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SOYBEAN CHEMISTRY AND TECHNOLOGY

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FOREWORD

IN THE long stream of agricultural history, few events are more fascinating than the astonishing rise of the soybean in America.

From a minor forage crop little over a decade ago, production has doubled and doubled time and again until, last year, it topped the huge total of 209 million bushels, a magnificent contribution to the war effort.

In production of edible oil, it is now a leader in the field, having surged ahead of the great cottonseed oil output.

Production of soybean oil meal, a superior protein ingredient for livestock and poultry feeds, has swollen to figures undreamed of a few years ago.

And now soy protein has pushed into the human food field, with production capacity estimated by the government at the end of 1943 as one and a half billion pounds. Soy flour, soy grits and soy flakes are moving in a steady stream to allied nations; they are going into the rations of our fighting men; they are included in bakery and innumerable other food products, and are being packaged for direct sales by stores to the housewives of the nation. As a meat supplement, soy protein is gaining ground.

Such is the record of the versatile oriental bean in a short span of time.

Much of the credit must go to the men of the laboratory, who, staring into test tubes with repressed excitement, have made new discoveries, and new contributions, one after another, to the forward stride of the industry.

There has been a tremendous public demand for more scientific facts—for the chemistry and technology of the soybean and its products.

At last, the present work has been concluded and will be hailed everywhere for its clarity of approach and its thoroughness of execution. It was a monumental task, discharged as could be done only by scientists of broad perspective and infinite patience for detail.

The volume will be on the "must" list of all technical libraries here and abroad; professors, students, research workers, industrialists engaged in vegetable oil and protein trades, all will find it an indispensable mine of factual information. It is perhaps the most complete work of its kind on the ancient soybean, which pre-dates the Pyramids and was hoary with age before the building of the Tower of Babel, and centuries before Solomon fashioned his temple.

SOYBEAN NUTRITIONAL RESEARCH COUNCIL
EDWARD JEROME DIES, *President*

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Part I

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INTRODUCTION

THE soybean, Soja max. (L.) Piper,[349] * also referred to by botanists as Soja hispida (Moench) and Glycine hispida (Moench) Maxim., is one of the oldest crops cultivated by man. Its early history is lost in antiquity. According to Morse and Cartter,[287] the plant was extensively cultivated in China long before written records were kept. According to these authors, the first record of the plant is contained in a materia medica written by Emperor Sheng Nung in 2838 B.C. Throughout the history of China and down to the present day, the soybean has been the most important cultivated legume, and probably the most important crop, to the existence of the Chinese people and to the Chinese civilization.

From China, the soybean has spread over a considerable portion of the world. The principal soybean producing countries are China, Manchuria, United States of America, Chosen, Japan, and Netherlands Indies in the order named. In the last few years, increasing quantities of soybeans have been grown in Europe, especially in Germany, the Balkan States, and the Union of Soviet Socialist Republics. England, South Africa, British East Africa, Algeria, Egypt, New South Wales, and New Zealand have experimented with soybeans, but commercial production has been negligible. The trend of soybean production, in various countries, is shown

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*** Small numbers refer to "Literature Cited," on pages 119 and 249.**

in Table 1, which is reproduced from *Foreign Crops and Markets.*[440]

TABLE 1

SOYBEAN PRODUCTION IN SPECIFIED COUNTRIES FROM 1935 TO 1941

(Compiled from official sources and unofficial estimates.)

Country	1935 1,000 bushels	1936 1,000 bushels	1937 1,000 bushels	1938 1,000 bushels	1939 1,000 bushels	1940 1,000 bushels	1941[a] 1,000 bushels
China[b]	184,415	215,728	213,189	207,600	203,900	216,800	c
Manchuria ..	141,793	152,375	159,907	157,445	144,952	140,617	c
United States	44,378	29,983	45,272	62,729	91,272	77,374	106,712
Chosen	20,738	17,937	20,205	18,333	c	c	c
Japan	10,719	12,485	13,473	c	c	c	c
Taiwan	139	162	158	146	c	c	c
Netherlands Indies	7,448	9,090	9,880	10,567	c	c	c
Rumania ...	424	1,367	2,584	1,803	3,532	3,600[d]	c
Bulgaria	c	179	419	246	613	1,415	c
Yugoslavia ..	36	22	54	140	103	294	c
Hungary	c	c	c	c	125	194	c
Total[e] ...	410,500	439,700	466,000	473,000	477,500	483,500	c

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[a] Preliminary.

[b] Excluding Kwangsi Province, for 1935 to 1937, which normally produces about 2,500,000 bushels.

[c] Not available.

[d] Assuming that Bessarabia produces 80 per cent of the total.

[e] Includes a small amount for other minor-producing countries, but excludes the Soviet Union.

Although, China usually produces more soybeans than any other country and approximately as much as the two next largest producers, Manchuria and the United States, it is not a factor in world trade as practically the total production is domestically consumed. In addition to domestic production, China normally takes important quantities of soybeans and soybean products from Manchuria. The latter country is the most important factor in the world soybean trade, although, in 1939, the United States exported 10.5 million bushels to European oil centers, principally the Netherlands and Scandinavian countries. Japan has been one of the largest importers of soybeans from Manchuria, but these imports have been decreasing. Germany's imports of soybeans have increased rapidly in recent years, reaching approximately 800,000 metric tons in 1938. Most of these imports came from Manchuria, but the United States, Rumania, and other Balkan States also contributed to the total. The world production for 1937 has been estimated at 12,454,000 metric tons or approximately 457,500,000 United States bushels. Data, covering imports and exports of soybeans and soybean oil, for all principal producing and consuming countries for the period of 1930 to 1937, are contained in the *Report of the Imperial Economic Committee*[193] to which the reader is referred for detailed information on this subject.

In the Orient, especially in China and Japan, soybeans are grown principally for the seed which has served for centuries as an important source of food. For this purpose, the beans are utilized in the preparation of numerous fresh, fermented, and dried products. Most familiar to Occidentals is the fermented product known as shoyu or soy sauce which is but one of the numerous derivatives of this versatile seed. Besides soy sauce, the beans are used in the form of flour, vegetable milk (fresh, condensed, and dried), curd or tofu, from which a variety of products is prepared, cheese, and the important fermented product known as miso. Large quantities of beans are also crushed for oil which is used for food and numerous industrial purposes, and the resulting cake or meal is used chiefly as a fertilizer and as feed for animals. The roots are often dug and dried for fuel, especially in Manchuria, and the leaves, stalks, pods, and other refuse are used for feeding cattle. The use of soybean stalks, as a source of cellulose pulp,[249, 18] has been proposed, and a plant, capable of producing 15,000 tons of pulp annually, was erected at Kaiyan, Manchuria, in 1939. A Japanese patent,[283] covering the use of soybean refuse mixed with powdered coal and lime and pressed into briquets for fuel, has been granted.

In contrast to the food uses in the Orient, European countries have for many years imported considerable quantities of soybeans from Manchuria for the production of oil and meal. In the United States, the soybean has been used primarily for forage purposes, being either preserved extensively as hay or silage or cut and fed in the green state. It is also pastured extensively with hogs and sheep and used, to some extent, as a green manure or cover crop. More recently, soybeans have been grown extensively in the United States for the production of oil. During the last 15 years, both the total acreage, sown to soybeans, and the acreage, harvested for commercial beans, have greatly increased as is evident from Table 2.

"The marked increase in the production of soybeans in the Corn Belt has been conditioned by several factors. These include the ability of the soybean plant to withstand drought, its relative freedom from pest hazards, its adaptability to crop rotations, the possibility of harvesting the beans with a small combine, and the fact that soybeans provide an additional source of cash income for many farmers. The necessity for finding a more profitable crop than oats and, in some cases, corn has been important in bringing about increased soybean production. In the South, where cotton acreage has been reduced considerably in recent years, soybeans, harvested mostly for hay, forage, and as a green-manure crop, also have been useful for replacement purposes." [444]

TABLE 2

ACREAGE, YIELD, AND PRODUCTION OF SOYBEANS IN THE UNITED STATES FROM 1924 TO 1943 *

Year	Acreage Grown Alone for All Purposes 1,000 Acres	Acreage Harvested for Beans 1,000 Acres	Average Yield Per Acre Bushels	Production 1,000 Bushels
1924	1,567	448	11.0	4,947
1925	1,539	415	11.7	4,875
1926	1,871	466	11.2	5,239
1927	2,057	568	12.2	6,938
1928	2,154	579	13.6	7,880
1929	2,400	708	13.3	9,398
1930	3,010	1,008	13.4	13,471
1931	3,738	1,104	15.2	16,733
1932	3,595	977	15.3	14,975
1933	3,365	997	13.2	13,147
1934	5,572	1,539	15.0	23,095
1935	6,640	2,697	16.5	44,378
1936	5,811	2,132	14.1	29,983
1937	6,171	2,549	17.8	45,272
1938	7,262	3,105	20.2	62,729
1939	9,506	4,417	20.7	91,272
1940	10,513	4,779	16.2	77,374
1941**	10,146	5,881	18.0	105,587
1942**	13,879	10,008	18.7	187,155
1943**, †	14,762	10,820	18.1	195,762

* U. S. Department of Agriculture, *Agricultural Statistics*, p. 196 (1942).

** Crop Reporting Board, Bureau of Agricultural Economics, U. S. Department of Agriculture, *Crop Report; Annual Summary* (1942 and 1943).

† Preliminary.

The marked increase in the production of soybeans, in the United States, has led, in the last few years, to the development of numerous food, feed, and industrial uses for both the meal and the oil. There are at present over 100 oil mills processing soybeans * and several times that number of concerns are engaged in the manufacture of soybean flour and other food products and in the manufacture of various industrial products. Table 3, prepared by Mr. W. J. Morse of the United States Department of Agriculture, shows the diversity

TABLE 3

SOYBEAN UTILIZATION

- **SOYBEAN**
  - **Plant**
    - **Forage**
    - **Green manure**
    - **Pasture**
      - **Ensilage**
      - **Fuel**
      - **Furfural**
      - **Hay**
      - **Soilage**
  - **Bean**
    - **Meal**
      - **Celluloid substitutes**
      - **Core binder**
      - **Feeds**
        - **Cattle**
        - **Dogs**
        - **Fish**
        - **Hogs**
        - **Poultry**
        - **Rabbits**
        - **Sheep**
      - **Fertilizer**
      - **Glue**
      - **Human food**
        - **Beer brewing**
        - **Flour—see dried beans**
        - **Seasoning powders**
        - **Soy sauce**
        - **Vegetable milk**
      - **Plastics**
      - **Water paints**
    - **Oil**
      - **Candles**
      - **Celluloid**
      - **Core oil**
      - **Disinfectant**
      - **Electrical insulation**
      - **Enamels**
      - **Food products**
        - **Butter substitutes**
        - **Cooking oils**
        - **Lard substitutes**
        - **Salad oils**
        - **Medicinal oil**
      - **Fuel**
      - **Glycerin**
      - **Insecticides**
      - **Lecithin**
        - **Cocoa**
        - **Emulsifier**
        - **Margarine**
        - **Medicines**
        - **Textile dyeing**
        - **Candy**
        - **Chocolate**
      - **Lighting**
      - **Linoleum**
      - **Lubricant**
      - **Oilcloth**
      - **Paints**
      - **Printing ink**
      - **Rubber substitutes**
      - **Soaps**
        - **Hard**
        - **Liquid**
        - **Soft**
      - **Varnishes**
      - **Waterproofing cement**
      - **Waterproof goods**
    - **Green bean**
      - **Canned**
      - **Frosted**
      - **Green vegetable**
      - **Salad**
    - **Dried bean**
      - **Baked**
      - **Boiled**
      - **Breakfast foods**
      - **Feeds**
        - **Cattle**
        - **Hogs**
        - **Poultry**
        - **Sheep**
      - **Flour**
        - **Baked products**
        - **Breakfast foods**
        - **Candies**
        - **Chocolate**
        - **Diabetic foods**
        - **Health drinks**
        - **Ice cream cones**
        - **Ice cream powder**
        - **Infant foods**
        - **Macaroni products**
        - **Meat products—filler**
      - **Roasted**
        - **Candied**
        - **Coffee substitute**
        - **Salted**
      - **Soy sauce**
      - **Sprouts**
      - **Vegetable milk**
        - **Casein**
          - **Paints**
          - **Paper size**
          - **Textile dressing**
          - **Waterproofing**
        - **Condensed**
        - **Curd**
          - **Canned**
          - **Dried**
          - **Fermented**
          - **Fresh**
          - **Smoked**
        - **Foods**
        - **Powder**

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* See list of oil mills in Part II.

of uses to which the different products of the soybean are put.

The soybean is an annual summer legume, requiring from 75 to 200 or more days to reach maturity. The plant, which grows to a height of from 2 to more than 6 feet, though more usually from 2 to 3½ feet, has rather woody and branched stems (Fig. 1).

The stems, leaves, and seed pods are covered with short reddish-brown or gray hairs. The flowers are small and inconspicuous, either white or purple and clustered in the axils of the leaves. The pods are from 1 to 2½ inches long and contain two to four seeds. When mature, the seeds may be yellow, green, brown, or black in color; and in shape, round, oval, or flattened like the lima bean.

The varieties of soybeans are very numerous and many hundreds of types and strains are known. They may be divided into three general groups with respect to their uses, namely, vegetable varieties, hay varieties, and grain or industrial varieties. The unusually large number of known varieties and strains of soybeans appears to be the result of the peculiar sensitivity of the plant to changes in soil and climate. The recognition of the sensitivity of the soybean to environment has been the basis of much of the breeding and adaptation studies which have been carried on in various countries of the world, particularly in the United States, Japan, Manchuria, China, India, Chosen, Germany, the Union of Soviet Socialist Republics, and other European countries. The chief objective of these studies has been to increase the yield of beans under local conditions; but, more recently, similar work has been conducted with a view of increasing the quality of beans, especially for industrial utilization.

The factors or characters which are included in the term

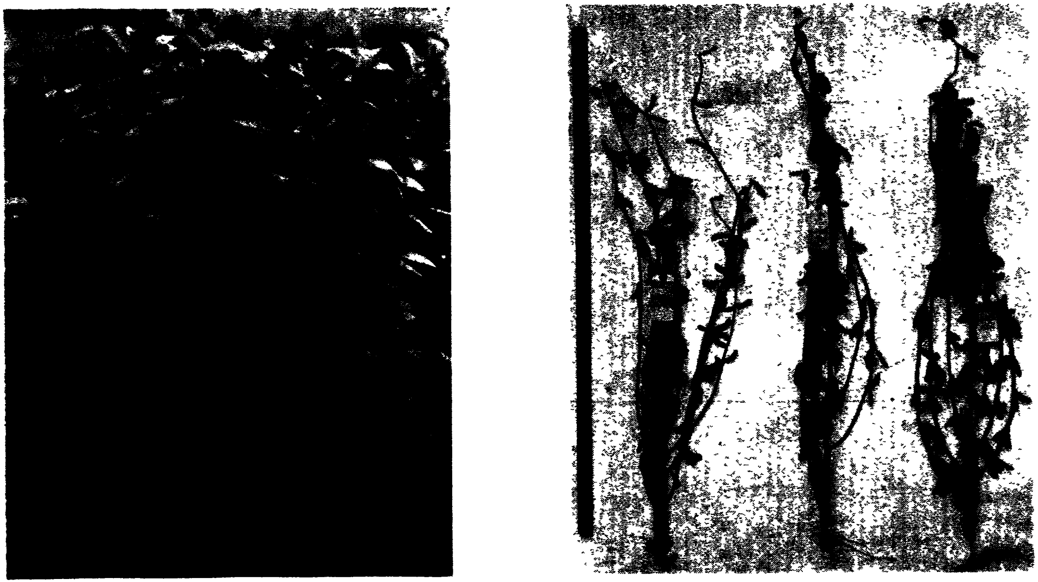

FIGURE 1

The Soybean Plant

In Foliage

Mature

quality, as applied to the industrial uses of soybeans, are principally oil content, iodine number of the oil, phosphatide content, and protein content. In response to the demand by oil mills for varieties of high oil content, breeding and selection from foreign introductions into the United States have led to the development of yellow-seeded varieties such as Illini, Dunfield, Mukden, Mandell, Scioto, Mansoy, Manchu, Mamredo, Delsta, Mandarin, Seneca, and many others which are particularly adapted to a given agricultural region.

The literature, pertaining to the effect of variety, climate, soil type, and maturity on the yield and quality of protein and oil, is very extensive and has been reported from every country in which the soybean has been grown. A similarly extensive literature, pertaining to the cultural practices, including harvesting and handling of the mature seed intended for commercial processing, is readily available.

COMPOSITION AND PROPERTIES

FROM the chemical point of view, most seeds are extremely complex, containing, as they do, all the elements and compounds necessary to reproduce and nourish the new plant until it can form the necessary system of roots and leaves to obtain from the soil and atmosphere the materials essential for growth and maturation. The nature and chemical composition of some of the numerous products, stored by seeds, are known and their functions, in the reproduction of the plant, are understood. However, many substances, which are present in seeds, have not been completely characterized chemically and their probable functions provide food only for speculation.

To this general statement, the soybean is no exception and despite the considerable study, which has been devoted to the composition of the soybean seed, it may be said that only its grossest aspects are known and much is yet to be learned of the finer and less obvious details of its chemical structure. It is well known, for example, that the soybean seed consists principally of protein, oil, carbohydrates, and mineral constituents. It is also known that the protein is made up of a number of amino acids; that the oil contains a variety of mixed fatty acid glycerides and phosphatides, as well as unsaponifiable materials such as sterols, ketones, and hydrocarbons; that the carbohydrates are present in the form of sugars, cellulose, and various glycosides; and that the mineral constituents consist of potassium, calcium, phosphorus, and similar elements. Moreover, the soybean seed contains many minor constituents such as pigments, vitamins, enzymes, and antioxidant bodies, many of which have been isolated in pure form. Little is known regarding their structure, function, and use. Still other substances are undoubtedly present in the soybean seed, but only a guess may be hazarded as to their identity.

Not only are the chemical constituents of the soybean numerous and complex, but their relative proportions often vary markedly as a result of differences in variety, state of maturity, soil, fertilizer treatment, cultural and climatic conditions, as well as other environmental factors. The literature, pertaining to the effect of the above-mentioned factors on the chemical composition of the soybean, is voluminous and has been reported from every country in which the soybean has been grown.

Typical of these investigations may be mentioned the work of Arasimovich, Artemieva, and Pavlova[19] who noted that the protein content decreased when soybeans were grown under irrigation. Cartter and Milner[75] found the yield of protein and oil varied with different varieties of soybeans when grown in the same locality, and also when the same variety was grown in different localities. Hall[*] examined a large number of soybeans, representing shipments of the 1935 crop, received at various United States terminal markets, and found that the protein content varied from 32.8 to 45.0 per cent, and the oil content from 18.5 to 22.1 per cent, calculated on an oven-dry basis. McClelland[257] examined 160 varieties of soybeans and found the oil content to vary from 13 to 23 per cent. O'Kelly and Gieger[331] observed marked variations in the content of oil, protein, nitrogen-free extract, ash, and crude fiber of the same variety of soybeans as a result of differences of maturity, crop year, and soundness of the seed, as well as similar marked differences when the same variety was compared for different crop years.

Piper and Morse[349] state that the principal varieties in the United States vary from 34.1 to 46.9 per cent in protein content.

Tsukunaga and Nishino[439] followed the changes in composition of soybeans from 53 to 54 days after blooming until time of normal maturity and found the nitrogen-free extract, crude fiber and ash content decreased with increased maturation, whereas the protein and oil content increased. Sessous[390] reported a variation in protein content from 31.7 to 41.9 per cent and in the oil content from 16.5 to 21.3 per cent for all varieties grown at Geissen from 1929 to 1936. Similar vari-

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[*] **Wallace L. Hall, *Some Analyses of Commercial Soybeans,* U. S. Bureau of Agriculture Economics, 5 pp. (1937; mimeographed).**

ations in the protein and oil contents were observed by Webster and Kiltz[450] for Oklahoma-grown soybeans and by Shutt[397] for seed grown in Canada. Smirnova and Lavrova[399] examined a number of varieties of soybeans to determine the effect of geographic location on their protein, oil, ash, and enzyme content. Viljoen[441] examined a number of varieties of soybeans, with regard to the effect of seasonal conditions and soil types, and concluded that variations in the fertility of the soil, as ordinarily encountered in farm practice in South Africa, had little or no effect on the composition of the bean, but variations in climatic conditions had a very pronounced effect. According to the observations of Viljoen, for every degree Fahrenheit rise or fall in the minimum temperature, a corresponding increase or decrease of 0.44 per cent in the oil content may be expected. No correlation was found between the maximum temperature and percentage of oil and protein, or between rainfall and these two characters. Woodworth[470] found the oil content of Illini soybeans ranged from 18.95 to 21.02 per cent when grown in different parts of Illinois.

Bailey, Capen, and LeClerc[25] summarized the results of hundreds of analyses of soybeans as indicated in Table 4.

TABLE 4

CHEMICAL COMPOSITION OF SOYBEANS

	Minimum Per Cent	Maximum Per Cent	Average Per Cent
Moisture	5.02	9.42	8.0
Ash	3.30	6.35	4.6
Fat	13.50	24.20	18.0
Fiber	2.84	6.27	3.5
Protein	29.60	50.30	40.0
Pentosan	3.77	5.45	4.4
Sugars	5.65	9.46	7.0
Starch-like substances by diastase	4.65	8.97	5.6

These authors state that soybeans consist of 6 to 8 per cent of hull, 90 to 92 per cent of cotyledons, and 1.5 to 2 per cent of germ, having the composition given in Table 5.

TABLE 5

COMPOSITION OF THE COMPONENT PARTS OF SOYBEANS

	Proportion of the Seed Per Cent	Moisture Per Cent	Protein Per Cent	Carbohydrates Per Cent	Fat Per Cent	Ash Per Cent
Cotyledons.	90	10.57	41.33	14.60	20.75	4.38
Germ	2	12.01	36.93	17.32	10.45	4.08
Seed coat ..	8	12.53	7.00	21.02	.60	3.83

MINERAL CONSTITUENTS

THE ash content of soybeans varies considerably with the variety and the amount and availability of the mineral constituents of the soil, but five per cent may be taken as a fair average for air-dry beans (see Table 6). They contain more calcium and phosphorus than any of the cereal grains, and few foods excel soybeans as a source of iron, four-fifths of

TABLE 6

MINERAL CONTENT OF SOYBEANS (AIR-DRY BASIS)*

	Per Cent		Per Cent
Ash	5.06	Phosphorus	0.59
Potassium	1.91	Sulfur	0.41
Sodium	0.34	Chlorine	0.024
Calcium	0.21	Manganese	0.0028
Iron	0.0074	Zinc	0.0018
Copper	0.0012	Aluminum	0.0007
Magnesium	0.22		

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* The figures for copper, manganese, and zinc are taken from Winton's *Structure and Composition of Foods.*[466] Aluminum reported by Paul Meunier.[278] The other figures are from Forbes, Beegle, and Mensching.[122]

which is biologically available according to Sherman, Elvehjem, and Hart.[394]

Hirano and Mikuno[184] have reported the presence of 15.896 mg of copper per kilogram of soybeans, 30 to 40 per cent of which is found in the seed coat. In view of the fact that a few parts per million of copper salts (oleate) adversely affects the stability or keeping quality of most refined oils, it would be of interest to know how much of the total copper, contained in soybeans, finds its way into the refined oil. Spectrographic analysis has shown copper to be present in refined soybean oil, but the amount and manner of its combination are unknown.

At one time, it was presumed that the phosphorus in soybeans was present solely in the form of phosphatides, but according to Earle and Milner,[105] only a relatively small portion of the total phosphorus is actually present in this form as is evident from the results shown in Table 7. In fact,

TABLE 7

DISTRIBUTION OF PHOSPHORUS IN DUNFIELD SOYBEANS, CONTAINING 6.02 MILLIGRAMS PHOSPHORUS PER GRAM OF WHOLE BEAN

Sample No.	Phosphatide phosphorus mg	Inorganic phosphorus mg	Phytin phosphorus mg	Phosphorus in residue mg	Total accounted for mg
1	.80	.27	4.45	.24	5.76
2	.77	.26	4.25	.33	5.61
3	.91*	..	4.44	.36	5.71
4	.91*	..	4.29	.37	5.57
5	.74	.26	4.33	.33	5.66
6	.74	.28	4.26	.32	5.60

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* Also includes inorganic phosphorus.

approximately 75 to 80 per cent of the phosphorus contained in the beans is present in the form of phytin.

The plant phytins are the calcium, magnesium, and potassium salts of phytic acid, mesoinositol hexaphosphoric acid, and their amount present in the soybean is normally sufficient to account for practically all of the calcium and magnesium. McCance and Widdowson [256] have shown that 20 to 60 per cent of ingested phytin is excreted unchanged that may, therefore, account for the apparent calcium deficiency of soybeans which has been noted by various investigators. Crystalline calcium oxalate has been observed to occur in the cells of the seed and has been known to precipitate from water extracts of soybean protein.

PROTEIN AND OTHER NITROGENOUS CONSTITUENTS

MEISSL AND BÖCKER [270] appear to have been among the earliest workers to make a systematic study of the chemical components of the soybean seed. Applying the procedure outlined by Ritthausen [373] for the fractional separation of the proteins of oilseeds, these authors extracted ground soybeans with water, dilute acids and alkalies, salts, etc., and examined the various extracts thus obtained. Based on the results of these examinations, Meissl and Böcker concluded that the soybean contained 30 per cent soluble "casein," 0.5 per cent "albumin," 7 per cent insoluble "casein," no gluten, and only small amounts of amido compounds. Of the protein soluble in dilute alkali, they found 86.3 per cent to be "casein" and 1.7 per cent to be "albumin."

Little additional information, concerning the nature of the proteins present in the soybean, was forthcoming until the appearance of the classical work of Osborne and his co-workers. Osborne and Campbell [343] investigated the proteins derived from soybeans and proposed the name glycinin for the globulin which they considered to represent 80 to 90 per cent of the total crude protein. A second and more soluble globulin, similar to phaseolin, was isolated, and an albumin-like proteid, which they designated as legumelin, was estimated to make up 1.5 per cent of the total protein fraction. Osborne and Clapp,[344] in their analyses of glycinin, the principal protein of the soybeans, found the content of amino acids was similar to the values reported for casein, the principal protein of milk.

Tadokoro and Yoshimura [419] fractionated the proteins present in soybeans by means of water, 10 per cent sodium chloride solution, and 0.2 per cent sodium hydroxide solution and obtained a number of products which they designated as glycinin, legumelin, and glutelin. They determined the chemical and physical properties of the protein fractions including the ash, phosphorus, and nitrogen content, the specific rotatory power, hydrochloric acid combining power, and the nitrogen distribution.

Jones and Csonka [212] obtained five protein fractions from soybeans by fractional precipitation at definite concentrations of ammonium sulfate within a range of 33 to 70 per cent of saturation. In order to determine which fraction represented glycinin, a salt-extract of soybean meal was dialyzed. From the protein fraction which precipitated, two globulins were separated. One was precipitated from a 10 per cent sodium chloride solution by ammonium sulfate at 55 per cent of saturation and did not coagulate even at boiling temperatures. This fraction was called glycinin since its properties agreed with those given by Osborne and Campbell for glycinin.

Csonka and Jones [90] analyzed the chief protein, glycinin, from seeds of several varieties of soybeans and found it to differ considerably in amino acid content, with greatest variations occurring in the content of cystine, which shows a low value of 0.74 per cent for the Illini variety and a high value of 1.45 per cent for the Manchu variety. Csonka and Jones [91] were the first investigators to report on the amino acid distribution contained in the whole (non-protein extracted) defatted soybean meal. Again cystine was found to be the most variable amino acid of the varieties tested. Values ranged from 0.287 per cent for the Illini up to 0.491 per cent for the Herman variety. The chief protein, glycinin, of the soybean contains the following percentage of amino acids: Glycine 0.97, valine 0.68, leucine 8.45, proline 3.78, phenylalanine 3.86, aspartic acid 3.89, glutamic acid 19.46, tyrosine 1.86 to 4.55, arginine 5.12, histidine 1.39, lysine 2.71, tryptophane 1.94 to 2.84, cystine 0.74 to 1.45, and methionine 1.84.

Hibino [177] separated albumin, glycinin (globulin), and glutelin from soybeans and studied the products derived from them after hydrolysis under various conditions. Hamilton, Uyei, Baker, and Grindley [147] determined the nitrogen distribution in a sample of soybeans containing 6.79 per cent of this element. The basic nitrogen, amounting to 28.94 per cent of the total, was found to be present as ammonia nitrogen 9.38 per cent, humin nitrogen 2.87 per cent, arginine nitrogen 15.70 per cent, cystine nitrogen 1.46 per cent, histidine nitrogen 5.60 per cent, and lysine nitrogen 6.18 per cent. The monoamino nitrogen amounted to 48.28 per cent, non-amino

2.43 per cent, ether-soluble 0.16 per cent, alcohol-soluble 0.58 per cent, and non-protein 5.55 per cent of the total nitrogen. Sasaki [378] reported the nitrogen distribution of a sample of Korean soybeans as follows: Total nitrogen 7.03 per cent, protein nitrogen 6.48 per cent, non-protein nitrogen 0.55 per cent. From the water extract of five kilograms of soybeans, Sasaki obtained adenine (picrate) 1.40 g, guanine 0.31 g, histidine (dichloride) 0.62 g, arginine (nitrate) 9.55 g, choline (gold salt) 25.35 g, trigonelline (hydrochloride) 0.33 g, and an unidentified base 0.30 g.

Tomiyama [432] found soybeans to contain cystine 1.05 per cent, methionine 3.01 per cent, and tryptophan 1.35 per cent. Sasaki [379] hydrolyzed whole soybean protein with 25 per cent sulfuric acid for 32 hours and removed the diamino acids with phosphotungstic acid and the dicarboxylic amino acids with alcoholic barium hydroxide. The monoamino acids were then fractionated with the results shown in Table 8.

Okano and Beppu [329] examined soybean oil foots (probably obtained in the alcohol extraction process) and found them to contain arginine, aspartic acid, glutamic acid, hydroxyglutamic acid, and an unknown amino acid lactone, having the formula $C_7H_{19}O_7N_3$. The lactone was obtained in the form of colorless prisms melting at 245° C. and was found to contain two carboxyl and two amino groups.

ENZYMES

ENZYMES are the biochemical catalysts of all living organisms. Chemically, the enzymes are proteins or substances closely related to proteins, and in physical aggregation, they are colloidal as they occur in nature. The presence, in the soybean, of a number of enzymes has been detected and reported by various workers, but a comprehensive study of the nature and activity of the enzymic systems, present in the different organs of the soybean, still remains to be made.

TABLE 8

RESULTS OF FRACTIONATION OF MONOAMINO ACIDS OF SOYBEAN PROTEIN

Amino Acid	Form in which separated	Per cent by weight of protein	Per cent of total N (16.6 per cent N in protein)
Glycine	Picrate	0.23	0.26
Alanine	Copper salt	4.12	3.90
Valine	......	2.56	1.84
Leucine	......	10.02	6.45
Isoleucine	Copper salt	2.38	1.53
Proline	Picrate	3.94	2.86
Phenylalanine	Hydrochloride and benzoic acid	5.21	2.66
Tryosine	......	3.82	1.78
Aspartic acid	Copper salt	15.09	3.23
Glutamic acid	Hydrochloride	16.60	9.44
Oxyglutamic acid	......	13.20	6.87
Serine	......	not found	...
Hydroxyproline	......	not found	...

Urease: Perhaps the most thoroughly investigated enzyme, found in soybeans, is urease which is characterized by its specific action on urea. It is found, in varying amounts, in all leguminous plants and was the first enzyme to be obtained in crystalline form.

Takeuchi [420] investigated the presence of urease in the soybean and later Annett [17] reported its presence in all the varieties of soybeans which he examined.

According to Onodera,[337, 338] the urease of soybeans loses its activity on dialysis, but it is restored again by the addition of a small amount of fresh urease, indicating that the fresh urease contains a coenzyme. Heat, acid, and alkali were found to effect the coenzyme but not the enzyme. In germination, urease accumulates in the germs of soybeans in large proportion, but the free coenzyme is absent.

The most comprehensive investigation on the soybean urease was reported by Wester in a series of communications extending over approximately five years. In the course of these investigations, Wester [452–459] examined the effect of bacteria, germination, age, variety, and other factors in relation to the urease activity of soybeans. He determined the urease content of 48 varieties of soybeans and found that all of them, regardless of age, possessed strong ureolytic activity.

Based on the examination of a number of varieties of soybeans, Dox [104] concluded that differences existed in the urease activity of soybeans, but these differences appeared to bear no relationship to the germinating power or the protein content of the seed. Urease activity was observed in seeds which were almost completely devitalized.

Kennaway [224] described, in detail, a method for the estimation of urea in blood, using soybeans as a source of urease. Recently, Granick [183, 184] reported the results of the distribution and variation of urease in various organs of the soybean as a function of maturation. Sizer [398] investigated the kinetics of urea hydrolysis with urease from two commercial preparations of soybean flour and found that, at all temperatures, carbon dioxide liberation was a linear function of elapsed time. The activation energies were found to be identical whether unextracted soybean or the purified enzyme was used.

Amylase: The presence of amylase in the soybean, which had been reported as early as 1886 by Stingl and Morawski,[405] was confirmed by Street and Bailey.[408]

Orestano and Zummo [340] subjected dry, ground soybeans to various elevated temperatures for periods of half an hour and extracted them with physiological salt solution, after which, their amylolytic activity was determined. It was concluded that their results did not support the hypothesis of the existence of two different enzymes, one of which caused liquefaction and the other saccharification of starch.

Later, Artom and Orestano [20] studied the rate of starch liquefaction as a function of the change of viscosity and found it to be proportional to the square root of the temperature and approximately proportional to the concentration of the enzyme. Equations, for the course of liquefaction and saccharification reactions, were devised. Still later, Orestano [339] reported that the soybean contained only one amylase, probably β-amylase. Teller,[423, 424] however, concluded that soybeans contained two types of sugar-forming diastase which have different activities in starch media of different pH and at different temperatures. One of these diastases is of the type characteristic of normal wheat flour and is designated as "reserve" diastase. It was found in the cotyledons of soybeans in all stages of maturity. The other type, which predominates in the bran of germinating cereals and in plant parts most closely associated with active vegetation, is designated as "vegetative" diastase. It was found to be present in the hull of soybeans and also in the pods and leaves.

Newton and Naylor [318] developed methods for preparing amylase concentrates from soybeans and for the determination of the saccharogenic power of soybeans and soybean concentrates. The application of these and other methods to soybeans indicated that the concentrates contain principally β-amylase. In a subsequent publication, Martin, Naylor, and Hixon[264] reported the results of an investigation of the action of β-amylase from soybeans on corn, wheat, rice, potato, and tapioca starches.

Katagiri and Mugibayasi[219] investigated the maltase, saccharifying, and liquefying enzymes of germinated and ungerminated, mature and green soybeans. Maltase and the liquefying enzyme were found to be absent in both the mature and germinated seeds.

Lipase: Falk[118] investigated the action of lipase from soybeans, using the same methods as had been previously used for the lipase from castor beans. Soybean lipase was found to act on triacetin in various substrates in a manner quite comparable to castor bean lipase. Heat and desiccation were likewise found to effect both lipases similarly.

Barton[28] studied the range and activity of lipase from soybeans and concluded that it was identical with lipase from castor beans, but less intense in its activity, owing to the smaller amount in the former seed. Smirnova and Lavrova[399] have reported that, although the lipase activity of soybeans varies but little with the variety, the peroxidase activity varies from 7.56 to 88.02 units, and the urease activity from 26.86 to 60.76 units. André and Hou,[14-16] and Horovitz-Vlasova and coworkers[189] reported the presence of a lipoxidase in soybeans.

Protease and other enzymes: Street and Bailey[408] found evidence of the presence of a protease of the peptoclastic type, as well as ot a peroxidase and a lipase, but negative results were obtained for the presence of sucrase and protease of the peptonizing type. Blagowestschenski and Melamed,[88] however, found that various proteolytic enzymes were present in the soybean.

Hibbard[176] reported an extensive study of the various enzyme systems, including catalase, peroxidase, invertase, amylase, and reductase, of the soybean plant, especially in relation to photoperiodism.

Ito[197] reported the presence of an ascorbic acid oxidase in the soybean.

CARBOHYDRATES

Despite the nutritional, technological, and economic importance of the carbohydrates present in soybeans, these substances have not been completely characterized, and even the total amount of them, which is present in the seed, has not been agreed upon. According to Piper and Morse,[349] the total carbohydrates amount to 22 to 29 per cent, but exactly what carbohydrates are included is not stated. Many investigators have reported data on the presence of nitrogen-free extract and crude fiber in soybeans, but such determinations shed little light on the specific nature or composition of these carbohydrate materials. For example, O'Kelly and Gieger[331] have reported data, covering a large number of determinations of nitrogen-free extract, which were found to vary from 17.73 to 30.18 per cent for sound, mature beans. Determinations of crude fiber gave values of 4.37 to 13.17 per cent, and similar variations have been reported by other workers.

The difficulty, in obtaining satisfactory quantitative data, may be appreciated when it is realized that the carbohydrate substances are present in the soybean in many different forms, including celluloses, free sugars, pentosans, hexosans, glycosides, and probably other forms.

The cellulosic fraction appears to have received little attention aside from crude fiber determinations, and no attempts appear to have been made to separate the various celluloses or cellulose complexes such as ligno-cellulose or cuto-cellulose if such are present.

The presence, in soybean seeds, of the tetrasaccharide, stachyose, $C_{24}H_{42}O_{21}$, was first demonstrated by Tanret[421] who showed by hydrolysis that the sugar was a polysaccharide composed of one molecule of levulose, one molecule of glucose, and two molecules of galactose. This sugar is obtained as a by-product in the alcohol extraction process for the production of soybean oil.

Street and Bailey[408] reported the presence of the following carbohydrates in the soybean: Galactan 4.86, pentosan 4.94, invert sugar 0.07, sucrose 3.31, raffinose 1.13, starch 0.50, cellulose 3.29, undetermined hemicelluloses 0.04, dextrin 3.14, total 21.28. Sato[380] reported the presence of 21.66 per cent of carbohydrates, distributed as follows: Sucrose 5.90, stachyose 3.52, araban 3.80, galactan 4.62, crude fiber 3.82. Kraybill, Smith, and Walter[238] reported the isolation of crystalline sucrose from soybeans. Iwasa[198, 200-202] obtained a sirup as a by-product in the alcohol extraction of soybeans which, on examination, was found to contain water 17.43 per cent, carbohydrates 70.09 per cent, protein 5.20 per cent, and fat 2.28 per cent. The carbohydrate fraction contained glucose, fructose, galactose, rhamnose, arabinose, glucuronic acid, sucrose, and stachyose. The ratio of sucrose to stachyose was found to be 3.50 to 1.90.

Burrell and Wolfe [70] reported the variation in composition of five varieties of edible soybeans which were grown, harvested, and stored under comparable conditions. Appreciable differences were found in the content of the various carbohydrates, especially reducing sugars, sucrose, raffinose, pentosans, and galactans. No effort was made to determine the amount of stachyose which was present.

Considerable difference of opinion exists concerning the presence of starch in soybeans. A number of investigators have reported its presence in amounts up to 3 per cent, whereas an equal number of investigators have reported their inability to demonstrate its presence. The discrepancies may, perhaps, be reconciled by differences in maturity of the beans used in the various experiments. In any event, the amount of starch is quite small.

