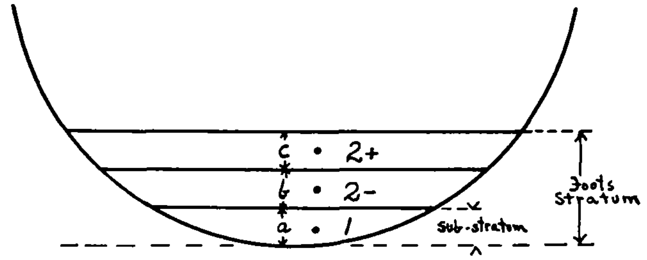
of the foots stratum may be plainly seen through the glass wall and read on the engraved scale thereon, as shown in the photograph.



Substrata Thickness (a=b=c)	Total Foots Depth (a+b+c)	Volume Ratios		
		c/a	b/a	a/a
2"	6"	2.3	1.8	1
3	9	2.3	1.8	1
4	12	2.2	1.8	1
6	18	2.2	1.8	1

Cross Section of the Lower Part of Tank Car Containing Foots. Geometrical basis for the proportions specified in Case 3 of the proportional foots method. Thus, within the rather extreme limits indicated, (which should cover all cases encountered in practice), and for all practical purposes, the ratio of the volumes of the top third, based on depth, and of the middle third of any foots stratum, to the volume of the bottom third, is substantially two-to-one.

Technique. If the proportional foots method appears to be rather complicated, it is really simple and logical to a technically-trained person though it may seem difficult to the average workman. Tankcar sampling, however, should always be under the close supervision of the laboratory, when price settlements or claims are concerned; and where there is indicated a method of sampling which may require unusual care in application as compared with the usual ones, if it cannot be applied under the direct supervision of a laboratory man or someone thoroughly familiar with the principle involved, then the workman who does use it unobserved should be qualified by thorough instruction.

On the other hand, what this method may lose in being somewhat complicated in principle, from the workman's point of view, it more than makes up by being less time-consuming; and once the idea of the right proportion has been mastered it should be more easily applied, especially when we consider that it requires drawing only a few portions from the tank-car, as compared with the federal specifications method's minimum of 40 withdrawals.

Summary

The general problem of taking a representative sample from a tank car containing foots is discussed, and the shortcomings of various methods in wide use are noted. A new method based upon a clear recognition of the difficulties involved and the application of simple geometry to the problem has been proposed.

Acknowledgment

The author expresses grateful acknowledgment to A. L. Hall of the Buffalo Testing Laboratories and to Victor B. Shelburne, for aiding and supervising the first trials of the proportional foots method, as described.

He is grateful also to Charles V. Bacon, inventor of the Bacon Bomb Sampler, for corroborating the basic points made in this paper when it was presented at the 1948 Fall Meeting of the Society in New York. Since Dr. Bacon has applied these principles (and probably others also have), no claim of originality for the basic concept is made.

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Flavor Reversion in Hydrogenated Soybean Oil.* I. The Effect of Double-Degumming. II. The Effect of Unsaponifiable Matter

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THE results of research work in this field fall into two general groups with respect to the cause of flavor reversion. One group considers materials other than pure triglycerides to be the offending factors whereas the other places the responsibility on the triglycerides proper. This apparent contradiction is largely due to the ambiguous use of the term "soybean oil flavor reversion" and particularly to the failure to make proper distinction between the flavor found in soybean oils held at moderate temperatures (20-60°C.) and the entirely different flavor and odor developed by heating hydrogenated soybean oils to the elevated temperatures required for culinary purposes.

The different methods used to develop the two types of reversion as well as the lack of uniformity in panel evaluations add to the confusion and have made it virtually impossible to compare the results of various workers. As has been pointed out repeatedly in the literature (1, 2, 13, 14), the use of the term "flavor reversion" is unfortunate since these flavors are not the same as the original ones. This is particularly true of the heated flavor of soybean oils hydrogenated to shortening consistency since this strong-peculiar-lasting taste is in no way reminiscent of natural soybean oil.

