Soy-Bean Oil: Factors Which Influence Its Production and Composition^{1,2}

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PHYSICAL AND CHEMICAL PROPERTIES

Soy-bean oil is more like linseed than most oils. In chemical properties, however, it is not unlike corn oil, but if it is to be used for paint manufacture special driers are desirable.³ A tungstate drier, such as a mixture of precipitated lead and manganese salt of tung oil, is excellent. A hard, dry, resistant film is produced with 5 to 7 per cent of drier, in 24 hrs. Soy-bean oil contains about 95 per cent of glycerol esters of fatty acids in proportion as follows: palmitic, 15 per cent; oleic, 50 per cent; linolic, 19 per cent; and linolenic, 5 per cent. It is to the latter three *unsaturated* acids that the oil owes its drying power. After hydrogenation, soy-bean oil can replace linseed in the manufacture of hard soaps. As an average of sixteen determinations, the iodine number of sixteen samples of imported and domestic oils was 129.2. The range was from 120 to 135. Soy-bean oil decreases the iodine number of linseed oil when mixed with it, but not appreciably until approximately 20 per cent of the former has been added.^{4,5}

The results of tests made on soy-bean oil are given in Table I. There was considerable variation in color and appearance of the samples used for this work. The imported samples were composites of equal quantities of each of three distinct lots. The prepared samples were obtained by crushing and extracting with ether four different lots of each of the varieties being tested. Official methods were abandoned in several determinations because of the greater simplicity of Thompson and Morgan's⁶ methods.

TABLE I

Source of Sample	Sp. Gr.	Refractive Index 25° C.	Iodine Number	Saponification Number	Acid Number	Drying Power
Warren Co. No. 1	0.924	1.4748	130.1	194.6	0.8	Fair
Warren Co. No. 2	0.923	1.4750	128.2	195.8	2.1	Fair
Warren Co. No. 3	0.922	1.4736	131.3	190.2	0.3	Poor
Warren Co. No. 4	0.925	1.4740	125.7	191.3	2.6	Poor
Mid Green Soybeans	0.925	1.4739	123.2	193.8	0.3	Poor
Black Eyebrow Soybeans	0.924	1.4726	125.0	195.0	0.2	Good
Houston Soybeans	0.925	1.4732	128.1	193.5	0.17	Fair
Blackbrook Soybeans	0.924	1.4740	128.1	191.8	0.3	Good
Barth-Hansen Soybeans	0.926	1.4720	128.0	193.0	0.2	Fair
Tarheel Soybeans	0.926	1.4741	132.3	193.0	0.55	Poor

Additional determinations were made upon two samples, particularly for the purpose of comparing imported Manchurian oil with domestic oil.

TABLE II

Source of Sample	Reichert-Meissl No.	Hehner No.	Neutralization Value	Unsaturated Fatty Acids	Saturated Fatty Acids	Ether No.
Warren Co. No. 2 Imported	4.3	94.3	190.3	85.7	8.6	190.1
Black Eyebrow Soybeans (Composite of 16 samples)	5.2	95.0	195.2	84.9	9.2	187.2

These data show the close similarity which exists among different lots of soy-bean oil. The specific gravity is prac-

tically constant at 0.925 and the refractive index varies but little from 1.474. The iodine number is more variable, ranging from 123.2 to 132.3. Some investigators have maintained that imported oils have a higher value and hence better drying properties than domestic oils, but these data do not bear out this contention. Nemzek¹ points out that iodine value and drying power do not necessarily go hand in hand, although such is often the case.