GLYCOSIDES

THE glycosides, present in soybean seeds, comprise a heterogeneous group of complex carbohydrate substances. At least three distinct carbohydrate-containing classes of compounds * have been isolated from the soybean. One of these groups of compounds is known as the saponins which consist of an aglycone of the trimethylnaphthalene or triterpenoid hydropicene series, combined with one or more molecules of sugar; another group comprises the phytosterolins, the agly-

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* The term glycoside is used here as a general name for the group, irrespective of the sugar present; glucoside is the specific name used for those glycosides, the sugar constituent of which is known to be glucose.

cone portion of which is represented by a sterol, likewise combined with a sugar molecule; and the third group comprises the isoflavone glycosides or yellow pigments contained in the cells of the cotyledon. The aglycones of this last group consist of di- and tri-hydroxy isoflavones which are combined with glucose.

Although differing in the aglycone portions of the molecule and, hence, in the chemical classification generally assigned to these substances, it is nevertheless convenient to treat them as a group, on the basis of the carbohydrates which they contain.

Saponins: The saponins are widely distributed in plants and are generally characterized by their solubility in dilute alcohol and aqueous acids and alkalis, foaming or lathering properties, bitter taste, and, in many cases, by their hemolytic action.

In 1923, Muramatsu [300] isolated what he assumed to be a hydroxy acid which he named hispidic acid. The product melted at 224° C., gave a hexaacetyl derivative, melting at 155° C., and corresponded to the formula $C_{34}H_{68}O_{17}$. Later, he isolated from soybeans a compound [301] having the formula $C_{50}H_{50}O_{20}$ which melted at 240° C. and which he also presumed to be a new hydroxy acid. In reality, these compounds were a mixture of saponins as was shown by later workers. By neutralizing a 70 per cent alcoholic solution of free saponin with sodium hydroxide, Sumiki [410, 411] isolated from soybeans the sodium salt of a saponin, melting at 222–4° C. and corresponding to the formula, $C_{52}H_{80}O_{21}$. The hemolytic power of the saponin was found to be relatively weak compared to standard Merck saponin. Hydrolysis of the saponin yielded the equivalent of one molecule of sapogenin melting at 228–241° C. and corresponding to the formula $C_{32}H_{50}O_3$, together with one molecule each of glucose, rhamnose, arabinose, and an acid which was presumed to be mesoxalic acid.

Walz [445] isolated three saponins from soybeans which he designated as glycosides C, C_1, and C_2. The saponins were obtained as white, characteristic, crystalline products, melting at 272, 225, and 278–280° C., respectively. Preparation C, when tested with canine erythrocytes, gave a Kofler hemolytic index [232] of 1 : 1600, 1 : 200, 1 : 51200 for pH values of 6.0, 8.5, and 10.0. Saponin C_1 gave an entirely negative reaction, and C_2 was not examined for its hemolytic action. After hydrolysis, crystalline sapogenins, melting at 235–6° C. and 243–5° C., were obtained from saponins C and C_1, respectively, and glucose was detected qualitatively.

Okano and Ohara [328] examined the alcohol extract of soybeans, from which the oil was removed, with the object of identifying the soluble glycosidic materials. The alcohol solution was treated with sodium chloride solution, and the resulting precipitate separated by filtration and extracted with ether. The ether-insoluble portion was repeatedly crystallized from 80 per cent ethanol whereby a crystalline saponin was obtained which melted at 225–7° C. and corresponded to the formula $C_{48-50}H_{77-81}O_{18}$. On hydrolysis, there was obtained a crystalline sapogenin corresponding to the formula $C_{30-32}H_{48-52}O_3$, glucuronic acid, galactose, and rhamnose.

From the alcoholic mother liquors of the crystalline saponin, a second and amorphous saponin was obtained which melted at 216–18° C. and corresponded to the formula $C_{49-51}H_{79-83}O_{19}$. Five isomeric sapogenins were obtained, depending on the degree of hydrolysis of the original saponin.

Neither of the original saponins exhibited any hemolytic power.

Hattori, Ogimura, and Okumura [168] isolated two saponins from soybeans which they designated as saponins I and II. Saponin I melted at 265° C. and gave, on hydrolysis, a sapogenin melting at 249° C., whereas saponin II melted at 217–218° C. and gave a sapogenin melting at 241° C.

Burrell and Walter [69] likewise isolated a saponin from soybeans, which melted at 220–225° C., and, after prolonged hydrolysis, obtained and identified the sugars as galactose and probably rhamnose. Although the saponins isolated by all these workers gave different aglycones, Burrell and Walter assumed that their product and those of Sumiki, Walz, and Okano and Ohara were probably identical. In 1937, Miyasaka [284] demonstrated that the apparently homogenous saponin, derived from soybeans, could yield at least three different sapogenins, depending on the conditions of hydrolysis, and about the same time, Nozoye and Katsura [323] reported the isolation of four different sapogenins from soybean saponin. Miyasaka assigned formulas corresponding to C_{29}, C_{27}, and C_{23} to his products, whereas Nozoye and Katsura assigned C_{30}- formulas to all four of theirs. The properties of the seven sapogenins differ but little despite the apparent differences in composition.

Ochiai, Tsuda, and Kitagawa,[324] in a comprehensive investigation of the saponins of soybeans, separated the crude product in the form of a calcium salt from an alcohol extract of soybeans which had been freed of oil and phosphatides. The crude calcium salt contained, in addition to saponins, the phenolic glycoside, genistin. (See isoflavone glycosides.) The purified crystalline saponin, obtained from the calcium salt, melted at 222° C. After hydrolysis with acid and subsequent chromatographic adsorption, four sapogenins were obtained, melting at 311, 259, 239, and 298° C.; having the formulas $C_{30}H_{50}O_4$, $C_{30}H_{50}O_3$, $C_{30}H_{50}O_2$, and $C_{30}H_{50}O_3$, respectively. Analyses and the physical properties of a considerable number of derivatives of these products led Ochiai, Tsuda, and Kitagawa to conclude that the first three of their products were identical with those obtained by Miyasaka, and with three of the four products obtained by Nozoye and Katsura. In a second communication, Ochiai, Tsuda, and Kitagawa [325] reported the results of selenium dehydrogenation of the four sapogenins from which they concluded that the sapogenins, obtained from soybean saponin by acid hydrolysis, were triterpenoid alcohols, genetically related to one another, and to the many similar sapogenins, belonging to the hederagenin series. Further confirmatory work on the structures of the sapogenols was reported by Tsuda and Kitagawa,[437, 438] and by Tsuda and Ichikawa,[436] which leaves no doubt concerning the triterpenoid hydropicenic nature of these compounds.

Iwasa [199] examined the saponin obtained as a by-product in the alcohol extraction method for the production of soybean oil. The product was a crystalline substance decomposing at 220–225° C. and gave, on hydrolysis with surfuric acid, rhamnose, arabinose, glucuronic acid, and a sapogenin.

Phytosterolins: The second group of glycosides, which are present in soybeans, is represented by the phytosterolins or sterol glycosides. Jantzen and Gohdes [209] examined the white flocculent precipitate which separated at the interface when the saponification mixture from soybean oil was shaken with petroleum ether. From the crude product, they isolated sitosteryl-*d*-glucoside. Glucose was identified in the form of its diphenylhydrazone after hydrolysis of the glucoside. The sterol was identified as sitosterol, but the melting point, 138.4–138.90° C., would seem to indicate that the product was, in reality, a mixture of sitosterols and stigmasterol. The same glucoside was isolated from crude soybean phosphatides which are especially rich in this material. According to Jantzen and Gohdes, crude soybean oil contains only about 0.03 per cent of the sterol glucoside, whereas phosphatides, prepared by washing the oil with water, may contain up to 3.0 per cent and the phosphatide-free oil will contain none at all.

Kondo and Mori [234] reported the isolation of sitosteryl-*d*-glucoside from soybean foots which were apparently produced as a by-product during the alcohol extraction of soybean oil by the Honen Oil Manufacturing Company. Soybean oil foots (12.0 kg) were extracted with acetone, and the insoluble portion successively extracted with methanol and ethyl ether. The insoluble residue was a tan-brown powder which consisted principally of phospholipids and phytosterolin. The phytosterolin was separated from the crude product by extraction with boiling 80 per cent ethanol. On cooling the ethanol solution, sitosteryl-*d*-glucoside was obtained as a white powder, melting, after recrystallization, at 252–254° C. and corresponding in analysis to the formula, $C_{35}H_{60}O_6$. The tetraacetyl derivative was prepared by heating the product with pyridine and acetic anhydride. The recrystallized sitosteryl-*d*-glucoside tetraacetate was obtained as brilliant, leaf-like crystals melting at 166–166.5° C. and corresponded to the formula $C_{43}H_{68}O_{10}$.

A portion of the sitosteryl-*d*-glucoside was hydrolyzed with amyl alcohol and hydrochloric acid, and the free sterol recovered. After recrystallization from 80 per cent ethanol, sitosterol was obtained in the form of cubic crystals melting at 138° C. This product gave, on reduction with metallic sodium in amyl alcohol, dihydrositosterol melting at 175° C. Glucose was recovered from the hydrolysate in the form of the phenylosazone melting at 205° C.

Thornton, Kraybill, and Mitchell[426] prepared the mixed sterol glucosides from crude expeller oil by treating the oil with an absorbent and subsequently extracting the glucosides from the absorption agent. The sugar, combined with the sterols, was quantitatively recovered after hydrolysis of the glucosides and identified as *d*-glucose. The aglucone portion was found to consist of sterols similar to those which occur, in the free state, in soybean oil.

Isoflavone glycosides: The third group of carbohydrate-containing substances, present in the soybean, is represented by a series of yellow isoflavone glycoside pigments. Walz[445] isolated two yellow pigments from soybeans and proved them to be identical with the isoflavone glycosides, genistin and daidzin. By extracting 10 kg of soybean meal with 90 per cent methanol, and working up the extract, he obtained 15 g of genistin and 0.7 of daidzin. According to Walz, genistin, $C_{21}H_{20}O_{10}$, melted at 254–256° C. and had a rotation $[\alpha]^{21}_{D} = -27.7°$ in 0.02 *N* NaOH. It gave a hexaacetyl derivative melting at 188° C., a hexabenzoyl derivative melting at 132° C., and a trimethyl derivative melting, with decomposition, at 200–205° C. Hydrolysis of the glycoside gave 1 mole of glucose and 1 mole of the aglycone, genistein, $C_{15}H_{10}O_5$.

Ochiai, Tsuda, and Kitagawa[824] likewise isolated the phenolic glycoside, genistin, but reported it to have a melting point of 298–300° C. Previous to its isolation from soybeans, genistein was synthesized by Baker and Robinson[26, 27] who established it to be identical with prunetol and 5, 7, 4′-trihydroxyisoflavone.

Daidzin was found to melt at 234–236° C. and had a rotation $[\alpha]^{20}_{D} = -36.4°$. It crystallized with one molecule of water, gave an acetyl derivative melting at 203° C., a benzoyl derivative melting at 145–150° C., and a monomethyl derivative melting at 206° C. Hydrolysis yielded glucose and the aglycone, daidzein, which proved to be 7, 4′-dihydroxyisoflavone, melting at 315–320° C. The diacetyl derivative melted at 182° C. and the dimethyl derivative at 154° C.

Okano and Beppu[330] isolated four different isoflavones from the alcoholic extract of soybeans. Lecithin was salted out from the solution and a crude saponin was precipitated from the alcoholic filtrate by the addition of acid. The saponin-pigment complex was dissolved in alcohol, and the saponin precipitated by the addition of lead acetate. The lead-saponin complex was removed by filtration and the excess lead discarded from the filtrate, after which, the pigments were fractionally separated. A mixture of ethanol and ethyl ether was added to the solution which resulted in the separation of yellow, insoluble needles, melting at 265° C. The product corresponded to the formula $C_{21}H_{20}O_{10}$ and was named isogenistin. On hydrolysis, glucose and an aglycone, isogenistein, melting at 302° C. were obtained. The aglycone corresponded to $C_{15}H_{10}O_{5}$ and gave a triacetyl derivative melting at 189° C. and a dimethyl ether melting at 120–125° C. On the basis of these results, isogenistein was presumed to be 5, 7, 2′-trihydroxyisoflavone, isomeric with genistein.

The soluble portion yielded three other crystalline products. One of these, which was designated as tatoin, consisted of colorless needles, melting at 318° C. and having the formula $C_{16}H_{12}O_4$. It gave a diacetyl derivative melting at 185° C., a monomethyl ether melting at 160–163° C., and a dimethyl ether melting at 165° C. These and many other reactions indicated the probable identity of tatoin with 8-methyl-5, 4′-dihydroxyisoflavone.

The second product, which was designated as methylgenistein, consisted of faintly yellow needles melting at 298° C. The product was characterized by the preparation and analysis of a large number of derivatives, on the basis of which, it was concluded that methylgenistein was probably 8-methyl-5, 7, 4′-trihydroxyisoflavone.

The third product, consisting of faintly yellow, lustrous needles, melting at 255° C. and corresponding to the formula $C_{22}H_{22}O_{10}$, was designated as methylisogenistein. On hydrolysis, it yielded glucose and an aglucone, melting at 301–302° C. and corresponding to the formula $C_{16}H_{12}O_5$. The aglucone was converted into a series of derivatives, the analysis of which indicated it to be 8-methyl-5, 7, 2′-trihydroxyisoflavone, isomeric with methylgenistein.

PIGMENTS

THE soybean presents a remarkable range of colors, resulting from a diversity of pigments distributed throughout the various parts of the seed. The pigments, responsible for the color of soybeans, comprise four different types, namely the red-yellow carotenoids, the yellow isoflavone glycosides, the blue-purple anthocyanins, and chlorophyll.

Piper and Morse [349] have described this unusual variation in pigmentation as follows: "Most varieties of soybeans have unicolored seeds in the following colors: Straw yellow, olive yellow, green, olive, brown, and black, the last really a dark violet. Straw-yellow seeds are in some varieties very pale, especially when old, and are sometimes erroneously called white, but no truly white seeds are known in soybeans. In several varieties, like the Mammoth, the seeds have a greenish tinge, if harvested before maturity, making it difficult to distinguish them from varieties whose fully mature seeds are greenish-yellow. The latter again merge by very fine gradations into olive and from this into brown. Bicolored seed occurs in but few varieties. The commonest are green or yellow with a saddle of black, the latter not sharply delimited. Some varieties have their seeds brindled brown and black, the two colors somewhat concentrically arranged. One variety has black seeds faintly marked with minute brown specks. On heterozygote plants, the seeds are often irregularly bicolored and, in some cases, tricolored. Among recent introductions from Chosen (Korea) were several black and a few brown varieties with the outer layer of the testa broken by numerous cracks so as to expose the inner white layer. In the case of the black sorts, this splitting has a net-like appearance, giving the beans a black and white color.

"The hilum or seed scar may be of the same color as the seed coat, as in the case of black, brown, and a few yellow-seeded varieties, or it may range from a pale brown to black in most straw-yellow, olive-yellow, and green-seeded sorts.

In the latter case, the color of the hilum is often of value in distinguishing varieties having the same outer color. In a few varieties, as in Ito San, there is a minute brown spot on the micropyle which is diagnostic."

Despite this remarkable variation in color and its genetic significance, little effort appears to have been directed toward the isolation and identification of the individual pigments. By means of microreactions with a series of reagents, Kondo [233] examined the colored contents of the palisade cells and concluded that the blue color of the Japanese seed was an anthocyanin, the brown color of the black Chinese seed a tannin-containing anthocyanin, the olive-green color of the Japanese green seed chlorophyll, and the yellow-brown color of the dark wine-red Japanese seed probably tannin. He concluded that the palisade cells of yellow seeds contain no pigment, the color being located in the cotyledon. According to Alexandrov and Alexandrova,[5] the basic type of pigmentation consists of a blue anthocyanin in the cell sap and of the chlorophyll of the plastids. According to these authors, the yellow coloration of the cell walls results from the presence of phlobaphene, but since the phlobaphenes are usually deep red in color, it is more than likely that the yellow color has its origin in the previously mentioned isoflavone pigments. In addition to the pigments of the palisade cells, there are present in the oil droplets of the cotyledon various carotenoid pigments which impart to the expressed oil its characteristic reddish-yellow color. These pigments will be discussed under the sections on oil and vitamin A. Chlorophyll, which occurs in the plastids, will be discussed under oil properties since it affects the color of the oil removed from the seed during pressing or solvent extraction.

VITAMINS

THE term vitamin is used to designate those substances, which, in addition to fats, proteins, carbohydrates, and mineral salts, are required, in very small amounts, to maintain normal growth and health. Chemically, there is no basis for placing vitamins in one group because, generally speaking, they are as unrelated as simple sugars, terpenes, pyridine, pyrimidines, and sterols and consequently, no generalization can be made with respect to their chemical properties. They are, however, alike in one respect, namely, the absence from the diet of any one of the vitamins causes a specific disease.

Vitamin A: Vitamin A is a growth vitamin and prevents xerophthalmia or hardening of the membrane of the eye and cornea, hence is referred to as the anti-xerophthalmic vitamin. Certain carotenoids, particularly β-carotene, can be converted, in the animal organism, into true vitamin A which is stored in the liver often in considerable quantities.

Although a number of workers have reported the presence of vitamin A in soybeans or soybean oil, the amount, in which it is present, has not been satisfactorily decided upon. Most vitamin assays of vegetable oils, in general, indicate the presence of but little vitamin A or D. De Gironoli,[98] who was one of the earlier investigators of the vitamin A potency of soybeans, concluded from a clinical study on infants that soybean oil contained no vitamin A. Scheunert [381] reported that soybean phosphatides contained no antirachitic vitamin and only negligible traces of vitamin A. Ohtomo[327] reported that soybean cake contained some vitamin A, whereas Tso [485] stated that soybean milk was comparable to cows' milk in vitamin A and richer in vitamin B, although inferior in mineral content. Wan[446] reinvestigated the dietary properties of soybean milk and concluded, contrary to the findings of Tso, that, as measured by rat assays, soybean milk contained less vitamin A than cows' milk. A diet of soybean milk powder (⅓) and white wheat (⅔), with added salt, did not result in as good growth, even when supplemented with vitamins A, B, and D, as did a similar diet, containing cows' milk in the form of Klim. The poorer growth, observed with soybean milk, was attributed to protein deficiency in the case of the vitamin supplemented diet.

Hayward,[170] however, states that examination of fifty varieties of soybeans showed the presence of 10 to 210 γ of carotene per 100 grams, equivalent to 0.16 to 3.5 international units of vitamin A per gram. Assays of expeller meal, containing 8 per cent fat, and extracted soybean flour, containing 3 per cent fat, indicated the presence of 0.36 and 0.30 international units of vitamin A, respectively, and 0.165 and 0.132 international units of vitamin D per gram. He concludes from these results that soybean flours or meals are not reliable sources of these vitamins for feeding livestock or poultry.

Lantzing and Van Veen[244] analyzed sixteen samples of soybeans, representing a number of different varieties, for their content of provitamin A. The beans were ground, treated with alcohol, extracted with petroleum ether, and the extract allowed to separate into an epiphysical and a hypophysical phase. The composition of the two phases was determined by chromatographic adsorption of the pigments followed by spectrographic and colorimetric analyses.

It was found that the epiphysic phase consisted of β-carotene, whereas the hypophysic phase consisted of xanthophyll. The various samples of soybeans, which were examined, gave results varying between 40 and 80 γ of carotenoids per 100 grams or approximately 70 to 180 international units of provitamin A per 100 grams of ground beans. The β-carotene content was equivalent to 70 to 130 international units per 100 grams of ground beans.

Wilber, Hilton, and Hauge[462] reported that soybeans appeared to suppress the transference of vitamin A from dairy rations to the butter when soybeans constituted part of the feed. In a later communication, these authors[169] concluded that there was present in soybean oil and soybean oil meal, obtained either by pressing or solvent extraction, an unknown factor which suppressed the transfer of vitamin A from the rations to butter and that prolonged extraction with ether and alcohol failed to completely remove this factor from the bean.

Frey, Schultz, and Light[127] found that shaking carotene solutions with ground soybeans, in the presence of oxygen, led to the complete decolorization of the carotene. When 0.09 ml portions of carotene solution, equivalent to 272 U. S. P. units, after they had been shaken with a suspension of 10 mg of active soybean in one ml of water, were fed daily to assay animals, no response was observed, whereas 0.001 ml portions of untreated carotene solution, equivalent to 3 U. S. P. units, gave a normal growth response. These authors also reported that 99 per cent of the vitamin A, present in codliver oil, was destroyed by treatment with active soybean. However, Kishlar[226] states that more than a hundred assays have been made of carotene-soybean meal mixtures, and no abnormal destruction of carotene was found.

A recent investigation, by the Bureau of Agricultural Chemistry and Engineering,[230] has clarified the problem of the alleged destruction of vitamin A by the action of an oxidase in raw soybeans. A series of feeding experiments, employing a raw-soybean diet and daily administration of the vitamin supplements apart from the diet, indicated that there was no marked destruction of the vitamins as a result of their contact with raw soybean meal, under the conditions of the experiments. It was concluded, therefore, that the unsatisfactory rate of growth, with raw soybeans alone, was attributable to a protein, rather than a vitamin, deficiency.

Sherman and Salmon [395] have reported the results of the determination of the carotene content of a large number of different varieties of green and mature soybeans. Most varieties of soybeans, in the green stage, were found to be very good sources of carotene with a range from 212 to 705 γ per 100 gram fresh sample. The carotene content of different varieties of mature soybeans ranged from 18 to 243 γ per 100 gram air-dry sample. Excessive weathering of soybeans, produced by allowing plants to stand in the field two or three weeks after the seed reached maturity, caused a destruction of as much as 50 per cent of the carotene in several varieties of mature soybeans.

In a subsequent report, Sherman [398] correlated the carotene content with biological assays for five varieties of soybeans. Chromatographic analyses of the biologically active carotenoid pigments, extracted from the mature seeds, demonstrated that the pigment, contained in the purified extract, was 80 to 88.8 per cent β-carotene and 2.5 to 11.8 per cent α-carotene. Cryptoxanthin was not found in any of the soybeans analyzed.

Sherman concluded that, "The carotene content of many varieties of soybeans at maturity is as great as that of yellow corn. In terms of total vitamin A activity, however, the yellow corn, because of the presence of relatively large amounts of cryptoxanthin, was superior to all varieties of mature soybeans studied." The superiority of yellow corn to soybeans, as a source of vitamin A, has been reported by Mitchell and Beadles.[281]

Halverson and Sherwood [145] reported the vitamin A activity, obtained by means of rat-growth assays, in fifteen samples, representing nine varieties of soybeans. They found the vitamin A content per gram of soybeans varied from 0 to 1.3 international units and concluded, therefore, that none of the varieties examined contained any appreciable quantity of vitamin A.

Snyder and Moore [401] determined the content of carotene in the whole soybean plant, at weekly intervals, from the time just prior to the formation of flowers until the stalks were completely mature and dry. The carotene content was found to increase to a maximum of 432 micrograms per gram of dry matter by the time the pods began to fill and then decrease to 7.9 micrograms per gram of dry matter at final maturity.

Vitamin B complex: In view of the confusion existing in the literature relative to the nomenclature of the various components of the so-called vitamin B complex, it is necessary to discuss briefly its nomenclature prior to reviewing the published investigations on the occurrence of this nutritional factor in the soybean.

In the course of the early investigations on the cause and prevention of beriberi, the terms water-soluble B, vitamin B, beriberi vitamin, and antineuritic vitamin were used by various authors to refer to the dietary factor essential to protect against the disease. As research on this factor continued, it became evident that vitamin B was not a single substance but a complex group of chemical entities, the absence of one or more of which resulted in different pathological conditions in experimental animals.

A number of the factors of the B complex have now been isolated in pure form and their structure determined and verified by synthesis. The members of the B complex have been designated as follows: *

"Vitamin B_1 is a factor which prevents and cures beriberi in man and polyneuritis in animals. It has been isolated and synthesized and is now called thiamin. The crystalline, synthetic compound is thiamin chloride. Vitamin B_1 is also called aneurin.

"The term 'Vitamin B_2' has been used in various ways and now has no generally accepted meaning. It has been used to refer to the compound now known as riboflavin, to refer to all components of the vitamin B complex other than vitamin B_1, and, in some instances, other individual components of the vitamin B complex.

"Nicotinic acid (nicotinamide or nicotinic acid amide) is synonymous with the pellagra-preventive factor, which is also specifically for the prevention or cure of blacktongue in dogs.

"Riboflavin, which has also been known as vitamin B_2 and G, is a compound necessary for growth in rats and chicks and which prevents a specific dermatitis and cataract in rats. It has also been shown to be effective in the treatment of

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* E. M. Nelson. Private communication to the authors dated May 17, 1940.

lesions of the mouth of man, called cheilosis, as well as keratitis. It is a component of an oxidation-reduction system in living cells.

"Pantothenic acid, a compound necessary for growth in rats and chicks, and which prevents chick dermatosis.

"Vitamin B_6, also called pyridoxine, essential for preventing dermatosis in rats, and necessary for growth in rats and chicks.

"Vitamin B_3, a factor necessary for rapid gains in weight and normal nutrition of pigeons.

"Vitamin B_4, a factor for prevention of a specific paralysis in rats and chicks.

"Vitamin B_5, a factor necessary for maintenance of weight in pigeons.

"Factor W, a factor necessary for growth in rats."

Wan[446, 447] concluded from a comparative study of soybeans and milk that soybeans contain three times as much vitamin B_1, but only two-thirds as much vitamin B_2 (flavine), as does dried milk. Chen[79] concluded, on the basis of rat assays, that salted egg white, beef, and dried soybean curd were good sources of vitamin B_1. Miller and Robbins[277, 278] reported that cooked beans were a good source of vitamins A, B, and G, but a poor source of vitamin C. Scheunert and Schieblich[882] found that fresh soybeans, grown near Leipzig, contained practically no vitamin A but did contain significant amounts of vitamin B_1 and vitamin B_2. The content of vitamin B_1 corresponded to about $\frac{1}{40}$ of the amount found in a very good dried brewers' yeast, while that of B_2 corresponded to about $\frac{1}{8}$. Consequently, 1 g of fresh soybean contains the equivalent of about 1.5 international units of vitamin B_1. Hayward[170] reported that a sample of solvent-extracted meal assayed 2.8, and a hydraulic-process meal 1.0 international units of vitamin B_1 per gram of solids. Mitchell and Beadles[282] found that 20 per cent of soybeans, in the diet, furnished sufficient vitamin B for maximum growth and maintenance of health in rats. They concluded that 20 to 30 per cent of soybeans in the diet was as effective as 70 per cent or more of corn as a source of vitamin G, or that soybeans contained two to three times as much of this vitamin as does corn.

Sherwood and Halverson[392] reported soybean meal to be a good source of vitamin B. According to these authors, soybean meal contains 1.1 international units of vitamin B compared to 5.4 international units per gram for linseed meal. In a later communication, Halverson and Sherwood[145] reported the examination of fifteen samples representing nine varieties of soybeans, from which, it was found that the vitamin B_1 content varied from 3.2 to 4.8 international units per gram.

Norris and coworkers[321, 468] have shown the essential nature of riboflavin in the diet of chicks and demonstrated its necessity for hatchability of fertile eggs. They introduced the term "Chick Unit" as a measure of riboflavin in the feed mixture which is roughly equivalent to 1 microgram of flavin. They determined that chicks need approximately 290 units of vitamin G per 100 grams of feed in order to attain normal weight at eight weeks' age. Hens require about 230 units per 100 grams of feed, in order to produce eggs that will hatch well. As small an amount as 130 units per 100 grams of feed is sufficient for normal egg production. The quantity of vitamin G, found in soybean oil meal, compared with other feedstuffs used in poultry feeding, as determined by these authors, is recorded in Table 9.

TABLE 9

RELATIVE VITAMIN G CONTENT OF COMMON FEEDSTUFFS USED IN POULTRY FEEDING

Feedstuffs	Units of Vitamin G per Gram
Dried pork liver	100
Dried yeast	35
Dried whey	30
Dried skim-milk	20
Alfalfa meal, dehydrated	16
Alfalfa meal	11
White fish meal	10
Sardine fish meal	7
Meat scrap	6
Menhaden fish meal	5
Wheat germ	4
Soybean oil meal	3
Wheat middlings, standard and flour	2
Wheat bran	2
Wheat red-dog flour	1
Yellow corn	1
Wheat, hard and soft	0.5
Barley	0.5
Buckwheat	0.5
Oatmeal	0.5
Oats	trace
Corn-gluten meal	0

Levine and Remington[253] report the presence of 2.4 to 3.2 Bourquin-Sherman vitamin G units per gram of soybeans. Kishlar[226] reported the presence of 2.5 Sherman rat units of vitamin G per gram of high grade expeller meal and concluded that soybean meal of good quality has approximately half the vitamin G content of dried skimmed milk and about twice the vitamin G content of 55 per cent protein meat scrap or 60 per cent fish meal, and 20 times as much as common cereals. These conclusions are at variance with the above-mentioned results reported by Norris and coworkers.

The flavin deficiency of expeller-pressed soybean meal in chick rations has also been demonstrated by Christiansen, et al.[84] These authors conclude that "the protein of the grains supplemented solely by soybean oil meal is inefficient and requires additional supplementation with other protein for maximum efficiency." The protein materials, which were effective in supplementing soybean oil meal, were found to be those high in flavin which would indicate the observed deficiency resulted primarily from insufficient flavin rather than from a protein deficiency.

According to Schneider, Steenbock, and Platz,[384] rat acrodynia can be cured either by vitamin B_6 or linoleic acid, and vegetable oils containing this acid. Although, soybean oil does not contain vitamin B_6, it does contain a very considerable amount of linoleic acid in the form of glycerides and may, therefore, be considered effective in curing acrodynia in rats. In this connection, it should be mentioned that contrary to earlier reports, no untoward symptoms were observed in growing chicks until the soybean oil content of the ration amounted to 10 per cent or more.[173]

Vitamin C: Vitamin C, or the antiscorbutic vitamin, is water-soluble and is found particularly in fresh fruits and certain green vegetables. It was the first vitamin to be obtained in crystalline form and its constitution has been proved by total synthesis. Chemically, it is *l*-ascorbic acid, $C_6H_8O_6$.

It is very sensitive to oxidation and heat, and is the most easily destroyed of all the known vitamins.

The literature, relative to the occurrence of vitamin C in soybeans, is not very extensive. Lee and Read [247] found that soybeans germinated in the dark at 25° C. formed ascorbic acid in increasing amounts up to about the tenth day. The maximum amount formed was nearly 0.4 mg per seedling. The largest amounts were found in the cotyledons, and it was present mainly in the reversibly oxidized form. Sunlight caused a production of about twice the amount formed in the dark. Dry soybeans are reported to be relatively poor in vitamin C. Similar results were reported by Sugiura.[409]

Vitamin D: Vitamin D, or the antirachitic vitamin, occurs in the liver. Before it was isolated and properly characterized, a different antirachitic principle was obtained by irradiating ergosterol with ultra-violet light. This second vitamin D has been obtained crystalline and is designated as calciferol or vitamin D_2. It is isomeric with ergosterol, one of the sterols contained in yeast.

Vitamin D from liver oil, vitamin D_3, is closely related to the product of irradiating ergosterol. Vitamin D_3 can also be derived from 7-dehydrocholesterol by exposing it to ultraviolet light. Both calciferol (vitamin D_2) and vitamin D_3 are strongly antirachitic.

Heilbron, Kamm, and Morton [172] examined a wide variety of oils with respect to the possible presence of their pro-vitamin D absorption spectra. No evidence of absorption bands characteristic of these substances was found in soybean oil.

Bacharach [28] found that refined soybean oil was moderately rich in vitamin A, but devoid of vitamin D. About the same time, Izume, Yoshimaru, and Kimatsubara [204] reported antirachitic properties for hydraulic-pressed, alcohol-extracted, and benzine-extracted soybean oils. They found that refining did not appreciably alter the activity of the oil, and that the activity was increased by irradiation. Irradiation of the unsaponifiable fraction produced well-defined absorption bands, characteristic of ergosterol. In a later communication by Izume, et al.,[203] it was claimed that 20 per cent of the unsaponifiable fraction of soybean oil consisted of ergosterol which was effective, after irradiation, in curing rachitis in mice in daily doses of 0.01 mg compared to 0.1 mg for the irradiated oil. Despite the reported vitamin D activity, extensive investigation of the sterol fraction has failed to reveal the presence of ergosterol in soybean oil.

Campos, Cavalcanti, and Santos [74] could find no evidence of the presence of an antirachitic factor in soybean oil.

Vitamin E: Vitamin E or the antisterility vitamin is fat-soluble. Evans, Emerson, and Emerson [117] isolated, from wheat-germ and other vegetable oils, two alcohols, α- and β-tocopherol, having the formulas $C_{29}H_{50}O_2$ and $C_{28}H_{48}O_2$, respectively. These alcohols are oily liquids which form crystallizable derivatives. Both tocopherols possess vitamin E activity, but the former is about 2.5 times as active as the latter. Deficiency of vitamin E in female animals renders them incapable of bearing viable offspring.

Sahashi [877] appears to have been the first to observe, from the anatomical examination made on rats at the termination of feeding experiments that soybean oil possessed vitamin E activity. In a subsequent communication by Suzuki, Nakahara, and Sahashi,[417] it was reported that, when soybean oil was used as the only source of vitamin E, testicular degeneration was prevented, in contrast to the marked degeneration which occurred when peanut, coconut, sesame, palm, and blubber oils were fed under the same conditions. The soybean oil, used in these experiments, was freshly expressed in the laboratory and had an iodine number of 142.5, which is considerably higher than that of most commercially produced oils in this country.

In a still later communication, by the same authors,[418] it was concluded, on the basis of breeding tests with seven albino female rats, that soybean oil contained antisterility vitamin E. However, the experimental evidence is not very convincing since three of the females never became pregnant; another gave birth to one litter of four, none of which survived; still another became pregnant but died prior to completion of gestation; a sixth gave birth to one litter of seven young, all of which died due to failure of lactation and a second pregnancy led to abortion; the seventh gave birth to three litters all of which died, within two to three days, due to failure of lactation. Based on the interruptions of gestation, the amount of vitamin E in soybean oil was assumed to be relatively small.

In 1936, Goettsch and Pappenheimer [131] observed that certain vegetable oils, including corn, cottonseed, peanut, and soybean, when added to a causative diet, provided a protective factor against nutritional encephalomalacia in chicks. The disease was not thought to be a manifestation of vitamin E deficiency since addition of natural foodstuffs, rich in vitamin E, did not protect the chicks.

Coombes, Elvehjem, Phillips, and Hart [86] reported that encephalomalacia, a type of chick paralysis or crazy chick, was caused by an unknown nutritive factor in the ration, and that soybean oil, but not cottonseed oil, provided excellent protection against the disorder. Ni[319, 320] likewise reported that Chinese gelatin as well as soybean oil would prevent the disease and concluded, therefore, the factor was non-lipoidal in nature.

Jukes and Babcock[216] concluded, on the basis of extensive feeding experiments, that when alfalfa meal was added to the diet, it was more active than soybean oil in improving growth and preventing paralysis in chicks. It was further concluded that there were two different forms of the same active factor since protection against paralysis was observed either by a fat-soluble fraction prepared from soybean oil or by a water-soluble fraction prepared from fat-extracted alfalfa meal.

Recently, Pappenheimer, Goettsch, and Jungherr[346] have published a monographic report on their studies of nutritional encephalomalacia in chicks. The pathological changes resulting from feeding chicks a synthetic diet, containing all the factors known to be necessary to normal rat nutrition, except vitamin E, were described and defined, and the disease designated as nutritional encephalomalacia.

The protective factor was concentrated from soybean oil by extraction with 95 per cent alcohol. It was found to be present in the unsaponifiable fraction when due precaution was taken against oxidation and the proper solvents were used for extraction. The fatty acid and water-soluble fractions were found to be inert. Protection was also afforded when α-tocopherol (vitamin E) from vegetable oils or synthetic *dl*-α-tocopherol acetate was included in the diet. The above results would seem to indicate that soybean oil does, in fact, contain vitamin E, but at present, the amount cannot be expressed in quantitative units.

Pappenheimer and Goettsch[345] observed that the addition of soybean oil to the diets of dystrophic rabbits resulted in the production of viable offspring which could be raised to maturity, whereas its omission, from an otherwise similar diet of the parent, resulted in death of the offspring within one day of birth. Autopsy showed the presence of lesions identical with those found in certain stages of adult nutritional muscular dystrophy.

Later, it was found by Goettsch and Ritzmann[132] that naturally occurring α-tocopherol prevented the development of muscular dystrophy in young rats when it was fed from the tenth to the twenty-fifth day after birth, whereas control rats, under similar conditions, but without the supplement of α-tocopherol, showed symptoms of muscular dystrophy at the end of the test period.

Mackenzie and McCollum[261] and also Morris[286] showed that natural α-tocopherol, from wheat-germ oil, was effective in curing muscular dystrophy in rabbits, and in addition, Morris demonstrated that synthetic α-tocopherol was equally, if not more, efficacious than the natural product. He found the lower limit of a single curative dose to be about 20 milligrams of synthetic α-tocopherol per animal.

On the basis of the evidence mentioned above, it may be assumed that (1) vitamin E is more than an antisterility factor; (2) soybean oil possesses this factor, although to a much less marked degree than does wheat-germ oil; and (3) the factor is contained in the unsaponifiable fraction of soybean oil from which it can be produced in concentrated form by extraction with suitable solvents.

Vitamin K: During the course of some experiments on the sterol metabolism of the chick, Dam[93, 94] observed that chicks, raised on certain artificial diets, became anemic, had large subcutaneous and intramuscular hemorrhages and in one chick the blood-clotting time was markedly increased. Later he reported [77] that the hemorrhagic condition was not relieved by the addition to the diet of vitamin C or any other of the then known vitamins or essential dietary factors. He suggested that the hemorrhages were due to the lack of a new fat-soluble factor, which he named vitamin K.

It has been shown that this antihemorrhagic factor is widely distributed in green leaves and vegetables and is especially abundant in dried chestnuts, spinach, cabbage, and alfalfa leaves. Almquist and Stokstad [7, 8] reported in 1935 that the addition of 0.5 per cent of dry alfalfa to the deficient diet prevented the appearance of symptoms, and since that time, alfalfa has been one of the main sources of this vitamin.

Almquist and Stokstad [10] were the first to report the presence of vitamin K in soybean oil. The blood-clotting time of two-week-old chicks, fed a diet supplemented with a hexane extract of alfalfa, was 1.7 minutes; with one per cent soybean oil 15.6 minutes; with two per cent soybean oil 3.7 minutes; with five per cent soybean oil 1.3 minutes, compared with the control group having a blood-clotting time of 12 minutes. It was concluded,[407] therefore, that 2 to 3 per cent of soybean oil, added to the chick diet, provided an adequate level of vitamin K.