Soybean oil reversion is usually referred to in terms of flavor. We have found, however, that the flavor developed in hydrogenated soybean oils at elevated temperatures is characterized by a similar distinct odor; and in the panel evaluations to be discussed later participants have used the flavor and/or

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[*] Presented at 22nd annual fall meeting, American Oil Chemists' Society, Nov. 15-17, 1948, New York City.

the odor as the individual member preferred. Usually odor has proven to be a more satisfactory criterion. For purposes of simplicity, flavor is used in this discussion as a common term to include both flavor and odor. The term "heat flavor reversion" refers only to the flavor and odor developed in soybean oils which have been hydrogenated to shortening consistency and heated at 140°C. in open beakers in a dark oven for four hours.

A great deal of previous experimental work in our laboratories has indicated that the glycerides themselves are the precursors of "heat flavor reversion," and, as brought out by others (3), moderate variations in processing, including degumming, etc., have failed to effect any marked improvement in the reversion characteristics. Nevertheless, in view of recent papers on this subject (4, 5, 9) which attribute soybean oil flavor reversion to unsaponifiable matter, etc., we have made additional experiments on the effect of unsaponifiable matter and material that may be removed by degumming.

I. THE EFFECT OF DOUBLE-DEGUMMING

Recent reports on German processing methods (4) and experimental work in this country (5) indicate that proper handling of oil seeds and oils coupled with double-degumming of the extracted oils before refining may improve the reversion characteristics of unhydrogenated soybean oils. Tests have recently been completed in our laboratories to determine if this treatment will improve the reversion of hydrogenated soybean oils. In the investigation at the Northern Regional Laboratory (5), 0.01% citric acid added before deodorization was tried in conjunction with the degumming. In our work on degumming this reagent was omitted since it is a separate factor which to evaluate properly would require duplicate tests with and without citric acid in the deodorizer. The time involved in such a test appeared prohibitive.

Experimental

In order to be sure that the oil used would be of exceptional quality it was extracted from No. 1 yellow beans in the laboratory and processed promptly with particular care being taken to protect the material from exposure to light, air, and excessive heat at all times.

The oil was extracted from the beans with chemically pure petroleum ether in a large Soxhlet-type extractor heated with a Glas-Col mantle. The entire apparatus was enclosed in a black cloth screen to eliminate exposure to light and the maximum temperature of the miscella was 60°C. Each lot of beans was cracked in a food chopper just prior to extraction. Twenty-one batches were handled, and each was extracted an average of 15 times, yielding 7,718 grams of miscella containing 3,930 grams of crude oil from 27,920 grams of beans. This left only about 2% oil in the meal. The petroleum ether was distilled from the miscella in a bath of hot water, using vacuum to remove the residual solvent. The crude oil was degummed twice with 2% H_2O at 65°C., separating the gums each time with a laboratory-model Sharples Super-Centrifuge. After degumming, the sample was refined with 0.2% excess NaOH as 16° Bé lye.

The refined stock was bleached with Special Filtrol earth at 120°C. in vacuo, hydrogenated to about 75 I.V. at 125°C. in a steel vessel, filtered, and then cleaned with 0.5% of neutral clay. The hardened stock was deodorized in an all-glass apparatus for several hours at approximately 200°C., employing high vacuum and a normal amount of steam. The finished samples and the controls were heated at 140°C. in open beakers in a dark oven for four hours. They were then evaluated by an experienced-calibrated panel according to the method explained in detail by Handschumaker (6).

Briefly, the sample to be tested and five controls—100% hydrogenated cottonseed oil (about 75 I.V.), the same cottonseed stock containing 25%, 50%, and 75% hydrogenated soybean oil and 100% hydrogenated soybean oil (approximately 75 I.V.)—were coded from A through F and each panel member was asked to arrange the six beakers in order of increasing bean characteristics by odor and/or flavor. The evaluation was kept as objective as possible by not informing the observers what samples were being tested as well as withholding the identity of the sample and controls. Each panel member made his selection without other members being present and, after completing the sample arrangement, reported his result on a piece of paper which was held in a ballot box until all the results were in. The sample and controls were then scored according to the method of Fisher and Yates (7). In addition to the foregoing test, doughnuts were fried in the special sample (extracted-degummed-processed) at 195°C. and evaluated by a panel of 20 experienced tasters.

Results

The extracted oil analysis shown in Table I appears normal for a good-quality extracted crude. The degummed stock had a free fatty acid of 0.15% and a Lovibond color of 35Y-12.4R. The bleached color on the refined oil was 25Y-1.7R while the color of the hydrogenated product was 4Y-0.4R and the F.F.A. 0.018%.

