Rice Bran Oil. III. Utilization as an Edible Oil

R. O. FEUGE and P. B. V. REDDI,[1] Southern Regional Research Laboratory,[2]
New Orleans 19, Louisiana

RELATIVELY minor amounts of rice bran oil have been marketed in the United States over a period of years. The greater portion of this oil has been of low quality—dark in color, high in free fatty acid content, and difficult to refine and bleach. There are no established uses for this oil, and it has been employed for such diverse purposes as food and soap stock and as an emulsifier for asphalts.

Potentially, rice bran oil can be of considerable economic significance in the rice milling industry. Concentration of the latter in a few centers in the rice growing regions of the United States is favorable to the establishment of extraction plants capable of producing a steady supply of the oil. Recent work (10) has shown that solvent-extracted oil obtained from freshly milled rice bran has a low free fatty acid content and that the crude oil can be converted by conventional refining and bleaching procedures into a clear light-colored product having good odor and flavor. The most logical outlet for this oil is therefore in the edible field.

Data with respect to the composition and characteristics for rice bran oil which are presented here were obtained from products prepared in the laboratory and pilot plant from crude oil obtained by extracting fresh rice bran with commercial hexane as described in a previous publication (10). The object of the present work has been to compare rice bran oil and derived products with other typical edible oil products.

Cooking Oil

When crude rice bran oil is of good quality, its odor and flavor are bland and pleasant, and the oil could be used in certain instances without purification. However, in the United States the almost universal preference is for bland, light colored, neutral oils. Rice bran oil can be processed to produce a tasteless, odorless, and neutral product by the usual processes of alkali refining, bleaching, and deodorization.

The fatty acid composition, iodine value, and content of unsaponifiable of typical refined peanut, cottonseed, and rice bran oils are compared in Table I. The data recorded in this table shows that the fatty acid composition and iodine value of rice bran oil is similar to that of cottonseed and peanut oils. In fact, the degree of unsaturation of rice bran oil is intermediate between that of the other two oils. The glycerides in rice bran oil are such that the oil will not solidify at ordinary temperatures, and the unsaturated fatty acids are such that the oil is not unduly subject to oxidative rancidity or polymerization.

The smoke, flash, and fire points of a rice bran oil were determined according to the official method of the American Oil Chemists' Society, using a gas-heated, Cleveland open cup. Since the presence in an oil of minor amounts of free fatty acids markedly lowers the smoke, flash, and fire points (8), refined and bleached oils containing only a few hundredths of 1% of free fatty acids were used in each case for these determinations. The thermal properties (Table II) of rice bran oil as measured by the standard tests does not appear to be significantly different from that of choice cooking oils of comparable quality.

TABLE I

Fatty Acid Composition, Iodine Value, and Content of Unsaponifiable Matter of Refined Rice Bran, Peanut, and Cottonseed Oils

Analysis	Rice bran oil	Peanut oil	Cottonseed oil
Fatty acid composition:			
Saturated, %	17.6	20.0	24.0
Oleic, %	47.6	50.0	24.6
Linoleic, %	34.0	30.0	51.0
Linolenic, %	0.8	0	0
Iodine value of oil	102.3	95.0	109.2
Unsaponifiable matter, %	2.7	0.5	0.5

TABLE II

Thermal Stability and Crystallization Constants of Rice Bran, Peanut, and Cottonseed Oils After Refining and Bleaching

Characteristic	Rice bran oil	Peanut oil	Cottonseed oil
Smoke point, °F., (A.O.C.S.)	415	445	425
Flash point, °F., (A.O.C.S.)	615	625	613
Fire point, °F., (A.O.C.S.)	665	680	683
Cloud point, °F., (A.S.T.M.)	34	40	38
Solid point,[a] °F., (A.S.T.M.)	18	34	28

[a] Modified by examination of the sample at intervals of 2° rather than 5°F.