Dam and Glavind [95] determined the amount of vitamin K in many types of plants. Soybean seeds, dried in vacuum desiccators at room temperature, were found to contain 25 units of vitamin K per gram of dry material. The method of assay was that described by Schnheyder [386] and developed by Dam and Lewis.[79]

Evidence, for the existence of a fat-soluble factor required by the chick for the integrity of the gizzard lining, has been presented by Almquist and Stokstad.[9] Almquist [6] showed that the gizzard factor was present in soybean oil and, to a less extent, in soybean meal. He also demonstrated the instability of the factor to heat and ethyl alcohol by replacing an active soybean oil with the same oil, after heating with ethyl alcohol, or by heating the oil in vacuo for 24 hours at 120° C. whereupon it was observed that the activity of the protective factor was markedly reduced or completely destroyed. The gizzard factor does not appear to be identical with vitamin K.

OIL AND OIL-SOLUBLE CONSTITUENTS

SOYBEANS normally contain from 13.5 to 24 per cent of lipids extractable by fat solvents such as ethyl ether, hydrocarbons, chlorinated hydrocarbons, alcohols, or carbon disulfide. Over ninety-five per cent of this fatty material is found in the cotyledons, and the remainder in the germ and seed coat. The oil or fat, obtained by extraction of the seed, consists principally of the glycerides of saturated and unsaturated fatty acids, mixed with a number of other lipid materials. The latter include phosphatides, sterols, long-chain hydrocarbons, alcohols and ketones, free fatty acids, pigments, vitamins, and antioxidants, as well as small amounts of non-lipid, gummy or mucilaginous substances. The type and amount of the various lipids, which may be present in the oil, depend somewhat on the variety of seed, environment during growth, methods of harvesting, handling, and storage of the beans, and especially on the manner of processing the seed and subsequent refining the oil. Probably, no commercially important vegetable oil is produced by the variety of processing practices to which soybeans are subjected.

It is not surprising, therefore, that the physical and chemical characteristics of crude soybean oils show considerable variations, resulting from combinations of the various factors enumerated above. Individual oils, derived from specific varieties of seed, may show wide variations in physical properties and chemical composition, but commercial soybean oils are much more uniform, owing to the mixing of different lots of seed, or of different batches of oil during processing. Furthermore, the numerous refining operations tend to eliminate much of the secondary materials, especially gums, phosphatides, free fatty acids, unsaponifiable matter, and pigments.

The existing literature, pertaining to soybean oil, is voluminous and widely scattered; also much of it is superficial with respect to objective and execution. Systematic and comprehensive examination of individual soybean oils, with respect to all or even a considerable number of their physical and chemical properties, is not extensive. Data, relative to the variations of such properties as specific gravity, viscosity, refractive index, and specific heat as a function of temperature, pressure, or other variables, are either non-extensive or non-existent. Systematic and comprehensive chemical analyses, especially with respect to the non-glyceride constituents of the oil, are similarly non-extensive. Apparently, most of the investigations, reported in the literature, refer to laboratory preparations, usually solvent-extracted crude oils, and in many cases, the variety or previous history of the seed is unknown or is not recorded. No doubt, many industrial concerns have amassed considerable data relative to oils produced in their own plants, but, for the most part, such information is not available in the scientific and technical literature.

PHYSICAL AND CHEMICAL CHARACTERISTICS OF SOYBEAN OILS

MOST vegetable oils, and soybean oil is no exception to the general rule, are evaluated as to quality, freedom from associated impurities or added adulterants, adaptability to various processes or uses, by means of certain inherent, physical and chemical characteristics or properties. Some of these properties have been made the basis of trading rules for buying and selling oils, and procedures for their determination are set forth in so-called official methods. Many determinations of these more common properties are made by and for oil mills, refiners, and consuming industries.

Other properties, especially those of importance in highly specialized applications or processes, are determined with less frequency and often by arbitrary or improvised methods, or under conditions applicable to or closely simulating, the process in which the oil is to be employed. In some cases, the results of these determinations are published, but more often they are not.

In assembling the available data on the physical and chemical characteristics of soybean oil, as has been done in the following pages, several defects are evident, notably, the narrow range of environmental conditions over which a given property has been measured; the lack of specificity of the material examined; the variety of methods which have been used by different investigators; and the variety of units in which the results have been expressed.

In the following enumeration of the chemical and physical properties of soybean oil, an effort has been made to include, wherever available, information concerning the type or origin of the oil and the method applied in determining a given property.

Acetyl value: See Hydroxyl number.

Acid value: See Free fatty acids.

Break: The so-called "break" material, found in most crude soybean oils, consists principally of phosphatides, pigments, and mucilaginous materials which are removed from the seeds along with the oil. The various methods of pressing and extracting soybeans result in marked differences in the amount of extraneous or non-glyceride material which accompanies the oil. The temperature and pressure of pressing, and the temperature, moisture content, and type of solvent influence the quantity and composition of non-glyceride substances which are removed from the seed. The method and degree of clarification (settling, filtering, centrifuging, or washing) likewise affect the quantity of extraneous materials which remain in the crude oil. Where the phosphatides are to be recovered, their presence in the crude oil is desirable and advantageous, but much of the oil, especially in America, enters directly into the edible or drying oil industry where excessive "break" material is objectionable because it leads to increased refining losses.

The percentage of "break" material is determined by the modified Gardner acid-heat-break method [11] which consists, essentially, of adding three drops of hydrochloric acid to a 25 g sample of oil, heaing rapidly to 288° C., cooling, and diluting the sample with carbon tetrachloride. The "break" material, which separates, is filtered, washed, dried, and weighed. The amount of "break" material, obtained under these conditions, normally varies from 0.04 to 0.20 per cent for extracted oils and from 0.20 to 1.00 per cent for expeller oils. It was originally supposed that the amount of "break" material, found by the heat-break method, was correlated with the loss sustained in refining the oil. Such a relation exists with respect to many soybean oils, but numerous exceptions are found (Table 10) especially in the case of solvent-extracted oils.

The standard specifications,[312] governing the purchase and sale of domestic, crude soybean oil, impose a maximum limit of 0.60 per cent on the content of "break" material and provide a penalty of 0.2 per cent of the purchase price for each 0.1 per cent, or fraction thereof in excess of 0.60 per cent.

Color: The color of soybean oil is usually determined by matching in a tintometer a column of oil, 25 mm deep, in the case of crude oils, and 133 mm deep, in the case of refined oils, against a combination of red and yellow Lovibond color glasses. The results are expressed in terms of red and yellow units on the Priest-Gibson (N″) color scale.[129, 130, 259]

Although satisfactory for many purposes, color values, obtained by matching an oil against standard yellow and red glasses, do not reveal the complete color characteristics of an oil. In order to obtain a true measure of the color of an oil, it is necessary to know its absorption or transmittance characteristics over the entire visible spectral range. Transmittance curves (figures 2, 3, and 4) of a number of typical crude and refined soybean oils are produced from the data of

Bickford, Anderson, and Markley.[34] Inspection of these curves and reference to others in the original publication, from which they are reproduced, provides ample evidence of the manner in which soybean oils may vary in their color characteristics.

The color of crude soybean oil may vary considerably with the source of seed and the method of producing the oil, but normally a 133 mm column of oil is found to range from 70 yellow and 10 red units to 70 yellow and 30 red units on the N″ color scale. Occasionally, the color of a crude oil may depart from these values if, for example, the soybeans, from which it is produced, are immature and contain unduly large amounts of chlorophyll, or when the oil is overheated or otherwise improperly treated during processing. Also oil produced from green, brown, and black varieties of soybeans will show abnormal color if the colored seed coat is not removed before processing for oil.

Refined oils may vary appreciably in color, depending on the use for which they are intended. For example, in mayonnaise or salad dressings, a bright yellow oil may be desired, whereas for use in shortening, light colored varnishes, or synthetic resins, a minimum of color is desired. Highly refined, edible quality soybean oil is generally produced with a color of 15 to 35 yellow units and 1.5 to 3.5 red units on the N″ Lovibond scale when measured in a 133 mm cell. When hydrogenated for use in shortening, the color is further reduced to approximately 10.0 yellow units and 1.0 or less red units. Commercial, varnish-grade soybean oil is often sold on a guaranteed color of 30 yellow and 3 to 5 red on the Lovibond scale.

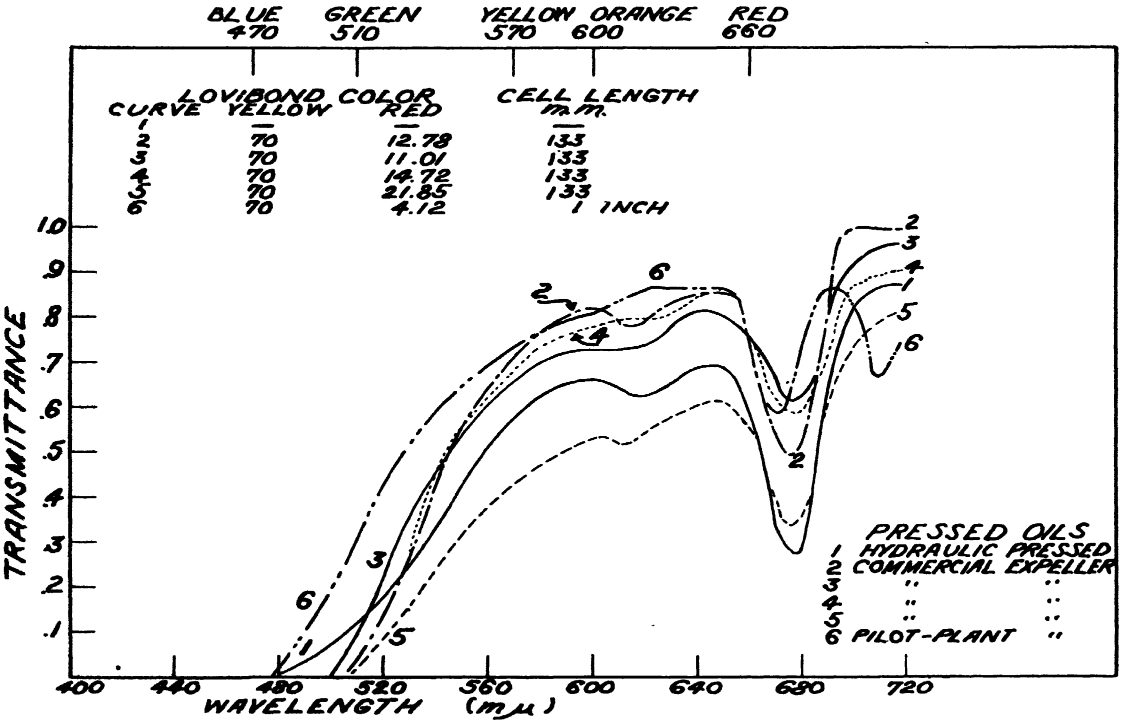

FIGURE 2
Spectral transmittance of crude pressed soybean oils

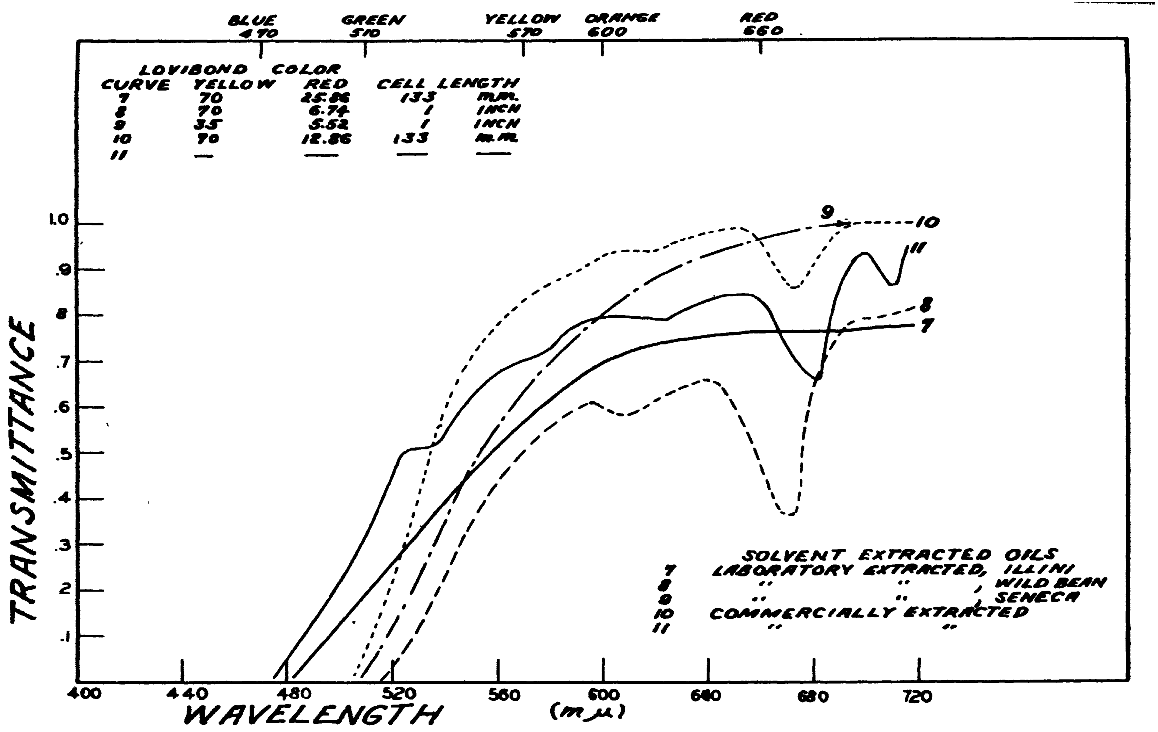

FIGURE 3
Spectral transmittance of crude, solvent-extracted soybean oils

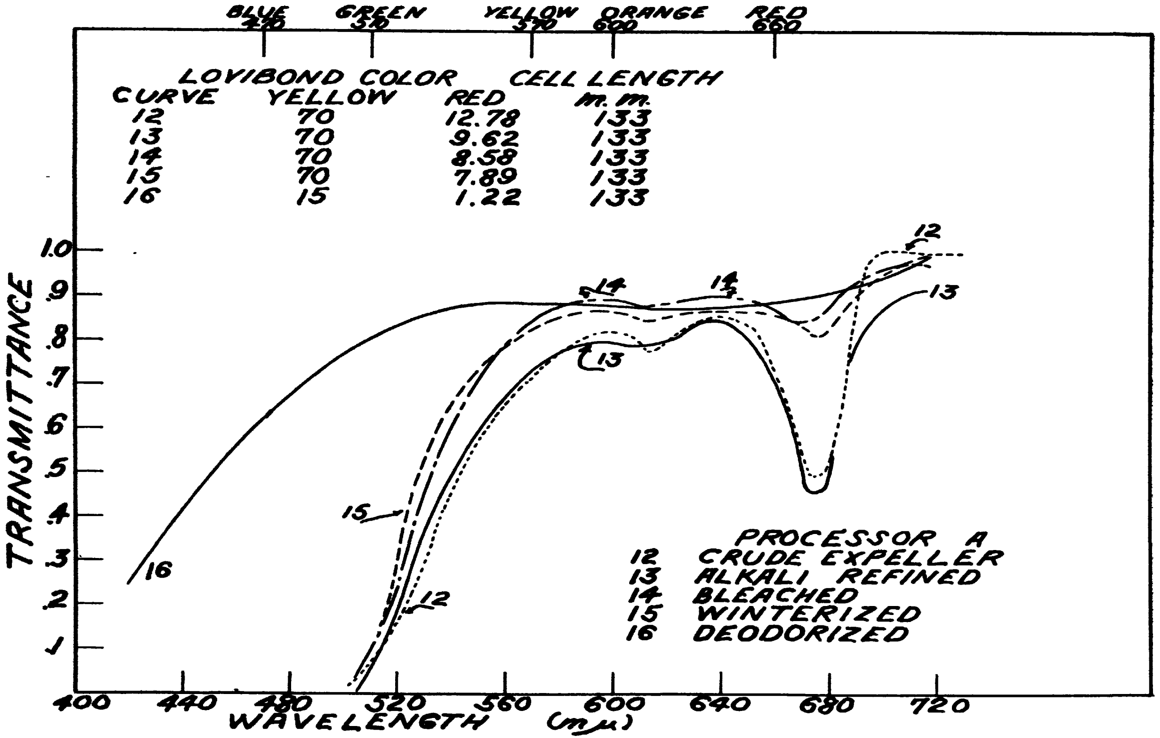

FIGURE 4
Spectral transmittance of a soybean oil at various stages of processing

TABLE 10

FACTORS AFFECTING THE REFINING LOSS OF CRUDE SOYBEAN OILS

Sample No.	Type of oil	Free fatty acid	Refining loss	Break	Phosphorus
		%	%	%	%
48	Expeller-pressed	0.35	3.7	0.26	0.097
49	Expeller-pressed, roasted beans	0.52	6.5	0.58	....
56	Expeller-pressed, commercial	0.61	3.9	0.06	0.059
57	Commercial-pressed, clarified	0.45	4.3	0.15	0.021
59	Expeller-pressed	0.87	4.2	0.30	0.046
60	Expeller-pressed	0.42	3.3	0.26	0.043
61	Expeller-pressed, commercial	0.60	5.1	0.48	0.083
62	Expeller-pressed	1.02	5.4	0.36	0.058
63	Expeller-pressed	0.91	4.8	0.26	0.054
64	Expeller-pressed	0.75	4.1	0.28	0.044
65	Expeller-pressed	0.73	4.2	0.28	0.044
66	Expeller-pressed	0.81	4.1	0.24	0.042
67	Expeller-pressed	1.10	4.9	0.32	0.050
68	Expeller-pressed	0.78	3.9	0.26	0.044
69	Expeller-pressed	0.86	4.2	0.24	0.038
70	Cold-pressed, commercial	0.43	4.3	0.37	....
72	Solvent-extracted, commercial	1.65	6.8	0.07	0.012
73	Expeller-pressed	0.83	4.8	0.26	0.045
74	Expeller-pressed	0.84	4.3	0.23	0.041
75	Expeller-pressed	0.86	4.0	0.25	0.041
80	Solvent-extracted, commercial	0.35	3.0	0.34	0.084

In Table 11, there are recorded data obtained at the Regional Soybean Industrial Products Laboratory, which illustrate the normal variation observed in the color of various grades and types of soybean oils.

Congealing temperature: The temperature, at which soybean oil freezes or congeals, has been reported to vary from –8.0 to –18° C.

Density: The density of soybean oil has been variously reported to range from 0.922 to 0.934, at 15° C. and 0.915 to 0.920 at 25° C. The specific gravity, at 25/25° C. for seven samples of solvent-extracted, crude soybean oil, which were examined at the United States Regional Soybean Industrial Products Laboratory, was found to vary from 0.9159 to 0.9219. Johnstone, Spoor, and Goss [211] reported the density in grams per cubic centimeter of a completely refined soybean oil, at 25, 37.8, and 50° C., to be 0.9171, 0.9087, and 0.9004, respectively. These authors have also reported data for the density of soybean oil solutions in hexane, ethylene dichloride, and trichloroethylene throughout their miscibility range and for temperatures of 25, 37.8, and 50° C.

TABLE 11

COLOR VARIATION OF SOYBEAN OILS IN PRIEST-GIBSON (N") COLOR UNITS

Type of oil	Number of samples	Low	High	Cell length mm
Expeller-pressed crude	23	70Y— 4.04R	70Y—10.03R	25
Expeller-pressed crude	7	70Y—13.16R	70Y—30.75R	133
Solvent-extracted crude	7	70Y— 3.50R	70Y— 6.64R	25
Solvent-extracted crude	7	70Y—12.60R	70Y—29.35R	133
Alkali-refined	24	70Y— 6.34R	70Y—11.42R	133
Completely processed	13	10Y— 0.92R	35Y— 3.17R	133

The density of soybean oil has been related to other physical properties as, for example, iodine number. These relationships are discussed under the correlated property.

Diene numbers: The diene number was originally proposed as a measure of the conjugated double bonds of the fatty acid glycerides of vegetable oils. Diene numbers ranging from 8.5 to 8.9 have been reported by Kaufmann, Baltes, and Büter [228] for soybean oils. Bickford, Dollear, and Markley [86, 87] were unable to confirm these results, except in the case of blown soybean oils. The latter authors found that good-quality, refined oils had diene values ranging from 0.7 to 2.0. Furthermore, they established the fact that the presence, in fats and oils, of hydroxyl groups, peroxides, and possibly other oxidation products influences the magnitude of the diene number, apparently as a result of the reaction of these substances with maleic anhydride, under the conditions specified for the determination of diene numbers.

Fatty acids: (see also titer value) The mixed fatty acids, obtained by saponifying soybean oil, have been reported to melt at from 20 to 29° C. and solidify at 14 to 25° C. The mean molecular weight of the mixed fatty acids is about 290, and the iodine number has been found to vary from 106 to 158.

Flash and fire points: Detwiler and Markley [101] examined a number of representative soybean oils with respect to their smoke, flash, and fire points. Average values, which were found by the Cleveland open cup method for a number of typical soybean oils, are given in Table 12.

TABLE 12

AVERAGE SMOKE, FLASH, AND FIRE POINTS OF SOYBEAN OILS

Type of soybean oil	Average smoke point °F.	Average smoke point °C.	Average flash point °F.	Average flash point °C.	Average fire point °F.	Average fire point °C.
Expeller-pressed crude	380	183	573	300	664	351
Solvent-extracted crude	411	210	602	316	672	355
Alkali-refined	467	242	624	329	681	361

The results, obtained by these authors, indicated that expeller-pressed crude soybean oils generally exhibit lower smoke, flash, and fire points than do mechanically refined or alkali-refined soybean oils. Solvent-extracted crude oil likewise appeared to be superior to expeller-pressed crude oil with respect to these properties. Alkali-refining was found to result in improvement of the thermal stability of soybean oil, whereas subsequent processing, such as bleaching and deodorization, had little additional effect on this property. It was concluded that good-quality soybean oil, free from excessive quantities of free fatty acids and foots, usually could be heated with safety to 600° F. (315° C.) and, in some cases, even slightly above this temperature without undue risk of fire.

Fluorescence: Most vegetable oils, when subjected to ultra-violet irradiation, emit fluorescent light which imparts to them color qualities different from those observed in ordinary light. For example, irradiation of soybean oil by a quartz light produces a light lilac fluorescence.[142] Marcille[263] found that soybean oil, like olive, peanut, and other seed oils, exhibits a violet fluorescence and concluded that although some oils, as found, will fluoresce when irradiated with ultraviolet light, for the most part, fluorescence is an acquired characteristic and is dependent on the treatment to which the oil is subjected during the various processing operations.

Free fatty acids: Soybean oils contain variable amounts of free fatty acids. In the case of freshly produced crude oils, these acids may have pre-existed in the uncombined form in the seed at the time they were harvested, or they may have developed in the seed after harvesting and before processing. Their presence in aged oils may be attributed to the above causes and also to hydrolysis of the glycerides after their extraction from the seed. Regardless of the manner, in which the free fatty acids originated, it is of importance to know the amount of these substances which is present in the oil.

The quantity of free fatty acids, which are present in an oil, is expressed by the acid number. It is defined as the number of milligrams of potassium hydroxide required to neutralize the free fatty acids in one gram of an oil. Examination of a large number of freshly produced soybean oils has shown variations in acid number as follows: Solvent-extracted oils 0.35 to 3.85; expeller-pressed oils 0.86 to 2.10.

Alkali-refining results in a reduction of the free fatty acid content, and carefully refined and deodorized soybean oil should have an acid number of 0.10 or less. However, freshly refined and deodorized soybean oils have been produced with acid numbers as great as 0.40. The acid number changes with conditions which tend to produce hydrolysis or splitting of the glycerides and, in due course of time, under adverse storage conditions, the acid number may become relatively large.

Instead of the acid number, the trade prefers to express the content of free fatty acids in an oil on a percentage basis, which, in the case of soybean oil, is calculated as oleic acid. Trading rules [312] limit the maximum free fatty acid content of crude soybean oil to 1.5 per cent, and impose a penalty of 0.5 per cent of the purchase price for each 0.5 per cent in excess thereof.

Hehner number: The Hehner number expresses the percentage of water-insoluble acids which are found in an oil after saponification, neutralization, and extraction of the liberated acids with water. Values of 93.0 to 94.3 have been reported for soybean oils.[119]

Hexabromide number: When the fatty acids, prepared from soybean oil, are brominated in ether solution, an insoluble precipitate of hexabromostearic acid is obtained which, when freed from impurities, melts at 180–181° C. The weight of the precipitate times 100 divided by the weight of fatty acids gives the percentage of hexabromides or the hexabromide number. Hexabromide numbers of soybean oils, varying from 2.2 to 9.65, have been reported by Steele and Washburn,[403] Bailey, and Baldsiefen,[24] Kaufmann [222] and others. These values were once presumed to represent the relative percentages of linolenic acid present in soybean oils, but it has been shown by Shinowara and Brown [396] and Kaufmann [222] that the yield of hexabromides varies with the composition of the other fatty acids present in the mixture and is, therefore, not a reliable index of the content of linolenic acid.

Hydroxyl number: The hydroxyl number and the related acetyl value are intended to measure the amount of hydroxyl groups present in an oil, presumably, in the form of the glycerides of hydroxy acids. In a freshly refined oil, such groups may represent naturally occurring hydroxy acid glycerides, but in aged oils, hydroxyl groups may be present as a result of the oxidation of unsaturated acids or hydrolysis of triglycerides to mono- and diglycerides.

The hydroxyl number is defined as the number of milligrams of potassium hydroxide equivalent to the hydroxyl content of the sample of oil, whereas the acetyl value is defined as the number of milligrams of potassium hydroxide required to neutralize the acetic acid produced on saponification of one gram of acetylated oil. Both values are found to vary with the method used in their respective determinations. Acetyl values for soybean oil, varying from 4.9 to 20, have been reported in the literature, but the higher values are improbable, except in the case of aged or oxidized oils.

The hydroxyl number of a series of crude, semi-refined, and completely refined soybean oils, obtained from soybeans of different varieties and grown under different soil and climatic conditions, were determined at the Regional Soybean Industrial Products Laboratory by the method of West, Hoagland, and Curtis.[451] The values, found for these oils, varied from 2.6 to 6.7. Mild oxidation of a freshly refined, edible-grade soybean oil, by aeration at 98° C. in a Swift stability apparatus, was found to result in a gradual increase in the hydroxyl number as follows: Time of aeration 0, 6, 8, and 10 hours; hydroxyl number 3.9, 4.2, 6.1, and 11.5, respectively. The increase in hydroxyl number results from the oxidation of the double bonds of the unsaturated acids present in the form of glycerides.

Iodine number: The iodine number is defined as the number of grams of iodine which 100 grams of fat or oil is capable of absorbing. Although varying somewhat with the method and conditions, under which it is determined, it provides information, concerning the total unsaturation of most vegetable oils, containing non-conjugated ethenoid linkages. The so-called official Wijs method is generally accepted as most reliable for use with soybean oils. Examination at the Regional Soybean Industrial Products Laboratory of hundreds of samples of commercial and laboratory-processed oils, including crude, semi-refined, and completely refined oils, derived from many varieties of soybeans grown under different soil and climatic conditions, has revealed iodine numbers ranging from 103 to 151. The majority of commercial soybean oils were found to have iodine values within the range 130 ± 3. Crude oils and the corresponding refined soybean oils differ only slightly in their respective iodine numbers.

Soybean oil of a minimum iodine value is preferred by the edible oil trade as it is believed that increased unsaturation is detrimental to keeping quality, and also because the greater the degree of unsaturation the greater is the consumption of hydrogen, during the hydrogenation or hardening process. On the other hand, the drying oil trade prefers soybean oil of maximum iodine value, because superior drying and film-forming properties are associated with a high degree of unsaturation.

Various relationships have been established between the iodine number and other physical properties of soybean oil, as, for example, iodine number and density, and iodine number and refractive index. Yokota and Tachimori [476] have shown that the relation between the density and the iodine number of soybean oils is nearly constant. For the relation between the iodine number and refractive index of soybean oil, see section on refractive index.

Optical rotation: Most fats and oils show very slight optical rotation, unless they contain acids with monovalent polar groups such as are present in castor oil. Such optical activity, as they may possess, is generally attributed to the sterols which are normally present in the oil in small amounts. However, the optical behavior, observed by Suzuki, Inoue, and Hata,[413] is difficult to explain on this assumption. These authors observed that a number of freshly produced vegetable oils, including soybean oil, possessed a small optical rotation which gradually decreased to zero, on standing. Soybean oil, for example, when freshly isolated, was found to possess an optical rotation of +0.25 which gradually and regularly decreased to zero in the course of a few days. Since crude soybean oil contains up to 0.3 per cent or more of mixed sterols, it is to be expected that the oil might have a slight optical rotation, but since these sterols are quite stable and do not change appreciably with age, their presence offers no explanation of the observed decrease in rotary power, on standing.

Refining loss: Refining losses are caused by the presence of free fatty acids, phosphatides, and extraneous non-glyceride materials which are present in the crude oil. The apparatus and conditions for the laboratory determination of the refining loss for expeller, hydraulic, and extracted soybean oils are set forth in the *Official and Tentative Methods of the American Oil Chemists' Society.*[11] Examples of typical laboratory refining losses are recorded in the annual reports of the Refining Loss Committee of the American Oil Chemists' Society.[12]

Refractive index: When a beam of light passes from one transparent medium to another, it is deviated or refracted and the ratio of the sines of the angles of the incident and of the refracted light is a constant at the boundary between the two media. This constant ratio, for any two given media, one of which is usually a glass prism, is known as the refractive index. It is an important property of fats and oils, not because of any direct interest in the refraction of light by the lipid, but because the index of refraction is relatively easy to determine, and is characteristic of a given oil, and because, it can be correlated with other, less easily determined properties.

The refractive indices of hundreds of samples of oil, derived from soybeans representing many different varietal and cultural conditions, have been determined over a period of several years at the Regional Soybean Industrial Products Laboratory. These refractive indices have been found to range from $N_D^{25} = 1.47084$ to $N_D^{25} = 1.47423$.

Considerable effort has been devoted to correlating the refractive index with other properties of soybean oil such as iodine number, density, and the oil content of the seed.

Pickering and Cowlishaw [348] were probably the first to establish a quantitative relationship between the refractive index and iodine number of soybean oil. They found, as the result of the examination of hundreds of samples of fresh soybean, linseed, refined cottonseed, and peanut oils, that the refractive index could be related to its respective iodine number by the equation: $N_D^{40} = 1.4515 + 0.0001171$ iodine number. It was stated that the equation applied only to fresh oils, free from oxidation and having a low content of free fatty acid and unsaponifiable matter.

More recently, Majors and Milner [262] correlated the results of the determinations of refractive indices and iodine numbers of a very large number of soybean oils and studied the effects of variation of different factors on the accuracy of the correlation. These factors included, among others, the method of obtaining the oil from the seed, age of the sample of seed, the content of free fatty acids and of unsaponifiable matter of the oil.

These authors established the fact that the corrêlation curves varied from year to year, but were remarkably constant for a given crop year. They concluded that the iodine number of soybean oil can be determined by calculation from the refractive index, with an accuracy comparable to any chemical method, provided that the refractometer used is sufficiently accurate, the measurements are carefully made, and that for any given crop year, a correlation curve is established.

Leithe and Müller [248] devised a method for determining the percentage of oil in soybeans, based on the differences in the refractive indices of the solution of the oil and that of the pure solvent.

Zeleny and Neustadt [477] investigated the determination of the oil content of soybeans by refractometric and solvent-extraction methods. They proposed a method for the determination of the oil content of soybean seed, based on the refractive index of a mixture of soybean oil, having a refractive index, $N_D^{25} = 1.47302$, and a solvent, consisting of halowax (α-chloronaphthalene) and α-bromonaphthalene adjusted to have a refractive index, $N_D^{25} = 1.63940$. For oils deviating in refractive indices from the standard oil, they constructed a table of corrections to be added to or substracted from the observed values.

Johnstone, Spoor, and Goss [211] published data for the refractive indices of various soybean oil-solvent solutions over their entire miscibility range at 25° C. The solvents comprised hexane, ethylene dichloride, and trichoroethylene and the oil represented a highly refined, edible grade.

Reichert-Meissl number: The Reichert-Meissl number is defined as the number of milliliters of 0.1 *N* potassium hydroxide solution required to neutralize the water-soluble, volatile fatty acids obtained from 5 grams of fat or oil. Values ranging from 0.2 to 2.8 have been reported for soybean oil. It is not an important characteristic of soybean oil and is only seldom determined.

Saponification number: The saponification number or Koettstorfer number is defined as the number of milligrams of potassium hydroxide required to saponify one gram of fat or oil. The saponification number of freshly produced, solvent-extracted, crude soybean oils, which were examined at the Regional Soybean Industrial Products Laboratory, were found to vary from 188.8 to 193.5.

Smoke point: See flash and fire points.

Specific heat: The specific heat of a sample of soybean oil, having an iodine number of 134 and an acid number of 2.3, was determined by Long, Reynolds, and Napravnik[254] over a temperature range of 75 to 287° C. (167 to 548.6° F.). The data are given in Table 13.

TABLE 13

SPECIFIC HEAT OF SOYBEAN OIL

Temperature °C.	Temperature °F.	Specific Heat Cal./Gram
75	167	0.568
85	185	0.579
130	266	0.582
140	284	0.591
140	284	0.606
151	303.8	0.589
159	318.2	0.596
161	321.8	0.597
171	339.8	0.603
181	357.8	0.623
190	374.0	0.640
193	379.4	0.630
220	428.0	0.618
230	446	0.655
240	464	0.681
250	482	0.682
250	482	0.698
280	536	0.759
287	548.6	0.765

Thiocyanogen number: The thiocyanogen number determination was proposed by H. P. Kaufmann [220, 221] on the supposition that the thiocyanate radical added quantitatively to but one of the two double bonds of linoleic acid and to but two of the three double bonds of linolenic acid, whereas iodine and other halogens added quantitatively to both of the double bonds of linoleic acid and all three of the double bonds of linolenic acid. On this assumption, therefore, it became possible to calculate the composition of the unsaturated acid fraction of fats and oils from the determined values for the iodine and thiocyanogen numbers.

Unfortunately, for the accuracy of the fatty acid composition calculated in this manner, it has since been shown by Riemenschneider and Wheeler,[372] Kass, Loeb, Norris, and Burr,[218] and Hilditch and Murti [181] that the addition of the thiocyanate radical is far from quantitative for linoleic and linolenic acids and esters, under the conditions of the Kaufmann method. However, by substituting in the equations, used for calculation, new constants obtained experimentally on highly purified linoleic and linolenic acids, it is possible to obtain accurate values for the composition of many fats and oils, including soybean oils. The last mentioned authors presented data for the different values obtained in the unsaturated acid fraction of soybean oil when calculated by the use of the original Kaufmann constants and the revised constants. Higher values were found for linoleic acid and lower values for oleic and linolenic acids when calculated by the new constants as compared with those calculated by Kaufmann's constants.

A very considerable number of soybean oils, representing many varieties of seed and types of processing, has been examined at the Regional Soybean Industrial Products Laboratory. Variations of from 78.0 to 90.5 were observed in thiocyanogen numbers compared with 103 to 151 for the iodine numbers of the same oils.

Titer: The solidification point of the mixture of fatty acids and unsaponifiable matter, obtained by saponifying, acidulating, and washing the water-insoluble fraction of fats and oils, is known as the titer. It is determined by an arbitrary, but very specific method which provides information of value and utility to the manufacturer of soaps and candles. Titers varying from 22 to 27.5° C. have been reported for soybean oil. Manufacturers generally offer soybean fatty acids for sale, with a titer of 22 to 26° C.

Unsaponifiable matter: The unsaponifiable fraction of soybean oil includes all those substances which are not saponified by alkali but which are soluble in ether or petroleum ether. Included in this fraction are the sterols, some phytosterolines, hydrocarbons, alcohols, and ketones. The average content of unsaponifiable matter found in 153 samples of soybean oils, examined at the Regional Soybean Industrial Products Laboratory, was found to be 0.75 per cent, with individual variations ranging from 0.52 to 1.61 per cent.

Standard specifications [312] for crude, domestic soybean oil limit the maximum content of unsaponifiable matter to 1.5 per cent, for special technical uses.

Viscosity: Viscosity measurements have been reported for only a few soybean oils. They are given in various units and for different temperatures as shown in Table 14.

TABLE 14

Viscosity of Soybean Oils

Temperature °C.	Units		Reference
37.78	164.6	S.U.S.	Hufferd *
98.89	51.4	S.U.S.	Hufferd
148.89	38.9	S.U.S.	Hufferd
37.78	35.26	K V (Centistokes)	Hufferd
98.89	8.00	K V (Centistokes)	Hufferd
148.89	3.998	K V (Centistokes)	Hufferd
25.0 **	51.0	Centipoises	Johnstone, Spoor, and Goss [211]
37.8 **	31.5	Centipoises	Johnstone, Spoor, and Goss
50.0 **	21.36	Centipoises	Johnstone, Spoor, and Goss
15.5	0.797	Poises	Inter. Crit. Tables [311]
25	274	Redwood	Jamieson [206]
25	8.26–8.43	Engler	Jamieson

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* Hufferd, R. W., Kendall Refining Company, private communication.

** Corrected figures. Viscosity data in reference are in error and must be multiplied by square of specific gravity to obtain correct values.

Miscellaneous data: In addition to the properties of soybean oils, which have been discussed in the preceding pages, there are several conversion factors derived directly or indirectly from these properties which are of considerable practical value. These factors are grouped here for convenient reference and are as follows:

Weight of soybean oil per gallon 7.67 pounds.
Weight of soybean oil per standard U. S. tank car, approximately 61,000 to 62,000 pounds.
Volume of soybean oil per standard U. S. tank car, approximately 8,000 to 8,060 gallons.

Fatty Acids and Glycerides

The percentage distribution of the fatty acids, is found in various petroleum ether-extracted soybean oils, is shown in

Table 15. In each case, the composition of the unsaturated acid fractions was calculated from the iodine and thiocyanogen numbers, on the assumption that only oleic, linoleic, and linolenic acids were present in this fraction. However, Hilditch and Jasperson [178, 179] have found that normal soybean oils contain about 0.5 per cent of hexadecenoic acid and it is not known in what amounts this acid may be present in abnormal oils. The literature contains a number of reports on the analyses of soybean oils by other methods which have yielded results that are in substantial agreement with those given in Table 15. For example, Smith,[400] Baughman and Jamieson,[29] Jamieson, Baughman, and McKinney,[207] Cruz and West,[89] and Griffiths and Hilditch [139] employed the hexabromide number in determining the percentage of linolenic acid, whereas Hashi [165] and Hilditch and Jasperson [179] employed the fractionation of the methyl esters to determine the composition of a soybean oil. The last mentioned authors reported the presence of C_{14}-and C_{16}-unsaturated acids in these oils amounting to 0.64 and 1.44 per cent, respectively, before deodorization, and to 0.53 and 1.60 per cent, respectively, after deodorization.

The last seven samples of soybean oil, referred to in Table 15, were prepared in the same manner under the same experimental conditions and were analyzed by identical methods throughout.[29] Inspection of the data indicates that there is a remarkable constancy in the ratio of saturated to unsaturated acids of these soybean oils, which appears to be wholly independent of the iodine number of the oil from which the acids were derived. Of the seven soybean oils, having iodine numbers ranging from 102.9 to 151.4, the saturated acids were found to comprise 12.7 ± 0.8 per cent and the unsaturated acids, 87.3 ± 0.8 per cent of the total acids present. It is also to be noted that within the limits of experimental error, the percentages of linoleic and linolenic acids increase more or less regularly with increasing iodine numbers of the oils, whereas the reverse is true of the oleic acid, which decreases progressively with the increase in iodine numbers of the oils.