Although the constants on the deodorized stock indicate a soybean oil of unusually good quality, the heat-flavor reversion score was identical with that of the 100% commercially processed soybean oil control as shown in Table I. Likewise the specially degummed and processed sample exhibited no improvement in doughnut frying inasmuch as it scored the same as the regularly processed soybean oil.

Discussion

The fact that low-temperature extraction and double-degumming failed to improve the heat reversion charateceristics of soybean oil hardened to shortening consistency indicates strongly that phospholipids removed by degumming are not the precursors of this type of reversion.

On the surface these data may appear contradictory to those of Dutton et al. (5), but actually this is not the case since the type of reversion developed by holding unhardened soybean oil at 60°C. is entirely different from the flavor developed in hydrogenated soybean oil heated at elevated temperatures.

It is logical to expect the reversion precursors of hydrogenated and unhydrogenated oils to be different since both the basic compositions of the starting materials and the reverted flavors are different. Obviously, the significance of the work depends upon the accuracy of the reversion evaluations. The dependability of the results is indicated by an examination of our method of evaluation (6).

TABLE 1

Crude Oil

% Free Fatty Acid as Oleic	0.30
% Break	0.14
% Acetone Insoluble	0.29
% Volatile Matter (Hot-Plate Method)	0.22
Iodine Value (Wijs)	135.1
Thiocyanogen Value	81.7

Deodorized Stock

Lovibond Color	2Y-0.2R
% F.F.A. as Oleic	0.006
Peroxide Number	0.0
Flavor	Bland
Rancidity Stability Index	7.6
Rancidity Stability Index for Four Other Soybean Oils Processed Concurrently	8.3
Iodine Value (Wijs)	74.9
Thiocyanogen Value	69.2

Scores on Panel Evaluation of Soybean Oil Reversion

Sample	Score
100% Hydrogenated Cottonseed Oil	6.99
25% Soybean Oil	4.03
50% Soybean Oil	1.64
75% Soybean Oil	—1.20
100% Hydrogenated Soybean Oil	—5.73
Special Soybean Oil	—5.73

It should be noted that the "heat-flavor reversion" panel had been reduced to a few persons who were selected on the basis of their ability to discriminate between flavors on a large number of tests over a period of months. Moreover this calibration of the testers is based upon their proven ability to evaluate reversion without regard to previous experience or reputation in oil grading. We have found that, in addition to the native ability to detect flavors and odors of the heat-reversion type, considerable experience is required before an individual is able to make satisfactory distinction between the flavor levels of the five controls.

The system of five controls with each sample serves as an additional check on each panel member at the time of the test; and in the rare case in which the tester's arrangement of the controls was inaccurate, the results are not included in the scoring. This method of testing is quantitative as well as qualitative and the results have proven to be reproducible.

II. THE EFFECT OF UNSAPONIFIABLE MATTER

It was shown in the preceding section that nonglyceride materials removed by water-washing were not the cause of heat flavor reversion in hydrogenated soybean oil of shortening consistency. Obviously, this does not eliminate the possibility that unsaponifiable matter may be responsible since this material was present in the finished product.

In view of divergent opinions (2, 3, 8, 9) concerning the role played by this material an investigation has been made as to its effect on the heat-reversion characteristics of hydrogenated soybean oil. The original plan was to test the unsaponifiable fraction by adding it to cottonseed oil and comparing this with a glyceride made from the unsaponifiable-free soybean oil fatty acids. When it was found that heat-treated esterified samples have peculiar flavors and odors which are not present in heated hardened natural oils, the experiment was extended to include preparation of a reconstituted cottonseed oil to act as a carrier for the unsaponifiable material as well as reconstitution of cottonseed and soybean oil controls for comparison.

In this section, as in Part I, the term "heat-flavor reversion" refers only to the characteristic flavor and odor developed in soybean oils hydrogenated to shortening consistency when heated at 140°C. for four hours.

Since from a commercial standpoint "flavor reversion" is a problem of the glycerides as they occur naturally rather than of the fatty acids, it was considered best to make all reversion tests on samples in the glyceride state and this procedure was followed throughout. The unsaponifiable matter was removed from refined oil and added to the cottonseed oil carriers after refining, but before bleaching, hydrogenating, etc., so that this material was subjected to the same processing as it is when soybean oil is made into shortening.

