

# Hydrogenation of Soybean Oil with Copper-Chromium Catalyst: Preliminary Plant-Scale Observations

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## ABSTRACT

Four commercial hydrogenations were carried out on 20,000 lb batches of soybean oil with 0.25, 0.5, and 1% fresh copper-chromite catalyst and 1% used catalyst. Hydrogenations proceeded smoothly at catalyst levels of 0.5 and 1%, but the reaction was slow at a 0.25% concentration. Kinetic, selectivity ratio ( $K_{Ln}^{Lo}$ ) and fatty acid compositional data were acquired during several of the hydrogenation runs. Nickel contamination, confirmed by analysis of used copper catalyst, lowered selectivity. Copper content of the oil rose during hydrogenation, but normal processing steps, particularly bleaching and winterization, removed it to below levels (0.01-0.02 ppm) detectable by direct atomic absorption spectroscopy. Both copper and chromium remaining in the oil after processing were concentrated by winterization in the stearine fraction. Organoleptic, oxidative, and room odor tests showed that oils of good stability can be produced on a commercial scale by copper hydrogenation and winterization. Information was gained regarding problems involved in the plant use of copper-chromite catalyst for hydrogenating soybean oil for edible purposes.

## INTRODUCTION

Soybean oil is the major edible oil in the U.S. During 1970, more than 6 billion lb were consumed as shortening, margarine, and salad and cooking oils (1,2). Although consumption as a cooking oil has increased steadily, further improvement in quality is desirable (3). When heated to frying temperatures, unhydrogenated soybean oil imparts an odor to a room that is different from cottonseed, safflower, and peanut oils (4). Hydrogenation improves the room odor of soybean oil used for frying, and this improvement correlates well with a decrease in linolenate content (4,5). However, basic technical problems with the nickel hydrogenation process prevent production of a liquid soybean cooking oil free of linolenate (6). Commercial soybean salad and cooking oils typically contain ca. 3% triene (3,6).

Studies conducted at the Northern Laboratory and abroad (8-13) have established that certain copper containing catalysts possess high selectivity for the hydrogenation of linolenate; i.e. linolenate is reduced from 7-12 times faster than linoleate. In addition, monoenes are not reduced much (14,15). Cowan, et al., (4) compared copper- and nickel-reduced soybean oils containing 0 and 3.3% linolenate, respectively, and found the former was superior to the latter in accelerated storage and room odor tests. More work (16) has shown that after exposure to fluorescent

light, copper-reduced oils perform better than nickel-reduced oils in room odor tests.

Copper hydrogenation offers an approach toward improving dual purpose soybean cooking and salad oils. The objective of this research was to hydrogenate soybean oil on full plant commercial scale with a copper-chromium catalyst. Unfortunately, what happened, as will be understood by all operating plant engineers, was that traces of residual nickel catalyst left from previous runs in the catalyst make-up tank, pumps, and lines, contaminated the copper catalysts; and obscured the hoped-for high selectivity of copper catalysts. However, despite this deficiency, a high selectivity of five was obtained, and the hydrogenated, winterized oil was found to be of high flavor stability. What follows is a description, as clearly as can be determined, of the operating condition for plant-scale hydrogenations of soybean oil with a nickel-contaminated copper catalyst and a stability evaluation of the resulting oils.

## MATERIALS AND METHODS

### Oil and Catalyst

Hydrogenations were conducted on a single lot of once-refined and bleached soybean oil. Its fatty acid analysis, as determined by gas liquid chromatography (GLC), was palmitic 10.8, stearic 4.4, oleic 22.7, linoleic 54.1, and linolenic 8.0; calculated iodine value (IV) was 133.5. The linoleate and linolenate contents determined by alkali isomerization were 54.4 and 7.3%, respectively.

A commercially supplied catalyst (Harshaw 1106P) was used for hydrogenation. It contained 39, 43.5, and 10% copper, chromium, and barium oxides, respectively. Activity of the catalyst was established in earlier pilot-plant tests.