The cloud and solid points were determined according to the A.S.T.M. standard method for lubricating oils except that the solid point determination was modified to include examination of the oil at intervals of 2° rather than 5°F. The results are compared with those obtained on samples of comparable refined and bleached peanut and cottonseed oils. The cloud point of rice bran oil (Table II) appears to be somewhat below that of peanut and cottonseed oils. The wax normally present in rice bran oil was removed in this particular case by permitting an oil which had been stored in a refrigerator to come to and remain at room temperature for 24 hours and then filtering it through a diatomaceous filter aid.

The surprisingly low solid point found for the rice bran oil may indicate that the distribution of the fatty acids in the glycerides follows the even distribution rule (5) more exactly than either cottonseed or peanut oil. A less likely explanation is that the approximately 2 or 3% of unsaponifiable material still present in heavily refined, washed, and bleached rice bran oil may serve as a protective colloid to retard crystallization at low temperatures.

One of the principal requisites of a good quality edible oil is good shelf-life or keeping quality. Three or four rice bran oils examined to date were decidedly more resistant to oxidative rancidity than average good quality cottonseed and peanut oils. The stability of refined and bleached rice bran oils was found to be approximately 15-16 hours when measured by the active oxygen method (11) at 97.7°C. and using a peroxide value of 100 milliequivalents

[1] Department of Industries and Commerce, Government of Madras, India.

[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

per kilogram as the end point. The crude oils had a keeping time of 24-25 hours. Even at 100 milliequivalents of peroxide the rice bran oils showed no organoleptic evidence of rancidity. Plots of peroxide value *vs.* time showed no induction periods and were essentially straight lines. This type of curve is indicative of the presence of greater than optimum amounts of antioxidants in the oil.

It has been stated (6) that imported rice bran oil had a tendency to darken on processing. Color measurements were made on rice brain oils after each processing operation, and it was found that they behaved normally during refining, bleaching, deodorization, winterization, and hydrogenation. For example, the Lovibond color (1) of a refined, washed, and bleached rice bran oil was reduced from 35 yellow and 2.91 red to 20 yellow and 1.91 red, on deodorization for one hour at 450°F.(232°C.) and at a pressure of 1.5 mm. of mercury.

Winterized Oil

Large quantities of winterized or destearinized edible oils are marketed in the United States. Cottonseed oil is the most widely used winterized oil in this country. A comparison of the winterization of rice bran and cottonseed oils was made by the customary method of winterization in which the oil is cooled to 42°-45°F.(7°-8°C.), held at this temperature range for some time, and filtered. In commercial practice the process is slow and critical, and great care must be exercised in the handling and chilling of the oil. Usually three to six days are required to chill and filter a batch of oil.

Examination of rice bran and cottonseed oils after simultaneous storage in a refrigerator indicated that the former remained partially liquid under conditions under which the cottonseed oil appeared to solidify completely. A sample of rice bran oil was shock-chilled to 39°F.(4°C.) and held at this temperature for 17 hours. The liquid oil obtained on filtration amounted to 82.6%. The cold test (1) for the liquid oil fraction was less than 5½ hours, and therefore was incompletely winterized. It was found, however, that rice bran oil could be successfully winterized in a comparatively short time by the following procedure: About 300 g. of oil was warmed to 120°F.(49°C.), cooled to room temperature, placed in a chilling flask which was immersed in an ethanol bath, and the temperature of the bath reduced from 80°F.(27°C.) to 54°F.(12°C.) at a constant rate of six degrees per hour. The temperature of the bath was then lowered to 42°F.(7°C.) at a rate of three degrees per hour. After holding the oil at 42°F. (7°C.) for 18 hours, filtration under vacuum was started, using a fritted glass disc approximately 6½ cm. in diameter and of medium porosity. Filtration was carried out without removing the oil or apparatus from the cooling bath. About half of the total filtrate passed through the filter at the end of two hours. Filtration was continued for an additional 11 hours to obtain a yield of 94.5% of winterized oil having a cold test of 9 hours.

Cottonseed oil was winterized by exactly the same procedure, but the filtration rate was much lower than that of rice bran oil. Filtration of the cottonseed oil was considered complete after 21 hours, and the final yield was 57.7% of filtrate having a cold test in excess of 30 hours.