In order to minimize variations due to processing all procedures were standardized as described below. In each case an attempt was made to choose the procedure that would ensure the best quality in the finished sample. In addition, the processing steps were calibrated by means of controls with the single exception of the effect of potash treatment on the soybean oil unsaponifiable matter. It is realized that alkali treatment may change the nature of the unsaponifiable material, but this is not considered important since the purified fatty acids themselves retained the heat-reversion characteristics.

All processing steps were performed in glass apparatus and care was taken to protect the materials from undue exposure to light and air. Insofar as possible, high temperatures were avoided.

Processing Procedures

Acidulation. An excess of 1:1 HCl was added and after clarification, the oily layer was washed five or more times with hot water.

Drying. Oils and fatty acids were dried under vacuum at temperatures less than 100°C.

Esterification. The method of Feuge, Kraemer, and Bailey (10) using stannous chloride catalyst and C.P. glycerine under an atmosphere of hydrogen at pressures of 20 mm. Hg absolute or less was employed.

Hydrogenation. All samples were hardened in glass at atmospheric pressure using electrolytic hydrogen and nickel catalyst at a temperature of approximately 140°C.

Refining. 16° Bé NaOH was used with excesses varying from 0.2% to 0.3% of NaOH calculated on the oil weight. Temperatures not greater than 65°C. were used.

Bleaching. Bleaches were made under a pressure of less than 25 mm. Hg with earths and temperatures as designated.

Postbleaching. 0.5% natural clay at 80-85°C. in vacuo was employed.

Deodorization. An all-glass apparatus was used. The pressure was 5 mm. Hg or less, using 10% steam by weight at 185° or 210°C. during the four-hour period.

Experimental

Two thousand two hundred fifty grams of refined extracted soybean oil containing 0.48% unsaponifiable, as analyzed by the A.O.C.S. method, was treated with 900 grams of KOH in five liters of commercial ethyl alcohol. After adjusting to a water-alcohol volume ratio of approximately 4:1, the soap solution was divided and extracted semi-continuously with petroleum ether in two five-gallon bottles. After 90 hours of extraction 0.21% unsaponifiable still remained in the soaps and the extraction was continued for a total of 110 hours. At the end of this period the petroleum ether was still removing color from the soap so the solution was transferred to 18 one-gallon bottles and extracted 11 times using 600 ml. of petroleum ether to each bottle every extraction. At this point, the petroleum ether layer still contained a little color, but this was attributed to slight solubility of soap since analysis showed no more than a trace of unsaponifiable.

After evaporating the extract to dryness in a hot-water bath under vacuum, the residue was resaponified with 30 grams of KOH in 950 ml. of alcohol with 90 minutes of refluxing. The soap solution was adjusted to a volume ratio of two parts of water to one part of alcohol for extraction with petroleum ether, using a volume ratio of petroleum ether to soap solution of approximately 2:5 for each wash. This mixture was extracted 40 times, taking great care to prevent soap from being carried over into the extract. In all three of the above extractions no emulsion difficulty was encountered. Although the number of extractions may appear excessive, the extra effort was made to be sure that all reasonable precautions were taken to ensure the purity of the separated constituents.

The purified dried extract weighed 15 grams, which was 0.67% of the original soybean oil weight. This material had an iodine value of 143.2 and a thiocyanogen value of 67.2. The reason for the difference between the 0.48% unsaponifiable matter found in the soybean oil by analysis and the 0.67% actually recovered has not been investigated. The purity of the unsaponifiable was checked, however, by washing a petroleum ether solution with 10% alcohol solution. There was no loss of material by the wash and the washings were neutral to phenolpthalein.

This final extract was redissolved in 1,000 ml. of petroleum ether and stored in the dark at 60°F. until used. It was found that a part of the extracted material was only sparingly soluble in petroleum ether and a small amount of solid matter failed to dissolve in the 1,000 ml. used.

The fatty acids were recovered from the soap remaining after removal of the unsaponifiable matter and after drying, were molecularly distilled between 95°C. and 118°C. under 9 μ pressure or less. Only the 82.5% middle portion was esterified, refined, hydrogenated to approximately 75 I.V., postbleached and deodorized at 185°C. This material is designated as Sample 1.