### Hydrogenation and Processing

A typical large scale hydrogenation was carried out as follows: Soybean oil (20,000 lb) was charged into a stainless-steel converter. Hydrogen was introduced and the temperature brought to 280 F. The catalyst (200 lb) and filter aid (100 lb) were slurried in 25 gal soybean oil and introduced into the converter by a small pump. The converter was vented, hydrogen was blown through the oil for 5 min, and the vent was closed. The temperature of the oil was raised to 310 F, and the hydrogen (at 30 psi) was circulated from the converter headspace to the sparge inlet in the oil.

Hydrogenation proceeded after an induction period of 6 min. During the run, small samples were taken periodically for subsequent analysis. The IV drop was monitored by changes in refractive index. During sampling, hydrogen recirculation was stopped, but slow agitation was continued. Operating time means the time when hydrogen was being recirculated to the converter.

Samples taken from the hydrogenation runs were

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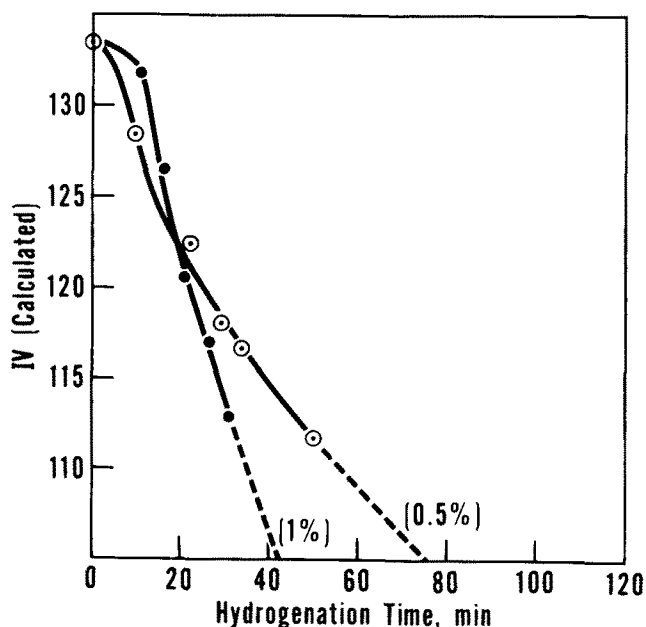


FIG. 1. Effect of copper-chromite catalyst concentration upon the reduction in iodine value (IV) of soybean oil with time. Solid line = experimental and dash line = extrapolated.

bleached in the laboratory with 2% activated clay and deodorized in all glass equipment, as described previously (17).

#### Analysis of Hydrogenated Products

Methyl esters were prepared by transesterification with  $\text{BF}_3\text{-MeOH}$  reagent (18). GLC analyses were carried out, as described previously (19). Wijs IV, *trans*-acids and conjugated acids were determined by official AOCS methods Cd 1-25, Cd 14-61, and Ti 1a64, respectively (20). Selectivity ratio values were calculated as reported by Butterfield and Dutton (21). Trace metals were determined by atomic absorption spectroscopy (22,23).

Flavor and oxidative evaluations were carried out according to the procedures of Moser, et al. (24). Room odor tests were conducted according to the method of Evans, et al. (25).

## RESULTS

The effect of copper catalyst concentration upon the rate of soybean oil hydrogenation is shown in Figure 1. After short induction periods, hydrogenation proceeded smoothly and both catalyst levels were active. The 1 and 0.5% catalyst levels required 36 and 50 min, respectively, to reduce the IV from 133.5 to 112.5. Hereafter, these oils will be referred to as batches 1 and 2, respectively. Induction periods, during which no hydrogenation occurred, probably were related to activation of the catalyst.

Compositional data from the hydrogenation runs are given in Figure 2, where fatty acid composition is plotted against calculated IV. Parts A and B represent oils produced from catalyst levels of 1 and 0.5%, respectively. Data points represent oils taken directly from the hydrogenation converter. Linolenate and stearate scales have been expanded 10-fold.

Figure 2 shows that stearate slightly increased in both runs. Such increases had not been observed in pilot-plant or laboratory studies (15,19).

Selectivity values (selectivity is defined as the ratio of linolenate hydrogenation rate to linoleate hydrogenation rate) for the 1 and 0.5% catalyst runs are given in Table I.