Although these data are limited, with respect to the number of samples of soybeans which have been examined, nevertheless, in view of the randomness of their selection, they indicate that the distribution of the saturated and various unsaturated fatty acids, in the soybean seed, bears a definite relation to the iodine number of the oil, and their formation in these proportions appears to be governed by a specific and relatively invariable biochemical process, independent of varietal, climatic, or pedological conditions. These observations may be summarized as follows:

(1) The ratio of saturated to unsaturated acids, in soybean oil, is fairly constant, irrespective of the total amount of oil present in the seed and of the iodine number of the extracted oil.

(2) The distribution of the unsaturated acids varies in a specific manner with the iodine number of the oil derived from the seed, but is independent of the total amount of acids which are formed during growth and maturation and stored by the seed in the form of various lipids.

Earlier workers, including Smith,[400] Baughman and Jamieson,[29] Wallis and Burrows,[443] Pfahler,[347] Heiduschka and Eger,[171] and others, have reported values for the saturated fatty acids of soybean oil varying from 9 to 17 per cent, but this apparent variation results from the different methods of analyses which were applied rather than from actual differ-

TABLE 15

Composition of Solvent-Extracted Soybean Oils *

		Oil			Fatty Acids					
Source	Variety	Iodine number	Thiocyanogen number	Unsaponifiable matter	Unsaturated	Saturated	Oleic	Linoleic	Linolenic	Worker
				%	%	%	%	%	%	
Manchuria	Unknown	137.05	80.5	1.2	84.6	15.3 **	21.3	55.2	8.2	Kaufmann [222]
Manchuria †	Unknown	132.2	78.3	0.6	84.2	15.8 **	25.9	51.2	7.1	Kaufmann
United States	Unknown	130.5	80.4	0.65	84.9	15.1 **	24.7	53.7	6.5	Kaufmann
United States	Mammoth	134.2	81.9	0.57	85.2	14.8 **	24.7	50.5	10.0	Kaufmann
Manchuria	Unknown	133.8	79.7	0.54	88.2	11.8	25.9	58.8	3.8	Kimura [225]
United States	Dunfield	102.9 ‡	78.0	0.84	88.0	12.0 ††	60.0	25.0	2.9	Dollear, et al.[103]
United States	Dunfield	127.3	80.2	0.66	86.9	13.1 ††	34.8	46.0	6.0	Dollear, et al.
United States	Dunfield	124.0	79.6	0.70	86.8	13.2 ††	34.0	49.1	3.6	Dollear, et al.
United States	Illini	131.6	81.3	0.84	88.0	12.7 ††	27.7	53.7	5.9	Dollear, et al.
United States	Peking	137.8	84.5	0.93	87.6	12.4 ††	24.4	56.2	7.3	Dollear, et al.
United States	Seneca	139.4	85.1	0.61	88.1	11.9 ††	24.7	55.4	8.0	Dollear, et al.
United States	Wild Beans	151.4	87.4	2.20	86.5	13.5 ††	11.5	63.1	12.1	Dollear, et al.

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* Calculated on the basis of total fatty acids as 100 per cent and not as glycerides.

** Bertram's oxidation method.

† Refined oil.

†† Twitchell's lead salt alcohol method.

‡ Abnormal oil.

ences in composition of the magnitude indicated by these figures. For example, the content of saturated fatty acids, in soybean oils, was found by Kaufmann[222] and by Earle and Milner[106] to be approximately 15 per cent, by the Bertram oxidation method, which value is 2 per cent greater than that obtained by the Twitchell lead salt-alcohol method.

The content of myristic acid has been reported to vary from 0.6 to 1.07 per cent, palmitic acid from 6.5 to 8.5 per cent, stearic acid from about 3 to 6 per cent, and arachidic acid from 0.2 to 0.7 per cent.

According to Hilditch's rule of random distribution of the fatty acids among the glycerol molecules of seed-fats and liquid vegetable and animal fats, soybean oil should contain no fully saturated triglycerides. From a study of the composition of non-hydrogenated and fully hydrogenated soybean oil, Hilditch and Jones[180] concluded that the original non-hydrogenated oil contained, on a mole-per cent basis, less than 1 mole-per cent of fully saturated, 0 to 13 mole-per cent of mono-unsaturated, 20 to 25 mole-per cent of di-unsaturated, and 75 to 87 mole-per cent of tri-unsaturated glycerides. The fully hydrogenated oil yielded 75 per cent tristearin and 25 per cent palmitoglycerides.

Previous to the work of Hilditch and Jones, Hashi[166] isolated oleodipalmitin from soybean oil by extraction with acetone. By brominating soybean oil and fractionating the resulting mixed bromides from petroleum ether, ethyl ether, and benzene, Suzuki[412, 415] isolated the following bromides: dilinoleolinolenin bromide, m.p. 78° C.; two linoleodilinolenin bromides melting at 117 to 118° C. and 158° C.; dilinoleolein bromide (oil); three oleodilinolenin bromides, m.p., 6, 5, and 3° C.; and linoleodiolein bromide, m.p. 3° C.

Neither triolein nor trilinolein bromides were found. Hashi [167] likewise attempted to separate the corresponding brominated glycerides from soybean oil by fractionation from various solvents. He obtained three bromides, melting at 154, 147, and 74 to 75° C. and concluded, from an examination of their properties, that they consisted of linoleodilinolenin bromide, a mixture of oleodilinolenin bromide with dilinoleolinolenin bromide or with linoleodilinolenin bromide, and a mixture of trilinolein bromide with oleolinoleolinolenin bromide, respectively.

STEROLS AND OTHER UNSAPONIFIABLE CONSTITUENTS

THE unsaponifiable fraction from soybean oil, amounting to from 0.5 to 2.2 per cent, has been incompletely investigated and, except for the sterols, little is known concerning its composition. Klobb and Bloch [229] isolated a sterol, designated as soyasterol, from the unsaponifiable fraction of soybean oil which melted at 169° C. Matthes and Dahle [265] found the unsaponifiable matter of soybean oil (0.7 per cent) to contain about 55 per cent of crystalline materials and 45 per cent of unsaturated, oxygenated compounds. From the crystalline portion, they separated two sterols, sitosterol and stigmasterol, melting at 139 and 169° C., respectively. Bonstedt [63] effected the separation of stigmasterol and sitosterol from the crude sterols derived from soybean oil by means of the Windaus and Hauth bromination method. Stigmasterol constituted 25 per cent of the sterol fraction. The analysis of the hydrochloric acid addition product of sitosterol indicated the probable presence of dihydrositosterol, the separation of which was effected by fractional crystallization. The dihydrositosterol melted at 144° C. and had a rotation of $(\alpha)_D = +28°$. Repeated fractionation of the acetylated residue from the mother liquors gave an acetate, melting at 143° C. and having a rotation of $(\alpha)_D = -46.8°$, which, on saponification, yielded a sterol melting at 142° C. and having a rotation of $(\alpha)_D = 44.8°$. This sterol was not identical with Anderson's γ-sitosterol. Bonstedt concluded that sitosterol from soybean oil evidently consisted of an almost inseparable mixture of several sterols which formed mixed crystals when fractionated from solvents.

Following the determination by Fernholz [120] of the constitution of stigmasterol from soybean oil, this sterol became an important source material for the preparation of various natural and synthetic hormones. Butenandt and coworkers [72, 74] prepared the corpus luteum hormone, progesterone, and related substances from stigmasterol and at practically the same time and by exactly the same methods, Fernholz [121] reported the independent synthetic preparation of progesterone from this sterol. Shortly afterwards, Butenandt and coworkers [71] also prepared dehydroisoandrosterone, the second male sex hormone isolated from urine, using both stigmasterol and cholesterol as raw materials.

Because of the interest in stigmasterol as a source material for the preparation of various sex hormones, the recovery of this sterol from soybean oil has attracted considerable attention. Although present in small amounts in crude soybean oil, it may be obtained in fair yields by bromination and fractional crystallization, according to the method of Windaus and Hauth,[464, 465] of the mixed sterol acetates derived from the unsaponifiable fraction of this oil. Detailed directions for the preparation of stigmasterol, from 1000 kilo quantities of soybean oil, are given by Steiger and Reichstein.[404]

The commercial recovery of crude sterols from soybean oil dates from the earliest application of continuous solvent extraction of soybeans in Germany. One of the early processes, for the continuous extractions of soybeans, employed the method of countercurrent washing of the oil with cold alcohol to remove free fatty acids and produce a neutral oil.[40] During the recovery of the alcohol by distillation, the crude, mixed sterols concentrated in the residue and often crystallized in the still.

Holtz [188] mentions the fact that sterols are found in the phosphatidic sludge from solvent-extracted soybeans but points out that acidulated soapstock, obtained during alkali refining, is a much better source of these substances. Holtz found that practically all of the sterols, present in solvent-extracted soybean oil, accumulates in the soapstock during alkali refining, where it forms 2 to 3 per cent of the total. Ten kilograms of soapstock was found to yield 185 grams of mixed, crystalline sterols, melting at 138–139° C. Advantage has been taken of this fact to produce crude soybean sterols from so-called still pitch, which remains on distillation of the fatty acids, recovered by acidulation of refinery soapstock.

The recovery of crude sterols, from the alcoholic extract of soybean oil, the acetone extract of soybean lecithin, and the steam condensate from the deodorization of soybean oil, has been described in a patent by Schwieger.[388] Crude sterols can also be recovered from soybean oil by molecular or short-path distillation.[351, 431]

Wolff [467] has called attention to the loss of sterols and hydrocarbons on filtration and neutralization of soybean oil.

Kraybill, Thornton, and Eldridge[240] have described a method of obtaining crude, mixed sterols by adsorbing them on aluminum silicate[236-239] during passage of the oil through a packed tower, or by mechanical agitation of the oil and adsorbent, followed by extraction of the adsorbent with acetone to recover the adsorbed sterols.

Besides the sterols mentioned above, the only other substances, isolated from the unsaponifiable fraction of soybean oil, have been a ketone and an unsaturated hydrocarbon. Schmalfuss and Treu[383] isolated methyl-*n*-nonyl ketone by steam distilling saponified soybean oil and extracting the condensed distillate with ether. The ketone was identified by preparation of the corresponding semicarbazone.

Nakamiya[302] isolated an unsaturated hydrocarbon, $C_{18}H_{32}$, from the unsaponifiable fraction of soybean oil. The same hydrocarbon was previously isolated from fish liver oil and named gadusene. On hydrogenation, the hydrocarbon gave gadusañe, $C_{18}H_{38}$, b.p. 85 to 86° C., $N_D^{20} = 1.4632$.

OIL-SOLUBLE PIGMENTS

THE pigments, present in soybean oil, have been incompletely characterized, and very little is directly known relative to the nature or the amount of these substances which are present in various types of soybean oils. On the basis of the spectral transmittance curves of many samples of crude and refined cottonseed oils, as well as a smaller number of soybean oils, McNicholas[259, 260] concluded that these oils contained various amounts of green (chlorophyll), reddish yellow (carotenoid), and brown pigments. The work of McNicholas has been substantiated and extended by Bickford, Anderson, and Markley [34] who examined a variety of crude, semirefined, and completely refined soybean oils with respect to their absorption spectra as has been previously mentioned under the subject of the color of soybean oils.

Considerable effort has been directed toward the measurement of the color of soybean oil in terms of various color scales; [144, 350, 430] studies relative to the effect of chemical and physical reagents on color values have been carried out; [448] and technological processes for the reduction or removal of color have been devised.[107, 313, 314] However, very little effort appears to have been made to isolate and identify the various pigments which are present in the oil and which are responsible for its color.

As a result of considerable interest in the vitamin A content of soybeans, a few quantitative determinations have been made of the carotenoid content of the seeds. For example, Lantzing and Van Veen [244] identified the carotenoid pigments of soybeans, grown in the Netherlands Indies, as β-carotene and xanthophyll. The total carotenoid content of the varieties, which they examined, were found to vary from 70 to 180 international units and the β-carotene portion from 70 to 130 international units per 100 grams of ground soybeans. Sherman and Salmon [395] found that soybeans, in the green stage, contained 212 to 705 γ per 100 grams of fresh material, whereas mature beans contained 18 to 243 γ per 100 grams. They also concluded that the principal carotenoid pigment, in the soybean extract, was β-carotene and that, if cryptoxanthin was present at all, it occurred in negligible amounts. In a later publication Sherman [393] reported that the carotenoid pigments, extracted from mature seed of five varieties of soybeans, consisted of 80 to 88.8 per cent β-carotene and 2.5 to 11.8 per cent α-carotene.

In a series of four publications on the unsaponifiable fraction of soybean oil, Nakamura and Tomita [304, 305, 306, 307] claim to have isolated from this oil a fucoxanthin-like pigment, taraxanthin, lutein, eloxanthin-like pigment and several other carotenoids.

The type and amount of pigments, present in crude soybean oils, vary markedly with the variety of beans and the method of producing the oil. A high moisture content and the use of certain solvents lead to an increase in the amount of chlorophyll extracted, whereas a low moisture content and the use of other solvents repress the removal of chlorophyll. The conditions of pressing, likewise, markedly affect the color of the oil, e.g., cold-pressed oils are generally lighter in color than hot-pressed oils. With increasingly high temperatures of the expeller barrel, the expressed oils become darker red and, in extreme cases, brown or nearly black.[13] Part of this increased color is probably caused by the removal of additional colored substances with increased pressure, but a greater part is undoubtedly due to the decomposition of the thermally unstable pigments, carbohydrates, and other materials present in the seed.

During the process of alkali refining and, subsequently, during bleaching with various activated carbons and earths, the color of soybean oil is markedly reduced. The processes of deodorization and hydrogenation likewise affect the color but to a lesser degree. According to McNicholas,[259] the green pigments are the most fugitive to the bleaching action of light and chemicals, and are nearly completely removed by treatment with fuller's earth or exposure to sunlight.

Commercial bleaching results in considerable reduction in the brown and red pigmentation, whereas the yellow pigments are the most resistant to complete removal. It is possible, however, to produce nearly colorless soybean oil by laboratory refining and bleaching with certain types of adsorbents. The effects of alkali refining, bleaching, deodorization, and winterization, on the reduction of the color of soybean oil, have been reported by Bickford, Anderson, and Markley.[34] Based on the examination of the spectral transmittance curves of 84 samples of soybean oils, representing various types of processing and different refining procedures, they concluded that: (1) Chlorophyll, which is present in various concentrations in crude soybean oil, is completely absent from the finished oil so far as spectrophotometric evidence is concerned, and (2) the concentration of carotenoid pigments is greatly reduced during refining operations, with the greatest loss occurring during deodorization.

ANTIOXIDANTS

IT HAS long been recognized that soybeans and crude soybean oil contain antioxygenic bodies which are effective inhibitors of oxidative rancidity. The identity and chemical configuration of the substances, which are responsible for this protective action, are at present unknown; however, various products, including the meal and flour, pigments, sterols, phosphatides, and even refined hydrogenated soybean oil itself, have been claimed to be the actual inhibitor or, at least, to act as inhibitors to rancidity.

Green and Hilditch[185] found that, if solvent-extracted soybean meal was first digested with dilute solutions of organic acids, e.g., 2 per cent acetic acid in water or acetone, and then heated with methyl alcohol, it yielded about 10 per cent of soluble material. It was found that part of this methyl alcohol-soluble material was soluble in cold acetone to the extent of about 2 per cent on the basis of the original meal, and that it consisted of a viscous gum having marked antioxygenic properties. When 0.2 per cent of this product was added to the distilled esters of olive oil, their stability at 97.5° C. was increased 4 to 8 times. In a subsequent publication by Hilditch and Paul,[182] evidence was advanced to indicate that the antioxygenic substance was a basic oxygenic compound rather than a basic nitrogeneous compound, but its exact nature could not be determined.

Musher [288, 289, 290] claims that soybean flour or meal, either untreated, or after bleaching, or after solvent extraction, when added to lard or other fatty products, imparts to them protection against rancidification. Musher [291, 292, 293] further claims that the addition of 0.1 to 0.5 per cent of a concentrated water extract or an alcoholic extract of soybean flour which has previously been extracted by fat solvents, when added to lard and other food products, will prevent or retard rancidification.

Dahle and Nelson [92] attempted to determine the active fraction of oat and soybean flours with only partial success. The phospholipid fraction and the alcoholic extract exhibited greater antioxygenic properties when added to dry fresh milk fat than did the aqueous acetone, ether, or hexane extracts. In every case, the oat flour extracts appeared to have greater protective powers in dry, fresh milk fat than did the corresponding extracts of soybean flour.

Grettie[137] claims in a patent that the use of one to ten per cent of crude soybean oil as such or after hydrogenation, when added to lard or other shortening, will stabilize it with regard to rancidification. In further patents,[138, 195, 280] the use of hydrogenated, refined soybean oil is claimed to inhibit rancidity in shortening, lard, oleo oil, and products containing these substances.

Carotenes, which are known to be present in soybean oil, have been claimed by some investigators to be antioxidants, whereas other, equally competent investigators have found them to be proöxidants. Franke[124] observed that carotene and related compounds catalyzed the autoxidation of linoleic acid to about the same extent as did ergosterol. All of the carotenoids, including vitamin A, carotene, lycopene, xanthophyll, and zeaxanthin, were found by Franke[125] to function as positive catalysts toward free fatty acids, e.g., oleic and linoleic, but were without effect on their glycerides, e.g., olive oil, linseed oil, and cod-liver oil. Monaghan and Schmitt[285] found that carotene greatly inhibited the oxidation of linoleic acid, but oxidized carotene slightly accelerated this process. Newton,[317] on the other hand, found that carotenes, in the form of concentrates, or some substance associated with them in nature, acted as antioxidants for certain fats. High-temperature treatment of the fat, to bleach it, increased the antioxidant effect. According to French, Olcott, and Mattill,[126] purified carotene, from any source, slightly reduced the induction period of fats and increased the rate of subsequent oxidation.

Nakamura and Tomita[310] observed very small stability indices, 0.95 to 1.41, with six different carotenoid pigment fractions which were added to refined soybean oil in concentrations of 0.05 per cent. One fraction was considered as a proöxidant, and one (lutein) as a strong antioxidant. The other four fractions were considered as weak antioxidants.

The conflicting observations, concerning the effect of carotenoid pigments on the stability of vegetable oils, can be explained on several grounds, namely, the purity of the preparations used and the presence or absence of light during the experimental work. Bradway and Mattill[65] found that purified carotene actually functioned as a proöxidant to shorten the induction period of autoxidizable fats, whereas crude carotene or carotene concentrates, by virtue of associated inhibitols, acted as antioxidants.

Franke[124] found that chlorophyll and chlorophyllides had little or no effect on the autoxidation of linoleic acid, presumably in the absence of light. Meyer[274, 275] investigated the effect of the presence of chlorophyll and other pigments on the photosensitized oxidation of a considerable number of unsaturated compounds, including oleic acid, undecenic acid, and ergosterol. In the photochemical oxidation of oleic acid, some terpenes and ergosterol, it was found that chlorophyll was an active catalyst and was even more effective than eosin. With chlorophyll as the catalyst, oleic acid and ergosterol took up 0.5 mol of oxygen to form hydroxyoleic acid, in the case of oleic acid, without the formation of any detectable peroxides.

From the work of Franke, Meyer, and of Bickford, Anderson, and Markley[85] and others, it may be concluded that any natural pigment, such as the carotenoids, chlorophyll, or its colored derivatives, or any fluorescent dye, contained in or added to a highly refined autoxidizable oil, will act as a proöxidant in the light, but will be inactive, or act as an antioxidant in the dark. These conclusions follow from the fact that the pigments mentioned above are capable of absorbing appreciable amounts of photochemical energy in the form of light, which energy may be transferred to and result in activation of other molecules present in the oil, thus enabling them to take part in oxidation reactions. On the other hand, in the absence of light, many of these pigments, being themselves readily susceptible to oxidation, absorb oxygen and thereby protect other readily oxidized constituents of the oil.

In a similar manner, the naturally occurring sterols of soybean oil have been considered to be antioxidants by some investigators, and to be wholly inactive by others. The only sterols, known to be present in soybean oil, are stigmasterol, sitosterols, and dihydrositosterol. Evans,[116] using the peroxide index of cottonseed oil catalyzed by cobaltic oleate at room temperature, found that cholesterol and stigmasterol had no antioxygenic activity but that sitosterol afforded considerable antioxidant protection.

Franke found cholesterol to have little or no effect on the autoxidation of linoleic acid whereas ergosterol was found to be active under the same conditions. Royce[375] demonstrated by several different methods that the mixed sterols, from corn oil and cottonseed oil, had no antioxidant activity in finished cottonseed oil.

Mattill and Crawford[267] attributed the observed antioxygenic effect of certain types of corn oil to the presence of sterols but later Mattill[266] concluded that purified cholesterol and sitosterol were ineffective as antioxygens and that the protection against oxidation, observed with these substances, was due to some antioxygenic constituent accompanying the sterols.

Roller [374] found that the antioxidant activity of wheat germ oil for fats and oils was independent of the sitosterol content of the germ oil.

Nakamura and Tomita [308, 309] found that although the unsaponifiable fraction, prepared by several different methods, possessed antioxidant activity when added to refined soybean oil, this was not observed to be the case with the sterols isolated from the same fractions. The crystalline sterol fraction melting at 139.5° C. and having a rotation $\alpha_D^{20} = -34°$ in chloroform solution was added to refined soybean oil in chloroform solution was added to refined soybean·oil in concentrations varying from 0.1 to 1.0 per cent. Comparison of the treated and untreated soybean oil showed no difference in stability.

Experiments at the Regional Soybean Industrial Products Laboratory, with the purified, mixed sterols from soybean oil and the corresponding pure sitosterols and stigmasterol, indicated that they afforded refined soybean oil no antioxidant protection under the conditions maintained in the Swift accelerated stability test.

The sterols, which are present in soybean oil, are quite stable products and relatively unreactive even in the isolated state, and it is not to be expected that they should be any more reactive in an oil system. It may be concluded, therefore, that the sterols, present in soybean oil, do not function as antioxidants under the conditions prevailing in the crude or refined oil.

Olcott and Emerson [383] have shown that the tocopherols are effective for lard. Thaler and Schulte [425] investigated the effect of pure *dl*-α-tocopherol and acetate on the aldehyde and ketone rancidity, when added to ethyl oleate and peach kernel oil in concentrations of 0.1 and 0.5 per cent. Antioxidant activity was observed with the tocopherol as well as with the acetate. Isler [196] found that α-tocopherol was autoxidized in a Warburg-apparatus at 38° C. and, therefore, it may be presumed to have antioxygenic activity. However, tocopherols have never been isolated from soybean oil and in view of the low vitamin E activity of this oil, it is unlikely that it contains any appreciable amount of tocopherols.

Bollman [41, 42] was perhaps the first to claim that phosphatides, in general, and commercial soybean lecithin, in particular, when added in amounts of 0.05 to 1.0 per cent to refined edible oils, prevented or retarded oxidative rancidity in these products. From time to time, other patents have appeared which claim that the addition of soybean phosphatides in various amounts, to such products as shortening, lard, bakery goods, gasoline, mineral lubricants, etc., will afford protection against oxidation changes. Many similar claims have been made in general articles relating to the use of phosphatides.[110, 461, 474]

According to many patents, the antioxidant activity of soybean phosphatides, containing added ingredients, is greater than that of the phosphatides alone. Mitchell [279] claims that the addition of one to ten per cent of hydrogenated, refined soybean oil and 0.05 to 0.2 per cent of lecithin to an oil affords marked antioxidant protection compared with the addition of either substance singly. Musher [294, 295, 296, 297, 298] claims that a mixture of carbohydrates and phosphatides affords superior antioxidant protection to lard and other fats.

Thurman[427, 428, 429] claims that corn oil and cottonseed oil phosphatides are superior to soybean oil phosphatides as inhibitors because the former contain acids of a lower degree of unsaturation than the latter. This claim is predicated on the fact that soybean phosphatides contain as part of the molecule, linolenic acid, which is readily susceptible to oxidation with the formation of off-flavors and -odors. A similar claim is made by Engelmann[112] who patented the stabilization of aqueous emulsions of soybean phosphatides by the addition of peroxides.

In another patent,[195] it is claimed that shortening can be stabilized against rancidity by simply mixing it with one to ten per cent hydrogenated, refined soybean oil. It is claimed in this patent that deodorization, at a temperature sufficiently high to destroy the lecithin, does not affect the antioxidant value.

Royce[376] claims that synthetic phosphatides, in which one hydroxyl group of the glycerol molecule is unesterified, are superior antioxidants to the natural product. The antioxygenic activity is attributed to the free hydroxyl group of the synthetic product. Shappirio[391] assumes that the antioxygenic portion of the molecule is betaine or some related trimethylamine derivative, and hence, he claims their use or the use of the corresponding synthetic alkylamino-alkylphosphoric acid esters as antioxidants. Eckey[108, 109] and Richardson[369, 370] have patented the use of phosphoric acid and related substances as antioxidants for the stabilization of fats and oils.

From the above cursory summary of the patent literature, it would appear that the phosphatides themselves as well as all of the component parts of the phosphatide molecule have been claimed to be responsible for the antioxidant activity of these substances.

On the experimental side Kockenderfer and Smith[281] reported that two commercial samples of soybean lecithin, which they examined, were found to be weak antioxidants, having indexes of 1.7 and 1.8, respectively, when added to fats in concentrations of 0.1 to 0.2 per cent. The antioxygenic index was defined as the induction period of the fat with added antioxidant divided by the induction period of the fat alone. Based on oven tests at 70° C., Royce[375] obtained somewhat similar results. The addition of 0.2 per cent of vegetable lecithin, to finished cottonseed oil, gave an antioxidant index of 2.0, whereas addition of 0.1 per cent of the same product, to hydrogenated shortening, gave an index of 1.5.

Roller,[374] and Triebold, Webb, and Rudy[433] reported that lecithin did not lengthen the induction period for oils. The latter authors found that choline, derived from lecithin, also failed to lengthen the induction period.

Evans,[116] using the peroxide index of a cobalt oleate-catalyzed cottonseed oil at room temperature, found vegetable lecithin to have relatively high antioxidant value. However, under the same experimental conditions, sitosterol, which is known beyond doubt to be inactive in this respect, was also found to have appreciable antioxidant value. Furthermore, the procedure by Evans, namely, the addition of the very active oxidation catalyst, cobalt oleate, to the test samples and admission of pure oxygen to the oil, once or twice each day, provides no information concerning the probable behavior of an oil under normal conditions of storage or use. Evans concluded that the antioxidant activity of vegetable lecithin probably resided in the free amino or hydroxyl group of lecithin or cephalin. However, he also concluded that the antioxidant property of vegetable lecithin is easily destroyed by heating to 65° C., which latter conclusion is not compatible with the former, since a temperature of 65° C. cannot have an appreciable effect on amino or hydroxyl groups. Also this temperature is below that prevailing in the various processing steps followed in the production of vegetable lecithin. An antioxidant, having protective action only at temperatures below 65° C., would be limited in its application in the field of fats and oils.

Holmes, Corbet, and Hartzler [186] found that hydroquinone and commercial soybean lecithin afforded protection against the destruction of vitamin A in halibut and cod-liver oils. Hydroquinone was found to be more active than the commercial lecithin, even in much smaller concentrations, but the combination of the two was found to be more active than either one separately. The results, obtained with vitamin A, do not appear to be comparable with those ordinarily observed with autoxidizable oils, since no induction period is apparent either with or without added antioxidants. In the case of the lecithin experiments, the destruction of vitamin A was found to be a straight-line function of time and, therefore, does not correspond to an autocatalyzed reaction such as occurs in the rancidification of oils. The two reactions, the destruction of vitamin A and autoxidative rancidification, appear, therefore, to be unrelated phenomena.

Olcott and Mattill [334, 335] found that commercial preparations of soybean lecithin had moderate antioxygenic action on refined cottonseed oil (antioxidant index 2 to 4 for 0.1 per cent lecithin), little effect on lard (antioxidant index 1.3

to 1.6 for 0.2 per cent lecithin), and none at all on mixtures of lard and cod-liver oil. Purified lecithin was found to have no antioxygenic action, whereas purified cephalin possessed some activity. No quantitative relation was found between the amount of purified cephalin used and the prolongation of the induction period. They concluded that the monobasic phosphoric acid radical of cephalin was probably responsible for the observed antioxygenic action.

Hilditch and Paul[182] found that carefully purified soybean phosphatides, containing phosphorus and nitrogen in almost exactly the proportions demanded by a diacid-glycerophosphoric ester of choline, were completely lacking in antioxygenic activity when added to the distilled esters of olive-oil fatty acids.

Nakamura and Tomita,[303] using highly purified lecithin and cephalin from solvent-extracted soybean oil, found them to be either inactive or weak antioxidants for refined soybean oil when used in concentrations varying from 0.20 to 1.06 per cent. The antioxidant index was found to vary from 1.05 to 1.17, and no relation was observed between the concentration and degree of activity of these substances in soybean oil.

Diemair, Strohecker, and Reuland[102] determined the antioxidant activity of lecithin and its components, including glycerol, oleic, and linoleic acids, glycerophosphoric acid, choline, and colamine. Commercial soybean lecithin, purified by a single precipitation from petroleum ether by addition of acetone, was added to olive oil in concentrations of 0.5, 1.2, and 4 per cent. In the case of the Kreis-Täufel reaction, no difference was observed between the treated and untreated samples, but other tests indicated that concentrations of 0.5 to 2.0 per cent were moderately effective, and concentrations of 2.0 to 4.0 per cent quite effective. The authors consider the latter concentrations impractical, and most patent claims specify 1.0 per cent as the maximum addition required for effective protection against rancidification.

Choline, in concentrations of 0.7, 1.25, and 5.0 per cent, was found to be an effective inhibitor, but it was stated the concentrations used were considerably greater than that corresponding to its occurrence in lecithin, and its use was followed, in a short time, by the development of a fishy odor resulting from the production of trimethylamine. The authors state that colamine, a component of cephalin, appears to be useless as an antioxidant. None of the other components of lecithin exhibited antioxidant activity.

Franke[124] found that lecithin and acetylcholine actually acted as catalysts in the autoxidation of linoleic acid.

From a theoretical point of view, it is not to be expected that pure lecithin should exhibit antioxygenic activity. Mattill and coworkers[146, 266, 332, 336] found that the antioxygenic substances, both natural and synthetic, comprised three general classes or types of substances: (1) acid-type inhibitors, (2) inhibitols and hydroquinone, and (3) phenols. These substances are characterized by the presence of polyhydroxy groups, polycarboxylic groups, hydroxy-carboxylic groups, or hydroxy groups in close proximity to ethenoid linkages.

If lecithin is assumed to contain a betaine linkage, none of these conditions exist in the lecithin molecule, whereas if a straight-chain configuration is assumed for the phosphoric acid ester portion of the molecule, it would contain two free hydroxyl groups. On the basis of the best available experimental evidence, it would appear that lecithin possesses a betaine or endo-salt structure.[140, 141]

Delezenne and Fourneau[99] claim to have proved that lysolecithin has an anhydride formula and Grün and Limpächer,[140, 141] likewise, claim to have established this structure for synthetic lecithin. Grün states that, without doubt, the phosphatides, isolated from natural products, are anhydride endo-salts, at least when completely dried. As further evidence, he states that the pure phosphatides react neutral and that the strong basic hydroxyl group of choline and the acidic hydroxyl radical of phosphoric acid cannot coexist in the same molecule.

If the natural pigments, sterols, and phosphatides are eliminated as possible sources of the antioxygenic activity which has been observed to reside in soybeans and crude soybean oil, what other substance or substances may be considered as the cause of this activity?

Olcott and Mattill[385] found that the unsaponifiable fraction of many vegetable oils contains compounds which are active antioxidants for lard and designated these unknown substances as inhibitols. They found that these inhibitols could be concentrated by processes of solvent extraction, saponification and extraction, fractionation to remove the carotenoid pigments and sterols, and finally recovering the inhibitol by fractional distillation within a temperature range of 90 to 220° C. at 0.002 to 0.2 mm pressure.[268] These inhibitols were found to be transparent oils which resisted crystallization. They contained at least one phenolic hydroxyl group and one double bond. Reagents, which attacked the hydroxyl group or saturated the double bond, were found to inactivate the inhibitol. The activity could, however, be regenerated by reestablishing the hydroxyl group and the double bond. The double bond was found to be resistant to hydrogenation but readily added chlorine and bromine. These inhibitols exhibited a strong absorption at 2940 Å which was roughly proportional to their antioxidant activity.

Similar inhibitol fractions were observed at the Regional Soybean Industrial Products Laboratory to collect in the first fractions from crude and, to a less extent, from refined soybean oils when these oils were submitted to short-path or molecular distillation.[33] The temperature of distillation was considerably below that at which the glycerides distilled, which, in turn, was below the temperature at which the phosphatides distilled. In fact, analyses of the distillates and undistilled residues for phosphorus indicated that the phosphatides gradually accumulated in the undistilled portions of the oil. The first distillates were found to contain sterols, carotenoid pigments, and a light colored oil similar to that described by Mattill and Olcott. The sterols and the light colored oil were separated by solvent fractionation and the original distillate, sterols, and oily residue were separately examined for antioxidant activity. The sterol fraction was found to be inactive, whereas, the original distillate and residual oil possessed marked antioxidant properties when added to refined, edible-grade soybean oil. Attempts to crystallize the oil or prepare crystalline derivatives were unsuccessful. A colorless amorphous solid was obtained by reacting the crude product with cyanic acid gas. The product was not identical with the allophanates of the natural tocopherols.

Green and Hilditch [185] reported previously unpublished work carried out by H. K. Dean, describing the preparation of an orange-colored syrup from the unsaponifiable fraction of linseed oil which possessed strong antioxygenic activity.

The syrupy oil was found to reduce Tollens' reagent and alkaline permanganate and readily absorbed bromine. It had an iodine number of 145 and possessed absorption bands at 2560, 4200, 4450, and 4750 Å, the latter three bands being attributed to the presence of carotenoids. Green and Hilditch obtained a viscous, gummy product by extraction of soybean cake, which, although it apparently contained other substances, resembled the oily, antioxygenic product described by Mattill and Olcott. They, like previous workers, were unable to isolate and identify the pure antioxidant present in the viscous oil.

Despite efforts to completely characterize the oily fraction obtained by Mattill and Olcott, and other workers, it would appear that this substance either is or contains a constituent which is responsible for the antioxidant activity observed in soybeans and crude soybean oil. It is also quite probable that the antioxidant activity, observed by various investigators with products such as unsaponifiable matter, sterols, carotene, and commercial phosphatides, results from the presence of this oily constituent in the semi-pure products used in their experiments. It also explains the fact that these products, when rigorously purified, are found to be inactive or, in some cases, accelerators of rancidity and autoxidation of fats and oils.

PHOSPHATIDES

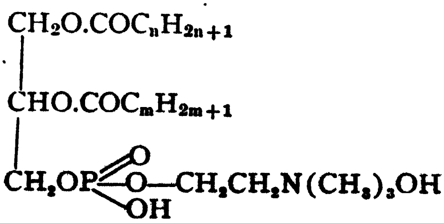
SOYBEAN oil contains a variable mixture of glycerophosphoric acid esters which are collectively designated as phosphatides, or, according to Chibnall and Channon,[80, 81, 82, 83] as phosphatidic acid esters. The apparent content of phosphatides of the oil varies with the method by which the oil is removed from the seed, but generally ranges from 1.5 to 2.5 per cent.

As has been previously mentioned, phosphorus is present in the soybean seed in the form of phytins, phosphatides, nucleic compounds (phosphoproteins), and inorganic salts, having different and varying solubilities in different solvents and under various conditions of extraction. The exact quantitative determination of the content of phosphatides in the seed is, therefore, extremely difficult as has been pointed out by Earle and Milner [105] and much confusion has been created by investigators who have been unaware of or ignored the difficulties of the problem.[111, 187, 205, 245, 352, 355] Only a small fraction of the phosphorus, present in the seed, is in the form of phosphatides, but practically all of the phosphorus of the oil appears to be present in this form.

Soybean oil contains both lecithins and cephalins, the former being present to the extent of about 30 to 35 per cent of the total phosphatides.

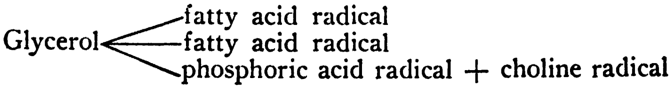
Lecithins are distinguishable from the cephalins by their ready solubility in alcohol, in contrast to the lesser solubility or complete lack of solubility of the latter in alcohol.

Since lecithins yield, on hydrolysis, two molecules of fatty acid, one molecule of phosphoric acid, and one molecule of choline, Strecker [217] proposed the general formula,

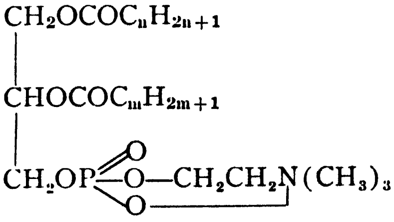


$$\begin{array}{l} CH_2O.COC_nH_{2n+1} \\ | \\ CHO.COC_mH_{2m+1} \\ | \\ CH_2O\overset{O}{\underset{OH}{P}}\text{—}O\text{—}CH_2CH_2N(CH_3)_3OH \end{array}$$

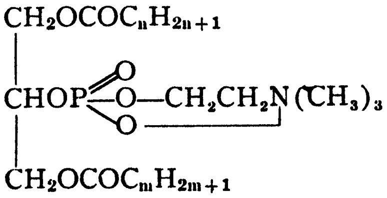
for these compounds, or more simply,



Unsaturated acid radicals may be substituted for one or both of the saturated fatty acid radicals and the phosphoric acid radical may occupy either the α- or the β-position in the glycerol molecule. If it is presumed that the choline radical is present in a betaine linkage, the naturally occurring lecithins are best represented by the formulas shown below.



α-Lecithins



β-Lecithins

If colamine (hydroxyethylamine, $CH_2NH_2CH_2OH$) is substituted for choline in the above formulas, a similar series of α- and β-cephalins is obtained. It is obvious that, by varying the fatty acid radicals of the lecithin and cephalin series, a very considerable number of isomeric and homologous phosphatides is possible. In fact, Suzuki and Yokoyama have calculated that seventy isomeric and homologous lecithins are theoretically possible with four different fatty acids.*

Prior to the work of Levene and Rolf[250, 251, 252] on soybean phosphatides, plant phosphatides were usually supposed to be varieties of lecithin, containing palmitic, stearic, and oleic acid components. These workers showed that the phosphatides, present in the soybean, consisted of a mixture of lecithins and cephalins, containing palmitic, stearic, oleic, linolenic, and linoleic acids. They prepared optically-active barium glycerophosphates from the lecithin and cephalin fractions and concluded, therefore, that the phosphoric acid was attached to an α-position in the glycerol molecule. Webster[449] recorded Hanus iodine values of the mixed fatty acids, present in the acetone-insoluble phosphatides, as 92.5, this indicating the presence of acids more unsaturated than oleic.

Suzuki and Nishimoto[414] separated a series of cephalins from soybeans which yielded, on hydrolysis, only β-glycerophosphoric acid and fatty acids. The fatty acids consisted of about 50 per cent stearic acid and a mixture of approximately equal parts of linoleic and linolenic acids. From the brominated cephalin, they obtained at least two forms of linoleostearo-β-cephalin and linolenostearo-β-cephalin.

