

**INCREASING THE DRYING PROPERTIES
OF SOYBEAN OIL**

By

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Signatures have been redacted for privacy

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TABLE OF CONTENTS

	Page
I. ACKNOWLEDGEMENT	2
II. INTRODUCTION	4
III. HISTORICAL	7
IV. EXPERIMENTAL	11
A. MATERIALS	11
B. METHOD OF PROCEDURE	12
C. METHODS OF TESTING	18
V. RESULTS AND DISCUSSION	19
VI. CONCLUSIONS	22
VII. LITERATURE CITED	24

INTRODUCTION

The soybean is an annual legume native to eastern Asia, where it has formed an important source of protein food for many centuries. (10) Its use in China dates back to the beginning of China's agricultural age, or at least 3000 B. C. (5) Later, its use spread to Japan, India, Ceylon, West Africa, South America, Australia, and the United States. (1) Seventeen years ago, China produced 80% of the world's soybean crop, 70% coming from Manchuria alone. The production at that time was 4,500,000 tons from 8,000,000 acres, which represented one fourth of the total cultivated area of China. (5) Since that time, the amount raised in the United States has grown to about 13,000,000 bushels of beans in 1930. (2)

The value of the soybean as a forage crop, stock food, and soil builder is very generally recognized. (8) In addition to these there is valuable oil available from the bean to the extent of up to 20% by weight. (10) Increased production in the United States has reduced the amount of imported soybean oil from 336,824,646 pounds in 1918 to 13,166,220 pounds in 1928, according to statistics from the United States Department of Commerce. (8) In 1932, the United States produced one and one half times as much as it consumed. (6)

Soybean meal, the ground bean from which the oil has been expressed or extracted, is a high grade stock food and a good fertilizer. Soybean flour is made by grinding the meal and is used extensively in human foods; it is especially valuable as a diabetic food because of the almost entire absence of starch. (10)

The oil of the soybean, which is classified as a semi-drying oil, has properties which adapt it to a wide variety of uses. As a food it is used in butter and lard substitutes, edible oils and salad oils; its non-food uses include paints, enamels, varnish, explosives, linoleum, celluloid, lighting, lubrication, printing inks, and soaps. (10) Extensive research is being carried on by many groups at the present time in an attempt to increase the utilization of soybean oil. The paint and varnish industries of this country are sponsoring research in an attempt to substitute the oil for linseed and tung oils. (4)

Paint containing a mixture of soybean oil and linseed oil has the advantage over pure linseed oil paint in that it does not turn yellow on aging and the film is considerably more elastic. Soybean oil is also cheaper than either linseed or tung oil at the present time. Furthermore, the United States is dependent on foreign countries for about 37% of the linseed oil used in this country. (10) The reason soybean oil cannot now displace linseed oil entirely

is because of its lower drying power.

It is the purpose of this research to increase the drying properties of soybean oil in order that it can be used to displace linseed oil to a greater extent.

HISTORICAL

The method of processing the soybean for oil is quite similar to the processing of cottonseed, linseed, and peanuts. In China much of the oil is produced in small domestic mills operated in a rather primitive fashion. (8) The beans are soaked in water, crushed between millstones, heated on stones or in iron pans, and pressed in wooden presses. This method yields about 8% to 10% oil. (1)

In this country the oil is removed by three general methods: the expeller method, the hydraulic press method, and the solvent extraction method. The expeller method is the generally prevailing one today, although solvent extraction removes a higher percentage of the oil, leaving a drier cake which is more satisfactory as a stock food. (10) The oil obtained by the expeller and hydraulic press methods, however, generally brings a slightly higher price than the extracted oil. (5)

The expeller method involves the use of a mechanical expeller, the beans first being dried and crushed. It is a continuous process and involves little labor cost, although the power requirement is large. The cake produced contains about 5% oil but is highly digestible. (10)

In the hydraulic press system, the beans are crushed and cooked, and then sent in batches to the hydraulic presses. This process requires a comparatively low investment cost, but the power and labor requirements are high. The cake produced has a high residual oil content, about 6%, and is undesirable from the stock feeding aspect. (10)