The data indicate selectivities of 5-6 were achieved,

TABLE I

Selectivity of Commercial Copper-Chromite Hydrogenations of Soybean Oil

| Catalyst level, % by wt | $\frac{\text{Ln}^a}{\text{Lo}}$ | IV  | % Ln |
|-------------------------|---------------------------------|-----|------|
| 1                       | 5.7                             | 113 | 1.2  |
| 0.5                     | 5.0                             | 112 | 1.2  |

<sup>a</sup>Selectivity ratio and iodine value (IV) calculated from last sample taken from converter. Percentage linolenate (Ln) determined by alkali isomerization. Lo = linoleate.

TABLE II

Copper and Chromium Contents of Hydrogenated (1% Catalyst) Oils before and after Bleaching<sup>a</sup>

| Sample (min)          | As received, ppm |                 | After 2% bleach, ppm |       |
|-----------------------|------------------|-----------------|----------------------|-------|
|                       | Cu               | Cr              | Cu                   | Cr    |
| 11                    | 2.7              | 0.48            | 0.02                 | Trace |
| 16                    | 16.1             | 0.50            | 0.16                 | 0.17  |
| 21                    | 21.8             | 0.53            | 0.41                 | 0.24  |
| 26                    | 22.7             | 0.72            | 0.67                 | ---   |
| 26 B1-2X <sup>b</sup> | ---              | ---             | <0.02                | 0.10  |
| 31                    | 12.3             | 0.54            | 0.03                 | 0.12  |
| Plant filtered        | 0.03             | ND <sup>c</sup> | <0.02                | ND    |

<sup>a</sup>Bleached in laboratory. Cu = copper and Cr = chromium.

<sup>b</sup>B1-2X = bleached twice.

<sup>c</sup>ND = none detected.

TABLE III

Copper and Chromium Contents of Hydrogenated Oils<sup>a</sup>

| Oil                             | Cu, ppm | Cr, ppm            |
|---------------------------------|---------|--------------------|
| Composite as received           | 0.26    | Trace <sup>b</sup> |
| Composite bleached <sup>c</sup> | <0.01   | ND                 |
| Composite winterized            | <0.01   | ND                 |
| Stearine                        | 0.54    | 0.14               |

<sup>a</sup>Cu = copper and Cr = chromium.

<sup>b</sup>Lowest detection limit of chromium by atomic absorption ca. 0.05 ppm.

<sup>c</sup>Bleached in laboratory with 2% bleaching earth. ND = none detected.

compared to ca. 2.0 for nickel catalysts (6). In laboratory studies, Koritala and Dutton (8) reported values as high as 12.2 for copper-barium-chromium oxide catalysts.

The relationship between *trans*-isomers formed during copper hydrogenation and calculated IV is plotted in Figure 3. Included for comparison are data from pilot-plant hydrogenations carried out with CuBaCr and nickel catalysts at 170 and 150 C, respectively. Plant hydrogenations produced substantially more *trans*-acids than did either copper or nickel hydrogenations run in the pilot plant. For example, at IV 115, pilot-plant runs had 9% *trans*-vs ca. 15% for the large scale plant runs.

The change in linolenate content in soybean oil vs reduction of IV is depicted in Figure 4 for plant size copper (1% catalyst), pilot-plant copper, and pilot-plant nickel hydrogenations. Commercial copper hydrogenation runs were intermediate in the removal of linolenate, falling between pilot-plant copper and pilot-plant nickel hydrogenations.

Since metals, particularly copper, are known to be strong prooxidants for unsaturated fats (26), studies were undertaken to determine the levels of copper and chromium added to oils during hydrogenation with a copper-