In Table III comparative results are given for a rapidly winterized rice bran oil and a winterized cottonseed oil obtained by the conventional process. As is evident from this table, rice bran oil gives a much better yield of winterized oil in a shorter time.

TABLE III

Comparison of Rapidly Winterized Rice Bran Oil and Conventionally Winterized Cottonseed Oil

Factor	Rice bran oil	Cottonseed oil
Chilling time, hrs.	26	36-120
Yield, %	94.5	65-75
Cold test,[a] hrs. (A.O.C.S.)	9	5-15
Cloud point, °F., (A.S.T.M.)	20	24-26
Pour point,[b] °F., (A.S.T.M.)	18	20-22

[a] Time required to cloud, at 32°F.(0°C.).
[b] Modified by examination of the oil at intervals of 2° rather than 5°F.

Hydrogenated Products

The hydrogenation of alkali-refined and bleached rice bran oil presents no unusual difficulties. The reduction in iodine value proceeds as easily and smoothly as it does with other high grade edible oils. The decrease in color during hydrogenation is quite marked in the case of rice bran oil. The rate of hydrogenation and reduction in color of a rice bran oil is shown in Table IV.

TABLE IV

Reduction of Color During Hydrogenation of Rice Bran Oil Under Normal Conditions[a]

Sample No.	Iodine value	Hydrogenation time, min.	Lovibond color	
			Yellow	Red
R-3-0	104.3	0	35	3.1
R-3-1	88.4	11¾	20	2.3
R-3-2	79.1	19¼	20	1.9
R-3-3	74.3	23¼	20	1.6
R-3-4	70.7	26	15	1.5
R-3-5	67.9	28	15	1.2

[a] At 350°F.(177°C.), 15 p.s.i.g., 0.10% nickel catalyst, and medium agitation.

At a given temperature the refractive index of many hydrogenated vegetable oils is very nearly the same for a given iodine value, and the hydrogenation process is often followed and controlled by measurement of the refractive index. The refractive index was determined on a series of samples withdrawn at intervals during hydrogenation under moderately selective conditions, i.e., at 350°F.(177°C.), 15 p.s.i.g. hydrogen pressure, 0.10% nickel catalyst, and medium agitation. The variation of iodine value with

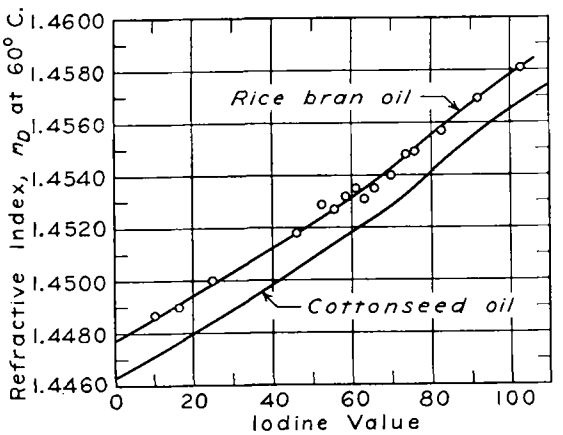

FIG. 1. Iodine value *vs.* refractive index of hydrogenated rice bran and cottonseed oils.

refractive index for this oil is reproduced in Figure 1 in comparison with that for cottonseed oil.

It has been pointed out by Bailey (2) that the iodine value-refractive index curves for cottonseed, soybean, sesame, and corn oils are practically identical because of the similarity in the average molecular weights of the fatty acids of these oils. Since the average molecular weight of rice bran oil fatty acids very nearly equals that of cottonseed oil fatty acids and since the curves representing the refractive index *vs.* iodine value for the two oils do not coincide, the curve for the rice bran oil must be regarded as somewhat peculiar. Data for the refractive index-iodine value relationship obtained on a series of samples prepared from another sample of rice bran oil were found to be practically identical with the data represented by Figure 1. The discrepancy in the behavior of rice bran oil is probably attributable to the relatively high content of highly unsaturated (iodine value 109) unsaponifiable matter of rice bran oil. Rice bran oil is derived from both the seed coat and germ of the rice grain, and it is possible that the oils from these two organs differ significantly in degree of unsaturation and glyceride configuration, and any marked peculiarity of this nature would influence the consistency of the product obtained on hydrogenation.