Suzuki and Yokoyama[416] separated from soybeans α- and

---

* For a general treatment of the chemistry, physiology, technology, and uses of phosphatides, especially those derived from soybeans, the reader should consult the chapter on phosphatides prepared by Ad. Grün which appears in the first volume of Hefter-Schönfeld's *Chemie und Technologie der Fette und Fettprodukte*[385] and also the chapter by E. H. Winterstein and A. Winterstein on phosphatides in Klein's *Handbuch der Pflanzenanalyse.*[227]

β-lecithins, on the basis of their differences in solubility in warm acetone, the β-forms being much more soluble. By hydrolysis of the cadmium chloride salt of lecithin, they obtained the barium glycerophosphate equivalent to 35 per cent of the β-acid. Hydrolysis of the α- and β-forms gave 24.3 and 20.1 per cent of palmitic acid, 32.4 and 53.8 per cent of dibromostearic acid, 42.2 and 24.8 per cent of tetrabromostearic acid, and 1.1 and 1.4 per cent of hexabromostearic acid, respectively. Similarly Yokoyama and Suzuki [475] isolated from soybeans a series of α-lecithins as the double salts of cadmium chloride which, on bromination and fractionation by means of ethyl ether and chloroform, gave four bromides. Three of the bromides, palmitolinoleo-α-lecithin, oleolinoleo-α-lecithin, and dioleo-α-lecithin, were oils and the fourth, dilinoleo-α-lecithin, a solid, melting at 113 to 114° C. The structures were established by hydrolysis and identification of the fatty acids.

Hilditch and Pedelty [183] examined the component acids, present in the alcohol-insoluble and alcohol-soluble fractions of phosphatides, derived from soybeans. The fatty acid distribution of the phosphatide fractions is shown in Table 16. From these results, it is evident that the phosphatides contain all the characteristic fatty acids which are present in the glycerides. The proportion of saturated acids is higher in the phosphatides than in the glycerides. It is also evident that linoleic acid is the chief acid of both the phosphatides and glycerides derived from soybeans.

Belozerskii and Kornov [81] found that the embryos of soybeans contained 3.15 per cent of phosphatides and the cotyledons, 2.1 per cent. Both cephalins and lecithins were isolated, the latter of which yielded, on hydrolysis, oleic, linoleic, and linolenic acids. Linoleic and linolenic acids were found to be present in greater amounts in the cotyledon-lecithin than in the embryo-lecithin.

Recently, McKinney, Jamieson, and Holton [258] have again raised the question of the probable occurrence of phosphatides in the form of glycosidal complexes. Rewald [356, 365, 368] has shown, however, that although phosphatides are closely associated with carbohydrates, the union is not a chemical one, since extraction with the proper solvent and other physical treatments are sufficient to separate the phosphatides, in relatively pure form, from carbohydrates or fats. Soybean phosphatides can be freed of carbohydrates according to Rewald [367] simply by suspending them in water and shaking the suspension with trichlorethylene. The phosphatides go into the trichlorethylene phase, whereas the carbohydrates remain in the water phase. In this connection, it might be

TABLE 16

COMPONENT ACIDS IN PHOSPHATIDES DERIVED FROM SOYBEANS

	Alcohol-insoluble		Alcohol-soluble	
Acid	Weight-per cent	Mole-per cent	Weight-per cent	Mole-per cent
Palmitic	11.7	13.1	17.3	18.6
Stearic	4.0	4.0	...	...
Arachidic	1.4	1.3	...	...
Hexadecenoic	8.6	9.6	5.5	6.0
Oleic	5.5	5.7	19.0	18.5
Linoleic	63.3 *	61.5	53.0	52.0
Linolenic	...	...	3.7	3.6
C_{20} unsaturated	5.5	4.8	1.5	1.3

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* Includes small amount of linolenic acid, not exceeding 4 per cent.

mentioned that Klenk and Sakai[228] isolated from the cephalin fraction of purified soybean phosphatides, after hydrolysis with hydrochloric acid, inositol, glycerophosphoric acid, and the brucine salt of inositolmonophosphoric acid, melting at 236° C. Other phosphoric acid esters were also found to be present.

It is to be expected, from a consideration of the nature of the carbohydrate materials present in soybeans, and of the properties and method of removal of the phosphatides, that the two should form difficultly separable mixtures. The carbohydrates are present in soybeans both as free sugars and as glycosides, e.g., saponins, phytosterolines and isoflavone glycosides. The relative solubility and emulsifying properties of the various carbohydrate materials, lecithins, and cephalins in water, alcohol, acetone, and other organic solvents are such that the preparation of carbohydrate-free phosphatides is extremely difficult. Much the same solubility relations hold for the non-phosphatidic nitrogenous constituents which are associated with the phosphatides. In fact, Hofer[185] has prepared synthetic lecithin-protein complexes, e.g., a serum-albumin-lecithin complex, which could not be broken up by ether extraction but which was readily soluble and could not be filtered. If ether and alcohol were added to a lecithin solution at pH 2.5, the lecithin was found to pass quantitatively into the ether and separate again at pH 7.0 when one per cent of potassium chloride was added to the solution.

Properties, preparation, and uses of phosphatides: The preparation and uses of phosphatides are inseparably associated with the physical and chemical properties of these substances and it is, therefore, advantageous to discuss these three subjects simultaneously. The production and purification of the commercial product is, however, deferred to the section on processing.

It is to be understood that by phosphatides is meant the mixture of lecithins and cephalins which are generally isolated from soybeans or soybean oil, in the laboratory. Commercial preparations of phosphatides, often referred to as vegetable lecithin, are stated to consist of a mixture of approximately 60 per cent phosphatides, 35 to 40 per cent soybean or other oil, and 4 to 6 per cent moisture. However, these preparations also contain various amounts of sterols, sterol esters, carbohydrates, glycosides, pigments, and many other minor lipid and non-lipid constituents.

The commercial product is usually a yellowish-brown, waxy solid, at room temperature, which is soluble in ether, petroleoum ether, benzene, and fatty oils, partially soluble in alcohol, and relatively insoluble in acetone and ethyl and methyl acetates.

The relatively oil-free mixture of soybean phosphatides, ordinarily obtained by laboratory preparation, or commercially, by special refining, is a yellow wax-like mass. When entirely freed of oil, it rapidly undergoes oxidation, on exposure to air, and turns black, whereupon, it loses its solubility in alcohol and ether and becomes somewhat soluble in water. Soybean phosphatides readily form addition compounds with the salts of heavy metals such as cadmium chloride, and advantage is often taken of this property as a means of fractionation and purification of the various lecithins and cephalins present in the mixture. They are readily saponified by strong alkalies and hydrolyzed by strong acids.

Soybean phosphatides are highly hygroscopic, swell in water, form colloidal solutions, and generally behave as colloids. One of their most important properties is their effectiveness in lowering the surface tension of aqueous solutions. Lecithin forms monomolecular films, and the interfacial tension, for the system benzene-water, containing lecithin, has been measured at various pressures by Alexander and Teorell.[4]

Soybean phosphatides are excellent emulsifying agents and it is to this property that they owe their greatest usefulness as will become evident later. They are also presumed to possess antioxidant properties for certain fatty materials which property, however, is somewhat secondary to the property of emulsification so far as their commercial use is concerned.

The scientific, technical, and patent literature is too voluminous to review here in its entirety, but the references, which follow, will provide a background for the general reader and serve as a basis for further inquiry for those interested in pursuing the subject in more detail.

Much of the earlier work of importance and interest on soybean phosphatides has been carried out by German and, to some extent, by Japanese investigators, especially with reference to the recovery and utilization of these substances. Workers in other countries, including a number in the United States, have likewise made contributions to this field.

Hentze,[175] Rewald,[360, 354] Kühl,[342] Working,[471, 472, 473] Horvath,[190, 191] Wiesehahn,[461] and Eichberg[110] have published brief informative résumés, dealing with the general aspects of the preparation, properties, and utilization of soybean phosphatides.

Much difficulty has been experienced, in the United States, in connection with the separation of phosphatides from certain crude oils. In Germany, where most of the soybean oil is produced by solvent extraction and then treated for the recovery of phosphatides, this difficulty is not encountered. In the United States, where the bulk of the crude oil is produced by pressing, the formation of sludge, especially during storage and transportation prior to refining, is often times a serious problem. Sludge formation may also occur in solvent-extracted oils if they are not subsequently treated to remove phosphatides. The phosphatides, which are soluble in the crude oil at the time of pressing, are gradually hydrated, on standing, and subsequently settle to the bottom of the tank car or storage vessel.

Jamieson and McKinney [208] reported the results of the examination of a number of American soybean oils, with respect to their content of phosphatides, and found that, generally, soybeans grown in North Carolina and Virginia contained less phosphatides than midwestern soybeans. The investigation of the relative content of phosphatides, in various American-grown soybeans, was undertaken in an effort to determine the reason for the observed separation of sludge from North Carolina oils, since sludge formation was presumed to be confined solely to eastern oils. Actually, the separation of phosphatidic sludges is a rather general phenomenon,[143] and is dependent on the rate and degree of their hydration. In regions or seasons of high humidity, the hydration of phosphatides results in increased sludge formation and at a more rapid rate than when the climate is relatively dry. Low temperatures accelerate the rate of separation of phosphatidic sludges and, once separation has occurred, it is extremely difficult or impossible to completely redissolve them in the crude oil, especially in storage tanks and tank cars. As has been shown by Kraybill,[235] Kraybill, Kleinsmith, and Thornton,[237] and Beck and Klein,[30] the presence of phosphatides in crude soybean oil is responsible for the separation of "break" material, when these oils are heated to approximately 315° C.

Applications: The proposed applications for phosphatides, especially those prepared from soybean oil, are numerous, indeed, and new uses are constantly being suggested as even a cursory survey of the scientific and patent literature of the subject will reveal. Most of the suggested uses may be classified in the following categories: (1) food modifier, (2) cosmetics and pharmaceuticals, (3) textiles, (4) leather goods, (5) plastic compositions, (6) soaps and detergents, (7) special emulsifiers, (8) petroleum products.

(1) *Food modifier:* Perhaps the largest outlet for soybean phosphatides, both in Europe and the United States, is in the field of food modifiers in the manufacture of oleomargarine, shortening, candies and confections, bakery, milk, and other products.[154, 322, 358, 360, 366] In Europe, the largest use of commercial preparations of phosphatides, derived from soybean oil, is in the manufacture of oleomargarine, especially when made principally with coconut and palm oils.[371] Phosphatide additions of 0.1 and 0.3 per cent to oleomargarine reduce spattering and sticking of milk solids to the pan, during frying. The dispersed water evaporates as the oleomargarine is heated, and the fat froths and browns like butter. The degree of reduction of spattering, during heating of phosphatide-treated oleomargarines, is used in Europe as a quantitative measure of the effectiveness of commercial phosphatide preparations. This method, for the comparative determination of the so-called "margarine effect" of phosphatide preparations, is described in detail by Ad. Grün.[385] Better

moisture and salt retention, in the package, is likewise claimed to result from the addition of phosphatides to oleomargarine. It is also claimed [88] that by the use of phosphatides, condensed and dried milk can be incorporated with fats, in the preparation of oleomargarine.

The preparation and use of lecithin, in vitamin compositions for use in the production of oleomargarine, has been described in various patents.[1, 2, 3]

Phosphatides are often added to shortenings, which, according to various patent claims, results in more homogeneous mixing of the compounded fats, improved air retention, better lubricating value, and better browning qualities.[113, 215, 428, 472, 473] Improvement of the characteristics of bakery goods, such as pastries,[276] cake fillings, icings, etc., especially with regard to texture and flavor retention, is also claimed to result from the use of phosphatides in these products.[214, 389]

Soybean phosphatides are used extensively in the chocolate industry, in the United States, as an aid in the preparation of various chocolate products, for the conservation of cocoa butter, and to improve the appearance of the finished product. The products, which are benefited by incorporation of phosphatides, include especially chocolate coatings for candies, ice cream bars, fillings, caramels and other hard candies. Due to the emulsifying action and lowering of the interfacial tension by the phosphatides, there occurs more complete mixing of sugar, fat (cocoa butter, butter, or shortening), water, and other ingredients.[22, 213, 471] According to Avent and Morgan, the addition of 1.0 per cent lecithin has the most marked effect on the reduction of the interfacial tension between cocoa butter and water.

It has been claimed that the addition of phosphatides to chocolates will result in the reduction of fat bloom or graying of the outer surface. According to Brown,[67] Harris and Shillaber,[164] and others, the development of bloom, which results from the diffusion of fat to the outside surface, can be prevented or retarded by the addition of 0.1 to 1.0 per cent of phosphatides to the chocolate. However, other investigators, notably Clayton, Back, Robert, and Morse,[85] conclude from experimental evidence that "Lecithin and lecithin substitutes, although exerting a profound influence on fluidity, exert only a slight (beneficial) effect in relation to fat bloom."

Erb and Collins [114] investigated the effect of the use of phosphatides in the application of chocolate coatings to ice cream bars. They reported that, in the absence of moisture, coatings, containing a large amount of fat, were unaffected by additions of phosphatides, but that the same coatings, containing a small amount of water, were markedly improved by the addition of approximately 0.4 per cent of these lipids.

A process for the production of cocoa powder, containing two per cent of anhydrous phosphatides, has been patented.[44] According to the claims of this patent, the beverage prepared from the cocoa-phosphatide powder, with milk or water, maintains the particles of cocoa in suspension and the cocoa butter in solution instead of separating, respectively, as a sediment on the bottom and oil droplets on the surface of the liquid.

According to another patent,[87] the addition of 1.5 to 2.0 per cent of commercial phosphatide-cocoa butter mixture or the fraction of soybean phosphatides, insoluble in 95 per cent alcohol, produces a superior type of chewing gum, especially with regard to increased smoothness and decreased tackiness and cohesiveness.

In addition to the products mentioned above, the incorporation of phosphatides is claimed to impart beneficial or desirable properties to a host of other food products. Among these products may be mentioned sandwich spreads, peanut butter, soups, sauces, ketchup, prepared milk products, cheese, ice cream, gelatin desserts, puddings of the corn starch and chocolate type, beverages, etc.[429] Dry carbohydrate-phosphatide preparations, containing various added sugars, such as lactose, maltose, and malt extracts, have been patented [159] as well as aqueous lecithin compositions, containing high percentages of carbohydrates such as glucose or sucrose.[243]

Many patents and technical articles mention, claim, or otherwise refer to the antioxidant protection which is afforded various food products by the addition of commercial soybean oil-phosphatide preparations. However, unequivocal evidence, obtained under rigidly controlled and readily reproducible conditions, of the antioxidant activity of such preparations, is still lacking. The subject of the antioxidants, which are present in soybean oil, is discussed in a separate section to which reference should be made for further details.

Wolff and Guellerin [468] have investigated the effect of refining operations on the reduction of phosphatides and unsaponifiable matter in edible oils and recommend the restoration to refined olive oil of phosphatides recovered from soybean oil. Grettie [186] has patented the addition of phosphatides to winterized cottonseed oil for the purpose of inhibiting crystallization.

(2) *Pharmaceuticals and cosmetics:* Ad. Grün [385] discusses numerous uses of oil-free phosphatides in therapeutic preparations, the various forms in which they are dispensed, and the methods of administration in the treatment of various human and animal diseases. Besides these uses, which are presumed to depend on the action in the animal organism of the phosphatides themselves or their metabolic products, other uses are made of phosphatides which depend on their emulsifying or surface-tension-lowering properties. Such uses include the preparation of ointments, salves, and vehicles for dispensing medicinals, tonics, vitamin preparations, liver oil emulsions, and similar products.[21, 210, 354] A specially dehydrated preparation of soybean phosphatides, suitable for dispensing in gelatin capsules, has been patented by Buer.[68]

The use of phosphatides is recommended in the preparation of facial, cleansing, and other types of creams and ointments and for emulsifying fats, waxes, hydrocarbons, and alcohols to form oil-in-water types of preparations, as well as in brushless shaving creams,[241] dentifrices, and similar products. Epstein and Harris [113] have patented a preparation of soybean phosphatides and diglycerides which, they claim, is particularly suitable for making solid lipstick, having the dye dispersed in a fatty medium of high melting point and, at the same time, providing increased wetting capacity, when applied to the tissue.

(3) *Textiles:* According to the claims made in the patent and technical literature, phosphatides are of value in the textile and textile specialty industries because of their solubilizing effect on fatty oils, their softening power and emulsifying properties.[45, 46, 52, 60, 62, 112, 149, 150, 163, 271, 361, 368]

Mecheels [269] and Tatu [422] discuss the various applications of phosphatides in the textile industry, including their use and effect in kier-boiling, as a spinning lubricant for cotton [100] and wool, addition to doubling solutions, in the mercerizing bath as a wetting-out agent, in the dye bath in rayon finishing as a leveling agent, and for increasing color in calico printing pastes.[157] Bollmann and Rewald [61] and others [153] have patented the use of phosphatides in dyeing cotton, wool, silk, rayon, and other textile materials and claim certain advantages such as increased brilliance, softer handle, and better penetration.

Ohl [326] discusses the use of phosphatides as a stabilizing agent in bleaching rayon and other synthetic yarns. In Europe, the use of phosphatides, as a wetting and softening agent and in the preparation of sizing and finishing pastes, has been patented.[52, 53, 192, 342] Bollmann and Rewald [51] and Rewald [364] have patented the use of phosphatides in printing textile fabrics and claim many advantages are to be derived therefrom.

The production and use of hydrated [442, 255] and sulfonated [49, 77, 78] phosphatides have been covered in a series of patents.

(4) *Leather:* In recent years, the use of phosphatides has been advocated or introduced as an assistant in producing oil- and chrome-tanned leathers.[32, 39, 76] They are recommended for use in fat-liquoring to facilitate the penetration of fats and oils into the hide, to reduce the amount of working required, and to make the finished leather more pliable.[353] The use of soybean phosphatides, in tanning preparations, softening oils, leather dressings, and greases, is described in a considerable number of patents which should be consulted for details of their application.[47, 54, 55, 56, 57, 58, 59, 161, 162, 341, 357]

(5) *Plastic compositions:* The use of soybean phosphatides has been recommended for the production of various plastic compositions, including vulcanized rubber,[115, 362] linoleum, and sound records.[123] According to claims in the literature, phosphatides are especially useful in the production of putty, casein paints, in the vulcanization of rubber, for reducing foaming in latex, and decreasing the rate of aging in linoleum.

Merz and Wagner,[272] and Stock[406] have discussed the application of phosphatides in the manufacture of oil paints and casein water paints. The use of phosphatides, as a binder in paints, has been patented by Bollmann and Rewald,[50] Fincke,[160] and others.

The New York Paint and Varnish Production Club[315, 316] has reported studies on the wetting and dispersion of pigments in oils, containing added phosphatides. The production of asphalt and tar emulsions, in which soybean phosphatides are employed as emulsifying agents, has been patented both in the United States[387] and abroad.[152, 158]

(6) *Soaps and detergents:* The effect of phosphatides, on the composition and physical properties of soaps, has been discussed by Lederer,[246] Genin,[128] and others. Inaba, Kitagawa, and Sato[194] observed that the addition of lecithin, to soap solutions, resulted in a lowering of the surface tension as measured by the drop number against kerosene. It was also found to affect the foam number, turbidity and transparency temperatures, and the gold numbers. Trusler[434] investigated the effect of the presence of phosphatides on the rate of catalytic splitting of fats and found the reaction to be inhibited by these substances. However, after treatment of the fat with dilute mineral acids, as for example with one to

three per cent hydrochloric acid, it was found catalytic hydrolysis could be effected.

The manufacture of soap, containing phosphatides, has been patented,[155] and soaps of this type are said to have better foaming properties, especially when they contain excessive amounts of sterols. The presence of phosphatides serves as an aid in superfatting and, in general, to impart improved texture to fine toilet soaps. Braun and Rosenbusch [66] have patented a liquid preparation, consisting of phosphatides, castor oil fatty acids, and polyethanolamines, for use in the production of soaps.

(7) *Special emulsifiers:* Since the primary action, exerted by phosphatides in aqueous and other solutions, is one of lowering surface tension and increasing emulsifying action, it is not surprising that numerous applications, in this field, have been investigated and patented. In addition to those already cited in connection with various food, cosmetic, and textile preparations, many others might be cited, particularly with reference to certain special applications.

The use of phosphatides, in the production of adhesives, has been described [148] and the addition of phosphatides to insecticide and fungicide preparations, containing mineral oil and water-soluble substances, e.g., copper salts, has been patented.[48, 359] Bousquet [64] has patented the use of crude soybean phosphatides in contact sprays containing nicotine, rotenone and pyrethrum. According to the claims of the patentees, the presence of phosphatides results in better dispersion of the phases and greater adhesion of the applied spray. However, Woodman,[469] on the basis of extensive studies of numerous polyphase systems containing lecithin, concluded, "An aqueous dispersion of lecithin has been demonstrated to form dual emulsions with certain non-aqueous liquids, the water-in-oil type only with oleic acid, and oil-in-water only with certain bases. Generally speaking, therefore, lecithin is an unsuitable emulsifier for the preparation of insecticidal and ovicidal spraying emulsions."

According to a patent of Bollmann and Rewald,[62] emulsions of phosphatides, with or without added oils, can be prepared solely with such solvents as benzyl alcohol, ethylene, propylene and amylene glycols, and many aromatic alcohols. Similar preparations have been patented by others.[151]

An alkali peroxide-stabilized emulsion, consisting of crude, undried phosphatide-soybean oil mixture, has been patented by Engelmann.[112] Dry, powdered preparations of phosphatides, with lime and with solid sodium hydroxide, have been patented, respectively, by Bollmann[43] and by Schwieger.[387]

(8) *Petroleum products:* It is claimed in patents by Sollmann[402] and others[156] that the addition of phosphatides to gasoline will prevent or, at least, retard the formation of gums. Hendrey[174] has patented the use of phosphatides in lubricating oils and claims that the addition of 0.1 to 1.0 per cent of phosphatides to such oils has been found to reduce their ring-sticking behavior when used in lubricating automotive engines. Musher[209] claims that the combination of commercial soybean lecithin and a polyhydroxy compound decreases sludge formation in lubricating oils.

White and Vaughan[460] found that the addition of 0.25 to 2.0 per cent of phosphatides to wood-preserving oils, such as creosote and mineral oil, increased the penetration and improved the distribution of the preservative in the wood.

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Part II

PROCESSING OF SOYBEANS AND SOYBEAN PRODUCTS

DEVELOPMENT OF THE SOYBEAN PROCESSING INDUSTRY

THE processing of soybeans, to produce oil and meal, is a very old industry in the Orient,[12] * where rather primitive equipment is still widely used. In the United States, the soybean processing industry is a comparatively new one, having been developed almost entirely within the past 20 or 25 years. Soybeans have been grown more or less experimentally in various sections of the country for over a hundred years, and it is, therefore, possible that some of the cottonseed oil mills, in the southern or southeastern part of the country, crushed small amounts of soybeans earlier than those operations which have been recorded.

The first soybean crushing in the United States, for which records are available,** however, appears to have been on Manchurian beans in about 1911. The soybeans were imported by the Albers Brothers Milling Company and sold to a Mr. Herman Meyer who operated a small hydraulic press oil mill in Seattle, Washington. The establishment was later known as the Pacific Oil Mills, but it is no longer in existance. The meal, produced in these operations, was sold as a feed ingredient under the name of "Proteina." It was found, however, that the oil and meal could be imported more cheaply than they could be domestically produced from im-

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*** Bibliography on page 249.**

**** L. W. Eilertsen, personal communication.**

ported raw materials, and the crushing operations were, therefore, discontinued when the initial shipment of beans had been processed.

The earliest recorded crushing of American-grown soybeans * took place at the cottonseed oil mill of the Elizabeth City Oil and Fertilizer Company in Elizabeth City, North Carolina. This mill was later operated by the Eastern Cotton Oil Company, but its operations were discontinued in the early 1930's. The first soybean crush was largely a test run, extending from December 13 to 20, 1915. During that time, 10,000 bushels of local soybeans were pressed in the six expellers with which the mill was equipped, and the resulting meal was reported to be of excellent quality, containing 5.0 to 5.5 per cent oil. The test was conducted by Mr. W. T. Culpeper, manager of the firm, as part of his activities toward encouraging local soybean production. The experiment was so successful that the company continued to process local soybeans, as supplies became available, and they reportedly offered production contracts with the growers in advance in order to induce farmers to grow more of this crop. In spite of their efforts to develop the production of soybeans sufficiently to assure regular operations, difficulties were encountered, from time to time, in obtaining enough beans to warrant crushing them. In 1916, for example, it is said that German interests bought and exported the entire available supply, at prices as high as $4.50 per bushel.

In late 1917 or early 1918, the Chicago Heights Oil Manufacturing Company ** experimentally processed a small

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* W. J. Morse, personal communication.

** E. J. Dies, *Gold from the Soil* (The Macmillan Co., New York, 1942).

amount of soybeans in expellers which were originally designed for crushing corn germs. During 1918, this company is said to have added two expellers specifically for crushing soybeans. These expellers had a combined capacity of 600 bushels per day and were used intermittently during the ensuing years as supplies of beans became available. In the fall of 1922, the same company is said to have experimented with hydraulic press equipment which had been used for producing linseed oil. The Chicago Heights Oil Manufacturing Company continued its pioneering efforts toward the establishment of a soybean industry in the present "soybean belt" until August of 1923 when it went out of business. The equipment was purchased by Funk Brothers Seed Company of Bloomington, Illinois, during the following year, and the latter company has since been continuously engaged in the soybean processing business.

On September 30, 1922, the A. E. Staley Manufacturing Company [183] of Decatur, Illinois, commenced operations in a mill which was equipped with expellers designed for crushing soybeans. This company has been in the soybean processing business continuously since that date. The Staley development was soon followed by others of a similar nature, and the early twenties saw the establishment of a permanent soybean processing industry.

Not all the earlier ventures proved successful. For example, the Piatt County Soybean Cooperative Company (sometimes referred to as the Monticello Grain Company) was organized in 1922 in Monticello, Illinois, and installed batch solvent extraction equipment for processing 300 bushels of soybeans per day.[6] The solvent used is said to have been benzol. This ill-fated undertaking was apparently unable to cope with the scarcity of beans and was in operation for only about six months during the period 1923 to 1924.

Another early attempt, at solvent extraction of soybeans, was undertaken during the years of 1924 and 1925 by the Eastern Cotton Oil Company at Norfolk, Virginia.* A Bollmann type of continuous extractor, having a capacity of approximately 80 tons per day, was used on soybeans obtained from North Carolina, but the supply proved to be inadequate. Difficulty was also encountered in adapting the German-manufactured equipment to the processing of American-grown soybeans. After exhausting the available stocks of soybeans, the mill's operations were transferred to the extraction of Argentine flaxseed, but this was said to have been found unprofitable.

At about the same time, soybeans were solvent-extracted by the Prossco Oil Company, also in Norfolk, using Scott rotary extractors. Their operations, however, consisted mainly in the extraction of cocoa butter and other fats, and only a small amount of soybeans is said to have been processed. Others, who engaged in soybean processing during the early twenties, include the Seeds Oil Company in Indianapolis and the Jonathan Havens Oil Company at Washington, North Carolina.

The foregoing instances are but a few of the many examples of the pioneer effort carried out by those who possessed the courage and foresight to enter what was then an unknown and untried field. These efforts, however, were the outgrowth of and were made possible by still earlier pioneering along agronomic and educational lines. It is a

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* A. K. Schwartz, personal communication.

well-recognized fact that the one development, which made possible the founding of a soybean industry in the present "soybean belt," was the introduction of varieties adapted to the soil and climate of the region. The present status of the soybean, as a major crop, is a tribute to the early research performed by the U. S. Department of Agriculture and the Agricultural Experiment Stations. No less credit is due to the small group of farmers who cooperated by taking up soybean cultivation, according to the practices recommended by the agronomists.[145]

The early processors were faced with the task of developing markets for their hitherto untried products. Initially, little was known concerning the value of soybean oil meal for feeding purposes. Stock feeders were persuaded to accept free batches of meal for feeding trials. Meal was sent to various state experiment stations and exhibited at state fairs, county fairs, etc. By the end of the twenties, these and other educational efforts had borne fruit, and soybean oil meal had established itself as a valuable protein supplement in the feed industry.

Similarly, the first domestically produced soybean oil found an unreceptive market. It was not known that soybean oil could be refined, bleached, and deodorized to produce a high-grade edible product, and its value in the drying oil industry was equally uncertain. Prospective buyers could cite dozens of reasons why soybean oil was not satisfactory, and it remained for the more farsighted oil processors and buyers to demonstrate to the prospective consumers that soybean oil could be used in both the edible and drying fields.

A large number of growers of soybeans and other individuals, interested in the industry, are organized in the

American Soybean Association. This organization has played a prominent part in the development of the American soybean industry and was founded in 1920 under the name of "The National Soybean Growers' Association."[1, 3, 4] The association adopted its present name in 1925.

In more recent years, there has been organized a group of soybean processors known as the "National Soybean Processors' Association." It was organized in 1930 and its original membership[7] was quite representative of those soybean processors who pioneered their industry.

At the present time, soybean oil and soybean oil meal are handled by processors, brokers, and others, in all parts of the country. Soybeans can be bought and sold for future delivery on the Chicago Board of Trade,* meal futures are handled by the Memphis Merchants Exchange, and trading in soybean oil futures is carried on by the New York Produce Exchange. For a more detailed description of the present economic position of the soybean processing industry, the reader is referred to references 51, 55, 60, 62, 76, 86, 109, 128, 184, and 197, in the bibliography (p. 249).

Soybeans are processed in large quantities in the Orient, Europe, and the United States, and it is, therefore, to be expected that processing practices would differ considerably from one country to another. Not only do processing practices vary from country to country, but in the United States, at least, considerable variations are encountered throughout the industry, no two plants being exactly the same. In Europe and the United States, the industry is highly mechanized.

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* Soybean futures trading was discontinued by the Chicago Board of Trade on February 20, 1943, because of wartime restrictions on oil-seed purchases.

This is also the case in the Orient, in the large oil centers at Dairen, Kobe, and Newchang. However, many primitive mills still continue to operate in districts away from the main centers of production. Although American methods of processing, prior to actual removal of the oil, vary from mill to mill, nevertheless, certain operations, such as storage and cleaning, are more or less common to the industry as a whole.

GRADING AND STORAGE

UNTIL comparatively recently, Government inspection and grading of soybeans was on a purely voluntary basis and was administered by the Inspection Service of the Grain and Seed Division of the Agricultural Marketing Service (formerly of the Bureau of Agricultural Economics), in accordance with the standards promulgated by the Bureau of Agricultural Economics.[196] The activities of the Inspection Service ordinarily cover such commodities as hay, straw, beans, peas, various seeds, etc. Effective November 20, 1940, an amendment to the United States Grain Standards Act provided for the inspection and grading of soybeans under the Administration of the Grain Standards Act as carried out by the Grain and Seed Division.[194] This amendment has had the effect of putting soybean inspection on the same basis as that of other grains such as wheat, corn, oats, barley, rye, and flaxseed, and it makes mandatory the use of the standards when grain is sold by grade in interstate or foreign commerce.

Present standards[195] designate five classes of soybeans: Class I, yellow; Class II, green; Class III, brown; Class IV, black; and Class V, mixed. In addition, soybeans are classified, according to their physical condition, into any one of five grades, as shown in Table 17.

In determining the grade, a single factor is sufficient to throw soybeans of one grade into a lower grade. For example, a lot, which grades No. 2 yellow in all respects, except that its moisture content is 16 per cent, would be graded as No. 3 yellow. It is often possible to mix two batches, one or both of which would alone receive a lower grade, in order to produce a blended lot that will meet the requirements of a higher grade.[17]

Soybeans are received at elevators by rail, truck, or boat. They are unloaded from cars and ships by means of automatic shovels, air hoses, or, in many large rail terminals, by automatic car unloaders. They must first be cleaned by running them through magnetic separators to remove tramp iron and through screening devices which remove stones, weed seeds, and other foreign material likely to cause heating in storage. If the moisture content is below 13 or 14 per cent, the beans can be run directly to the storage bins; otherwise, they must be dried to reduce the danger of heating.

Storing of soybeans resembles that of most of the other grains and presents no great technical difficulty.[2, 5, 8, 9, 10, 18, 140, 198] Although 13 per cent moisture is the generally accepted maximum, it is quite possible to store the beans at moisture contents as high as 16 per cent, or, sometimes, slightly higher, for short periods, if they are carefully watched and turned at the first evidence of heating. This is not the usual practice, and beans containing over 13 per cent will very likely heat during the "sweat" which occurs in the spring.[11] It is believed by many operators[199, 200] that if heating takes place in a small pocket of damp beans sur-

TABLE 17

GRADE REQUIREMENTS FOR YELLOW SOYBEANS, GREEN SOYBEANS, BROWN SOYBEANS, BLACK SOYBEANS, AND MIXED SOYBEANS

		Maximum limits of			
Grade No.	Minimum test weight per bushel Pounds	Moisture Per cent	Splits Per cent	Damaged kernels (soybeans and other grains) Per cent	Foreign material other than dockage Per cent
1*	56	13	10	2	1
2*	54	14	15	3	2
3	52	16	20	5	3
4**	49	18	30	8	5

Sample grade: Sample grade shall include soybeans of any of the classes Yellow Soybeans, Green Soybeans, Brown Soybeans, Black Soybeans, or Mixed Soybeans, which do not come within the requirements of any of the grades from No. 1 to No. 4, inclusive; or which contain stones and/or cinders; or which are musty, or sour, or heating, or hot; or which have any commercially objectionable, foreign odor; or which are otherwise of distinctly low quality.

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* The soybeans in Grade No. 1 of each of the classes Yellow Soybeans and Green Soybeans may contain not more than 2 per cent, and the soybeans in Grade No. 2 of each of these classes may contain not more than 3 per cent of black, brown, or bi-colored soybeans, singly or combined.

** Soybeans that are badly weathered or badly stained shall not be graded higher than No. 4.

rounded by dry beans, it will spread to the dry beans, but some elevator operators contend that this does not occur appreciably with soybeans.

For removing moisture from whole soybeans, the usual types of grain driers are satisfactory. The beans pass downward, over a series of baffles, counter-currently to an upward blast of hot air. In some driers, the air is heated indirectly, whereas others utilize the flue gases from a burner. Although practice varies considerably, the temperature of the air, entering a typical drying unit, is approximately 200 to 220° F., and the beans leave at a temperature of 180 to 200° F. Higher temperatures are likely to damage them for milling purposes. It is necessary to cool the dried beans immediately to 80 to 90° F. Accordingly, the lower part of a drying installation consists of a cooling section in which the beans continue their downward flow against a blast of cold air.

The usual storage facilities consist of a number of reinforced concrete silos and interstices which are served by horizontal belt conveyors overhead in the gallery and in the basement below the boots. Cleaning, elevating, and drying equipment is located in the head house at one end of the line of bins. The tanks often have thermocouples situated at various depths by means of which temperatures of the beans, at any point, may be determined from a central switchboard. Figure 5 shows a typical construction of this type having a total storage capacity of 2,500,000 bushels. Many mills have much smaller elevators and some have larger ones, but very few have sufficient capacity to hold a full year's supply of beans. Large amounts are also stored in smaller country elevators, usually nearer to the production areas. Considerable quantities of soybeans are occasionally stored in ship holds, particularly in Great Lakes steamers which must lie idle during the winter months.

Little has been published concerning the changes which occur in soybeans during storage and the effects which such changes have upon the subsequent processing operations. A number of theories, regarding these changes, are reviewed by Singer[178] and by Bredeman and Kummer.[47] The use of plant operating data to follow the variations in properties of stored seed is difficult because of the differences between the beans harvested in successive years. It is well known, however, that the yield of oil, from newly harvested beans, is less than would be obtained from the same beans after several months' storage, and that the operation of pressing equipment must be altered, at various times during the year, to conform to the ever-changing condition of the stored soybeans.

METHODS OF PROCESSING SOYBEANS

ONLY three methods are commonly used to process soybeans for oil and meal, namely continuous pressing (expellers and screw presses), hydraulic pressing, and solvent extraction. Table 18 contains data showing the relative importance of the three processes in the United States. The use of solvent extraction has gained in importance during recent years, and current construction work indicates that an even greater proportion of the 1941 and succeeding crops will be solvent-extracted. In the Orient, soybeans are crushed almost entirely by hydraulic presses or similar equipment, and in Europe, solvent extraction is used almost exclusively.

Those American mills, which use hydraulic presses, are or have been, for the most part, engaged primarily in crushing other oilseeds such as cottonseed and linseed. Such mills can be readily adapted to soybean crushing, but the unit crushing costs are said to be higher than those encountered in either the continuous press or the solvent mills. The higher costs

TABLE 18

SOYBEANS PROCESSED BY EXPELLER, SOLVENT, AND HYDRAULIC METHODS

Estimates based upon data compiled by Bureau of the Census in cooperation with U. S. Regional Soybean Industrial Products Laboratory, January, 1941

Crop Year (October to October)	Expeller		Solvent		Hydraulic		Total	
	Tons	Per cent	Tons	Per cent	Tons	Per cent	Tons	Per cent
1936–37	422,800	68.5	81,604	13.2	114,136	18.5	618,540	100.0
1937–38	637,532	70.1	155,591	17.1	116,167	12.8	909,290	100.0
1938–39	967,173	72.2	214,161	16.0	158,093	11.8	1,339,427	100.0
1939–40	1,274,016	74.4	346,055	20.2	92,081	5.4	1,712,152	100.0
1940–41	1,425,501	74.2	443,685	23.1	52,486	2.7	1,921,672	100.0

are due largely to the increased amount of hand labor required for a batch type of operation.

Solvent extraction of soybeans has been carried out in batch equipment of several types, using a variety of solvents, but all American soybean mills, which now use the solvent process, employ continuous systems. Although considerable effort has been expended toward developing solvent processes which can be safely and economically operated on a small scale, the solvent extraction systems, now used commercially, appear best suited for large-scale operation, i.e., 50 tons or more of soybeans per day. One of the advantages of the solvent system is the high recovery of oil. Whereas pressing methods yield residual meals containing 4.0 to 5.5 per cent oil, solvent-extracted meal contains 1.0 per cent or less oil.

Expellers and screw presses have capacities of approximately 20 tons of soybeans per 24 hours, and mills operate with any number of such presses installed side by side, de-

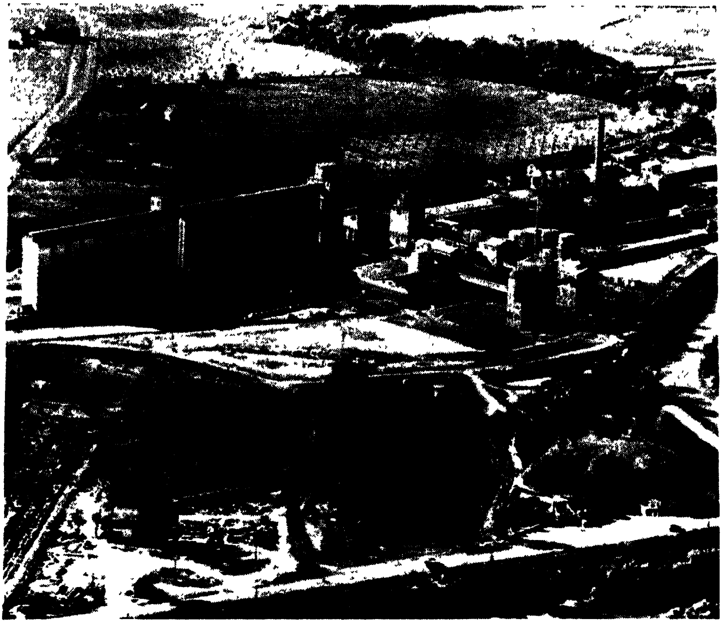

FIGURE 5
Elevators at a soybean processing mill
(Courtesy of Central Soya Company)

FIGURE 6
Cracking rolls used to prepare soybeans for pressing in expellers or screw presses (Courtesy of Allis-Chalmers Manufacturing Company)

FIGURE 7
Two steam-heated, rotary driers connected in series, for drying cracked soybeans (Courtesy of Allis-Chalmers Manufacturing Company)

pending upon the desired capacity. A few plants use only one press and, on the other hand, some of the large installations include several dozen units. Because of the lower operating costs, made possible by operating a large number of presses in a single mill, most operators of one-press plants have found it to their advantage to add one or more expellers or screw presses, if it is at all possible to obtain sufficient bean supplies to ensure their uninterrupted operation.