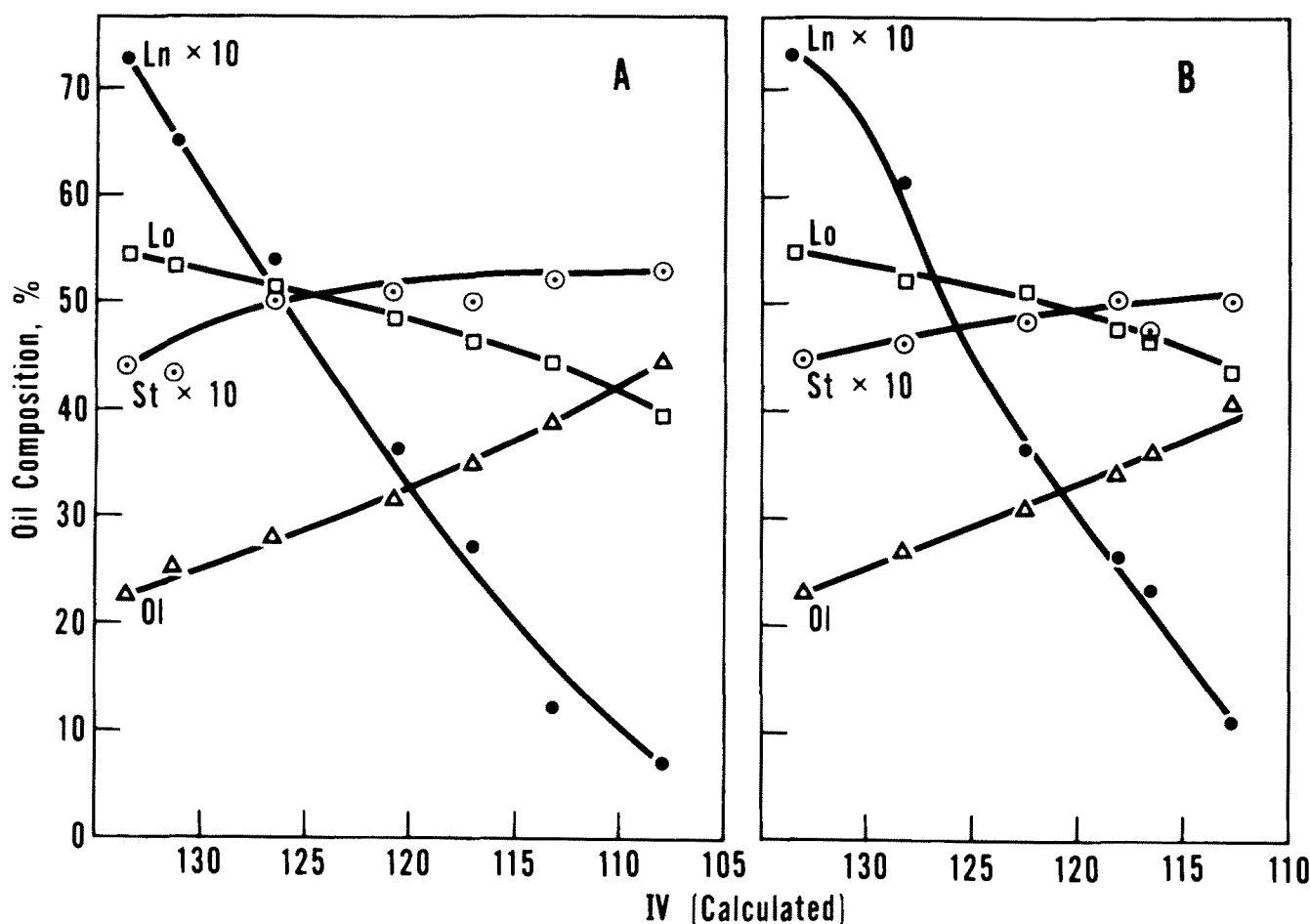


FIG. 2. Relationship between composition and iodine value (IV) of copper-reduced oils. (A) Oil prepared with 1% catalyst, (B) oil prepared with 0.5% catalyst. St = Stearate, OI = oleate, Lo = linoleate, Ln = linolenate.

chromium catalyst.

Copper and chromium contents of samples taken during one of the plant-scale hydrogenations are given in Table II. Those designated as received were withdrawn directly from the converter and filtered through paper to remove suspended catalysts. Samples were not cooled or protected with nitrogen, and some remained in contact with residual catalyst for some time. Thus, some oxidation of the fat undoubtedly occurred, and the copper levels reported may be artificially high. It has been observed repeatedly in our pilot-plant tests that oil has a copper content above 1 ppm after it is exposed to air in the presence of copper catalyst at temperatures above ca. 50 C. The maximum level of copper in as-received spot samples from all plant hydrogenation runs was ca. 23 ppm. Chromium levels were considerably lower than the copper, and, except for one sample, contents were rather constant throughout the run.