In the absence of any published data on the iodine value-consistency relationship for hydrogenated rice bran oil, a series of hydrogenated oils was prepared and consistency measurements made. The micropenetration determinations were made with the apparatus and procedure described by Feuge and Bailey (3). Essentially, this method consists of dropping a steel needle into a sample of fat chilled and tempered under specified conditions. The penetration of the needle into the fat is measured in tenths of a millimeter and recorded as the micropenetration value at the temperature of the test.

In Figure 2 micropenetration curves are given for samples of rice bran oil hydrogenated to different iodine values. Curves for peanut oils hydrogenated under similar conditions are included for comparison. For a given plasticity the iodine value of the peanut oil is slightly lower than for rice bran oil; however, this is to be expected in view of the originally lower iodine value of peanut oil. Over the temperature ranges shown, a given peanut oil first softens slightly more rapidly and then slightly less rapidly than the equivalent rice bran oil. When the

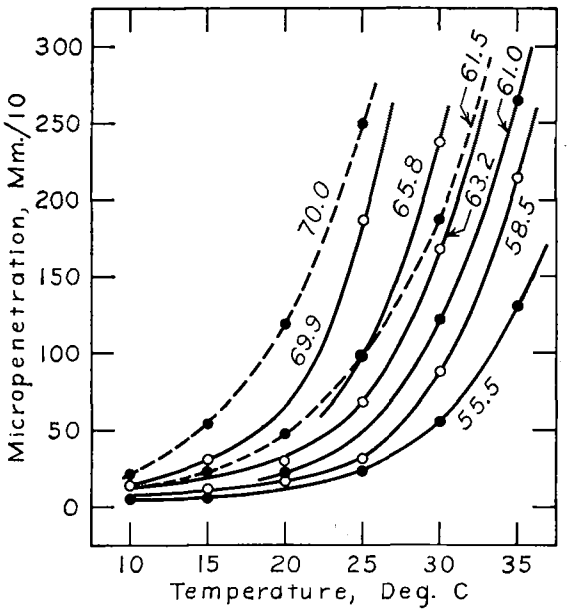

FIG. 2. Consistency of rice bran and peanut oils hydrogenated under identical conditions to varying degrees of hardness. The dotted lines refer to peanut oils and the solid lines to rice bran oils. The numbers on the curves are the iodine values of the oils.

plasticity of the hydrogenated rice bran oils was compared with those of a similarly hydrogenated cottonseed oil, no difference was observed. The curves for samples of equal iodine values practically coincided. The similarity of the curves for the three oils indicates that under similar conditions of hydrogenation the plastic behavior of rice bran oil is similar to that of cottonseed and peanut oils. These curves also indicate that in unhydrogenated rice bran oil the fatty acid distribution is of the even type generally encountered in vegetable oils.

The outstanding characteristic of rice bran oil, which sets it apart from other oils of similar type, is its superior resistance to oxidative rancidity. All samples examined to date have exhibited keeping qualities considerably greater than those expected of other vegetable oils of similar properties.

Hydrogenated rice bran oils also have been found to be exceptionally stable to oxidation; however, a valid comparison of hydrogenated products is slightly more involved. The stability or keeping quality of a hydrogenated product is related not only to its iodine value but also to the types and proportions of un-

TABLE V

Analysis and Keeping Quality of Hydrogenated Rice Bran Oils [a]