Because of the high overhead, associated with soybean processing operations, it is necessary to operate crushing equipment almost the year around, in order to achieve minimum conversion costs. An expeller mill, for example, in 300 days' operations, would require approximately 200,000 bushels of beans per press, i.e., the entire production of 10,000 acres of typical soybean acreage for each expeller. In general, the choice of the type, size, and location of a soybean processing mill revolves largely around the amount of soybeans available and the accessibility of the consuming markets for the products. The latter factor is determined in many, if not most, cases by freight rates and the applicability of milling-in-transit privileges.

PROCESSING BY MEANS OF CONTINUOUS PRESSES

AS SHOWN in Table 18, approximately 75 per cent of the annual soybean crush, in the United States, is now carried out by the use of expellers or screw presses. In this process; the beans are withdrawn from storage and conveyed to the mill where they are weighed, recleaned, and fed to corrugated rolls which crack them into small particles. The roller mills themselves are similar, in most respects, to those used elsewhere in the milling industry. They usually consist of two or three adjustable pairs of chilled steel rolls 9 or 10 inches in diameter and 14 to 42 inches long, depending on the capacity. Most of these rolls have saw-tooth corrugations running sharp-to-sharp with considerable differential in speed.[56]

The average size, to which beans are cracked, varies considerably from plant to plant, and although the particle size and the degree of size uniformity appear definitely to influence certain aspects of the performance of the presses, reasonably satisfactory operation can be secured over a very wide range of size. A sample, which yields a screen analysis averaging between 16 and 10 mesh, might be considered typical, although this should not, by any means, be regarded as standard. Figure 6 shows a set of cracking rolls commonly used for this operation.

In some mills, a large portion of the hulls is removed by screening, aspiration, centrifugal treatment, or other means, after the soybeans are cracked. This is usually the practice when the meal is destined for human consumption. In some cases, it has been found advantageous to remove the hulls of certain colored varieties of soybeans in order to obtain an acceptable color in the oil. The separated hulls can be ground and mixed with that portion of the meal which is sold for livestock feeding. Hull separation, however, is carried out on only a relatively small scale.

Satisfactory operation of continuous presses requires that the beans are both hot and dry, so the cracking rolls are immediately followed by rotary, steam-heated driers. A typical installation is shown in Figure 7. The more commonly used types employ rotating steam tubes and scrapers within a stationary shell, but a number of other types are also successfully used. They are often operated in banks of two or more units in series. Moisture is reduced to between 2 and 5 per cent, generally approximating the former figure, and temperatures of the discharged product are usually between 240 and 270° F. It is necessary to apply a certain amount of forced ventilation in order to remove water vapor from the driers. Satisfactory operation is obtainable with a draft barely sufficient to maintain the stack gases above the dew point. A dust separator is essential to such an installation.

The drying of granulated soybeans does not appear to have received much attention from a theoretical viewpoint. Design of the driers now used seems to have been accomplished principally by the "trial and error" method, and consequently, the literature contains little, if any, information relative to equilibrium moisture contents at various temperatures and humidities, to the causes and prevention of case-hardening, or to the effects of the controllable factors upon drying rates.

The present drying practice, as used in pressing soybeans, results in a non-uniform product, because insufficient time is permitted for equalization of unsteady-state temperature and moisture distributions set up within the individual grains. The usual practice, therefore, is to "temper" the dry beans, before pressing, by holding them at an elevated temperature for a period sufficient both for dissipation of the unsteady-state conditions and for "cooking" the protein to the proper physical condition for pressing. This operation is accomplished by slowly conveying the charge through one to three steam-jacketed troughs or bins designed to provide ample retention time. A separate set of tempering apparatus is attached to each press, and the cracked beans, discharged from the driers, are immediately transported to these by means of an overhead screw conveyor and spout system arranged to serve all the machines in the press line. In the typical press-room arrangement, the overhead conveyors terminate in an overflow or "run-around" bin at the end of the press line. This receives excess feed which the expellers are not able to handle, and the resulting excess is returned to the beginning of the line by means of the "run-around" screw conveyor located beneath the floor. The tempering troughs discharge directly into the pressing screws of the expellers or screw presses. Steam is ordinarily supplied to both the driers and tempering troughs at a pressure of approximately 125 pounds per square inch.

Although a considerable number of continuous presses are or have been on the market, only two makes are commonly used on soybeans in this country, i.e., the Anderson expeller and the French screw press. However, a number of other continuous presses have been placed on the market from time to time. The various makes include:

1. The Anderson expeller, manufactured by the V. D. Anderson Company, 1935 West 96th Street, Cleveland, Ohio.
2. The French screw press, manufactured by the French Oil Mill Machinery Company, Piqua, Ohio.
3. The Burrus rotor press, manufactured by the Davidson-Kennedy Company, 1090 Jefferson Street, N. W., Atlanta, Georgia.
4. The Hiller high-pressure, continuous press,[104] until

recently manufactured by the Santa Cruz Oil Corporation, San Francisco, California. Patents for this press are now reportedly owned by the V. D. Anderson Company.

5. The Sohler and Elbex screw presses, manufactured by the Fried. Krupp Grusonwerk Akt.-Ges., Magdeburg, Germany.
6. The MSP expeller press, manufactured by the Lenin Memorial Factory in U.S.S.R.
7. The Müller screw press, manufactured by Fritz Müller, Esslingen, Germany.
8. The Maxoil expeller, manufactured by Rose, Downs, and Thompson, Ltd., Hull, England.

The Anderson Expeller

Figure 8 shows the Anderson Super-Duo expeller. Pressing is accomplished by means of a worm shaft continuously rotating within a pressing cylinder or cage composed of closely spaced steel bars. The action is not unlike that of a household meat grinder. Pressure of 8 to 10 tons per square inch is developed partly because of an irregular design of the worm shaft and partly by means of an adjustable orifice or choke with which the cake-discharge opening of the pressing cylinder can be constricted. The internal pressure and high temperature plasticize the previously cooked protein and cause the oil to flow out between the barrel bars. Sufficient frictional heat is created to toast the residual cake to a brown color, and the higher temperatures, thus developed, are conducive to easy drainage of oil out of the compressed charge.

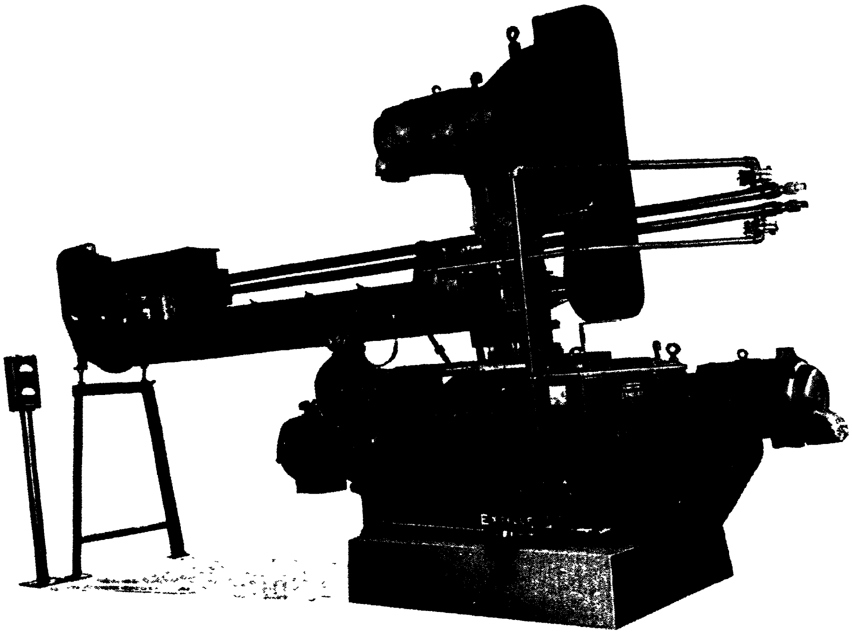

FIGURE 8

Anderson Super-Duo oil expeller (Courtesy of V. D. Anderson Company)

The Super-Duo expeller is one of the Anderson line of continuous presses which includes or has included models designated as No. 1, RB, Red Lion, Duo, Super-Duo, and Duplex Super-Duo. Of these, the Duo and Super-Duo are the most generally employed for soybeans, but many RB presses and a few No. 1's are still being used for this purpose. The Duo expeller resembles the Super-Duo in most respects but is of lighter construction and has a lower capacity.

Duo and Super-Duo presses actually employ two pressing cylinders. The main barrel is horizontal and is fed from a smaller vertical drainage barrel which receives hot beans from the tempering apparatus and subjects them to preliminary pressure, before forcing them into the main barrel. The horizontal worm shaft is driven at a speed of about 16 revolutions per minute by means of a 30 or 40 horsepower gear-motor, and its thrust is carried by a roller bearing located at the discharge end of the shaft. The vertical worm shaft is driven from above by a separate motor or bevel gear and chain drive combination called "hopper feeder mechanism." These presses, when installed to process soybeans, are usually equipped with three tempering troughs, 10 inches deep by about 10 feet long.

In order to maintain low barrel temperature, the Super-Duo employs so-called "oil cooling" which is illustrated in Figure 8. Oil, pressed in both cages, is collected beneath the main barrel where it fills a trough to the height of the "oil discharge" overflow opening. A small pump circulates the oil thus collected, at a rate of about 18 gallons per minute, through a heat exchanger where it is water-cooled to 170 to 200° F. The cool oil is then used to flush both barrels, lowering their temperatures from upwards of 300 to about 200° F., and, at the same time, washing the cages free of any accumulations of fine meal particles or "foots."

The French Screw Press

The French screw press, as shown in Figure 9, also uses a powerful worm, revolving within a press cage, but it differs considerably from the Anderson expeller in details of construction and operation. A single tempering trough, 28 inches

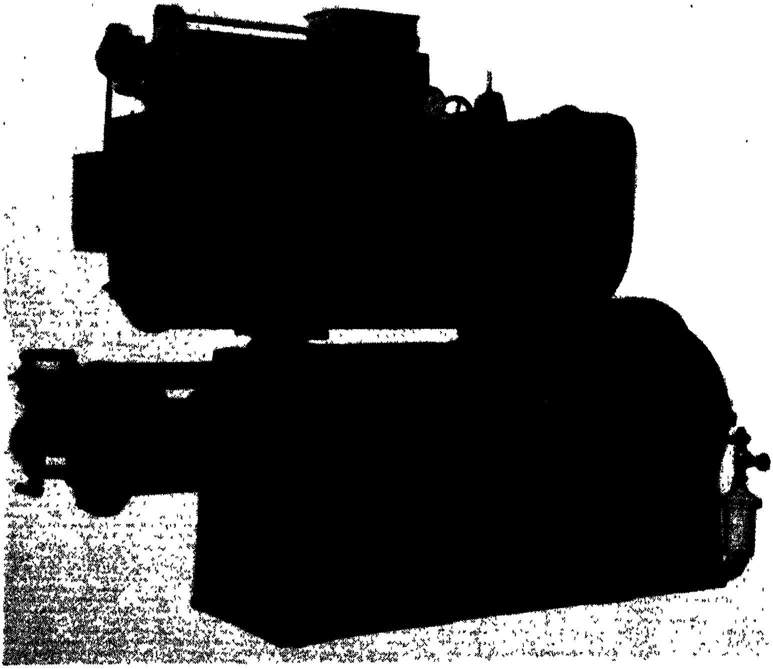

FIGURE 9

The French screw press (Courtesy of French Oil Mill Machinery Company) in diameter, is employed. Instead of a vertical worm for prepressing the material before it enters the main barrel, this machine uses two screws, revolving within the same horizontal barrel. The tempered beans fall from the steam-jacketed trough into the feeder worm which rotates at about 34 revolutions per minute and presses out approximately half of the oil. The charge is then forced into the main screw, revolving at 17 revolutions per minute, where it receives the final pressing and from which the cake is ejected through a cone type of adjustable-pressure orifice. The two worms turn concentrically about a common axis and are both driven from a gear box located at the inlet end of the machine. They are provided with separate thrust bearings located in the gear case.

In many French screw presses, coarse foots are removed from the oil, as it drips from the barrel, by straining through a slowly traveling, endless screen beneath the pressing cage. The retained particles (foots) are dumped into a conveyor which returns them, via the "run-around" bin, to be repressed after mixing with the feed. Most French screw presses are provided with water-cooled cages, the cooling water being circulated through ports in the steel rings which form the cradle supporting the barrel bars. There are numerous additional structural features wherein the French and Anderson machines differ, and for an elaboration of these, the interested reader is referred to the literature published by the respective manufacturers.

Operation of Continuous Presses

Regardless of the make of the continuous press employed, the resulting crude oil contains large amounts of suspended meal particles. A large part of these is removed by passing the oil through vibrating screens, revolving reels, or similar separating devices. The finest particles are filtered out, generally in filter presses, either with or without the addition of filter aids. The solids thus separated are fed into the "run-around" bin and are thus repressed. The filtered crude oil is run into storage tanks or to tank cars for shipment.[125]

The cake, produced by continuous presses, emerges as irregularly shaped fragments, which, while still hot, emit a strong and mildly pleasant odor, characteristic of soybean mills using this process. The odorous constituents are strongly adsorbed by articles of clothing, etc.

The freshly ejected cake contains 4 to 5 per cent of oil and approximately 2 per cent of moisture. Since it is quite hot, it cannot be stored in bulk without first being cooled nearly to room temperature. Otherwise, it rapidly heats, spontaneously, until combustion takes place, a phenomenon which has caused occasional destructive fires in processing mills.[14] Cooling can be accomplished by a wide variety of methods, the essential operations being thorough aeration and addition of sufficient water to produce a final meal containing 10 to 12 per cent of moisture. There are a number of cake coolers on the market, usually consisting of a horizontal, cylindrical shell which is well ventilated and which contains a rotor with stirring blades. The cooling is effected mainly by evaporation of water which is sprayed onto the hot cake. In some installations, cooling is accomplished simply by passing the cake through long, open conveyors, with the addition of water. In order to increase the ease of water absorption, the hot cake is sometimes first run through a corn crusher or similar type of cake breaker. The cooled cake is ground into meal in hammer mills and is then conveyed to storage bins, sacking machines, or bulk car loaders.

Many soybean mills are operated in conjunction with feed mixing plants, and a large portion of the meal, therefore, never reaches the market as such. It is often marketed in pellet form in various sizes, either alone or blended with a mineral supplement. In mixed feeds, it is sold in an extremely wide variety of products. Soybean meal shipments are ordinarily made either in 100-pound bags or in bulk.

In most respects, the operation of expellers and screw presses is an art concerning which no fixed rules can be given. The judgment of the operator, developed by years of experience, is usually the principal factor contributing to the efficiency of a mill's production. A skilled superintendent or foreman, however, relies, to a great extent, upon both physical and chemical measurements as guides toward the proper adjustment of the many items of process equipment throughout the mill. It is for this reason that all large processing plants include well equipped chemical laboratories and are provided with the many specialized instruments requisite both to intelligent operation on and accurate accounting of raw materials and products.[143]

The use of expellers or screw presses is, at present, a fairly standard method for processing soybeans, especially in those mills having a daily capacity of 50 tons or less. A mill can operate with any number of such presses, all receiving dried beans from the same conveyor system and discharging oil and cake into common pipes or chutes. Figure 10 shows the interior of a very large mill, using about fifty Anderson expellers, and Figure 11 shows an installation of six French screw presses in a mill which, in size, might be considered quite typical of the present-day American processing plants. By this method, one bushel of beans (60 pounds) yields approximately 9 pounds of crude oil and 48 to 49 pounds of meal, the latter containing 41 to 44 per cent protein and 12 per cent moisture.

The temperatures and moisture contents of the beans, at various stages in the process, vary considerably from plant to plant, but the following might be considered typical operating conditions:

Moisture content of beans entering drier	10–15	per cent
Moisture content of beans leaving drier	2.5	per cent
Moisture content of beans entering press cage	2.5	per cent
Temperature of beans leaving drier	270° F.	
Temperature of beans entering press cage	270° F.	
Temperature of barrel bars in uncooled cage	310° F.	
Temperature of surface of freshly pressed cake	310° F.	
Oil content of cake, on 10 per cent moisture basis	4.4	per cent
Protein content of cake, on 10 per cent moisture basis	43.0	per cent
Moisture content of freshly pressed cake	2.0	per cent

The storage and shipment of crude soybean oil is generally attended by difficulties, resulting from the formation of phosphatide-containing sludges in the tank bottoms. The maximum permissible amount of such sludge is specified in the trading rules which apply to soybean oil marketing, and sludge, in excess of that permitted, results in application of discounts. The amount of precipitate formed varies over wide limits and is governed by such factors as the quality of the beans, the storage conditions, the pressing technique, etc.[181] Crude oils, which have been freshly pressed and filtered to yield a crystal-clear product, gradually undergo precipitation of the dissolved phosphatides, unless some treatment is

Figure 10

An installation of Anderson expellers crushing soybeans (Courtesy of V. D. Anderson Company)

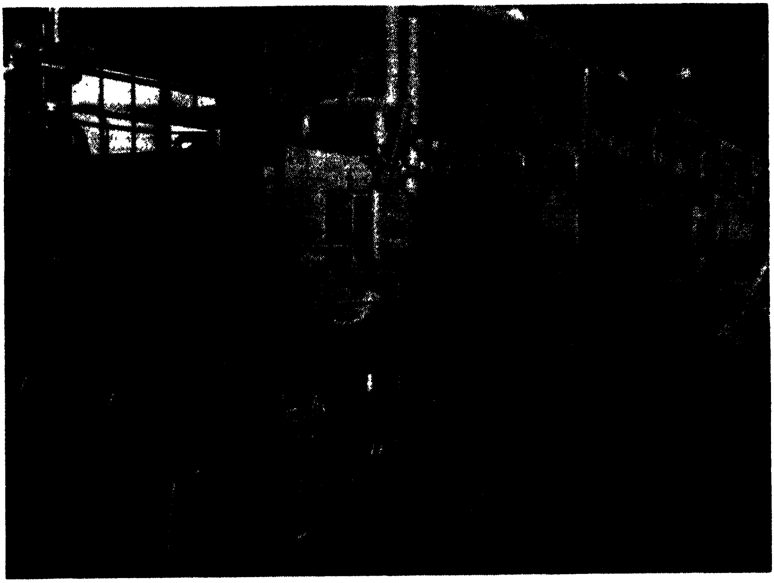

FIGURE 11

A battery of French screw presses crushing soybeans (Courtesy of French Oil Mill Machinery Company)

given to remove the sludge-forming materials.[87] This can be effected by washing the oil with water to hydrate the phosphatides, throwing them out of solution. The sludge thus formed can be rapidly separated from the oil by centrifuging. By using some alkali in the wash water, a partial refining can be effected, and some expeller-type mills have installed equipment for this purpose. More detailed information is given in the section describing phosphatides and phosphatide processing.

As is the case with many types of processing of agricultural products, the operation of expeller or screw-press soybean mills is subject to the danger of dust explosions. The relative explosibilities of various dusts encountered in soybean processing were reported by Price [146] and were compared with those of other dusts.

The drying and tempering of soybeans, for crushing in expellers or screw presses, appear to be necessary in order to have sufficient frictional resistance built up during the subsequent passage of the tempered beans through the pressing cage. In this respect, soybean crushing is different from that of most other oil-seeds wherein the precooking process is done in such a way that the seed meats are softened and the cell walls are weakened rather than toughened.[124, 136, 144, 205]

Several theories have been proposed to explain the roles of water, proteins, cell wall constituents, etc., in the process of precooking oil-seeds prior to the removal of the oil. These are reviewed by Heublum and Japhe,[98] Singer,[179] and Goldovskii.[83]

In Russia, two of the more modern, hydraulic-press methods of oil production have been developed as the result of chemical studies of the role of moisture during cooking. These are of interest because of their relation to research now being carried on in this country with a view toward improving the pressing processes used on soybeans, cottonseed, linseed, etc. The Skipin [180] process comprises the precooking of the oil-bearing material, in the presence of a very high percentage of water. Under these conditions, a large share of the contained oil is released and drains from the meats before the pressing operation. It has been successfully applied to the processing of castor beans, sunflower seed, hemp seed, cottonseed, cedar nuts, sesame seed, and peanuts in order to increase the capacity of a given press installation.

The Iljin process is employed to obtain a greater yield of oil from linseed, sesame seed, sunflower seed, etc. The material is treated with steam in such a way that it can be given a prepressing to remove 80 per cent of the oil at relatively low pressure and at a relatively high moisture content, without undue oozing or flowing of the cake. The residual cakes are broken up, treated with superheated steam, and repressed in the normal manner.

PROCESSING BY MEANS OF CONTINUOUS SOLVENT EXTRACTORS

AT present, about 20 per cent of the soybean processing, in this country, is carried out by means of volatile hydrocarbon solvents in a variety of equipment designed for continuous operation. Batch solvent extraction is still employed, to some extent, in other countries, but not in the United States. The continuous soybean extraction systems, now in commercial use in this country, include the Bollman (Hansa-Mühle), Hildebrandt, Allis-Chalmers, French, and Ford extractors. The variety and sequence of operations are more or less the same in all these systems, their most characteristic features being chiefly the designs of the individual extractors themselves, i.e., the methods of contacting beans with solvent in order to dissolve out the oil. A number of general references describing the use of solvent-extraction equipment are listed in the bibliography.[39, 45, 84, 94, 114, 135, 177, 192, 227]

Although continuous presses operate upon beans which have been subjected only to granulation, such material, when used in solvent equipment and ground sufficiently fine to secure efficient oil removal, tends to clog filters and to produce solvent channeling and consequent non-uniform extraction. It is, therefore, the practice to roll the beans into thin flakes similar, in some respects, to those produced in the hydraulic pressing of soybeans, cottonseed, etc. They are first cracked to a size which is determined by the desired dimensions of the final flakes and, if very dry, they are moistened by addition of direct steam. It is also customary to heat the beans, since the rolling operation is facilitated by both high temperatures and a high moisture content. Corrugated rolls of the same type as are used in pressing plants are used for cracking. In most mills, the flaking is accomplished with a single pair of smooth rolls, 1½ to 3½ feet in diameter and about the same in length as shown in Figure 11a. These are driven at approximately 400 revolutions per minute, either at equal speeds or with a differential which may be extremely slight or as high as 3 : 2. The desired characteristics of individual flakes, i.e., thickness, strength, size, etc., vary considerably, depending upon the type of extractor to be used, and they may be controlled by proper regulation of the precracking, moisture content, temperature, roll spacing, etc.

Soybeans are ideally suited for solvent extraction since they can be rolled into thin, firm flakes which are sufficiently rugged to withstand the solvent treatment, without disintegrating to a fine powder. One of the principal difficulties, encountered in the extraction of cottonseed,[131] linseed and other oil-seeds, results from the solution of the intercellular binder during extraction, with consequent disintegration of the individual flakes. The large amount of finely divided material thus produced results in compacting of the solids and uneven extraction due to channeling. It is for this reason that continuous solvent extraction has been applied to soybeans

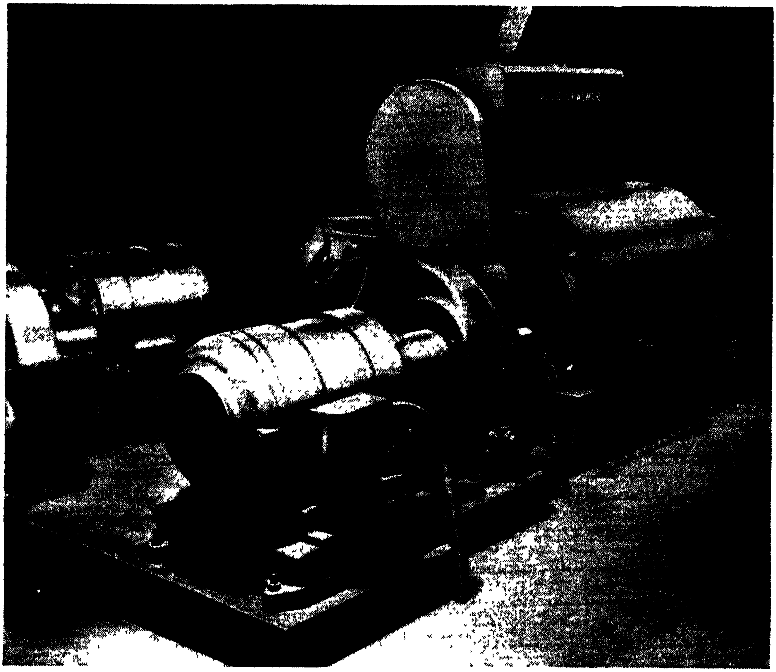

FIGURE 11a

Flaking mill, used for rolling cracked soybeans into thin flakes, in the solvent extraction process (Courtesy of Allis-Chalmers Manufacturing Company)

to a much greater extent than it has to other oil-bearing seeds.

In rolling soybeans for solvent extraction, it is essential to produce as thin a flake as possible, consistent with preserving considerable strength. In systems where mechanical agitation of the flakes is kept to a minimum, a thickness of about 0.007 inch is found satisfactory. In other systems where the flakes are subjected to considerable handling, as in extractors which propel the charge through the solvent with screw conveyors, flake thicknesses of 0.009 to 0.015 inch are commonly employed. In either case, maximum flake strength results from rolling moist beans through a single pass mill. The 5-high roller mills, used in the hydraulic milling of oilseeds, cause so much rupturing of cell walls by the repeated rolling that the resulting flakes are too fragile.

The Hildebrandt System

Although the results of individual operations, as carried out in various solvent systems, are somewhat similar, considerable variation exists in the equipment and method of carrying out the necessary steps of the process. For illustration, however, the Hildebrandt system [100, 101, 102, 103] is a satisfactory example. A flowsheet of this process, starting with the conveyor connecting the flaking rolls to the extraction tower, 1, is shown in Figure 12.

The extraction column is shown in greater detail in Figure 13. The unit is a U-shaped tube, 3, 5, 7, into which bean flakes enter at 1 and through which they are propelled by the perforated screw conveyors 2, 4, and 6. These are rotated at different speeds by means of explosion-proof gear-motors, the relative motions being controlled to produce considerable compacting in the "pressure chamber," 5. Guide rails, 8, may be provided in the ascending leg, 7, of the tower to prevent rotation of the charge as it is carried upward. The solvent, which is usually hexane, is pumped through the apparatus in countercurrent flow, entering at 10. The oil-solvent mixture, or miscella, is discharged at 12, after passing through the strainer, 11. The strainer is a cylindrical sheet perforated with vertical slots which are narrower at the inside edge than at the outside. This shape of opening prevents solid particles,

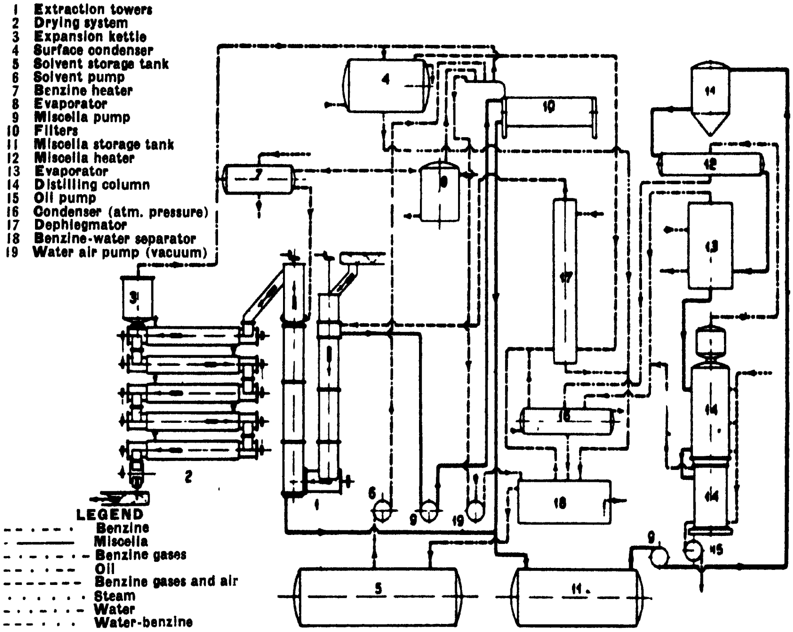

FIGURE 12

Flowsheet of the Hildebrandt system of solvent extraction (Courtesy of Sieck and Drucker, Inc.)

in the exit miscella, from clogging the openings. In addition, the screw flight, 2, is accurately machined to provide a clearance of only a few thousandths of an inch between its outer edge and the inner screen surface, providing a wiping or self-cleaning action.

The upper part of the ascending leg, 7, acts as a drainage zone for removal of most of the entrained solvent from the oil-free flakes. At 9, the wet extracted flakes are discharged into meal driers, shown at 2 in Figure 12. These are steam-jacketed conveyor sections wherein residual solvent is driven off to be condensed in the surface condenser, 4, and returned

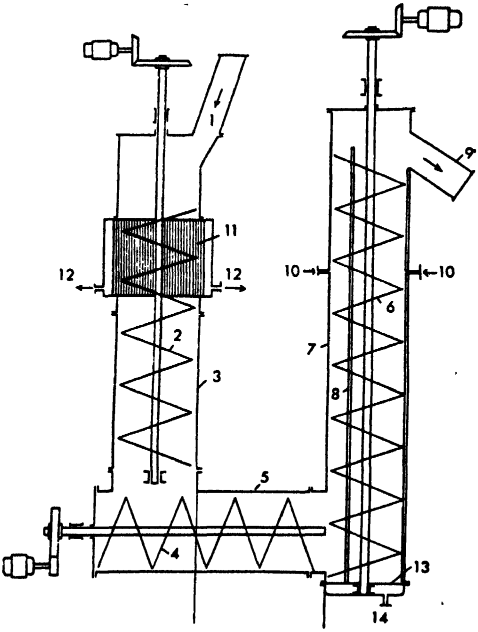

FIGURE 13

The Hildebrandt extractor (Courtesy of Sieck and Drucker, Inc.)

to the system. The expansion kettle, 3, is provided to minimize the amount of dust carried into the surface condenser by the solvent vapor. If protein dusts are permitted to enter the separator, 18, which removes water from the condensed solvent, serious emulsion formation will result.

The meal-drying equipment consists of five horizontal, steam-jacketed cylinders, arranged in series, through which the spent flakes are conveyed by rotating screws. A small amount of direct steam is often used in the final or fifth pass of the meal driers. The discharged meal contains 0.5 to 1.0 per cent oil and over 44 per cent protein. Since it is used almost entirely as a feed supplement, it is ordinarily given an additional toasting to increase its palatability and the nutritive value of the protein.[96]

Although it is claimed that toasting solvent-extracted meal greatly enhances its feeding value, the practice was introduced to the American industry largely as a measure toward overcoming the consumers' prejudice against oil-seed meals having a light color. As pointed out by Heublum and Japhe,[98] the production of a characteristic color, associated with "toasting" and the complete denaturing of the proteins, can be obtained by the combined effect of moisture and heat. Neither agent, per se, is very effective. The stack type of cooker, as used in other branches of the oil-seed processing industry, is well suited for heating extracted flakes, in the presence of a large excess of moisture. Although this equipment is not shown in Figure 12, it is described and illustrated under "Hydraulic pressing," in Figure 28.

The extracted flakes, from the meal driers, are introduced into the uppermost stack of the cooker, and the moisture content is raised to 15 to 18 per cent by adding steam and water. The cooking takes place in the lower compartments which are provided with some degree of ventilation. According to Hayward,[97] the flakes are in the cooker for approximately 75 minutes at a maximum temperature of 220° F. They emerge containing 10 to 12 per cent moisture and are passed through meal-cooling equipment to reduce their temperature to approximately 80° F.

Figure 12 indicates also the course of solvent (petroleum hydrocarbons, principally hexane) through the Hildebrandt system. From a tank, 5, it is pumped through a preheater, 7, where it is heated by steam to about 120° F. and from which it flows to the extractor. After countercurrently extracting oil from the flakes, the resulting miscella, containing approximately 20 per cent oil, leaves at a point so located that there is always a layer of fresh bean flakes above the miscella outlet sufficient to prevent escape of solvent vapor through the flake-charging mechanism. The ratio of solvent input to soybean input, on a weight basis, is roughly of the order of 1 : 1.

The complete removal of solvent, from the oil, must be performed with great care, particularly in the United States where the flavor standards for edible oils are very high. It is especially important to avoid over-heating the oil by continued exposure to hot surfaces. The solvent distillation is, therefore, carried out in several steps. The bulk of the solvent may be easily removed by any of a considerable variety of evaporating apparatus, but rather specialized distillation equipment is necesary for removing the last 5 or 10 per cent of solvent from the miscella. Bubble cap columns, vertical packed columns, and evaporators, constructed to maintain continuously moving thin films of oil over the evaporating surfaces, are effective for removing these last few per cent of solvent. It is also essential to reduce the amount of fines contained in the miscella so that the final distillation can be carried out effectively. This point is discussed by Bilbe[25] who describes settling, filtration, and centrifugal clarifying methods.

In the Hildebrandt system, the miscella is filtered through specially constructed filter presses, 10, and pumped to intermediate storage tanks, 11. It then passes through a preheater, 12, where it is warmed by vapors from the main solvent distilling equipment, and thence, in many installations, to a preliminary, steam-tube evaporator which removes about 10 per cent of the solvent. The rest of the solvent is removed in the distillation column, 14. In this apparatus,[37] the miscella enters at the top and passes downward successively through three evaporator sections, each of which is heated by a pancake steam coil. The vapors pass upward through a dephlegmator and then through the miscella preheater, 12. The undistilled product, from the lowest evaporator, contains approximately 10 per cent solvent and runs into the lower or stripping section. This contains several bubble-cap plates, and the oil is stripped of all traces of solvent by means of counterflowing steam. The solvent vapors pass to the condenser, 16, and the condensate runs into the water-separating tank, 18, from which it returns to the solvent-storage tank, 5.

The oil leaves the solvent-distillation equipment at a temperature of about 200° F. and is in the form of a very fluid emulsion with water. The formation of a water emulsion can be prevented, if desired, by the judicious use of superheated steam. However, the water causes the phosphatides to become hydrated and to be precipitated out of solution. By running the emulsion through a continuous separating centrifuge, the oil is clarified, and the phosphatides are discharged as an oily sludge which, in many mills, is used for the production of commercial lecithin. Crude oil, before centrifuging, usually contains 0.05 to 0.10 per cent of phosphorus, and the process of hydration and subsequent centrifuging, as generally employed, produces a clarified oil having a phosphorous content of 0.003 to 0.008 per cent. Such oil can often be sold at a slight premium over the unwashed crude oils.

Figure 14 shows a Hildebrandt extraction tower in side elevation, the second and third floors of the plant being cut

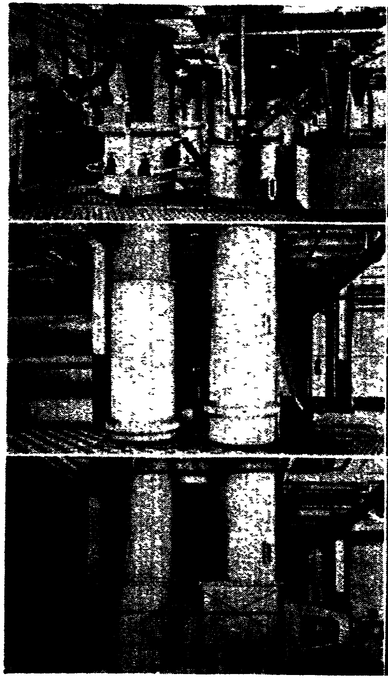

FIGURE 14
Side elevation on Hildebrandt extractor, with floors cut away to provide full view (Courtesy of Sieck and Drucker, Inc.)

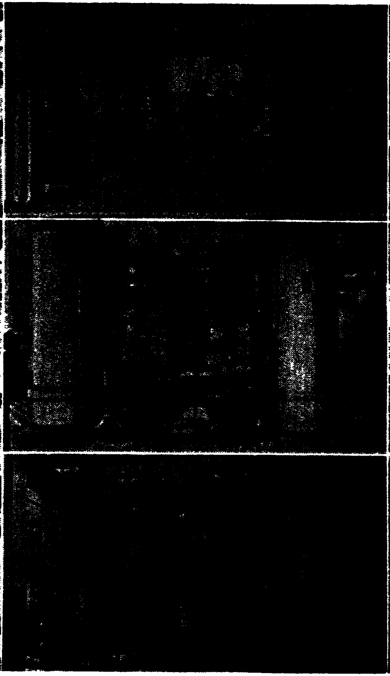

FIGURE 15
Installation of two Hildebrandt extraction units (Courtesy of Sieck and Drucker, Inc.)

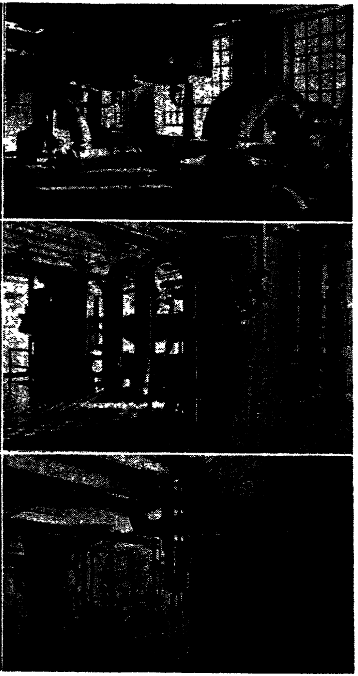

FIGURE 16
Solvent distillation equipment of Hildebrandt extraction system (Courtesy of Sieck and Drucker, Inc.)

away to provide an unobstructed view of the entire unit. Figure 15 shows a pair of these columns, with their respective sets of meal driers arranged vertically between them. The solvent-distillation equipment is shown in Figure 16. These units are regularly supplied in two sizes, having nominal capacities, respectively, of 55 and 110 metric tons of raw material per 24 hours. Where larger capacities are required, several units are installed.

The Bollmann System

The Bollmann or Hansa-Mühle extractor [27, 28, 29, 67, 91, 92] is shown in Figure 17. A number of baskets, b, having perforated bottoms, are attached to a pair of endless chains, a, which encircle and are driven by sprocket wheels. A charging hopper, c, introduces a predetermined amount of bean flakes into each basket as it starts down the descending side of the apparatus. Freshly filled baskets are moved slowly around the circuit, in the direction indicated by arrows, while the oil is dissolved from the beans by a spray of solvent. Upon reaching the top of the ascending side, the baskets automatically invert and dump the extracted meal into a discharge hopper, d. The filling and emptying mechanisms are shown more clearly in Figure 18. A pair of screw conveyors removes the spent flakes from the discharge hopper and feeds them to the meal driers which are located outside and alongside the vapor-tight, steel housing which encloses the complete basket system.