The saponification values are fairly constant between 190 and 195, a value which is near the average for neutral oils. This high number also indicates that the percentage of volatile acids is not high and that there is but little unsaponifiable matter. This is of great importance to the soap manufacturer. The acid value varies considerably in the several samples. Two high values were found in imported oils. Gardner,² in his repainting tests at Washington, D. C., showed that the acid value of a sample of soy-bean oil increased in 2.5 yrs. from 3.8 to 5.7. The drying power of the oils was determined by exposing oil films of uniform thickness on pine boards. This was merely to enable the writer to class the oils roughly as good, fair, or poor driers. Sample 4 imported oil, and Tarheel and Medium Green oils were markedly poorer than the rest. In the former, the iodine value is low and the acid value is high. The low Reichert-Meissl number shows but a very small percentage of volatile fatty acids to be present. The percentage of insoluble fatty acids plus the unsaponifiable matter gives the Hehner value of an oil. As Thompson and Morgan³ point out, this is a difficult determination to perform with soy-bean oil, since a solid cake of the fatty acids is hard to secure. Each result in Table II represents the average of four determinations. Since the per cent of unsaponifiable matter is so slight, the Hehner value practically represents the insoluble fatty acids alone. The proportion of unsaturated to saturated fatty acids is nearly 10 to 1. It is to the former that soy-bean oil owes its drying properties. It was observed that some of the oils examined remained perfectly clear, while others showed a considerable amount of flocs and were therefore inferior in quality. It was also observed that, in general, light colored beans gave a paler oil than the dark colored varieties, also the oil appeared to dry more quickly. It is realized, however, that no conclusions may be drawn from this mere observation.

According to Toch,⁴ cold-pressed soy-bean oil, heated to 500° C. for from 5 to 7 hrs., thickens like linseed oil and attains a specific gravity of 0.960 or more. Such an oil is certainly suitable for use in certain paints. In general, the latter are not as glossy and require somewhat longer to dry than linseed paints, but mixtures up to 33 per cent or even higher have given very good results in practical exposure tests. It is probably at its best when used in interior paints, baking japans, and in varnish. Soy-bean oil varnish requires longer to dry but is substantially like linseed varnish after a short exposure.

Analyses of two composite samples of soy-bean oil, obtained from sixteen different samples of Black Eyebrow soy beans were made, with the following average results: saturated fatty acids, 9.2 per cent; unsaturated fatty acids, 8.49 per cent. The values obtained by Thompson and Morgan⁵ on a composite sample agree very well with these.

¹ Educational Bureau, Paint Manufacturers' Association of the United States, Circular 37.

² *Ibid.*, 30; Bulletin 53.

³ *Loc. cit.*

⁴ *J. Soc. Chem. Ind.*, 31 (1912), 572; *Oil and Color Trades J.*, May 1913.

⁵ Delaware Agricultural Experiment Station, Bulletin 98 (1912).

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⁶ Work done at Rutgers College and the New Jersey Agricultural Experiment Station, New Brunswick, N. J.

¹ *J. Soc. Chem. Ind.*, 31 (1912), 572; *Oil and Color Trades J.*, May 1913.

² North Dakota Agricultural Experiment Station, *Special Food Bulletin* 23 (1913).

³ Quoted from "Soya," a bulletin published by A.M. Parks, Importers, The Hehrer, Philadelphia, Pa.

⁴ Delaware Agricultural Experiment Station, Bulletin 98 (1912).

OIL AND PROTEIN CONTENT OF VARIOUS SOY-BEAN VARIETIES

Since the amount of oil contained in several varieties tested was exceedingly inconstant, this point was studied further. The amount of oil present in the seed, as well as its drying power, are important from the standpoint of the paint or varnish industry. The greater number of samples were secured from the variety plot tests which have been conducted at the N. J. Agricultural Experiment Station for several years. A few were obtained from seed houses in Newark and Philadelphia. The samples were partly dried to facilitate grinding, ground to pass a 40-mesh sieve, and stored in glass sample jars until analyzed. It was found that the oil was incompletely extracted in samples ground coarser than 40-mesh size. The Soxhlet method of extraction was used. Electric bulbs enclosed in an asbestos box furnished the necessary heat. The oil was extracted in 8 hrs., and good checks were obtained. The extraction flasks containing the oil were dried from 30 to 50 min. in a constant temperature electric oven at 100° C. to constant weight. Too long exposure caused the absorption of oxygen and a resulting increase in weight. This had to be guarded against throughout the whole experiment.

Nitrogen was determined by the Gunning modification of the Kjeldahl method. With 5 g. K_2SO_4 , 1 g. $CuSO_4$, and 25 cc. H_2SO_4 , a complete digestion could be carried out in 30 min. Table III gives the result of these analyses.