The solvent extraction process involves dissolving the oil out of the flaked seeds with an organic solvent such as ether, naphtha, benzol, or trichloroethylene, and separating the oil from the solvent by distilling off the latter, recovering the solvent to be used again. This process also removes the fat-soluble vitamin and leaves it in the oil. (2) Steam and cooling water requirements are high and solvent losses are expensive, but the power requirement is not large. The cake produced contains only about 1% oil and is highly satisfactory for most uses. (10)

The crude soybean oil thus obtained is generally of a dark reddish brown color, is about neutral in reaction when fresh, and has an iodine number of about 130. The oil has considerable drying properties which fit it for acting as the vehicle for paints. The power of "drying" is the ability to combine with atmospheric oxygen, and this in turn depends primarily on the degree of saturation of the oil; the less saturated the oil is, the more quickly will it combine with oxygen and become dry.

Since the iodine number of an oil measures its degree of saturation, this number is generally taken as an index of the drying capacity of the oil. According to Picard (9), however, crude oils with the same iodine value may differ 300% to 400% in drying rate. He says this variation is due to the different amounts of lecithin present in the oil, the lecithin content varying widely depending on the extraction process. Lecithin is a distinct drier, and if removed from the oil there is no more variation in the drying of oils having the same iodine value.

The value of soybean oil as a paint vehicle has been recognized for many years. As early as 1912, Toch (11) in England wrote about the utilization of soybean oil for paint purposes. His work, as well as most of the work that has been done on the subject up to the present time, was on the problem of using chemical driers in soybean oil and in mixtures of soybean and linseed oils.

Gray (3) recognized the fact that soybean oil has the advantages of flowing more freely and working better than linseed oil, and of producing a glossy film which has far more elasticity and which does not tend to turn yellow with age.

Picard (9) says, "Soybean oil should not be used in too large amounts in paint, as fewer double bonds are formed. It is softer at the beginning and picks up dirt faster, but

chalks more quickly, releasing dirt, increasing in whiteness and becoming as hard as any type of paint. It is better than linseed oil, in that it does not crack, and the film holds better than straight linseed oil in high pigment concentration. Blown soybean oil brushes easier than blown linseed oil. If a lecithin-free soybean oil is bolstered with a large or small amount of other oils, china wood, perilla, linseed, etc., and with 5% to 10% of properly treated china wood oil, it becomes so near in properties to linseed oil that it is good for a normal line of house paints."

The purpose of this research is to endeavor to find a means of increasing the unsaturation of soybean oil, providing more double bonds and thereby increasing the drying rate. This should make possible the use of a higher percentage of soybean oil in paints, and possibly the use of a 100% soybean oil vehicle. It is the belief of the author that if this were possible a better and less expensive paint could be produced.

EXPERIMENTAL

Materials

Soybean oil

The crude soybean oil used in these experiments was produced by the solvent extraction plant in the chemical engineering laboratory at Iowa State College, Ames, Iowa. Trichloroethylene was the solvent used in extracting the oil from the flaked beans, and it is possible that there was a trace of this solvent left in the crude oil.

Chemicals

The aluminum oxide and tungstic oxide used as catalysts were standard chemically pure products that had been ground to a fine powder.

In the iodine number determination, the Hanus method as described in Mahin's "Quantitative Analysis" (7) was used. The iodine monobromide solution was made up according to the directions given, and all chemicals used were standard chemically pure products.

Method of Procedure

Apparatus:

The scheme used in these experiments was to mix a dehydrating catalyst intimately with the crude soybean oil, heat the oil to a high temperature, and subject it to a mild oxidation, using air as the oxidizing agent. Because soybean oil decomposes somewhat if it is kept for too long a time at the high temperatures employed, it was necessary to complete the process and cool the oil before it had a chance to decompose to any great extent.

In order to bring the oil into intimate contact with the air, a piece of one inch pyrex glass tubing eighteen inches long was filled with glass beads and used as a column. To the bottom of this column a distilling flask was attached to collect the oxidized oil, and compressed air was introduced at a slow rate through the arm of the flask. The crude oil, after being mixed with the catalyst, was heated with a Bunsen burner in another distilling flask. This flask was provided with a two-hole rubber stopper through which were inserted a thermometer to measure the temperature of the oil and a glass tube extending from the bottom of the flask up through the stopper and over to the top of the

column. The arm of the flask was connected to a source of compressed air, the air being used to force the oil up through the glass tubing and over to the top of the column. A thermometer was also inserted in the column, with its bulb about in the middle, to measure the temperature of the oil at that point.