Fresh solvent, e.g., hexane, is sprayed onto the ascending line of baskets near the top and percolates downward, successively washing the contents of each container in countercurrent flow. The resulting solvent-oil mixture collects in a sump, e, which comprises one side of the bottom of the housing. This so-called "half-miscella" is pumped to a storage tank, f, and subsequently is sprayed onto the top of the descending chain of baskets to wash them in parallel flow. "Full miscella" collects in a sump, g, whence it is pumped to bag filters and then to miscella-storage tanks.

The full miscella contains 20 to 30 per cent of oil and passes through a heat exchanger where it is preheated nearly to the boiling point by vapors from the distillation equipment. It is concentrated to approximately 50 per cent oil content in a series of two or three steam-tube evaporators. A further concentration to 90 to 95 per cent oil is then effected in a "drip" type of evaporator in which the oil runs, in thin films, down the inner surfaces of vertical tubes surrounded by steam. The "drip" tubes feed into a flash chamber, at the bottom. Final stripping of the solvent from the oil takes place in a packed tower or in an additional "drip" type of evaporator in which it is countercurrently scrubbed with steam under vacuum. The crude oil contains emulsified water and hydrated phosphatides which are removed by centrifuging, as previously described.

The spent flakes contain moisture and entrained solvent which are removed, the latter practically completely, by successive passages through six meal driers or "Schneckens." These are horizontal, steam-jacketed screw conveyors arranged in vertical banks. The bottom "Schneckens" feed into a deodorizing drum which is a jacketed steam drier, having a steam-heated rotating coil equipped with scrapers for propelling the charge. Direct steam is admitted to assist in the deodorization. Finally, the solvent-free flakes are toasted, in

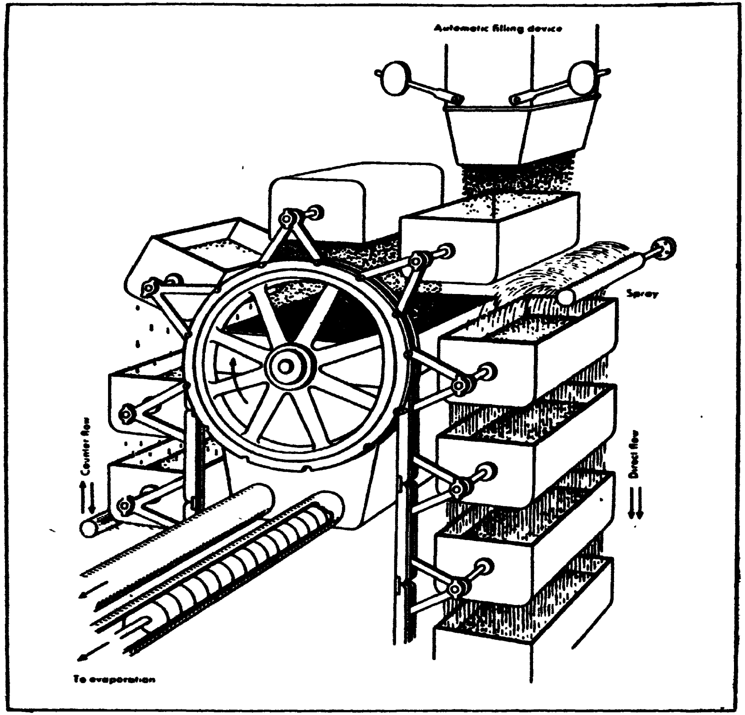

FIGURE 18
Basket filling and discharging mechanism of the Bollmann extractor (Courtesy of Albert H. Bruecke)

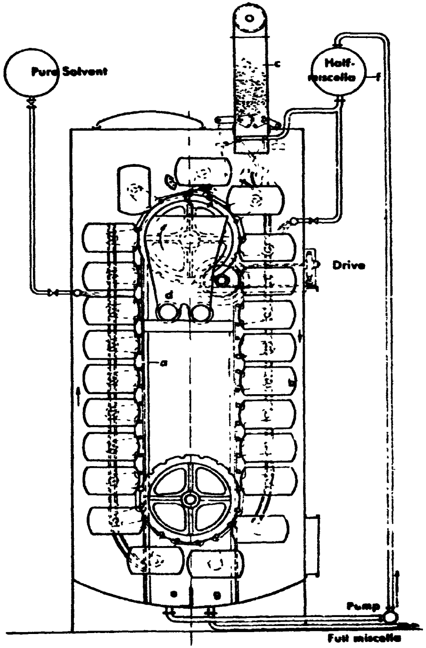

FIGURE 17
The Bollmann system of solvent extraction (Courtesy of Albert H. Bruecke)

the presence of large amounts of moisture in a stack cooker, as previously described. The vapors, given off from the meal driers, pass through dust-collecting equipment, before being condensed and fed into the water-separating tank.

In the Bollmann system, the flakes rest on perforated plates and are not agitated during the extraction process. The percolation method of operation affords considerable "self-filtration" of the miscella, minimizing the difficulties resulting from "fines" in the miscella. For these reasons, it is customary to use thinner and smaller flakes than are employed by the systems in which the flakes are completely immersed in and propelled through the solvent by screw conveyors. Usually, the baskets are moved through the extractor at the rate of about one revolution per hour, and solvent is sprayed onto the flakes at a rate corresponding to one pound of solvent per pound of beans processed. In European mills, slightly different operating conditions are employed, principally because Manchurian soybeans, which have heretofore constituted the bulk of their raw material, are quite different from American beans in their physical behavior during processing. The Bollmann or Hansa-Mühle extractor has been built in sizes, having capacities of from 50 to 500 tons of soybeans per day. Figure 19 shows an installation of the Bollmann system. Two vertical banks of "Schneckens," surmounting a deodorizing drum, may be seen immediately behind the stairway in the foreground.

Extraction System of The French Oil Mill Machinery Company

The Hildebrandt and Bollmann systems are both of German origin and manufacture and are widely used throughout

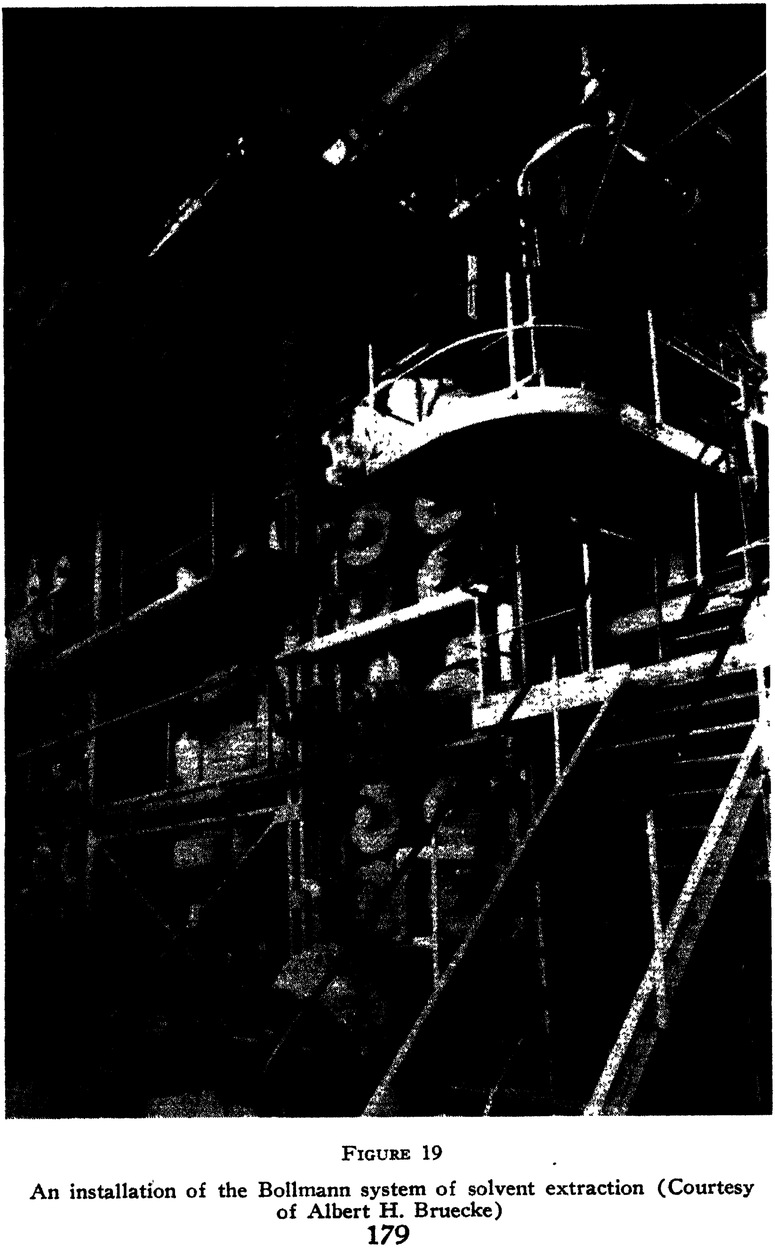

FIGURE 19

An installation of the Bollmann system of solvent extraction (Courtesy of Albert H. Bruecke)

Europe for processing a variety of oil-seeds and oil-seed press cakes. In recent years, there have been developed several American systems, some of which are now in successful operation.

The French Oil Mill Machinery Company has installed a solvent-extraction equipment which resembles the Bollmann system in most respects. Because of the close resemblance, a detailed description will not be given. The baskets have specially designed solvent ducts into which reciprocating solvent spray nozzles inject the solvent, while the baskets are in motion. The baskets are built with false bottoms constructed to distribute the solvent evenly over the next lower basket. This makes special precautions to avoid channeling unnecessary. The mechanical devices, for guiding, charging, inverting, and dumping the buckets, are also somewhat different from those employed by the Bollmann system. One installation of this system extracts approximately 130 tons of soybeans per day.

The Allis-Chalmers Extractor

An early edition of the Allis-Chalmers [38, 41, 42, 68] extractor is shown in greatly simplified form in Figure 20. A vertical, cylindrical column contains a series of horizontal circular plates, equally spaced and fixed to a central shaft which is slowly rotated by a gear-motor. The upper surface of each plate is wiped by a stationary scraper arm fastened to the inner wall of the cylinder. Slots are cut in the plates so that, during rotation, the stationary baffles sweep material, resting upon the disks, through the slots onto the plate immediately below. The slot arrangement is such that the material follows a helical path, in progressing downward through the equipment.

Bean flakes are introduced at the top, and while being slowly propelled downward, they are countercurrently washed with solvent which is pumped into the bottom of the tower. A thick layer of fresh flakes is maintained on the top plate, providing a filter bed to retain the fines dislodged in the lower parts of the column. Miscella overflows through a screen near the top and is filtered, centrifuged, or allowed to settle in conical tanks, before being fed to the evaporators. Spent meal is discharged at the base of the column by means of plug-forming, screw ejectors[44] which force the solids through cone-loaded orifices. The pressures, developed by the revolving screws, are so regulated that they form plugs sufficiently solid to prevent escape of the liquid contents of the column. Most of the solvent is also squeezed from the meal before final emergence so that a fairly dry product is delivered to the driers. Later designs of this extractor have replaced these devices with a totally enclosed conveyor which receives the flakes at the column base and bears them upward, outside the column proper, until they are above the solvent level.[25] The upper portion, i.e., that part which is above the solvent level, serves as a drainage zone so that, at the top of the conveyor, fairly dry material is discharged to the meal driers.

Removal of most of the solvent, from the oil,[43] is accomplished in calandrias which feed into a flash chamber. The oil is then countercurrently scrubbed with saturated steam in a bubble-cap tower, and, if desired, it is given a water-washing treatment to remove phosphatides. The Allis-Chalmers extractor has been built in sizes having capacities of 70 and 100 tons per day.

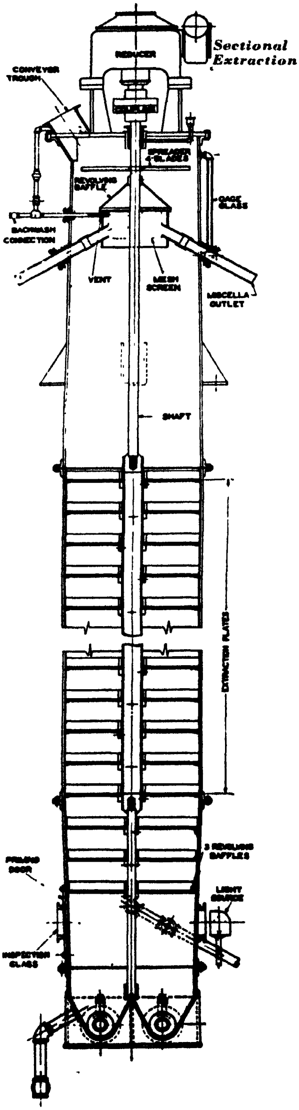

FIGURE 20

The Allis-Chalmers extractor

The Ford Extraction System

The Ford Motor Company has developed a soybean extraction system with the original intention of providing an inexpensive and easily operated apparatus which could be adapted to community operation. The only installations, to date, have been made by the Ford Motor Company, primarily to provide oil for their automobile finishes;[186] and it is expected that further research will lead to consumption of substantial quantities of the extracted meal within the Ford plant.

The complete system[113] is shown in Figure 21. The extractor itself is an inclined tube, enclosing a ribbon or helical conveyor and provided with two vertical standpipes at the lower end, one for admission of fresh flakes and the other for miscella overflow. The flakes are carried upward, against a counterflow of solvent, which fills only a little over half of the tube.

The upper portion of the tube is steam-jacketed to effect preliminary solvent removal, and immediately below is another steam-jacketed drier section to complete the separation of last traces of solvent. The newer and larger installations have the latter meal drier built horizontally, on the floor, beneath the extractor tube, and its length has been increased to permit any desired degree of toasting in the final product.

The miscella, containing 12 to 15 per cent oil, flows through a heat exchanger and then to a still. The latter is a steam-jacketed pot whose exit vapors pass directly into the heat exchanger. In the steam jacket there is a spiral coil through which the miscella flows and from which it is discharged, at a temperature considerably above the boiling point

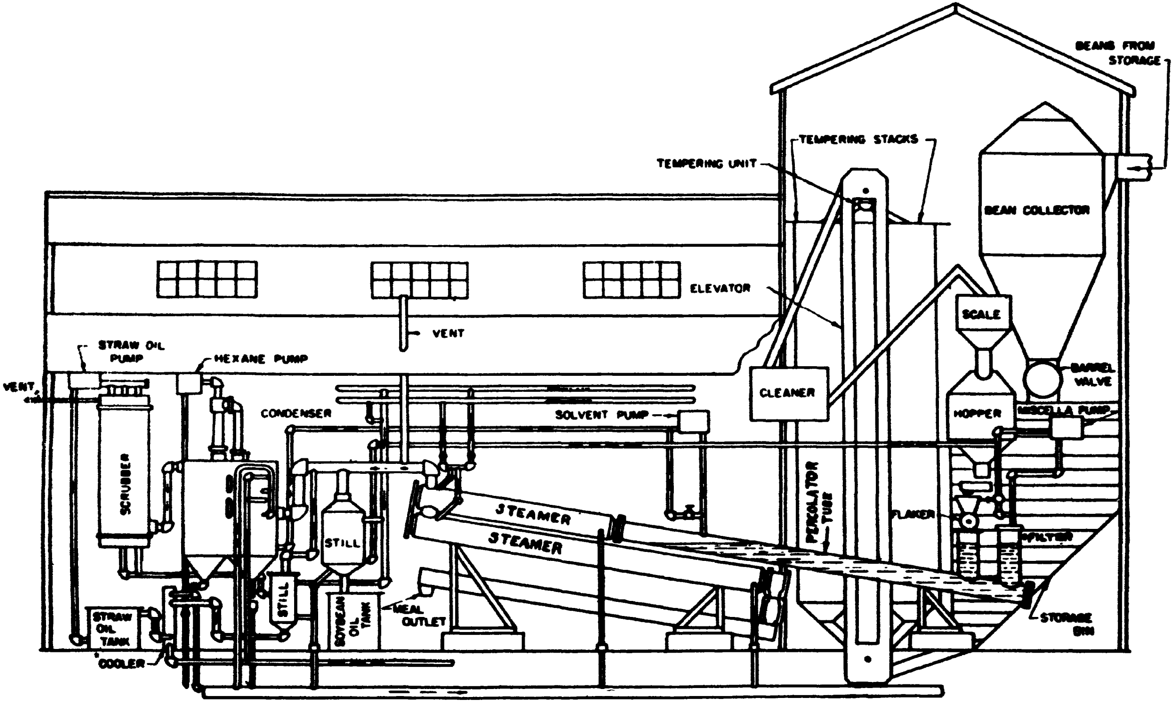

FIGURE 21

The Ford system of soybean extraction (Courtesy of Ford Motor Company) of the solvent, to flash into the top of the still pot. The unevaporated portions run downward, over baffles, into the bottom of the pot and then pass to a packed column in which the crude oil is countercurrently scrubbed with steam. The amount and quality of the steam are controlled to bring about

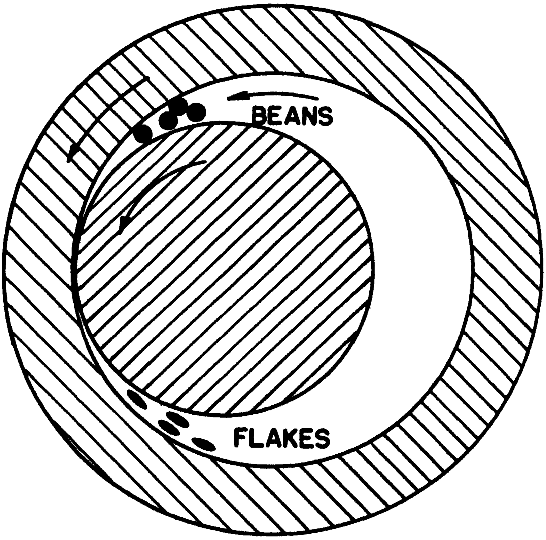

FIGURE 22

The horn-angle flaking rolls used in the Ford extraction system

hydration of the phosphatides which are removed by allowing them to settle out in the storage tanks. The supernatant oil is practically free of "break" materials.

Ford installations employ the "horn-angle" type of flaking equipment [73] in place of the conventional single pair of rolls. As shown in Figure 22, a cylindrical roll revolves inside an annulus having an inner diameter slightly larger than the diameter of the smaller roll. Such an arrangement provides an exceedingly small angle of nip and correspondingly higher capacity for a given roll diameter. At one time, the Ford system used an extrusion flaker in which a continuously revolving feed screw compressed the soybeans and forced them through a narrow annular opening.

The Ford extractor has been built in many small sizes for demonstration purposes, but the units, which are at present used to produce oil for the automobile factory, are said to have daily capacities of 6 and 24 tons, respectively. Figure 23

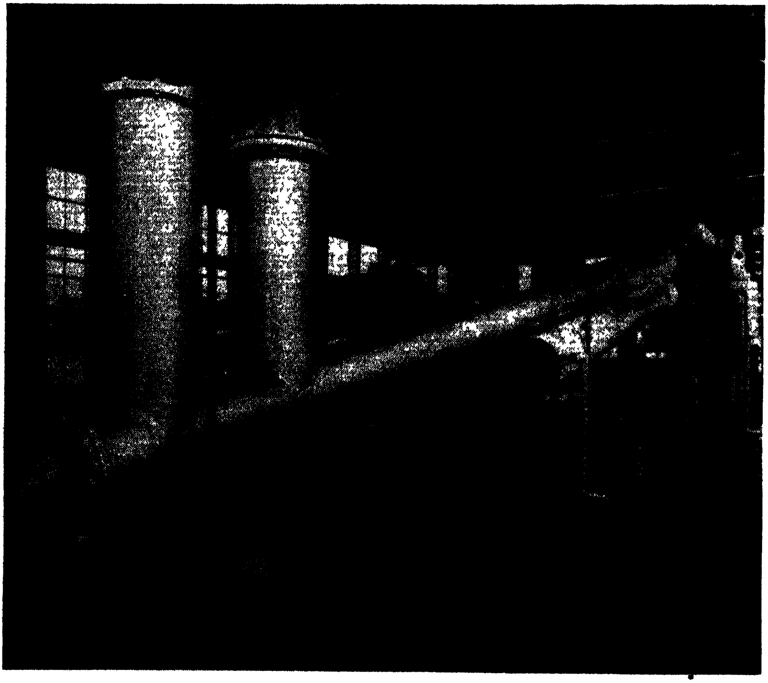

FIGURE 23

Interior of Ford plant at Saline, Michigan, showing soybean oil extraction columns (Courtesy of Ford Motor Company)

is a photograph of the interior of the plant at Saline, Michigan, in which two of the six-ton units are operated.

The Detrex Continuous Extractor

The Detrex Corporation, Detroit, Michigan, manufactures a solvent extraction apparatus, known as the Detrex oil-extractor, which uses non-inflammable trichloroethylene as the solvent (Figure 24). Briefly, the process, which is shown in a flow diagram in Figure 25, is as follows:

The beans are fed directly to the bean heater, which does not materially affect their moisture content, but merely heats them so that they become more pliable for flaking. After cracking and flaking, an elevator carries the prepared flakes to the flake hopper. From there, they are mechanically fed to the extraction tube, in which they are maintained in a loose condition, thereby allowing complete penetration of the solvent. Since the flakes are moved forward and constantly change their position, they come in contact with newly distilled solvent as they approach the discharge end of the extraction tube. The extracted flakes are drawn from this tube by means of an inclined screw which allows the solvent to drain from the flakes prior to their entering the drier tubes.

The driers are steam-jacketed and supplied with ribbon-type conveyors which move the meal through the path of the drying tubes. Super-heated live steam is injected at the exit-end of the drying tubes, which creates a counterflow of steam and solvent vapors from the meal and greatly facilitates thorough solvent removal.

The miscella flows from the extractor tube through a screening device and is collected in a surge or accumulation tank, from which, it is pumped to a preheater and evaporator. This preliminary treatment removes the bulk of solvent from the oil-solvent mixture. The final traces of solvent are then removed from the oil in a countercurrent steam stripping column. The solvent vapors, driven off from the various still sections, as well as those released from the meal in the driers, are condensed, cooled, passed through water separating devices, and returned free from water, to be reused in a continuous gravity system. An earlier version of this type of extractor is described by Hamilton and Perkins.[88]

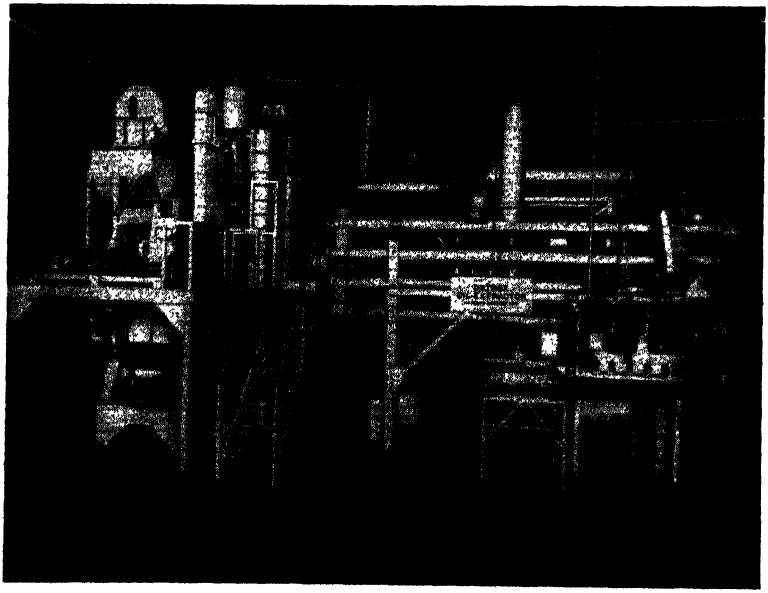

FIGURE 24

General view of the Detrex oil-extractor from the operating side

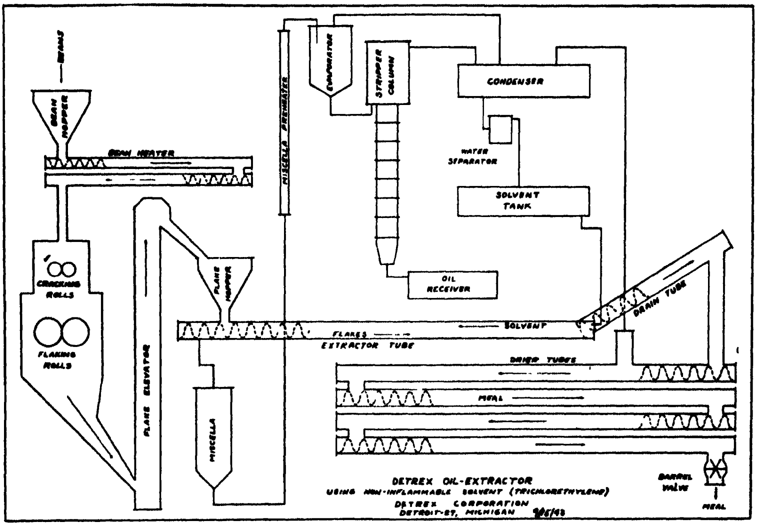

FIGURE 25

Flow diagram of Detrex oil-extractor which uses a non-inflammable trichloroethylene solvent

Other Solvent Systems

The patent literature is profuse with descriptions of solvent extractors, many of which have been used at some time on various forms of oil-seeds. Except for those already described, none is now being used commercially for processing soybeans in this country. There are a number of proposed systems, some used experimentally, which are available but have not yet been put into competitive operation.

The Kennedy extractor [115] is manufactured by the Wolf Company. In this system, a series of four-bladed paddle wheels rakes the flakes from one to another of a series of rounded troughs placed side by side. A paddle wheel revolves in each depression and its blades closely fit the circular contour of the trough. The solvent flows countercurrently and passes through perforations in the blades. One of these extractors is now being used for the commercial production of cocoa butter.

The Böhm system [26] of extraction is manufactured by Otto Wilhelm, Stralsund, Germany. It consists of two adjacent, vertical columns of rotating, perforated plates spaced in staggered positions. The material to be extracted is charged onto the uppermost plate, and the rotation causes it to be transferred, by means of a fixed scraper blade, to the next lower plate in the adjacent column. Here, a similar operation discharges the solids onto a still lower plate in the first column. The procedure is repeated on each of the six plates until the spent flakes are discharged at the bottom. Countercurrent extraction is secured by spraying solvent or partial miscella over each plate, pure solvent being used for the bottom stage and nearly full miscella for the uppermost one. After each step, the partial miscella is pumped to the next higher plate. The system is manufactured in sizes having daily capacities of from 30 to 200 metric tons of raw materials.

In the Fauth system,[69, 70, 71, 79, 80] extraction is carried out on a series of vibrating screens, the material being pressed between hollow, perforated rolls, after each stage. There are approximately six of these units, operating in Europe on a variety of oleaginous materials. The installations are said to have a capacity of 120 metric tons per day, each.

The Miag extractor, also German-built, is used in South America on a wide variety of oil-seeds and press-cakes. It consists of a large wheel, rotating in a vertical plane, having perforated compartments or "filter cells" on its periphery. An annular casing encloses the entire wheel in such a way that the "filter cells" continuously traverse a closed annulus, a stream of solvent being circulated in counterflow through the same annular raceway. The solid materials are introduced into the "filter cells" on the descending side, at a level about even with the wheel shaft, and are discharged after they have made three quarters of a revolution and are at the top of the wheel. The spent solids fall into a trough from which they are discharged by screw conveyors. The miscella leaves through a special strainer in the outside of the annular casing, the construction being such that the revolving wheel of "filter cells" provides continuous wiping action to prevent plugging the screen openings.

Solvents

So far as the authors are aware, there is only one extraction plant in the world now processing soybeans on a commercial scale with any other solvent than hydrocarbons or halogenated hydrocarbons. The single exception is a Manchurian plant using absolute alcohol. In this country, most of the solvent consists of hexanes, a typical, commercial grade of which has a boiling range of 146 to 158° F. and a specific gravity of 0.685 at 60° F. It is so flammable that its use, by any but experienced operators, is hazardous, and modern extraction plants are accordingly designed to afford the greatest possible protection from explosions.

Buildings should be well ventilated and provided with large areas of windows designed to open or shatter easily in order to relieve pressure in the event of an explosion. The plant should be located at some distance from the power house, and no open lights, flames, etc., should be permitted in the vicinity. Only explosionproof motors and related equipment are permissible, and electric wiring must conform to requirements of the National Electrical Code. Only sparkproof tools should be used in the building, and floors and stairways should be of the grating type. Bonotto[40] describes in some detail the precautions which should be followed. A number of both major and minor solvent explosions have occurred, two of which are described by Price and Brown[148] and by Price.[147]

An ideal solvent should, of course, be capable of penetrating the bean flakes and rapidly dissolving and removing the oil. Obviously, it must also be easily removable from the oil and the meal, leaving both products in satisfactory form for consumption. Other factors, entering into the choice, include cost, ease of recovery, fire and explosion hazard, corrosiveness, toxicity, and boiling range. The hexanes, now commonly used, possess most of the desirable characteristics, their only serious limitation being the extreme fire hazard.

Numerous solvents have been proposed and used experimentally, in efforts to reduce the danger of extractor operation. Of these, the chlorinated hydrocarbons have received a great deal of attention, and as previously pointed out, trichloroethylene is employed in one of the systems now being offered for sale. The use of trichloroethylene and similar solvents has been described by Hassel.[93] A number of fluorinated hydrocarbons are also now commercially available, and except for their expense, these appear to be desirable solvents.

The use of liquid propane, under pressure, has been proposed by Rosenthal and Trevithick.[158, 159, 160] The same authors reported[161] experiments suggested by German Patent

163,057, claiming the use of liquid carbon dioxide as an extracting solvent. It was concluded that liquid carbon dioxide has no solvent power for cottonseed oil. Obviously, it would also be of no use for extracting soybean oil.

Attention has recently been focused upon the use of solvents which exhibit two-liquid immiscibility with soybean oil. One such solvent is ethyl alcohol which dissolves the oil completely, at elevated temperatures, but in which the oil displays only limited solubility at room temperature. Such solvents are of interest because of their ability, in some cases, to dissolve selectively the more highly unsaturated portions of the oil. The use of sulfur dioxide, in this connection, has been patented.[61, 72, 85] In more recent patents, Freeman [74] claims the use of furfural and other liquids for the same purpose.

Hot Alcohol Extraction Process

The extraction of soybeans, by means of alcohol, was intensively investigated by Sato and coworkers,[162, 163, 164, 165] Okano and coworkers,[141] Ohtomo,[142] Mahino,[132] Iwasa,[133] and others.[50, 110, 111, 112] Based principally on the results of the earlier studies, a plant was erected, in Dairen, by the Manchuria Soybean Industry Company, for the alcoholic extraction of soybean oil and meal.

When soybean oil is dissolved in absolute ethyl alcohol at temperatures higher than about 150° F., a homogeneous solution is obtained. Upon cooling, two layers form, a lower one consisting chiefly of soybean oil with a small amount of alcohol and an upper layer which is mainly alcohol, containing a small amount of oil. The relative amounts of the two layers and their compositions depend upon the original solvent-oil ratio, the proof of the alcohol, and the temperature.

The plant at Dairen has a daily capacity of approximately 100 tons of beans which are processed in a battery of rotary extractors. The solvent is 99.8 per cent ethyl alcohol which is dehydrated at the plant. The beans are selected, cleaned, and, if necessary, they are warmed to a temperature of 85 to 105° F., before flaking. Since absolute ethyl alcohol is a dehydrating agent and loses its solvent power toward soybean oil in the presence of water, the flaked beans are dried to a moisture content of 3 per cent. They are then charged into the extraction battery and leached with the alcohol at a temperature of 175 to 180° F., under pressure.

The resulting miscella is cooled to about 75° F. and pumped into a conical separating tank where oil, containing 5 per cent alcohol, collects in the bottom. It is drawn off, and the solvent is removed in an evaporator.

The recovered oil is of semi-refined quality, having a light yellow color (30Y, 3R, 25 mm cell) and an acid number of 0.14 to 0.20. It has a salty taste and can be used for edible products, without further refining, although it is ordinarily further treated with fuller's earth and deodorized under vacuum.

The supernatant alcohol, in the settling cone, is returned to the extraction system, or, when it becomes too contaminated with water or non-oil extractables, it is transferred to a still for recovery of the by-products and subsequent rectification of the alcohol. During the evaporation in the still, sugars crystallize out, and by adding sulfuric acid, it is possible to recover saponins. Finally, phosphatides are salted out, 55 to 60 per cent pure. The residual meal contains 0.5 to 1.0 per cent oil and requires no refining for use in foodstuffs such as "miso," "shoyu," "ajinomoto," etc. It reportedly commands a price 25 per cent higher than meal produced by other methods.

The principal advantage of the alcohol-extraction method is the ease of by-product recovery. However, the American market, for the above-named by-products, is not highly developed and there has, therefore, been little incentive toward the introduction of the process into this country. The cost of alcohol, relative to that of hydrocarbons, the relatively high latent heat of evaporation of ethyl alcohol, and the high initial cost of the equipment are additional deterrents.

Extractor Design Data

The literature contains practically no data on the rates of extraction of soybean oil under various conditions, on the concentration of miscellas in equilibrium with partially extracted beans, on the diffusivity of soybean oil in various solvents under various conditions, etc. In other words, extractor design is now based almost entirely upon experience rather than upon any mathematical analyses of the processes taking place in the equipment. Many methods of approach to an analytical solution of problems in continuous extraction have been suggested. Among them, the solutions of Elgin [64] and Ravenscroft [149] are worthy of note. A simplified analysis as well as a detailed description of extraction of many types of solid materials is given by Donald.[57]

HYDRAULIC PRESSING

HYDRAULIC presses, or their more primitive, hand- or animal-powered counterparts, are used almost entirely by the Manchurian soybean oil industry.[12]

In the more remote, interior districts of that country, some small mills still employ presses which are actuated by hand-driven wedges. The beans are first crushed into wafers beneath a large, granite millstone, as shown in Figure 26, and then placed in coarse sacks, over a wooden grating which is laid upon pots of boiling water and steamed for about 15 minutes. The resultant mass is spread out in circular frames about six inches deep. Five of these frames are placed one above the other, in a vertical press, consisting of four upright posts, with cross-beams at the top and bottom. Pressure is applied by means of wedges driven between the cross-beams and beams placed on top of the frames, and the oil is thus expressed. One of these primitive installations is shown in Figure 27.

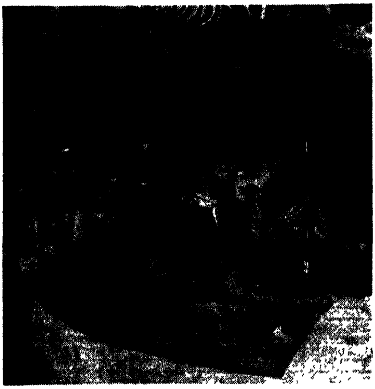

FIGURE 26

Crushing soybeans, preparatory to steaming and pressing for oil, in a primitive type of mill. On the left is a vat over which the crushed beans are steamed, before they are placed in the oil press (Courtesy of W. J. Morse)

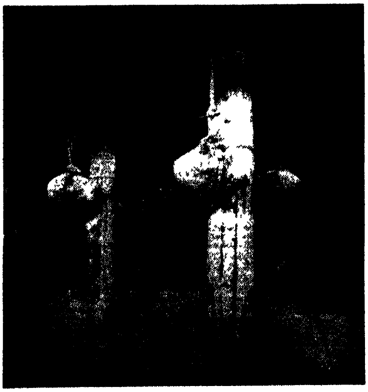

FIGURE 27

Old, wedge, Chinese oil presses used in remote villages of Manchuria (Courtesy of W. J. Morse)

The wedge press is one of three general types which produce so-called "round cakes." Most Manchurian mills employ the "screw system" in which hand-powered screws replace the wedges. Most of the operations, with the exception of the actual pressing, are more or less mechanized in the mills using this method. In the majority of the very large mills, particularly in the oil-producing centers such as Dairen, the screw system has been replaced by the hydraulic "round cake" process in which the screws are replaced by hydraulically operated rams. A few of the most modern mills employ the "plate cake" system which produces a flat, rectangular cake and which is essentially the same as the hydraulic methods used in the United States. An installation of round-cake, screw-type presses is shown in Figure 28.

The American soybean industry has, for the most part, abandoned hydraulic pressing, because of the relatively higher labor costs. There are, however, a considerable number of cottonseed mills and some linseed oil mills which use their equipment, wholly or in part, to crush soybeans. Since cottonseed processing is considered to be much more seasonal than that of soybeans, many mills run on soybeans, after the cottonseed crop has been consumed. The operations of a hydraulic mill require only slight modification in order to handle soybeans.

With soybeans, the steps of delintering and dehulling, as employed on cottonseed, are omitted. Beans are cleaned, weighed, and adjusted to a moisture content of approximately 12 per cent. They are then cracked by means of a disc huller or attrition mill and rolled into flakes by means of the usual five-high, crushing rolls which are universally used in hydraulic cottonseed oil mills.

The operation of a set of these rolls is illustrated diagrammatically in Figure 29. The five cylindrical rolls rest upon one another, and the bearings, upon which they rotate, are free to move up or down. The cracked material is fed at the top, and a series of scraper guides and cant-boards is so arranged on the rolls that the material passes downward, between successive pairs of rolls, in serpentine fashion. The pressure exerted on the beans, during any particular pass, is caused by the combined weights of the rolls above and, therefore, increases with each pass. The final product resembles irregularly shaped fragments of paper 0.007 to 0.008 inch thick. The purpose of this operation is to rupture as

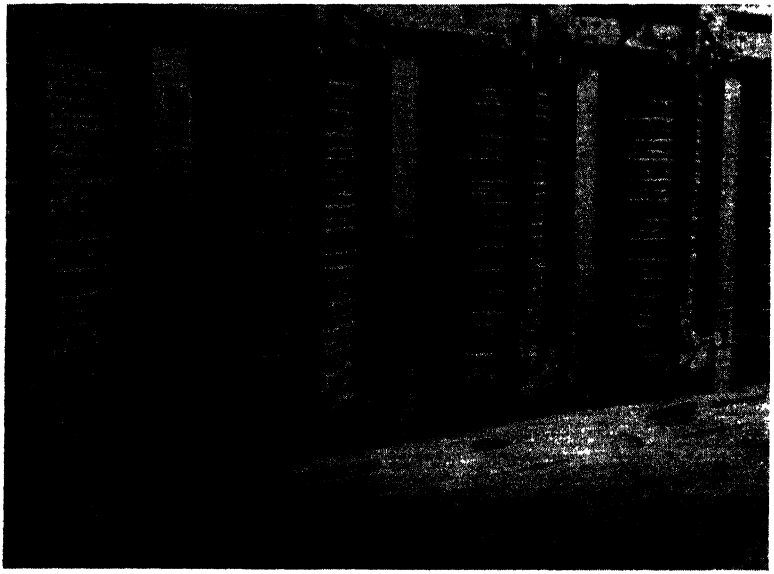

FIGURE 28

Screw presses in a soybean oil mill in Dairen, Manchukuo (Courtesy of W. J. Morse)

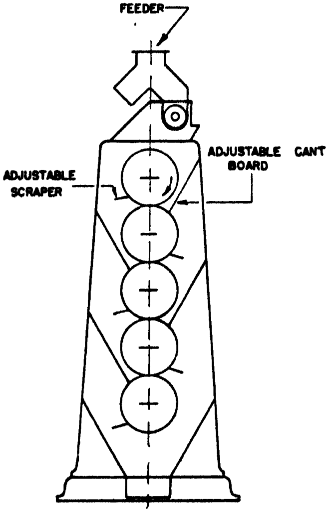

FIGURE 29

Five-high flaking rolls of the type used to prepare soybeans, cottonseed, and other oil-seeds for hydraulic crushing (sectional view)

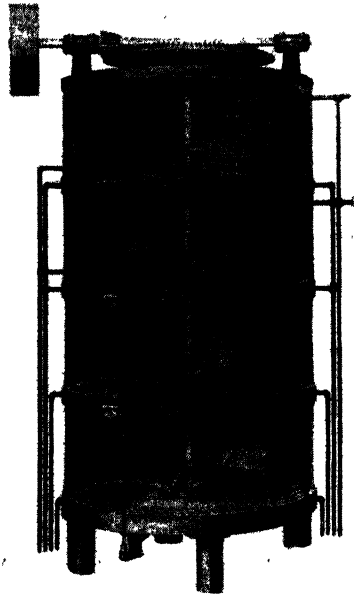

FIGURE 30

Phantom view of stack cooker used to prepare material for hydraulic pressing and for toasting solvent-extracted soybean flakes (Courtesy of French Oil Mill Machinery Company)

many as possible of the cell walls, in order to facilitate subsequent release of the oil.