The chromium values (for one hydrogenation run), given in Table II, represent the highest level found in any of the plant-scale hydrogenations. Samples taken from the other hydrogenation run contained levels ranging from ca. 0.05 ppm to the maximum of 0.24 ppm reported in Table II. The atomic absorption procedure for chromium (direct aspiration of a 25% oil solution in methyl isobutyl ketone) has a lower detection limit of ca. 0.05 ppm.

The plant processed oils were cooled in the hydrogenator and then received three separate filtrations (the third was a citric acid filtration), and batch 1 had a low copper content (0.03 ppm) (Table II). The other plant filtered sample (batch 2, data not shown) had a copper level of 0.15 ppm. A single laboratory bleaching (2% clay) removed residual copper from the as-received oils to low levels,

provided the initial levels were below 12 ppm. Above this value, a second bleaching was required to reduce copper to below the 0.01-0.02 ppm detection limit of atomic absorption. Bleaching was less effective for removal of residual chromium.

Trace copper and chromium contents of the hydrogenated oils are given in Table III. A blend of several plant oil samples had copper and chromium contents of 0.26 and 0.05 ppm, respectively. Winterization concentrated these metals in the stearine, which had 0.54 ppm copper and 0.14 ppm chromium. The winterized oil had a copper content of 0.01 ppm. The concentrating of metals in the stearine would indicate that the major part of the catalyst metal residue is particulate matter or soap, which offers nuclei for the initiation of crystallization.

Flavor and oxidative stability data for plant copper-hydrogenated oils are tabulated in Table IV. The original oil from which the hydrogenated oils were prepared had low flavor and oxidative stability as evidenced by initial flavor score (5.8) and active oxygen method (AOM) peroxide value (63.7). Addition of citric acid improved flavor scores and lowered AOM peroxide value (see table). Copper-reduced oils, batches 1 and 2, had high initial flavor scores and also received high scores after accelerated storage. Their low 8 hr AOM and low storage peroxide values are indicative of stable oils.

As usually found, citric acid helped to stabilize both hydrogenated and unhydrogenated oils.

Room odor scores and predominant odor responses, tabulated in Table V, were obtained by the procedure of Evans and coworkers (25). Percentage of tasters giving respective odors is shown in parentheses. Odor intensity

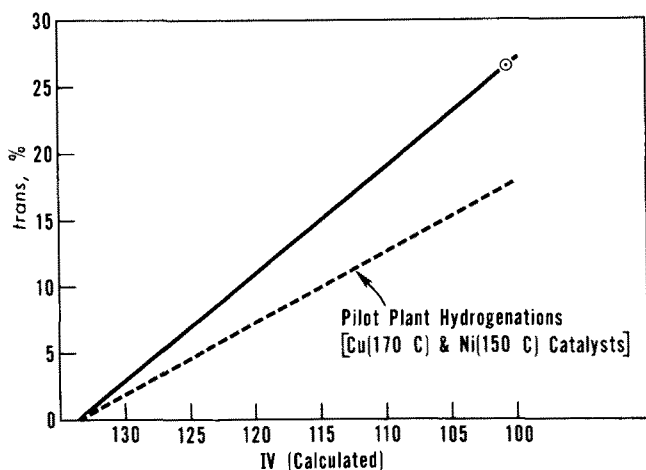


FIG. 3. Relationship between *trans*-formation and iodine value (IV) in plant scale and pilot-plant hydrogenations. Solid line denotes pooled data from plant scale copper hydrogenation; broken line denotes pilot-plant hydrogenations made with either 1% copper or 0.2% nickel catalyst.