Sample No.1:

About 400 cc. of the crude soybean oil was mixed intimately with 8 grams of tungstic oxide, and the mixture was heated to 175 degrees Centigrade. A change took place in the tungstic oxide at about 100 degrees, its color changing from bright yellow to dark green. This was probably caused by an oxidation of the oil, the oxide being reduced to a lower oxide of tungsten. When the temperature reached 175 degrees, the oil was run down through the column and the air was turned on to pass up through the column. The column was at room temperature when the oil was first introduced, and reached 140 degrees Centigrade at the end of the run. The average temperature of the middle of the column for the run was 80 degrees. The oil was run into the column a little too fast and piled up somewhat; the air had to be shut off twice to allow the oil to pass

out of the column. The oil was passed through the column in fifteen minutes.

Sample No. 2:

Sample No. 1 was heated again, this time to 190 degrees Centigrade, and was run through the column a second time. The average temperature of the center of the column for this run was 90 degrees Centigrade. The time taken for the passing of the oil through the column was again fifteen minutes.

Sample No. 3:

The same sample of oil was heated again, to 195 degrees Centigrade, and was again run through the column. The average temperature of the center of the column this time was 80 degrees, and the time of the run was twenty minutes.

Sample No. 4:

The same quantity of crude soybean oil, about 400 cc., was taken again and intimately mixed with 8 grams of tungstic oxide. This mixture was heated to 225 degrees Centigrade in the flask, and the tungstic oxide went through the

same color change again at about 100 degrees. At about 210 degrees another change took place, the green color of the tungstic oxide taking on a bluish tinge. At the same temperature a violent bumping began and a clear liquid boiled out of the oil and condensed on the upper part of the neck of the flask. It is believed that this was water which boiled out of the oil, although it could have been the extraction solvent, trichloroethylene, a small amount of which might have been left in the oil. When the oil was run through the column after its temperature had reached 225 degrees, it was seen that the tungstic oxide had coagulated into small clots and was no longer dispersed evenly in the oil. The average temperature of the center of the column was 90 degrees Centigrade. The oil was passed through the column in twenty minutes.

Sample No. 5:

In the belief that the passing of sample No. 4 through the column did little or no good, a sample was taken of this oil after it had been heated to 225 degrees and before it was passed through the column.

Sample No. 6:

Another sample of about 400 cc. of crude soybean oil was taken and was mixed with 8 grams of aluminum oxide. This mixture was heated to 225 degrees Centigrade in the flask and was then run through the column. The same boiling took place in the flask, beginning at about 210 degrees. No appreciable change was noted in the aluminum oxide except that it coagulated to a slight degree; this change was not nearly as much as took place with the tungstic oxide in the previous run, however. The average temperature of the center of the column for the run was 85 degrees Centigrade, and the time taken for the passing of the oil through the column was twenty minutes.

Sample No. 7:

A sample of the oil used in No. 6 was taken after it had been heated in the flask but before it was passed through the column.

Sample No. 8:

Another 400 cc. sample of the crude oil was mixed with 8 grams of aluminum oxide and heated in the flask to 225 degrees Centigrade. The same boiling was noted as with

the previous samples that were heated to this temperature. In this run an attempt was made to obtain a higher temperature in the column by heating the air that was passed up through the column. The air, before entering the column, was passed through a coil of copper tubing which was surrounded by a muffle and heated with a Bunsen burner. This heated air was passed through the column for about fifteen minutes before the oil was introduced. The temperature of the column for the run was constant at 100 degrees Centigrade; it was not possible to maintain a higher temperature because of radiation losses throughout the length of the column. The oil was passed through the column in twenty minutes.

Sample No. 9:

A sample of the oil used in No. 8 was taken after it had been heated in the flask but before it was passed through the column.