Sample	Iodine value	Thiocyanogen value	Fatty acid composition,[b] per cent			Saturated acid content, %		Keeping quality,[c] hrs.	Conjugated constituents on fatty acid basis, %		
			Sat.	Oleic	Linoleic	Betram [d]	Lead salt		Diene	Triene	Tetraene
R-3-0[e]	104.3	76.0	20.1	40.2	38.5	16.5	15.5	15	0.210	0.030	0.010
R-3-1	88.4	73.4	17.8	62.1	18.3	17.4	.....	34	1.550	0.003	0.004
R-3-2	79.1	72.7	16.1	75.9	7.5	17.9	18.0	76	0.520	0	0.002
R-3-3	74.3	71.7	15.9	81.8	2.2	18.9	.....	193	0.140	0	0
R-3-4	70.7	70.4	18.0	81.7	0.2	22.0	21.8	340	0.090	0	0
R-3-5	67.9	67.9	21.1	78.8	0	24.3	24.7	501	0.082	0	0
R-3-6	64.3	64.2	24.9	75.0	0	27.4	27.6	537	0.090	0	0
R-3-7	61.3	60.7	28.8	71.1	0	32.9	31.6	.....	0.087	0	0
R-3-8	56.3	58.1	34.6	65.3	0	.....	.....	627	0.094	0	0
R-3-9	51.8	53.9	39.8	60.1	0	.....	.....	680	0.091	0	0
R-3-10	41.0	38.2	52.4	47.5	0	.....	.....	910	0.098	0	0

[a] Hydrogenated at 350°F.(177°C.), 15 p.s.i.g., 0.10% nickel catalyst, and medium agitation.
[b] Calculated from spectrophotometric absorption data.
[c] Active oxygen method (11) employing a temperature of 97.7°C. and a peroxide value of 100 milliequivalents per kilogram of fat as the end point.
[d] Analyzed without removing the 3.14% of unsaponifiables present.
[e] Original, unhydrogenated oil.

saturated fatty acids combined in the glycerides and probably also to a slight extent to the conditions of hydrogenation.

To obtain stability data on hydrogenated rice bran oils of known composition, a refined and bleached rice bran oil was hydrogenated in an iron converter; samples were withdrawn at various intervals for determination of iodine and thiocyanogen value, fatty acid composition, content of conjugated constituents, and keeping quality. Part of the data with reference to the fatty acid composition and the amount of conjugated constituents were determined spectrophotometrically according to a tentative method of the American Oil Chemists' Society. Saturated acids were also determined by means of a slightly modified Betram oxidation method (9) and by the lead salt method of the American Oil Chemists' Society. Thiocyanogen values were determined by a modification (7) of the Kaufmann method. The results are summarized in Table V. The data on conjugated constituents indicates that the samples of oil were unoxidized and otherwize unaltered in processing. The fatty acid composition of the samples were calculated from the iodine and thiocyanogen values and were found to agree reasonably well with those determined by the spectrophotometric method. Discrepancies in the content of saturated fatty acids determined by the several methods of analysis were noted, especially in the case of the unhydrogenated oil, but they were of the order of magnitude observed in several other common vegetable oils to which the aforementioned two methods of determination have been applied.

The stabilities of cottonseed and peanut oils which were previously hydrogenated and analyzed under identical conditions (4) are compared with that of rice bran oil in Figure 3. Under conditions in which equal quantities of the various unsaturated fatty acids are present in all three oils, the superiority of rice bran oil is immediately apparent. When the stabilities of the hydrogenated products are compared on the basis of equal contents of glycerides of linoleic acid, the hydrogenated rice bran oil is decidedly more stable in spite of the fact that it contains the greatest amount of oleic acid glycerides. At iodine values below 65, the composition of the three oils are nearly identical; and here too the rice bran oil exhibits better keeping quality. The only sample comparing favorably with the equivalent sample of rice bran oil was a peanut oil with such a low iodine value that its keeping quality was of no practical importance. For products of a shortening-like consistency the rice bran oil is at least twice as stable as the other oils even though the peanut oil used for comparison is a better than average product.