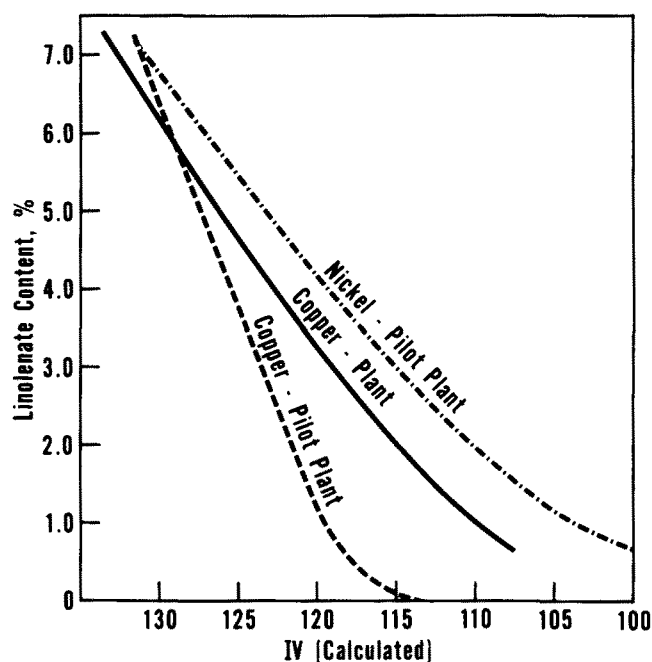


FIG. 4. Relationship between iodine value (IV) and linolenate content of soybean oils prepared in large scale and pilot-plant hydrogenation. Commercial (plant) copper and copper pilot-plant runs made with 1% catalyst. Nickel pilot-plant run made with 0.2% catalyst.

values (OIV) are weighted and averaged panel responses (4). When the original unhydrogenated oil is compared against batch 1, characteristically the room odor score for hydrogenated oil is higher. Hydrogenated oils were scored significantly higher than unhydrogenated, and responses were predominantly hot oil and rancid, rather than fishy.

Room odors developed by batch 1, copper-hydrogenated oil, indicate that undesirable fishy, rancid, and burned responses are considerably lower and probably less intense for the copper-reduced oils. The more desirable hot oil odor was predominant in the copper-hydrogenated oil. These room odor observations upon copper-reduced oils prepared in plant tests substantiate results reported earlier for laboratory prepared copper-reduced oils (4).

## DISCUSSION

The plant tests described here are apparently the first full commercial scale trials of hydrogenation with a copper catalyst to be reported. They demonstrate for the first time the technical feasibility of commercial hydrogenation of soybean oil with a commercially available copper-chromite catalyst, the successful removal from the oil of the small traces of copper dissolved from the catalyst, and the improved quality of the partially hydrogenated, winterized, deodorized oil which can be produced by this method.

The plant in which the copper runs were made was also in commercial production of regular nickel-hydrogenated

soybean oil stocks. The plant had several converters; only one of these was used for the copper hydrogenation runs. Common equipment was used to mix catalyst with filter-aid before hydrogenation for each converter, as well as common presses and pumps to filter the oil for removal of catalyst after hydrogenation. Likewise, common equipment of pumps, lines, and metering systems had to be used for placing each copper run in storage so that a composite sample could be obtained for a large scale plant (60,000 lb) winterization of the oil. The use of common equipment offered many opportunities for contamination of both the copper catalyst with nickel catalyst and the copper-hydrogenated soybean oil with nickel-hydrogenated oil stocks. The extent and seriousness of both types of contamination were greater than expected and will be discussed later together with the results.

Separate facilities would probably be the best solution to avoid any cross contamination of catalysts. When nickel- and copper-reduced oil are processed in the same plant, it should be apparent that nickel-hydrogenated oil would need to be kept separate or treated to remove copper, as

TABLE IV  
Flavor and Oxidative Stability of Copper-Hydrogenated Oils

| Days, 60 C                | Flavor scores                                 |  |                             |
|---------------------------|---|--|-----------------------------|
|                           | Original SBO <sup>a</sup> + 0.01% citric acid | Batch 1 <sup>b</sup> + 0.01% citric acid | Batch 2 + 0.01% citric acid |
| 0                         | 6.7 (0.0) <sup>c</sup>                        | 7.3 (0.0)                                | 7.7 (0.0)                   |
| 4                         | 5.7 (0.7)                                     | 6.0 (0.3)                                | 7.1 (0.7)                   |
| 8                         | 4.9 (9.6)                                     | 5.9 (3.2)                                | 5.6 (4.6)                   |
| PV, AOM <sup>d</sup> 8 hr | 6.1   | 2.0                                      | 3.5                         |

<sup>a</sup>SBO = soybean oil. Original oil used in plant hydrogenations. Oils deodorized in laboratory unless otherwise noted.