TABLE III

No. of Samples	Variety Soy Bean	Color	Average Per cent Oil	Average Per cent Protein (N $\times$ 6.25)	Color of Oil	Drying Power of Oil
8	Guelph	Green	21.2	38.1	Dark yellow	Poor
6	Ito San	Yellow	19.0	41.4	Straw	Fair
6	Cloud	Black	17.0	42.0	Dark straw	Poor
6	Hollybrook	Yellow	17.2	40.8	Straw	Good
6	Haberlandt	Yellow	19.2	38.3	Light straw	Good
8	Ebony	Black	14.6	43.6	Straw	Fair
4	Manhattan	Yellow	18.5	37.9	Straw	Good
6	Wilson	Black	18.8	37.3	Amber	Fair
6	Edna	Black	19.0	39.8	Straw	Fair
6	Tarheel	Black	16.1	39.0	Dark brown	Poor
6	Medium yellow	Yellow	19.6	39.3	Pale	Very good
6	Manchu	Yellow	21.6	40.5	Straw	Good
6	Ohio 9035	Yellow	21.5	37.3	Straw	Good
6	Swan	Yellow	19.1	42.5	Amber	Fair
6	Baird	Brown	17.9	43.0	Straw	Fair
172	Black Eyebrow	Black and yellow	20.2	38.7	Pale straw	Good
4	Ohio 7406	Yellow	17.0	40.1	Straw	Fair
16	Early Brown	Brown	19.5	40.3	Pale straw	Good
1	Habero	Yellow	17.2	41.4	Straw	Good
3	Amherst	Yellow	17.5	43.6	Straw	Good
3	Auburn	Black	21.6	40.0	Straw	Good
3	Manchuria	Yellow	23.2	36.9	Pale	Very good
1	O'Kute	Olive	25.6	35.7	Pale	Fair
6	Arlington	Black	16.7	43.4	Straw	Good
6	Peking	Black	17.9	37.3	Straw	Fair
1	Ogema	Brown	19.1	37.9	Straw	Good

The per cent of oil in soy beans is not at all constant, and the same thing is true of the nitrogen content. The range for oil in the twenty-six varieties tested is from 14.6 per cent in Ebony to 25.6 per cent in O'Kute.

The protein varies from 35.7 to 44.3 per cent. These data are valuable in that they show which varieties yield the largest quantity of oil as well as protein. Only high oil-yielding varieties should be planted by the farmer who is growing soy beans for their oil. Of course the question of yield per acre enters into any deliberations regarding the best oil producing varieties, and it is possible that some standard variety like Ito San or Ohio 9035 might actually give more oil per acre than O'Kute, with over 25 per cent oil. Still another factor must be considered, because the writer, as well as others, has noted¹ that, on account of the anatomical structure of the seed itself, the oil is more easily pressed from some varieties than from others. In those varieties where the oil content is high, it follows usually that the pro-

tein is low. For this reason the variety of soy bean that is best suited for oil production may not be best for feed.

There seems to be a correlation between the color of seed and drying power of the oil, but too much weight cannot be given this conjecture. In general, however, the dark-seeded varieties yielded oil of rather poor drying power. For example, Tarheel, Cloud, Black Eyebrow, and Guelph, all highly colored seeds, gave an oil which did not dry well. In the case of the Guelph variety, it seems certain that a portion of the coloring matter in the oil expressed from the seeds comes from the green seed coat.

The writer has shown elsewhere¹ that the inoculation of soy-bean plants with *B. radicicola*, var. *soy bean*, the nitrogen-fixing bacteria, causes a marked decrease in oil content of soy-bean seeds. A similar depression in oil content is noted where lime, in the form of the oxide or carbonate, is used as a soil amendment. Phosphates also increased the protein content of soy-bean seeds at the expense of oil. These differences are sometimes as great as 3 per cent in oil content—a factor of considerable importance.