Sample 2, cottonseed oil with soybean oil unsaponifiable added, was prepared as follows: A sufficient amount of the well-shaken petroleum ether solution of soybean oil unsaponifiable matter was added to refined cottonseed oil to make its concentration the same as found in the original refined soybean oil, i.e., 0.67%. Analyses by the standard A.O.C.S. method showed the unsaponifiable to be 0.77% in the cottonseed oil before and 1.27% after the addition. This analytical discrepancy is similar to the one mentioned previously and has not been investigated. After careful removal of the petroleum ether in vacuo over a hot-water bath the mixture was bleached with 1% activated earth, hydrogenated to about 75 I.V., postbleached and deodorized under the same conditions as Sample 1.

The two samples were then heat-treated and evaluated for reversion by the new improved method with five controls (6). It was immediately apparent that Sample 1, the reconstituted acids, had a distinctly different type of odor and flavor, and it was not possible to compare it with the normal controls. However, the two reverted samples were also compared with each other directly.

In order to prepare a test wherein all samples would be strictly comparable, reconstituted soybean and cottonseed oil controls were prepared, and a reconstituted cottonseed oil was used as a carrier for the soybean unsaponifiable. Sample 3 was prepared by saponifying refined cottonseed oil, acidulating, washing, and drying the acids. After the dried acids were molecularly distilled at 90-100°C. under 3 to 11 μ pressure, a 78% middle cut was esterified and refined, and to this was added sufficient petroleum ether solution to add 0.67% of the soybean oil unsaponifiable matter. After carefully removing the solvent, the mixture was bleached with 1% activated earth at 120°C., hydrogenated to the usual iodine value, postbleached and deodorized at 185°C.

The reconstituted controls were prepared from the regular controls by separation of the acids, esterifying, bleaching with 5% activated earth at 120°C., refining, cleaning with 0.5% neutral clay at 80°C. in vacuo and deodorizing at 210°C.

Results

In the evaluation of soybean oil unsaponifiable in natural cottonseed oil (Sample 2) as well as in the reconstituted oil (Sample 3), it was noted that while the samples definitely did not have the typical heat-reversion odor and flavor, they were not as bland as cottonseed oils alone. In other words, while the soybean oil unsaponifiable did impart some flavor and odor to the heat-treated hardened cottonseed oils, the samples did not develop the heat-reversion flavor typical of hydrogenated soybean oil. This point was clearly demonstrated in the direct comparison of two samples. When the unsaponifiable carried in natural cottonseed oil (Sample 2) was compared to the reconstituted purified soybean oil fatty acids (Sample 1), eight out of nine panel members picked Sample 1 (reconstituted purified soybean oil) to be more beany, i.e., as having more heat reversion. Actual statements on the ballots submitted in this comparison are listed in Table No. 2.

As mentioned previously, the reconstituted soybean oil exhibited a heated flavor that was different from

TABLE 2

Direct Comparisons Between a Heat-Treated Cottonseed Oil Sample Containing Soybean Oil Unsaponifiable Matter and a Heat-Treated Glyceride Prepared From Unsaponifiable-Free Soybean Oil Fatty Acids

Panel Member	Panel Member Statements	
	Sample 1	Sample 2
	Unsaponifiable-Free Reconstituted Soybean Oil	Soybean Oil Unsaponifiable in Natural Cottonseed Oil
1	Beany	Not Beany
2	Beany	Not Beany
3	1 twice as beany as 2	
4	1 definitely more beany	
5	Soybean Oil	....
6	Soybean Oil	....
7	1 beanier than 2	
8	2 more beany than 1	
9	Soybean Oil	....

natural oils. This was attributed to the esterification procedure and several subsequent tests on various reconstituted samples have confirmed this. With a sample such as No. 1 which has a flavor distinctly different from the controls, it is obviously not possible to place it accurately. Furthermore, if the observer does place the sample, the position is largely influenced by personal preference. The difficulty of this situation may be illustrated by a hypothetical situation where comparison of chocolate flavors is made by tasting chocolate-coated vanilla creams and then an attempt is made to place a sample having a strong peppermint-flavored center. Repetition of the heat treatment and evaluations of Sample 1 confirmed the flavor abnormality due to reconstitution.

