resin treatment. Properly conducted, each of the methods except alkali refining gives 95% or higher removal of copper introduced during hydrogenation. Ion exchange appears to be the most economical, but addition of about 0.01% citric acid during deodorization may be needed to inactivate traces of unremoved copper. Soybean oil hydrogenated with a copper-chromite catalyst, bleached or treated with an ion-exchange resin and deodorized with 0.01% citric acid added had low AOM peroxide values and acceptable flavor scores after eight days at 60 C which indicate that removal of residual copper from the oil should be adequate for the production of stable oils low in linolenic acid content.

Introduction

In processing soybean oil for edible use, the practice generally accepted is to avoid contact of the oil with equipment constructed of copper or copper alloys. If not removed or deactivated, minute amounts of copper dissolved in the oil from such contact can cause the oil to have poor oxidative and flavor stabilities. As little as 0.03 ppm of copper, in active form, has been shown by Evans et al. (4) to reduce significantly the flavor stability of soybean oil. Small amounts of copper and other metals found in crude vegetable oils are largely removed during refining and bleaching (9). These metals are apparently obtained from the seed during oil extraction.

Copper catalysts, such as the Adkins type (1), promote selective linolenate reduction during partial hydrogenation of soybean oil [Moulton, Moore and Beal, Manuscript in preparation (3,5,7,8)]. These findings have focused attention on a need to remove small amounts of copper from the oil. To produce a flavor-stable soybean salad oil low in linolenate content by copper-catalyzed hydrogenation, effective removal of trace amounts of copper is necessary. Five methods of copper removal were examined to compare their effectiveness and to consider their practicality.

Materials and Methods

Commercially refined, bleached soybean oils were used for all tests. The oils were partially hydrogenated in a 1 gal autoclave with a commercial copper-chromium catalyst to iodine values (IV) of 115-120. IVs were calculated from fatty acid composition data from GLC and by using the theoretical IVs for the pure acid glycerides (9). The partially

hydrogenated oils were filtered with about 2% of Hy-Flo SuperCel to remove the catalyst and obtain a clear oil.

The copper content of the hydrogenated oils varied from 0.3 to 3.8 ppm. Increase in copper appeared to be related to free fatty acid content of the oil, type and amount of catalyst used, and time of hydrogenation. The copper content of hydrogenated oils and of oils treated in various ways after hydrogenation was determined by ashing 100 to 200 g samples and analyzing for copper colorimetrically. Samples of oil were weighed into acid-washed porcelain evaporating dishes, which were placed on hot plates at low heat. As the oil samples started to decompose, the temperature was gradually raised but kept below the point where autoignition would occur. After the samples were converted to a dry, carbonaceous material, the evaporating dishes were placed in a furnace at 500 C for 16 hr and a light gray to white ash resulted. Ashing at temperatures higher than 500 C resulted in loss of copper. The ash was dissolved in dilute (1-4) nitric acid and the solution was diluted to 25 ml in a volumetric flask. Copper was then determined for a suitable aliquot of the solution by the diethyldithiocarbamate method of Andrews and Stringer (2). The method was checked by analyzing oil samples containing added copper. Samples containing 5.0, 1.0, 0.20 and 0.04 ppm copper (added as copper nitrate) analyzed 5.0, 0.75, 0.15 and 0.036 ppm by ashing at 500 C and colorimetric analysis, 4.68, 0.91, 0.16 and 0.036 ppm by low temperature dry ashing and colorimetric analysis (6), and 4.43, 0.837, 0.167 and 0.042 ppm by neutron activation analysis (6).

Copper Removal Treatments and Results

Either alkali refining plus bleaching or bleaching alone has been used to remove nickel from nickel-hydrogenated vegetable oils. Refining alone is not generally recommended because of the difficulty of washing out traces of soap left in the oil. Bleaching after refining removes substantially all traces of soap.

To study the effectiveness of refining, bleaching and other treatment methods for removing traces of copper from soybean oil, an oil containing 0.08% free fatty acid and 0.04 ppm copper was partially hydrogenated with a commercially available copper-chromium catalyst. The hydrogenated oil contained 3.4 ppm copper as shown in Table I.

To refine this oil, 200 g was vigorously mixed for 15 min at 25 C with 2 g of sodium hydroxide dissolved in 50 g of water. The resulting emulsified

TABLE I
Removal of Copper From Hydrogenated
Soybean Oil by Alkali Refining or Bleaching

Treatment	Copper content, ppm	Copper removed, %
Hydrogenated soybean oil	3.4
Refine, 1% NaOH (on oil) in 4% solution	1.5	60
Bleach		
½% Super Filtrol	0.52	86
1% Super Filtrol	0.23	93
2% Super Filtrol	0.20	95
2% Darco G-60 activated carbon	0.13	97

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TABLE II
Removal of Copper From Hydrogenated Soybean Oil
by Acid Extraction

Acid	Treatment				Copper content, ppm	Copper removed, %
	Strength, %	Amount, g solution/100 g oil	Mixing time, min	No. of extractions		
Original soybean oil					0.038
Hydrogenated soybean oil, Cu-Cr catalyst					3.80
Citric	2.0	65	15	1	1.10	71
H ₂ SO ₄	5.0	5	20	1	1.30	66
H ₂ SO ₄	5.0	50	5	1	0.52	86
HCl	1.0	15	1	3	0.17	95
HCl	2.5	15	1	3	0.19	95
H ₂ SO ₄	2.5	15	1	3	0.15	96
H ₂ SO ₄	5.0	5	20	3	0.17	95
H ₂ SO ₄	5.0	50	20	3	0.21	94

mixture was centrifuged without heating to separate the phases and the aqueous layer was removed. The refined oil contained 1.5 ppm copper. This amount corresponds to a removal of about 60% of the copper in the hydrogenated oil. Other refining conditions were not examined.