<sup>b</sup>Batches 1 and 2 represent runs at 1 and 0.5% catalyst, respectively. Samples obtained after citric acid filter press; bleached and deodorized in laboratory.

<sup>c</sup>Numbers in parentheses are peroxide values (PV) at time of tasting.

<sup>d</sup>AOM = active oxygen method, PV at 8 hr.

TABLE V  
Room Odor Tests with Hydrogenated Oils

| Oil                  | Odor score <sup>a</sup>                           | OIV                   |          |          |          |
|----------------------|---|-----------------------|----------|----------|----------|
|                      |   | Fishy                 | Rancid   | Hot oil  | Burned   |
| SBO <sup>b</sup>     | ** (3.6) <sup>c</sup><br>5.4) <sup>c</sup><br>6.0 | 0.9 (50) <sup>c</sup> | 0.6 (31) | 0.3 (12) | 0.5 (32) |
| Batch 1 <sup>d</sup> |   | 0.1 (6)               | 0.2 (19) | 0.8 (44) | 0.1 (13) |
| Plant Cu             |   | 0.2 (14)              | 0.4 (24) | 0.8 (52) | 0.4 (26) |
| HWSBO <sup>e</sup>   |   |                       |          |          |          |

<sup>a</sup>\*\*\* = Statistical significance at 1% level; + = no statistical significance; OIV = odor intensity value.

<sup>b</sup>Deodorized original soybean oil (SBO), unhydrogenated.

<sup>c</sup>Numbers in parentheses indicate percentage of panel that indicated this particular odor response.

<sup>d</sup>Oil prepared with 1% catalyst—laboratory deodorized.

<sup>e</sup>Composite of all batches of oil; oil processed entirely in plant equipment including, in addition to hydrogenation, bleaching, winterization, and deodorization. HWSBO = hydrogenated-winterized soybean oil.

well as residual nickel, contamination.

Compositional data (Fig. 2) for two large scale runs indicate that the copper-reduced oils were contaminated with oils of a lower IV. Presumably, contamination came from previous operations conducted in the processing equipment. Increases in stearic acid (runs A and B, Fig. 2) indicate that the major contamination of the copper-reduced oil occurred during passage through the citric acid filter presses which still contained nickel-reduced oil when regular operations were interrupted for the trial runs. Such contamination adversely affected the overall test by increasing the stearic and *trans*-acid content of the composite oil and, undoubtedly, contributed to the low yield of winterized oil (63%).

Laboratory (8) and pilot-plant studies (19) have shown that copper containing catalysts normally exhibit high selectivity for the hydrogenation of linolenate in soybean oil. Koritala (27) reported selectivity ratios ranging from 4-11 for copper-exchanged molecular sieve catalysts. Dejonge et al. (12) reported values of 7-10 for copper on Kieselguhr. By comparison, nickel catalysts show selectivity ratios of ca. 1.5-2.5 under similar operating conditions. Our results (Table I) for linolenate selectivity are somewhat lower than expected, suggesting possible contamination of the copper catalyst with nickel in the plant hydrogenator. Data from pilot plant tests indicate this amount of nickel would have been of the order of 0.1% of the copper catalyst (28).

Previous studies (29,30) indicated that residual traces of copper could be removed from copper-hydrogenated soybean oil through bleaching and winterization. Data presented in Tables II and III substantiate these previous findings. Trace metals can be removed in commercial processing to low levels. These reduced levels are below those that will adversely affect the stability of liquid hydrogenated-winterized soybean oil that is treated with citric acid. However, copper and chromium levels in stearine from winterization (Table III) show that this process concentrates copper and chromium, and they probably would be deleterious to stability. If used as an edible commodity, the stearine would require additional processing to reduce its metallic content to acceptable levels.

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formed some of the analyses.

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