To determine if the reconstituted controls were distinguishable, a sample of each and a 50/50 blend of the two were heat-treated, coded and evaluated. The panel was unanimous in placing them in the correct order, thus showing that it was possible to identify the heat-reversion odor and flavor despite the masking effect of the reconstitution flavor. A preliminary evaluation of the soybean oil unsaponifiable matter in reconstituted cottonseed oil (Sample 3) with only three controls, as above, placed the unsaponifiable sample ahead of the cottonseed oil control, indicating absence of any soybean heat reversion.

Portions of Samples 1 and 3 were heat treated and then evaluated using the standard procedure of five controls as described in Part I. In coding, the two experimental samples were given the same letter with their identities being known only to the person (not a member of the panel) setting up the test. First, one sample was placed with the controls and called Set No. 1 and after the tester had arranged these samples in order of increasing beaniness, the person in charge of the panel test (in the absence of the evaluator), replaced the first test sample with the second, and the tester again arranged the samples in order and recorded the results as Set No. 2. This method afforded an effective comparison of the two samples since they were evaluated at the same time with identical controls.

In this test Sample 3 (reconstituted cottonseed oil containing soybean oil unsaponifiable) placed between the cottonseed oil and the 25% soybean oil controls while the reconstituted unsaponifiable-free soybean oil (Sample 1) placed between the 50% and 75% soybean oil controls. The scores of the test are shown in Table No. 3. The difference between the two samples is perhaps more clearly demonstrated by a direct comparison between the two coded samples in which eight panel members unanimously picked the reconstituted unsaponifiable-free soybean oil to be more beany than the unsaponifiable matter in reconstituted cottonseed oil. See Table No. 4.

TABLE 3

Scores on Panel Evaluation of Soybean Heat-Flavor Reversion

	Set 1	Set 2
100% Reconstituted Cottonseed Oil	4.01	3.38
Sample 3—Soybean Oil Unsaponifiable in Reconstituted Cottonseed Oil	....	1.47
25% Reconstituted Soybean Oil	2.12	1.28
50% Reconstituted Soybean Oil	0.84	1.08
Sample 1—Reconstituted Soybean Oil Unsaponifiable-free	−1.47	....
75% Reconstituted Soybean Oil	−1.68	−2.12
100% Reconstituted Soybean Oil	−3.82	−4.45

TABLE 4

Direct Comparisons Between a Heat-Treated Reconstituted Cottonseed Oil Sample Containing Soybean Oil Unsaponifiable Matter and a Heat-Treated Glyceride Prepared From Unsaponifiable-Free Soybean Oil Fatty Acids

Panel Member	Panel Member Statements	
	Sample 1	Sample 3
	Unsaponifiable-Free Reconstituted Soybean Oil	Soybean Oil Unsaponifiable in Reconstituted Cottonseed Oil
1	Strong Bean	Not Beany
2	More Like a Bean	
4	1 more beany than 3	
6	1 more beany than 3	
7	Beany	Like Cottonseed Oil
8	Beany	Not Beany
10	....	Least Beany
11	Beany	Not Beany

Discussion

Aside from rancidity, at least three distinctly different flavors may be developed in hydrogenated soybean oils, only one of which is the subject of this discussion. One of the three is the flavor developed in some soybean oils on shelf storage or when held at moderate temperatures (9, 14) which may be found in stocks that are inadequately processed (1). A second is the extremely disagreeable light-effect flavor which is found in soybean and other oils (1, 11). The third is the subject of this study and is, in itself, a specific problem distinct from the other two.

While the present work is not primarily concerned with the first type, it was found that the presence of an analogous flavor in Samples 2 and 3 complicated the evaluation of the heat-reversion flavor. In both of these samples the addition of the soybean oil unsaponifiable matter increased the amount of flavor developed on heating, even though it was not of the typical heat-reversion type. This is in accordance with the results reported by Mattil (9) in which he found that soybean oil unsaponifiable matter caused flavor development in oils at 95°F. Light-effect flavor was avoided by protecting the samples from light exposure and was therefore not a factor in this experiment.

It becomes obvious that in addition to the weakness inherent in all organoleptic evaluations the detection and estimation of the heat-reversion flavor is complicated by the presence of contaminating flavors and odors. Of these the reconstituted flavor was most serious in this study and as reported by Golumbic (12, 15) was found to make appraisal of reversion flavors difficult.