To bleach the oil, 200 g of oil was heated to about 80 C. Bleaching clay or carbon was added and the temperature was raised to 105–110 C and held 15 min after which the oil was filtered and analyzed for copper. Bleaching with ½% clay was more effective for removing traces of copper than refining with 1% sodium hydroxide. Activated carbon and activated bleaching earth were, within experimental error, about equally effective for removing copper (Table I).

Washing the oil with dilute aqueous acid has been described as an effective method of copper removal (8). Results of several tests of acid washing are shown in Table II.

For these tests 200 g samples of soybean oil partially hydrogenated with a Cu-Cr catalyst and containing 3.8 ppm of copper were vigorously mixed with aqueous acid for several minutes by means of a magnetic stirrer. The resulting mechanical emulsion was centrifuged and the oil layer was washed with 10% distilled water, centrifuged and analyzed for copper. A single wash with a 2% citric acid solution (65 g/100 g oil) with 15 min mixing removed only about 70% of the copper. One wash with a 5% sulfuric acid solution (5 g/100 g oil) for 20 min was about equally effective. A larger amount of sulfuric acid was somewhat more effective. Three consecutive treatments with either 1.0% or 2.5% solutions of hydrochloric acid or a 2.5% and 5% solution of sulfuric acid removed about 95% of the copper. These data indicate that continuous countercurrent washing with a dilute acid should remove copper effectively. However, acid washing must be followed by very thorough water washing because traces of acid left in the oil adversely affect the flavor of the oil after it is deodorized.

The complexing effect of citric acid for trace amounts of iron and copper in soybean oil is widely

TABLE III
Removal of Copper From Hydrogenated Soybean Oil
by Citric Acid Chelation

Treatment		Copper content, ppm	Copper removed, %
Amount of citric acid, % of oil	Method of separation		
Hydrogenated soybean oil		3.4
0.01	Centrifugation	2.7	21
0.1	Centrifugation	1.3	62
0.1	Centrifugation + filtration	0.22	93
1.0	Centrifugation + filtration	0.04	99

employed commercially in producing a stable deodorized oil. Usually the metal complex is left in the oil after this treatment because it is extremely small in amount and gelatinous in nature, but it may be separated from the oil by filtration. Some oil processors accomplish this by filtering the oil after it is deodorized.

In tests summarized in Table III an aqueous solution of citric acid was added to hydrogenated soybean oil, and the oil was then heated to about 125 C under high vacuum to remove the water, passing steam through the oil to promote mixing and to prevent bumping. The oil was cooled under vacuum. In the first two tests of this series, the oil was treated with 0.01% and 0.1% citric acid (1% aqueous solution) and the water then removed under vacuum. The oil was centrifuged (15 min, 900 g), decanted and analyzed. These treatments gave only partial removal of copper. In the third and fourth tests in which the oil was both centrifuged and filtered after addition of citric acid solution and dehydration, almost all copper was removed. These and other data indicate that between 0.1% and 1.0% citric acid is required to remove copper from an initial level of 3.4 ppm.

The copper removed from the oil was accounted for quantitatively in two tests. In each test, 100 g of an oil, found to contain 2.4 ppm copper by ashing the oil, was treated with 1% citric acid in 10 ml distilled water, vacuum dried and filtered as described above. The flask in which the oil was dried was thoroughly rinsed with hexane and absolute ethanol. The solution was placed in a beaker and the solvent evaporated. The filter paper was added to the beaker and its contents ashed. Analysis of the ash (two samples) showed 2.8 and 2.5 ppm copper in the oil.

Treatment of acetone or hexane solutions of vegetable oils with cation-exchange resins reported is partially effective for removing metals (10,11) but no reports have been found describing the use of such resins in a vegetable oil-aqueous system.

Results obtained by using cation-exchange resins in the hydrogen form with a water-soybean oil system are summarized in Table IV. The oil used in this series contained less copper, 1.2 ppm, than oils used in previous studies; however, the ion-exchange resin treatment was highly effective when only 1% resin (dry basis) was used. This amount of resin has several hundred times the exchange capacity required to remove the copper. Oil was mixed with one-fifth its weight of water to which a weighed quantity of resin had been added. The oil-water-resin system was stirred for 15 min at room temperature and centrifuged to recover oil for analysis. It was found that adding the resin to the oil before adding the water frequently resulted in poor copper removal, as did the use of extremely high rates of agitation. Preferential wetting of the resin by the oil appeared to be responsible.