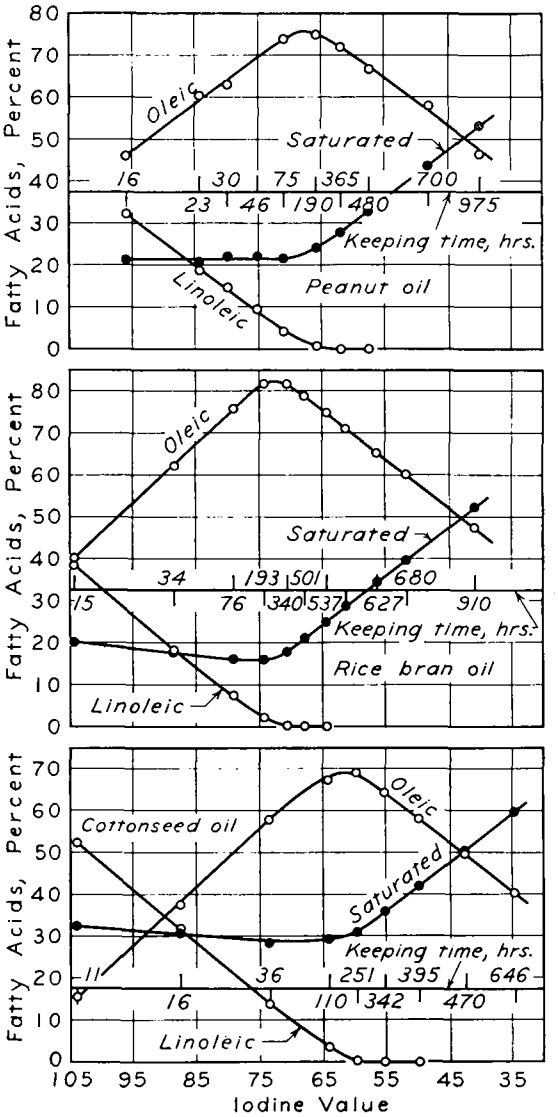

FIG. 3. Comparison of keeping time and composition of hydrogenated cottonseed, rice bran, and peanut oils.

Summary

1. Rice bran oil, which was produced on a pilot plant scale, has been examined for the purpose of determining its value as a cooking oil, winterized oil, and hydrogenated fat.

2. Rice bran oil is well suited for use as a cooking oil. An odorless, tasteless, and neutral product can be produced by conventional refining, bleaching, and deodorization. The smoke, flash, and fire points of the purified oil are comparable to those of other high quality edible oils. While the iodine values of rice bran and cottonseed oils are similar, rice bran oil solidifies less easily than either cottonseed or peanut oil. Rice bran oil is more resistant to oxidative rancidity than are the average cooking oils.

3. Rice bran oil can be winterized with relatively little difficulty. The yield of a well winterized oil is over 90% compared to 65-75% for well winterized cottonseed oil. Of the two oils, rice bran oil can be winterized more easily and rapidly.

4. During hydrogenation rice bran oil behaves like a typical vegetable oil with respect to ease of hydrogenation and reduction in color. The refractive indices of the hydrogenated products are higher than those of other natural oils having similar fatty acid compositions. The plasticity of hydrogenated rice bran oil is almost identical with that of hydrogenated cottonseed oil having a similar iodine value and produced under comparable conditions. The keeping quality of hydrogenated rice bran oil is decidedly superior to that of cottonseed and peanut oils of similar fatty acid composition.

Acknowledgment

The authors wish to express their appreciation to F. G. Dollear and Mrs. Josephine Loeb for assist-

ance in obtaining most of the compositional data reported here and to R. T. O'Connor and Miss Dorothy Heinzelman for the spectrophotometric analyses.