EFFECT OF DATE OF PLANTING UPON COMPOSITION AND MATURITY OF SOY BEANS

Mooers,² as well as Garner, Allard and Foubert,³ have shown that maturity in soy beans occurs much more rapidly when seed is planted late in the season. Working at Arlington, Va., the latter investigators found differences as great as 2 per cent in oil content between early and late planted seeds. This work was checked under New Jersey conditions as a result of the following experiments conducted with two varieties of seeds. The interval between plantings was about 2 wks. The criterion used for maturity was when most of the seed pods had turned brown. The data are presented in Table IV.

TABLE IV

No. of Plots	Variety	Date Planted	Date Matured	Days Required to Maturity	Oil in Seeds Per cent
2	Black Eyebrow	June 3	Sept. 10	99	18.92
2	Black Eyebrow	June 17	Sept. 15	90	18.70
2	Black Eyebrow	July 1	Sept. 23	84	18.30
2	Black Eyebrow	July 15	Oct. 4	81	17.20
2	Black Eyebrow	August 1	Oct. 12	72	17.00
2	Early Brown	June 3	Sept. 13	102	19.60
2	Early Brown	June 17	Sept. 17	92	19.50
2	Early Brown	July 1	Sept. 28	89	19.30
2	Early Brown	July 15	Oct. 8	85	18.72
2	Early Brown	Aug. 1	Oct. 21	81	18.68

¹ Frost hastened maturity and made observations more difficult.

These data show that the length of the growing season, or the number of days to maturity, is to a large degree dependent upon the time of planting. The yield of seed and forage was much less upon the late planted plots than upon those planted before July 1. The oil content of the seeds obtained by sampling the two plots of each series was higher in the case of the early plantings and fell off considerably as the date of planting became later and later. In the case of the Black Eyebrow variety, there was a difference of 2.9 per cent between the earliest and latest plantings. In the case of the Early Brown variety this difference amounted to but 0.92 per cent; yet in either case the difference is appreciable and constant. It seems therefore that for best results in growing soy beans for their oil, early, rather than late, plantings should be made.

SUMMARY

1—Soy-bean oil is a semi-drying oil consisting largely of the glycerides of palmitic, oleic, linolic, and linoleic acids. Chemically it resembles corn oil but dries much better.

2—It may be used successfully to replace linseed oil in part in the manufacture of paints and varnishes. When used with suitable driers, such as lead, cobalt or manganese tungstate or linoleate, it may be used alone, otherwise it is expedient to use

¹ *Soil Sci.*, **6** (1918), 81.

² Tennessee Agricultural Experiment Station, *Bulletin* **82** (1908).

³ *J. Agric. Res.*, **3** (1914) 227.

mixtures of soy-bean oil up to 50 per cent with tung or linseed oils.

3—Domestic soy-bean oil is practically identical chemically and physically with the imported oils. Excellent soy-bean oil has been produced in this country, the whole Southern section of which is admirably suited to the growth of the beans.

4—Samples of soy-bean oil from different varieties of beans, subjected to different methods of extraction, length of storage, soil conditions, and maturity of the seed when harvested, vary considerably in their physical and chemical properties.

5—The average amount of oil obtained from twenty-six different varieties of soy-beans was 18.3 per cent; Ebony

was lowest with only 14.8 per cent, while O'Kute was highest with 25.6 per cent. Such vast differences between varieties is of very great importance in growing soy beans for the oil market.

6—The length of growing season influences the oil content of soy-bean seeds. The oil content becomes less as the date of planting is later in the season. The number of days required to reach maturity is materially shortened when plantings are made during the middle and late summer. For growing soy beans as a catch crop or second crop on the same land, this fact is of prime importance.

7—There is considerable variation in the color and drying power of soy-bean oils derived from different varieties of soy beans.

The Alkalinity of Searles Lake Brine^{1,2}

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The article by J. E. Teeple³ on the operations of the American Trona Corporation at Searles Lake approaches the ideal, in the opinion of the writer, in divulging to the public the methods and accomplishments of a large company that has carried on considerable chemical research, while at the same time specifying the particular points that have been made the subject of patent applications. The writer visited the plant of this company at Searles Lake in the fall of 1920 and was given an opportunity to inspect the equipment and methods of operation that Mr. Teeple describes. It is a great pleasure to express appreciation of the courtesies shown at that time.