In the evaluation of one flavor component in the presence of other flavors our system of controls is particularly effective since the masking flavors are present in all samples and the differences are largely due to the heat-reversion factor.

The use of reconstituted controls substantially reduced the effect of the presence of this flavor but yet may account for the fact that Sample 1 failed to show more beaniness than the 75% soybean oil control. Likewise, the storage-type flavor imparted to the reconstituted cottonseed oil by the soybean oil unsaponifiable could account for the sample scoring similar to the 25% soybean oil control. In discussing the various flavors found in hydrogenated soybean oils, it should be mentioned that although 140°C. is used to develop heat reversion in our test, temperatures as low as 60°C. will develop the same flavor after extended exposure, usually more than three weeks.

While the system of five controls is very desirable from a quantitative and calculation standpoint, it should be realized that distinguishing between such narrow differences not only requires sharper perception on the part of the panel member but also necessitates more care and time to make the proper arrangement.

Also in such a system the inclination to place the samples in order of total flavor intensity rather than in order of quality can influence the evaluation. This, of course, is more likely to occur when the materials being compared have different types of flavors. For these reasons the preliminary three-control test and the direct comparison between the two samples (unsaponifiable matter versus unsaponifiable-free soybean oil) are important additions to the data.

In conclusion, this work presents strong evidence that neither the non-glyceride materials removed by water-washing nor the unsaponifiable matter is responsible for the heat-reversion flavor in soybean oil hydrogenated to shortening consistency.

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Deodorizer Catch Basin Sludges and the Metallic Soaps Found Therein*

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THE steam distillation method of deodorizing edible oils is a well known industrial process, which has been adequately described in the literature (1), (2), (3), (4). In the United States alone over one and a half billion pounds of vegetable and animal fats are deodorized each year. As a result of this process, there is produced a by-product which is known in the trade by various names such as deodorizer catch basin skimmings, deodorization sludge, hot well skimmings, deodorigation distillate, etc. All of these names refer to the sludge formed by emulsification of the highly complex mixture of organic compounds, distilled from the oil being deodorized, with water in the barometric condensers, and it will usually contain more or less dissolved soap formed by reaction with minerals in the water. The material appears first as small white flocs in the discharging water from the barometric condensers. The extent to which these flocs rise to the surface and form a recoverable sludge depends largely on the efficiency of the catch basin, but even the most efficient of catch basins would be expected to lose an appreciable proportion of the material on account of its physical condition.

Just how much of this by-product material is produced in the United States each year would be hard to say, but it is safe to assume that it is less than fifteen million pounds and certainly a much smaller amount is actually recovered. However, the composition of the sludge is of considerable interest in spite of the relatively small amount recovered. This is true for a number of reasons. Among others is the fact that all of the organic compounds found in the deodorization sludge were either present in the original oil or else their precursors were, and they are the compounds which contributed the flavors and odors to the raw oils. Too, in practical refinery operations the question of losses during deodorization is of considerable importance and certain substances, particularly soaps, if present in the sludge in appreciable quantities, may affect the results obtained in studies relating to these losses.

In spite of the obviously interesting character of deodorizer catch basin sludges, relatively little has been published regarding their composition. Jasperson and Jones (5) have made a study of the unsaponifiable constituents of some deodorizer distillates. Daubert and co-workers (6) have obtained some highly interesting results on soybean oil deodorization distillates produced in the laboratory, but these would differ somewhat from industrial materials, especially in their lack of metallic contamination. Hickman, in a series of U. S. Patents, (7) has described the recovery of tocopherol, sterols, etc., from deodorization sludges, and he gives general limits for free fatty acid contents. He also notes the presence of calcium and iron soaps and describes their removal by decomposition with strong acids. However, no exact data on the composition or percentage of metallic soaps present in deodorization sludges are given.

In the course of other work it was noted that deodorization sludge oil, which had been completely freed of insoluble material by filtering and bleaching, was nevertheless not completely soluble in cold Skellysolve-F, a commercial solvent consisting largely of pentanes, hexanes, and heptanes. When it was further found that the precipitated material represented a quantitative recovery of the calcium soaps present and that the fatty acids in these soaps were

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