REFERENCES

1. American Oil Chemists' Society, Official and Tentative Methods, 2nd ed., edited by V. C. Mehlenbacher, Chicago, 1946.
2. Bailey, A. E., Industrial Oil and Fat Products, Interscience Publishers, Inc., New York, 1945, pp. 610-611.
3. Feuge, R. O., and Bailey, A. E., J. Am. Oil Chem. Soc., *21*, 78-84 (1944).
4. Fisher, G. S., Bickford, W. G., and Dollear, F. G., J. Am. Oil Chem. Soc., *24*, 379-382 (1947). Fisher, G. S., O'Connor, R. T., and Dollear, F. G., J. Am. Oil Chem. Soc., *24*, 382-387 (1947).
5. Hilditch, T. P., The Chemical Constitution of Natural Fats, Wiley, New York, 1941.
6. Kester, E. B., and Van Atta, G. R., Oil & Soap, *19*, 119-125 (1942).
7. Lambou, M. G., and Dollear, F. G., Oil and Soap *22*, 226-232 (1945).
8. Morgan, D. A., Oil & Soap, *19*, 193-198 (1942).
9. Pelikan, K. A., and von Mikusch, J. D., Oil & Soap, *15*, 149-150 (1938).
10. Reddi, P. B. V., Murti, K. S., and Feuge, R. O., J. Am. Oil Chem. Soc., *25*, 206-211 (1948).
11. Report of the Committee on Analysis of Commercial Fats and Oils, Oil & Soap, *22*, 101-107 (1945).

Report of Seed and Meal Analysis Committee 1948-1949

THE Seed and Meal Analysis Committee has seven subcommittees engaged in the study of and/or collaborative testing of methods of analysis. Their activities and recommendations are given in this report.

Report of Subcommittee on Soya Flour Sampling

The committee is happy to report agreement on methods for sampling soya flour and the proposed methods are submitted herewith. No provision has been made for automatic sampling since investigation of current mechanical samplers has revealed operational incompatibilities of the devices with soya flour. Nevertheless, the work of the committee might well be extended towards a comprehensive examination of mechanical samplers vs. soya flour.

Soya Flour Sampling

Scope: Applicable to soya flour

I. PRODUCTION SAMPLING

A. *Apparatus:*

a. Small scoop (ca 1-2 oz.) of conventional design.

b. Closed container for retaining bag samples. It is suggested that the container have a diameter of ca 10", a height of ca 10" and be constructed from 26-28 gauge non-rusting sheet metal. The container should be equipped with a tight fitting lid which is replaced by a spouted cover during the actual sampling period. (See drawing.)

c. Sealable containers of ca 16 oz. capacity.

B. PROCEDURE:

1. Ca 1-2 oz. of flour is removed from bag by means of scoop at bagging point.
2. Sample is transferred to large, closed container through spout on cover of container.
3. Bags shall be sampled at regular intervals. Not less than 10% of bags in lot shall be sampled. If lot is composed of less than 100 bags, a minimum of 10 bags shall be sampled. Final composite sample shall not be less than five pounds.
4. Spouted cover on sample container is replaced by tight fitting cover on completion of the lot sampling.
5. The lot sample shall be mixed thoroughly by agitation and/or tumbling to give a homogeneous mass.
6. Portions of thoroughly mixed lot sample may be delivered to clean, airtight 16 oz. containers. The portions shall be scooped from various points around and in the lot sample.
7. Containers shall be filled to within 1/4" of top and be sealed immediately on completion of transfer.

II. SAMPLING AT LOADING, UNLOADING, STORAGE, OR TRANSIT POINTS

A. *Apparatus:*

a. Trier of stainless steel construction and equipped with a special cutting lip. The overall length of the trier is 31". The tube or body of the trier has an I.D. of 5/8" and a wall thickness of 1/32". Body of trier is slotted, the slot being 20" long and 1/4" wide. Right side of slot is slightly depressed while left side is somewhat raised, thus forming a cutting lip. A 2 1/2" tapered point is sealed off from the slot and body. A concentric, 5" wooden handle completes the trier, thus enabling the trier to be emptied by inversion.

b. Sealable container of ca 1/2 gallon capacity.

B. *Procedure:*

1. A number of bags equivalent to the square root of number of bags in lot, but not less than 10 bags must be sampled, i.e., 10 bags from 100 or less, 15 from 225, 20 from 400, etc.
2. Bags selected for sampling must be uniformly distributed throughout the whole lot.
3. From every bag selected for sampling, a core is drawn from a top corner of the bag