Portions of two resins, one Dowex 50, the other Amberlite IR-120, were used in copper removal tests. Each resin was then washed with a detergent solution, rinsed on a Buchner funnel, washed with 15% HCl and then with distilled water until the effluent from the filter was neutral. These regenerated resins were used to remove copper from a partially hydrogenated soybean oil containing 0.80 ppm copper. For 15 min 200 g of oil, 40 g distilled water and 2 g resin (dry basis) were rapidly mixed. Both treated oils contained less than 0.08 ppm copper.

TABLE IV
Removal of Copper From Hydrogenated Soybean Oil
by Cation-Exchange Resin

Treatment	Resin used, % of oil	Copper content, ppm	Copper removed, %
Hydrogenated soybean oil	..	1.2
Resin (Dowex)			
50-X8, 100-200 mesh	1	0.043	96
50-X8, 100-200 mesh	2	0.027	98
50-X8, 100-200 mesh	3	0.030	97
50-X4, 50-100 mesh	1	0.027	98
50-X4, 50-100 mesh	2	0.046	96
50-X4, 50-100 mesh	3	0.034	97

Several 1 gal batches of refined, bleached soybean oil were partially hydrogenated in the presence of a copper-chromium-barium catalyst and treated with 1% cation-exchange resin and 20% water for 15 min at room temperature. After treatment, respective batches contained 0.02, 0.03, 0.04, 0.06 and 0.02 ppm copper. The original unhydrogenated oil analyzed 0.06 ppm copper but analyses were not made on the hydrogenated oils before treatment.

Analyses of our samples by the Wisconsin Alumni Research Foundation showed that hydrogenation of soybean oil with a copper-chromium-barium catalyst increased the amount of all three metals in the oil. The oil samples were ashed at the Northern Laboratory, and the ash was analyzed by emission spectroscopy at Wisconsin. For example, a soybean oil containing 0.01 ppm barium, 0.046 ppm copper and <0.017 ppm chromium before hydrogenation contained 2.46 ppm barium, >0.85 ppm copper and 0.83 ppm chromium after hydrogenation. After a sample of the hydrogenated oil was treated 15 min with 1% resin and 20% water, it contained 0.5 ppm barium, 0.059 ppm copper and 0.049 ppm chromium.

Results and Discussion

Based on the data secured and economic considerations, a preliminary comparative evaluation may be made of the five methods which we examined for removing copper from soybean oil. Alkali refining under the conditions investigated is not adequate for copper removal, although removal achieved by refining followed by bleaching may be adequate. Treatments with citric acid by the method described above, or by the ion-exchange method, have been shown to lower the copper content of a soybean oil partially hydrogenated with a copper-bearing catalyst to about 0.1 ppm or lower. Bleaching and washing with dilute acid were slightly less effective, but properly conducted countercurrent acid washing should remove a greater amount of copper than our acid-washing results show. Bleaching entails a loss of oil, but the other methods of treatment are not expected to. Consideration must be given to other factors, such as reagent cost, equipment cost, heating requirements and waste disposal in the selection of the preferred method.

Oil Stability

One gallon of commercially refined, bleached soybean oil was hydrogenated to an IV (calculated from GLC data) of 118.0 in the presence of a commercial copper-chromium catalyst. The linolenate content was

TABLE V
Taste Panel Evaluation of Partially Hydrogenated Soybean Oil

Samples	Hydrogenated soybean oil			
	Cation resin treated		Bleached	
	Flavor score	Peroxide value	Flavor score	Peroxide value
Storage conditions				
Initial	7.7	0.0	7.8	0.0
Stored 4 days at 60 C	6.5	0.6	6.1	0.7
Stored 8 days at 60 C	6.0	5.5	6.4	3.0
AOM peroxide value		3.9		4.9
Copper, ppm		0.11		0.11

0.7% as determined by alkali isomerization. After removal of the catalyst, one-half of the oil was bleached 15 min at 110 C with 1% Super Filtrol, and the other half was treated with 1% Dowex 50-X4, 100-200 mesh, and 20% distilled water for 15 min at room temperature. The original oil contained 0.06 ppm copper and the hydrogenated oil 0.29 ppm copper. Both the bleached and cation-exchange resin-treated oils contained 0.11 ppm copper.

Two samples of the oil, variously treated, were deodorized in the laboratory with 0.01% citric acid added at 125 C during the cooling period; these consisted of partially hydrogenated, resin-treated oil and partially hydrogenated, bleached oil. Taste panel flavor and oxidative stability results for these oils are summarized in Table V. The initial flavor scores for the partially hydrogenated, deodorized oils were typical of good quality oils. After both four and eight days' storage at 60 C, the hydrogenated oils received about the same average flavor scores and were still in the range considered acceptable by the taste panel. They also had low peroxide values after four and eight days' storage and low AOM peroxide values. Comparison of flavor scores for the bleached and the resin treated oils indicates that the resin and bleaching treatments were about comparable with respect to their effect on flavor stability.

Of the several methods available for removing copper from partially hydrogenated soybean oils, the cation-exchange resin treatment in an oil-aqueous system appears very promising from overall considerations.

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