Methods of Testing

Iodine number:

As was stated above, the Hanus method as described in Mahin's "Quantitative Analysis" (7) was used for the iodine number determination. The iodine monobromide solution was made up according to the directions given; however, some difficulty was encountered in its use. The half-hour absorption time did not seem to be long enough to allow the oil to become completely saturated with iodine. This difficulty might have been due to some fault in the making up of the iodine monobromide solution. Some time was spent in standardizing the procedure, and constant results were finally obtained by using a smaller weight of sample than was recommended by Mahin and by allowing three days absorption time.

Drying test:

To determine the time of drying, the samples of oil were spread on clean watch glasses and allowed to stand until dry in air that varied from 25 to 35 degrees Centigrade. A sample was considered dry when the film no longer adhered to the finger and did not rub up appreciably when the finger was lightly rubbed across the surface.

RESULTS AND DISCUSSION

The following table shows the results obtained from the iodine number and drying tests.

EFFECT OF MILD OXIDATION OF CRUDE SOYBEAN OIL

Sample No.	Flask Temp. : Degrees C	Column Temp. : Degrees C	Iodine No.	Drying Time : Hours
Raw Oil	---	---	132	82
1	175	80	133	56
2	190	90	137	50
3	195	80	137	48
4	225	90	144	67
5	225	---	138	70
6	225	85	138	41
7	225	---	135	43
8	225	100	137	40
9	225	---	134	42

It is evident from the above data that the iodine number is not a very accurate index of the drying time. It is possible that the drying time was affected by the presence in the samples of small quantities of suspended alumina and tungstic oxide. The chemicals were not filtered

out of the oil, but were allowed to settle to the bottom of the sample bottle before the tests were made. In the first five samples, however, the oil used for the drying tests appeared to be perfectly clear. In the last four samples, the ones in which aluminum oxide was used, the time allowed for settling was only a few days, and it is quite probable that small quantities of suspended alumina were present in the oil used for the drying tests. This might have had some effect on the drying time, as the drying time of these four samples was substantially lower than the drying time of the other samples.

It is also evident from the data that re-heating the oil and passing it through the column a second and a third time increased the drying rate of the oil, although it had little effect on the iodine number.

A rather surprising result is that the passing of the oil through the column appears to do little good. The tests seem to indicate that practically all of the oxidation was done by the chemical reagent during the heating in the flask and that little further oxidation took place during the passing of the oil through the column. This was probably due to the low temperature of the oil in the column, and it is quite likely that much better results could be obtained if the column were insulated so that the temperature of the oil could be maintained at 200 degrees Centigrade or above.

In the last run an attempt was made to obtain a higher temperature in the column by heating the air that was run through the column, but because of the heat lost through the uninsulated glass the desired temperature could not be attained.

For future work on this subject, it is the author's suggestion that two different procedures be attempted. The first of these is to follow the procedure outlined in this report, but to maintain a higher temperature in the column by insulation or by some other means such as auxiliary heating of a jacket around the column. The second procedure recommended is to do away with the column, mixing larger portions of alumina or tungstic oxide with the oil and merely heating with agitation. Thorium and chromium oxides could also be tried. A means should be found of recovering the chemical reagents and re-oxidizing them if necessary.

CONCLUSIONS

The results of this investigation indicate that:

1. It is possible to slightly increase the unsaturation of soybean oil, thereby increasing its drying rate, by means of a mild oxidation with air at a high temperature and the use of a dehydrating catalyst thoroughly dispersed in the oil.
2. Tungstic oxide and aluminum oxide both gave fairly good results; aluminum oxide was a little the better.
3. The chemical reagents used, alumina and tungstic oxide, both apparently oxidized and dehydrated the oil when the mixture was heated in the flask.
4. If the temperature of the oil as it passes through the column is not above 100 degrees Centigrade, the air oxidizes it only to a very slight extent.
5. The iodine number of the oil is not a very accurate index of its drying rate.
6. The best drying rate obtained by the use of tungstic oxide was obtained by passing the same sample of oil through the column a number of times.
7. A better drying rate was obtained when alumina was used than when tungstic oxide was used, and was obtained when the highest temperatures were employed.

8. The treatment of soybean oil by this method darkens its color considerably, which might prevent its use in white paints.

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