The Searles Lake brine is a very interesting subject for investigation from a geochemical point of view as well as for its commercial value. Although it is recent, geologically speaking, it is changing so slowly, if at all, at the present time that the changes probably cannot be detected. It is possible, however, to determine the salts that separate on evaporation at various temperatures and the relation of certain physical properties of the brine to its components. The actual alkalinity of the brine, as measured by the H-ion concentration, is a property to which the writer has given some attention, with special reference to its use in arriving at a logical form of expression of the analysis of the brine. Very little has been published on the problem of determining carbonate and bicarbonate in the presence of borax and metaborate.

ANALYSIS OF BRINE

The sample of brine on which the experiments described below were made was collected from Well S6, at a depth of 35 to 40 ft., Sept. 20, 1913, by W. B. Hicks, of the United States Geological Survey. It had stood in a quart glass bottle without being opened until the present determinations were made. The H-ion concentration was then found to be 3.32×10^{-10} at 25° C., or, as usually expressed pH = 9.48. The apparatus used in making this determination has been

DETERMINATIONS, SEARLES LAKE BRINE

	Per cent of Brine
K ₂ CO ₃	2.46
Na ₂ CO ₃	12.32
NaHCO ₃	4.72
CO ₂	1.81
B ₂ O ₃	1.04
Specific gravity at 25°.....	1.204

1 cc. requires 13.1 cc. 0.1 N HCl with methyl orange.

1 cc. requires 12.85 cc. 0.1 N HCl with p-nitrophenol.

1 cc. requires 3.80 cc. 0.1 N NaOH to phenolphthalein end-point after removing CO₂ and making exactly neutral to p-nitrophenol.

¹ Received April 1, 1921.

² Published by permission of the Director of the U. S. Geological Survey.

³ THIS JOURNAL, 13 (1921), 219.

previously described.¹ The tabulated determinations were also made using the usual methods, such as are described in *Bulletin 700* of the United States Geological Survey.

CONVERSION OF ANALYTICAL RESULTS

The next problem is to convert the above determinations into the form of salts, which is the most logical form of expression for several reasons: First, the brine as it comes from the lake has been in contact with various salts, and similar salts can be obtained from it by evaporation. Second, after calculating the potassium to some one salt, such as potassium chloride, all the other salts may be expressed as sodium salts. Third, the actual pH alkalinity of the brine lies between the limits shown by solutions of sodium carbonate and sodium bicarbonate on the one hand and sodium tetraborate (borax) and sodium metaborate on the other. The special problem here is to convert the total CO₂ found into Na₂CO₃ and NaHCO₃ and the total B₂O₃ into Na₂B₂O₄ and Na₂B₄O₇. Titration methods are of no avail because there are four salts to be titrated and the titration curve gives no sharp breaks for the various salts. Modes of expression based on arbitrary assumptions lead to confusion unless the assumptions have some logical basis, and for this reason attempts to convert the CO₂ and B₂O₃ into only two or three salts are unsatisfactory, because the chemist realizes that any such that could be chosen would react on each other if dissolved, producing at least the four salts that have been mentioned. The writer has sought to overcome these difficulties by determining in separate experiments what proportions of the salts of each buffer pair, *i. e.*, the carbonates and the borates, would be required to give the same pH value as found for the brine. He has also shown that if the proportions found for one pair are taken to represent the concentrations of those two salts in the brine, the proportions for the other pair must be as determined. The results obtained appear to yield a form of expression that is free from the above objections.

ARTIFICIAL BRINE—An artificial brine containing only sodium chloride, potassium chloride, and sodium sulfate in the concentrations found in the Searles Lake brine was made up to serve as a medium to which buffer salts could be added in various amounts, thus making any possible "salt effect" constant and equal to that in the Searles brine. A set of pH determinations was made with this brine after adding various proportions of sodium carbonate and bicarbonate, keeping the total CO₂ equal to that found in the Searles brine. A similar set was made with mixtures of borax and sodium metaborate, keeping the total B₂O₃ the