The flaked beans are conveyed to a cooker, the usual type being the "stack cooker" commonly used in many types of oil-seed milling. Figure 30 shows a phantom view of one of these machines. It consists of several (usually 4 to 6) steam-jacketed, cylindrical kettles, stacked one above the other. A rotating central shaft extends vertically through all the compartments and has scraper arms attached. The shaft and arms carry ports to permit admission of moisture. Steam-jackets are provided not only on the sides, but also between the compartments, and the separate kettles are connected by damper-controlled doors which permit the charge to fall from one pan to another. The bean flakes are admitted at the top and work downward through the separate compartments, emerging from the lowest in a thoroughly cooked condition. The flakes are moistened to 12 to 15 per cent moisture content, before admission to the cooker, and during the cooking process, which lasts 70 to 90 minutes, the moisture content is reduced to 6 to 8 per cent. Although a higher moisture content tends to release the oil somewhat more easily, it imparts too soft a consistency to the cooked material for efficient pressing and results in rapid destruction of press cloths.

The cooker discharges into a hydraulically operated cake former which molds the hot material into a slab about 2 inches thick, 14 inches wide, and 3 feet long, and wraps it in a thick cloth, made of human hair or a special grade of wool. A typical cake former is shown in Figure 31. The cakes are placed into the boxes or between the plates of a hydraulic press, each press having approximately fifteen boxes or plates. A complete box type of press is shown in Figure 32. Figure 33 is a closer view of several press boxes. Boxes are used in mills which normally process cottonseed, and the plate type of press is found mainly in linseed mills. In the latter type, the plates have heavy rope mats on their surfaces. The cakes, encased in press cloths, are placed between the heavy mats on the plates. Pressure is applied to the cakes, and when the pressure of the oil in the hydraulic cylinder reaches 500 pounds, an automatic change-valve switches the system to a high-pressure pump. The ultimate pressure used is 4,000 to

4,500 pounds per square inch on a sixteen-inch-diameter ram and amounts to about 1,600 pounds per square inch at the cake. The pressing cycle consists of (1) drainage period of 15 to 30 minutes and (2) emptying and refilling the press, the latter operations requiring 8 to 10 minutes in all.

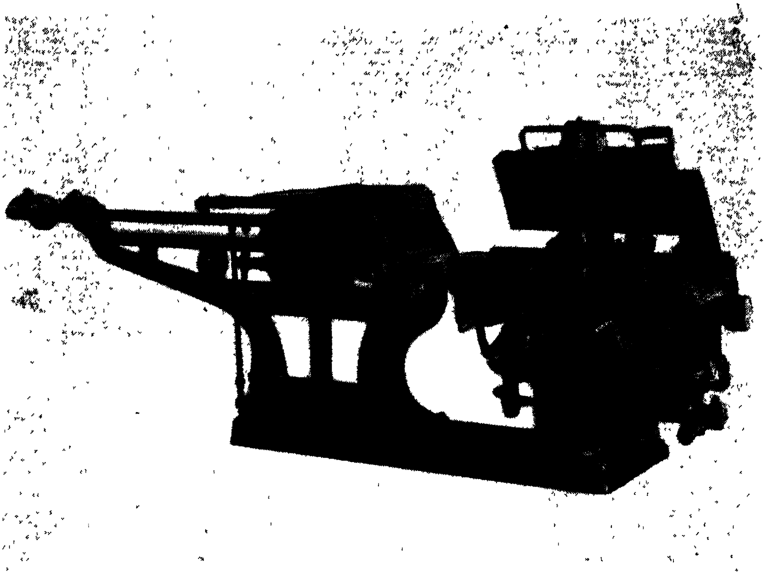

FIGURE 31

Cake former in which cooked soybean flakes are molded into flat cakes and wrapped in cloths, preparatory to hydraulic pressing (Courtesy of French Oil Mill Machinery Company)

The pressed cakes, still wrapped in the press cloths, are run through a cloth stripper, and the cloths are reused. The pressed slabs are passed through a cake trimmer which removes the less-thoroughly pressed edges to be reprocessed.

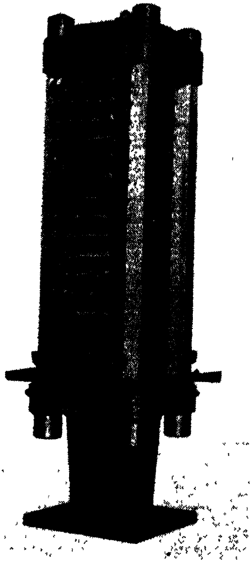

FIGURE 32

A hydraulic press

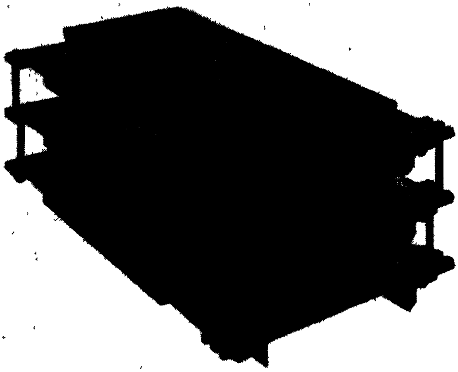

FIGURE 33

Hydraulic press boxes

(Courtesy of French Oil Mill Machinery Company)

The slabs of cake are fed to a cake breaker and then ground into meal in an attrition mill.

Cage presses, too, are used, to a small extent, on soybeans. Each press consists of a vertical, cylindrical pressing cage, composed of closely-spaced, steel bars or slotted, steel plates, into which a hydraulic ram is forced from below. The cages are filled with loose bean flakes from the top, as delivered from the cooker, a heavy cover is locked into place, and pressure is applied to the ram. After the drainage period, the cover is removed and the ram is further raised to discharge the press. It is customary to employ several cages, all fed from the same cooker. The cage type of press is used in mills which process special materials or a wide variety of oilseeds, because it develops much higher unit pressures on the oil-bearing material than can be realized in either the box or plate type of presses.

In a hydraulic press room, a great deal of manual labor is required for operating the cake former, carying cakes from the former to the presses and from the presses to the cloth stripper, loosening pressed cakes from the press boxes or plates, and operation of the cloth stripper and cake trimmer. In the more modern, continuous press installations and solvent extraction plants, the amount of hand labor is reduced to a minimum and the operating costs appear to be correspondingly lower. It is for this reason that there are few, if any, hydraulic mills, crushing soybeans, in the United States, except those which were originally built for processing other seeds, notably flaxseed and cottonseed.

Some observations of the effects of pressure, temperature, and time of pressing upon the rate of removal of oil from soybeans have been reported by Koo[119] who has also reported similar data for cottonseed and tung nuts.[118, 120]

MISCELLANEOUS PROCESSING METHODS

A PROCESS for removing oil from oil-bearing seeds, by bacterial action, has been patented and described by Beckman.[23, 24] The seeds are ground and mixed with water to produce a mush. Calcium carbonate is added to maintain a near-neutral pH, and the mixture is inoculated with Bacillus delbrueckia which is obtained from brewer's malt. The mixture is allowed to stand for 5 or 6 days at 50° C. while the organism attacks the sugars and produces lactic acid from them. The oil is released and floats to the surface. Although fair yields are obtained with copra and a few other oleaginous materials, Horovitz-Vlassova and Novotelnov [106, 107] report that they were unable to make the process work on soybeans, cottonseed, linseed, corn germs, and similar materials. The latter authors ascribe the release of the oil to the penetration of lactic acid into the cells whereas Beckman attributes it to the action of enzymes which are produced simultaneously with the lactic acid and which attack the proteins, degrading them into amino acids.

David and Felizat [52] have patented a method for extracting oil by beating the finely ground oil-seeds with water and floating out the oil. In their process, the comminuted materials are mixed with an alkaline solution, and the cellulosic constituents of the resulting slurry are removed by successive washings on a screen. The filtrate contains starch granules (if the particular oil-seeds contain starch) in suspension, proteins in a peptized form, and emulsified oil. The starch is separated by a relatively mild centrifugal treatment, and the oil is then removed in high-speed centrifuges. The protein is recovered by acid precipitation.

The use of a pulp beater, for a similar purpose, has been described by Freise.[75] In his experiments, a yield of 95 per cent of the oil, contained in soybeans, was obtained by feeding them at 40° C. through an experimental beater, at a density of 5 to 8 per cent. The power consumption was less than 2 kilowatt hours per bushel, and the filtered oil was said to be of good quality.

SOY FLOUR

CONSIDERABLE quantities of soy flour are produced by milling whole soybeans or the oil-free meal. It is used principally in the manufacture of sausage, dog food, miscellaneous meat products, and in bakery goods. In the production of bread, it is mixed with wheat flours in various proportions.

In the manufacture of soybean flour, it is necessary to remove the hulls, and this can be accomplished by subjecting cracked soybeans to an aspirating or a centrifugal treatment. It is also necessary to remove the beany flavor, generally associated with ground soybeans. Several "debittering" processes are referred to by LeClerc.* For the most part, they comprise treatment with heat, steam, or inert gases at elevated temperatures, often under vacuum or in the presence of an inert, protective coating of oil.

COST OF PROCESSING SOYBEANS

NO ATTEMPT will be made, in this discussion, to furnish costs of erecting and operating soybean mills, since information on this subject can more adequately be furnished by equipment manufacturers. Data on the items of expense, incident to soybean crushing, have been published by Sweeney and Arnold,[185] and by Torri,[191] as well as in various trade journals.[15, 21] However, what appear to be more accurate figures, for the bare costs of installing and operating both

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* J. A. LeClerc, *Partial list of processes for removing the bitter taste from soybeans,* U. S. Dept. of Agriculture, Bur. of Chemistry and Soils, Food Research Division, 1 p., October 11, 1938 (mimeographed).

solvent and continuous press types of mills, have more recently been tabulated by Bilbe.[52] In addition, the trade journals have published a number of descriptions of modern soybean mills.[13, 16, 19, 20]

For the convenience of those interested, Table 19 is appended, listing a number of manufacturers of soybean processing equipment. It is to be understood that the products of these manufacturers are not recommended more highly than those of other manufacturers who might be in the same business. No discrimination is intended nor is any guarantee of completeness implied. It must be realized that such a list is subject to continual change, however.

TABLE 19

MANUFACTURERS OF SOYBEAN PROCESSING EQUIPMENT

Continuous presses:
- V. D. Anderson Company, Cleveland, Ohio
- French Oil Mill Machinery Company, Piqua, Ohio

Hydraulic pressing equipment:
- French Oil Mill Machinery Company, Piqua, Ohio
- Davidson-Kennedy Company, Atlanta, Georgia
- Buckeye Iron and Brass Works, Dayton, Ohio

Continuous countercurrent solvent extractors:
- French Oil Mill Machinery Company, Piqua, Ohio
- Allis-Chalmers Manufacturing Company, Milwaukee, Wisconsin
- Sieck and Drucker, Inc. (Hildebrandt system), 9 South Clinton Street, Chicago, Illinois
- Detrex Corporation, 13005 Hillview Avenue, Detroit 27, Michigan
- The Wolf Company, Chambersburg, Pennsylvania
- Research Engineers, Post Office Box 1791, Houston, Texas
- Blaw-Knox Company, Post Office Box 1198, Pittsburgh, Pennsylvania

Milling equipment:
- Allis-Chalmers Manufacturing Company, Milwaukee, Wisconsin
- B. F. Gump Company, 441 South Clinton Street, Chicago, Illinois
- Great Western Manufacturing Company, Leavenworth, Kansas

Mill construction contractors:
Newell Construction and Machinery Company, Cedar Rapids, Iowa
Jones-Hettelsater Construction Company, 1012 Baltimore Ave., Kansas City, Missouri
James Stewart Corporation, 343 South Dearborn St., Chicago, Illinois
Ryan Construction Company, 2806 Taylor St., Omaha, Nebraska

In Table 20, there are listed those oil mills, in the United States and Canada, which may be classified as full- or part-time soybean mills.

TABLE 20

SOYBEAN PROCESSING MILLS IN THE UNITED STATES

The following list of soybean processing mills is divided into three parts: (1) mills in which soybeans regularly constitute the bulk of the throughput, (2) mills which are currently under construction or whose construction is being seriously considered, and (3) mills which are engaged in soybean processing temporarily or part time, or which have otherwise participated in the soybean program by signing a soybean processor contract. It must be realized that changes are occurring very rapidly at the present time, throughout the entire soybean processing industry.

Solvent extraction plants in group No. 1 are designated with an asterisk (*). Many of the solvent-type mills also contain expellers and screw presses.

After the name of each mill in group No. 1, the letter S, M, or L is used to designate whether it is a small, medium, or large installation. These ratings are only approximate and divide mills into three capacity groups: S, capacities less than 50 tons of soybeans per day; M, capacities between 50 and 200 tons per day; and L, capacities over 200 tons per day.

This list is furnished for the convenience of those interested in the soybean industry, but no guarantee of accuracy or completeness is implied, nor is any discrimination intended.

1. Mills Specializing in Soybeans

Arkansas:		
	West Memphis:	Arkansas Mills, Inc. (S)
	Wilson:	Wilson Seed and Feed Company (S)
California:		
	Oakland:	Albers Brothers Milling Company (S)

Illinois:		
	Bloomington:	Funk Brothers Seed Company (M)
	Cairo:	Swift and Company (M)
	Champaign:	Swift and Company (L)
	Chicago:	Archer-Daniels-Midland Company (M)* The Glidden Company (L)* Norris Grain Company (S) Spencer Kellogg and Sons (L)
	Decatur:	Archer-Daniels-Midland Company (L)* Decatur Soy Products Company (M) Spencer Kellogg and Sons (L) A. E. Staley Manufacturing Company (L)
	Galesburg:	Galesburg Soya Products Company (M)
	Gibson City:	Central Soya Company, Inc. (L)
	Monmouth:	Ralph Wells and Company (S)
	Peoria:	Allied Mills, Inc. (L)
	Quincy:	Quincy Soybean Products Company (M)
	Springfield:	Illinois Soy Products Company (M)
	Taylorville:	Allied Mills, Inc. (M)
Indiana:		
	Decatur:	Central Soya Company, Inc. (L)*
	Indianapolis:	Evans Milling Company (M)
	Lafayette:	Ralston Purina Company (M)
	Marion:	Hoosier Soybean Mills, Inc. (M)
	Mellott:	Knowles and Sons, Processors (S)
	Windfall:	Elevators and Mills, Inc. (S)
Iowa:		
	Cedar Rapids:	Honeymead Products Company (M)* Iowa Milling Company (M)
	Centerville:	Standard Soybean Mills (M)
	Clinton:	Clinton Company (M)*
	Des Moines:	Spencer Kellogg and Sons (M) Swift and Company (M)
	Fayette:	Wilbur Bell, Inc. (S)
	Fort Dodge:	Plymouth Processing Mills (M)
	Gladbrook:	Central Iowa Soybean Mill (S)
	Iowa Falls:	Ralston Purina Company (M)
	Quimby:	Simonsen Soybean Mill (M)
	Sioux City:	Sioux Soya Company (S)
	Waterloo:	Soy Bean Processing Company (M)
Kansas:		
	Emporia:	Kansas Soy Bean Mills, Inc. (M)

Kentucky:		
	Henderson:	Ohio Valley Soy Bean Cooperative Association (M)
	Louisville:	Buckeye Cotton Oil Company (L)*
	Owensboro:	Owensboro Grain Company (S)
Michigan:		
	Dearborn:	Ford Motor Company (M)*
	Milan:	Ford Motor Company (S)*
	Saline:	Ford Motor Company (S)*
Minnesota:		
	Mankato:	Mankato Soya Products Company (S)
	Minneapolis:	Archer-Daniels-Midland Company (S)
Missouri:		
	Galesburg:	Spring River Mill (S)
	St. Joseph:	Dannen Mills (M)
	St. Louis:	Ralston Purina Company (M)
Nebraska:		
	Fremont:	Pete Marr Soybean Processing Company (S)
	Omaha:	Allied Mills, Inc. (M)
New York:		
	Buffalo:	Spencer Kellogg and Sons (M)
	Oswego:	Oswego Soybean Products Corporation (M)
Ohio:		
	Cincinnati:	Drackett Company (M)*
	Circleville:	John W. Eshelman and Sons (M) Ralston Purina Company (M)
	Fostoria:	Swift and Company (M)
	Lexington:	Berea Milling Company (M)
	Marion:	Old Fort Mills, Inc. (M)
	New Washington:	Ohio Soya Company (S)
	Painesville:	A. E. Staley Manufacturing Company (L)
	Toledo:	Archer-Daniels-Midland Company (L) Toledo Soybean Products Company (M)
	Wooster:	Soya Processing Company (M)
Pennsylvania:		
	Jersey Shore:	Pennsylvania Soy Bean Cooperative Association (S)
Tennessee:		
	Memphis:	Buckeye Cotton Oil Company (M)
Virginia:		
	Norfolk:	Davis Milling Company (S)

	Portsmouth:	Allied Mills, Inc. (M) I. F. Laucks, Inc. (S)
Wisconsin:		
	Milwaukee:	Archer-Daniels-Midland Company (M)

2. Soybean Mills Under Construction or Contemplated

Illinois:		
	Colchester:	Colchester Milling Company
	Nashville:	Huegely Elevator Company
	Pana:	Shellabarger Grain Products Company
	Rock Falls:	Sterling Soybean Company
Indiana:		
	Danville:	Hendricks County Farm Bureau Cooperative Association, Inc.
	Shelbyville:	Indiana Grain Cooperative
	Vincennes:	Indiana Grain Cooperative
	Wabash:	Indiana Grain Cooperative
Iowa:		
	Belmond:	General Mills, Inc.
	Clinton:	Pillsbury Feed Mills
	Dike:	Farmers Cooperative Company
	Dubuque:	Dubuque Soy Products Company
	Eagle Grove:	Boone Valley Cooperative Processing Association
	Fairfield:	Fairfield Soybean Mill
	Hubbard:	Farmers Cooperative Elevator Company
	Manley:	North Iowa Cooperative Processing Association
	Martelle:	Farmers Cooperative Elevator Company
	Muscatine:	Muscatine Processing Corporation
	Plainfield:	Roach Soybean Mill
	Ralston:	Farmers Cooperative Association
	Redfield:	Iowa Soya Company
	Sac City:	Williams Feed Mill
	Sheldon:	Big Four County Cooperative Processing Association
	Spencer:	Honeymead Products Company
	Stratford:	Hamilton County Cooperative Association
	West Bend:	West Bend Elevator Company
Kansas:		
	Hiawatha:	J. J. Thomson and Son
	Kansas City:	Kansas Soybean Mills, Inc.

	Wichita:	Soybean Mills, Inc.
Minnesota:		
	Preston:	Wayne Fish and Company
	Worthington:	Honeymead Products Company
Missouri:		
	Kennett:	Hemphill Soy Products Company Sikeston Cotton Oil Mill
	Mexico:	Missouri Farmers Association Cooperative Grain and Feed Company
	St. Louis:	Blanton Company
Nebraska:		
	Lincoln:	Gooch Milling Company
North Dakota:		
	Grand Forks:	North Dakota Mill and Elevator
Ohio:		
	Springfield:	Farm Bureau Terminal Grain Elevator
South Dakota:		
	Sioux Falls:	Western Soybean Mills

3. *Temporary and Part-Time Soybean Mills*

Alabama:		
	Andalusia:	Southern Cotton Oil Company
	Birmingham:	Birmingham Oil Mill Farmers and Ginners Cotton Oil Company
	Boaz:	Elrod and Brock Oil Mill
	Dothan:	Dothan Oil Mill
	Enterprise:	Enterprise Cotton Oil Company
	Eufaula:	Eufaula Cotton Oil Company
	Headland:	Home Fertilizer and Cotton Oil Company
	Montgomery:	Buckeye Cotton Oil Company Southern Cotton Oil Company Swift and Company
	Ozark:	Mutual Cotton Oil Company
	Selma:	Buckeye Cotton Oil Company
	Sylacauga:	Southern Cotton Oil Company
	Uniontown:	Buckeye Cotton Oil Company
Arkansas:		
	Ashdown:	Temple Cotton Oil Company
	Blytheville:	Swift and Company Oil Mill
	Camden:	Camden Milling Company
	Fort Smith:	Cherokee Cotton Oil Company
	Helena:	Helena Cotton Oil Company

	Little Rock:	Buckeye Cotton Oil Company
		Rose City Cotton Oil Company
		Southern Cotton Oil Company
		Swift and Company Oil Mill
	Morrilton:	Morrilton Cotton Oil Mill
	Newport:	Southern Cotton Oil Company
	Osceola:	Ralston Purina Company
	Temple:	Temple Cotton Oil Company
	Wilmot:	Southern Cotton Oil Company
California:		
	Berkeley:	The Glidden Company
	Buena Park:	The Glidden Company
	Fresno:	Producers Cotton Oil Company
	Long Beach:	Procter and Gamble Company
		Spencer Kellogg and Sons
	Los Angeles:	Pacific Nut Oil Company
		California Cotton Oil Corporation
	Wilmington:	Vegetable Oil Products Company
Florida:		
	Pensacola:	Southern Cotton Oil Company
Georgia:		
	Americus:	Americus Oil Company
		McCleskey Cotton Oil and Peanut Mill
	Arlington:	Arlington Oil Mills
	Ashburn:	Southland Manufacturing Company
	Athens:	Hodgson Oil Refining Company
		Southern Cotton Oil Company
	Augusta:	Planters Cotton Oil Company, Inc.
		Southern Cotton Oil Company
		Swift and Company
	Camilla:	Camilla Cotton Oil Company
	Carrollton:	Mandeville Mills
	Columbus:	Southern Cotton Oil Company
	Cordele:	Southern Cotton Oil Company
	Dawson:	Dawson Cotton Oil Company
		Southern Cotton Oil Company
	Dublin:	Southern Cotton Oil Company
	Elberton:	Elberton Oil Mills
	Macon:	Buckeye Cotton Oil Company
		Central Cotton Oil Company
		Southern Cotton Oil Company
	Madison:	Caldwell and Company
	Moultrie:	Taylor Oil Mills
	Pelham:	Pelham Oil and Fertilizer Company
	Rome:	Southern Cotton Oil Company
	Savannah:	International Vegetable Oil Mill
		Southern Cotton Oil Company

	Sylvania:	Screven Oil Mill
	Thomasville:	Farmers Products Company
	Tifton:	Southern Cotton Oil Company
	Valdosta:	Southern Cotton Oil Company
	Washington:	Pope Manufacturing Company
Louisiana:		
	Alexandria:	Independent Mill and Gin Company
	Arcadia:	Arcadia Cotton Oil and Manufacturing Company
	Gretna:	The Southern Cotton Oil Company
	Lafayette:	Peoples Cotton Oil Company
	Minden:	Minden Cotton Oil and Ice Company
	Natchitoches:	Natchitoches Oil Mill, Inc.
	Opelousas:	Cotton Products Company, Inc.
	Shreveport:	Caddo-DeSoto Cotton Oil Company Southland Cotton Oil Company
	Tallulah:	Tallulah Oil Mill and Gin
	West Monroe:	Union Oil Mill, Inc.
Minnesota:		
	Minneapolis:	Northwest Linseed Meal Company
Mississippi:		
	Belzoni:	Humphreys County Oil Mill
	Brookhaven:	Refuge Cotton Oil Company
	Clarksdale:	Planters Manufacturing Company
	Corinth:	Buckeye Cotton Oil Company
	Greenville:	Greenville Oil Works Refuge Cotton Oil Company
	Greenwood:	Buckeye Cotton Oil Company Planters Oil Mill
	Vicksburg:	Refuge Cotton Oil Company
	Indianola:	Sunflower Cotton Oil Company
	Jackson:	Buckeye Cotton Oil Company
	Kosciusco:	Planters Oil Mill and Gin Company
	Leland:	Leland Oil Works
	Newton:	Newton Oil Mill
	Port Gibson:	Port Gibson Oil Works
	Rosedale:	Refuge Cotton Oil Company
	Shelby:	Shelby Oil Mill
Missouri:		
	Portageville:	Swift and Company
	Sikeston:	E. P. Coleman and Company Sikeston Cotton Oil Mill, Inc.
New Jersey:		
	Edgewater:	Archer-Daniels-Midland Company Spencer Kellogg and Sons
North Carolina:		
	Benson:	Benson Oil Mill

	Charlotte:	Buckeye Cotton Oil Company
		Southern Cotton Oil Company
	Clayton:	Central Oil and Milling Company
	Farmville:	Farmville Oil and Fertilizer Company
	Fayetteville:	The Southern Cotton Oil Company
	Fremont:	Fremont Oil Mill Company
	Goldsboro:	Southern Cotton Oil Company
	Hertford:	Southern Cotton Oil Company
	Kinston:	Lenoir Oil and Ice Company
	Laurinburg:	Laurinburg Oil Company
	Maxton:	Maxton Oil and Fertilizer Company
	Monroe:	Southern Cotton Oil Company
	New Bern:	New Bern Oil and Fertilizer Company
	Raeford:	Hoke Oil and Fertilizer Company
	Raleigh:	Buckeye Cotton Oil Company
	Rocky Mount:	Planters Cotton Oil and Fertilizer Company
		Southern Cotton Oil Company
	Selma:	Southern Cotton Oil Company
	Shelby:	Southern Cotton Oil Company
	Spring Hope:	Spring Hope Oil Mill
	Tarboro:	The Southern Cotton Oil Company
	Wadesboro:	Southern Cotton Oil Company
	Wilmington:	Wilmington Oil and Fertilizer Company
	Wilson:	Farmers Cotton Oil Company
		Southern Cotton Oil Company
Ohio:		
	Ivorydale:	Procter and Gamble Company
Oklahoma:		
	Altus:	Altus Cotton Oil Mill
	Anadarko:	Anadarko Cotton Oil Mill
	Ardmore:	Ardmore Cotton Oil Company
	Chickasha:	Chickasha Cotton Oil Mill
	Elk City:	Elk Cotton Oil Company
	Guthrie:	Guthrie Cotton Oil Company
	Lawton:	Chickasha Cotton Oil Company
	McAlester:	McAlester Cotton Oil Company
	Oklahoma City:	Southland Cotton Oil Company
		Terminal Oil Mill Company
	Shawnee:	Shawnee Cotton Oil Mill
	Tulsa:	Chickasha Cotton Oil Company
	Wynnewood:	Southland Cotton Oil Company
Pennsylvania:		
	Philadelphia:	Bisbe Linseed Oil Company

South Carolina:	Bishopville:	Palmetto Oil Company
	Camden:	Southern Cotton Oil Company
	Cheraw:	Carolina Oil Mill
	Columbia:	Southern Cotton Oil Company
	Lancaster:	Lancaster Cotton Oil Company
	Leesville:	Leesville Oil Mill Company
	Marion:	Marion Cotton Oil Company
	Ninety Six:	Ninety Six Manufacturing Company
	Spartanburg:	Caldwell and Company
	Union:	Union Oil Mills
Tennessee:	Colliersville:	Farmers Agricultural Products Company
	Memphis:	DeSoto Oil Company
		Southern Cotton Oil Company
		Swift and Company Oil Mill
	Nashville:	Nashville Cotton Oil Mill Corporation
	Tiptonville:	Lake County Oil Mill
Texas:	Amarillo:	Amarillo Cotton Oil Company
	Athens:	Athens Oil Mill
	Austin:	South Texas Cotton Oil Company
	Ballinger:	West Texas Cotton Oil Company
	Brownfield:	West Texas Cotton Oil Company
	Caldwell:	Womble Cotton Oil Company
	Childress:	Childress Cotton Oil Company
	Clarksville:	Clarksville Cotton Oil Company
	Commerce:	Commerce Oil Mill
	Corsicana:	Southland Cotton Oil Company
	Crockett:	Crockett Cotton Oil Company
	Dallas:	Planters Cotton Oil Company
		Trinity Cotton Oil Company
	Ennis:	Planters Cotton Oil Mill
	Gatesville:	Coryell County Cotton Oil Company
	Gilmer:	Gilmer Cotton Oil and Fertilizer Company
	Greenville:	Greenville Cotton Oil Company
	Hallettsville:	Lavaca Oil Company
	Hearne:	South Texas Cotton Oil Company
	Henderson:	Oil Mill and Fertilizer Works
	Honey Grove:	Honey Grove Cotton Oil Company
	Houston:	Fidelity Products Mill
		Houston Cotton Oil Company
		Houston Heights Mill
		Magnolia Provision Company

Hubbard: Union Oil Mill
Kaufman: East Texas Cotton Oil Company
Longview: Longview Cotton Oil Company
Marlin: Marlin Oil Company
Marshall: Marshall Cotton Oil Company
Mart: Brazos Valley Cotton Oil Company
Mexia: Munger Cotton Oil Company
Midlothian: Producers Cooperative Mill
Mineola: Wood Valley Cotton Oil Company
Mount Pleasant: Mount Pleasant Oil Mill
Paris: Lamar Cotton Oil Company
Southland Cotton Oil Company
Plainview: West Texas Cotton Oil Company
Richmond: Richmond Cotton Oil Company
Rule: Rule Yaton Cotton Oil Company
San Angelo: West Texas Cotton Oil Company
San Antonio: Alamo Cotton Oil Company
San Marcos: San Marcos Oil Mill
Sealy: Sealy Oil Mill and Manufacturing Company
Seguin: Seguin Cotton Oil Company
Seymour: West Texas Cotton Oil Company
Shamrock: West Texas Cotton Oil Company
Sherman: Kimbell Oil Mill
Sulphur Springs: Sulphur Springs Cotton Oil Company
Taylor: South Texas Cotton Oil Company
Temple: Southland Cotton Oil Company
Terrell: East Texas Cotton Oil Company
Texarkana: Farmers Cotton Oil Company
Texarkana Cotton Oil Company
Waco: Brazos Valley Cotton Oil Company
Waco Cotton Oil Company
Waxahachie: Southland Cotton Oil Company
Weatherford: Planters Cotton Oil Company
Wharton: Peoples Cotton Oil Company
Wichita Falls: Wichita Falls Cotton Oil Company
Winnsboro: Farmers Cotton Oil Company
Wolfe City: Ne-Tex Cooperative Mill

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PRODUCTION AND REFINING OF PHOSPHATIDES

THE industrial production of soybean phosphatides, on a large scale, has been a relatively recent development which resulted primarily from the introduction and general processing of Manchurian soybeans by German oil mills during the 1920's, and as a further consequence of which, the process and apparatus have been largely developed in Germany.

Since about 1900, many patents have been granted, especially in Germany, covering the recovery and purification of phosphatides from various plant materials, and particularly from oil-seeds and oil-bearing materials. The raw materials have comprised wheat, corn, rye, and barley germs,[207] and lupins,[49] peas,[99] soybeans, and other legumes. Ethyl and methyl alcohol were principally employed as solvents, and acetone and salt solutions as purification agents.

With the development of solvent extraction methods, in Germany, for the production of soybean oil, the industry was confronted with the problem of disposing of the sludge which separated from the oil when it was clarified by settling or other means. This sludge or foots comprised an emulsion of phosphatides, phytins, bitter principles (glucosides), sterols, mucilaginous substances, finely divided meal, water, and oil. Relatively large volumes of this sludge or foots accumulated at the oil mills. This disagreeable, malodorous mass soon underwent decomposition, with the formation of even more disagreeable odors, and its disposition became a serious problem to the industry.

Two groups of patents, each covering different processes for the recovery of phosphatides and oil from these sludges or foots, were granted about the same time to the firm of J. D. Riedel Akt.-Ges. and to the Hanseatische Mühlenwerke Akt.-Ges., respectively.

The process, covered by the patents of the J. D. Riedel Akt.-Ges.,[153, 154, 155, 156] was based primarily on the use of organic solvents for the extraction and purification of the phosphatides, contained in the by-product sludges, produced during the refining of soybean oil. It consisted of a series of steps wherein dehydration of the sludge in vacuum at 40 to 50° C. was followed by extraction and separation of the phosphatides and oil by means of methyl alcohol and acetone. A variation of the method comprised the following successive steps: extraction of the sludge with alcohol to remove the water, oil, and phosphatides; separation of the solvent and water by distillation of the extract; and removal of the oil and bitter principles from the phosphatide residue by washing it with acetone. In this method, the alcohol-insoluble phosphatides still remained in the residual sludge. In order to recover the alcohol-insoluble phosphatides, the sludge was reextracted with benzene, and the benzene extract treated with alcohol to precipitate the dissolved phosphatides.

The process never attained permanent industrial importance because of the development, at about the same time, of another process which was simpler, more efficient, and cheaper of operation. This second process, which was known as the "Bollmann Process," [32] soon assumed dominant importance in the industry and remains so at the present time. It obviates the use of solvents. The principal steps of the operation comprise removal of the solvent by distillation of the miscella, heating the residual oil, and treating it with wet steam, at 103° C. After about 15 minutes, the phosphatides begin to separate as a flocculent mass, containing oil and associated impurities.

The production and purification of soybean phosphatides have undergone various modifications and improvements since the process was first disclosed in the patent and scientific literature. In the original process, the solvent mixture, used for extracting the oil, consisted of alcohol and benzene,[31] although the use of other solvents was also claimed. Subsequent steps, in the purification of the recovered phosphatides, were described in later patents.[33, 35, 36, 151]

Because of the constant improvements, which were introduced in the industrial processing of phosphatides, and the consequent flow of patents pertaining thereto, the descriptions of the processes, which are found in the technical literature, vary somewhat in detail and are not always in accord with the practice actually followed at the time they were written.

Grün,[167] for example, described the process, as operated about 1935 at the plant of the Hanseatische Mühlenwerke Akt.-Ges., in Hamburg, somewhat as follows:

Soybeans are extracted in a Bollmann extractor with benzene, petroleum ether, or a mixture of the two, to which a little, or as much as 30 per cent, of alcohol has been added. The solvent is removed from the miscella by distillation, and the last traces removed by steaming. Additional water, usually in the form of steam, is admitted to the oil until precipitation of the phosphatides is complete, after which, they are separated from the oil by centrifuging. The separated phosphatides are transferred to distillation apparatus, with the possible addition of more water, and the water and odorous impurities removed by distillation under vacuum, at about

60° C. The distillation is continued until the residual phosphatides are freed from odor and bad flavor.[34] The product thus obtained contains 60 to 65 per cent of phosphatides. It is a brownish-yellow product of good odor and flavor. The Hansa-Mühle plant, in Hamburg, is said to have a daily capacity for the production of phosphatides from 1000 metric tons (35,000 to 40,000 bushels) of soybeans.

A somewhat similar description of the production of phosphatides is given by Horvath.[108]

Eichberg [63] gives a description of the process for the production of phosphatides which is more nearly in accord with present practices both in the United States and abroad. According to Eichberg and the patents cited by him, the process followed at present (1939) is as follows:

A single petroleum hydrocarbon solvent is used in the extraction of the oil from soybeans which contain 1.5 to 3.0 per cent phosphatides. The use of the single solvent does not remove all of the phosphatides from the beans, since the meal is found to contain about 1.0 per cent of residual phosphatides. However, the use of a single solvent yields a product which is relatively free of carbohydrates and entirely free of bitter substances, the presence of which, according to Sorensen and Bean,[182] results from the use of alcohol in the extraction process.

The oil, containing the dissolved phosphatides, is agitated with water at about 75 to 80° C. in order to flocculate the phosphatide emulsion, which operation requires about three quarters of an hour. The flocculent emulsion is separated from the oil by centrifuging, and the separated phosphatides, which actually consist of an emulsion of phosphatides, oil, and water, are subjected to vacuum distillation to remove the water and volatile odor and flavor constituents.[35] Simultaneously, they may be bleached with hydrogen peroxide,[36] or preferably dibenzoyl peroxide,[90] when it is desired to produce a light-colored product for certain special uses. The product thus obtained, which consists of a mixture of about 60 to 65 per cent phosphatides and 35 to 40 per cent soybean oil, is used, without further treatment, in a variety of products.

However, for use in certain products, and especially for use in the pharmaceutical and chocolate coating industry, further treatment is necessary. This treatment usually consists simply of removing the soybean oil, or of removing the soybean oil and replacing it with another fat or oil. In order to accomplish this, the bleached and dried phosphatide-oil mixture is agitated with acetone, in which the oil is soluble. The supernatant liquid consisting of a solution of oil in the acetone is drawn off from the undissolved phosphatides, and the acetone recovered by distillation.[89] The acetone-treated phosphatides are again treated under vacuum to remove the last traces of acetone and the oil-free product marketed for use in the pharmaceutical industry, or further treated for use in the chocolate coating industry. For the latter use, the product remaining after the removal of the bulk of the solvent, but prior to its complete removal by heating under vacuum,[151] is mixed with another oil, such as refined peanut oil, coconut oil, cocoa butter, or hydrogenated oils. The mixture of phosphatides and added oil is then subjected to vacuum and heat to remove the last traces of solvent. The finished product finds wide use in the preparation of chocolate coatings. The total production and consumption of soybean phosphatides, in the United States and abroad, is unknown, but a conservative estimate would be in the vicinity of ten thousand tons annually.

Various other processes have been proposed for the production and purification of phosphatides, but most of them have not found any appreciable industrial application. Among these other processes may be mentioned the cold solvent extraction proposed by Rewald,[150] which has for its object not only the recovery of undenatured phosphatides, but also the production of soybean meal with a minimum of denaturation of the proteins. Gensecke [78] proposed the use of acidified saline solutions for removing the phosphatides from the oil. Kelin and Tauboeck [117] proposed the use of silica gels and similar oxidic sols to recover phosphatides from the solvent, used to extract the dehydrated crude phosphatides. Gehrke [77] proposed the use of dehydration by means of glycerine, instead of vacuum distillation, for the separation of water from the crude phosphatides. The process of dehydration, with glycerine or concentrated aqueous sugar solutions, has been patented by the firm of Noblee and Thörl.[137, 138, 139] Schwieger [178] proposed a method for purifying crude soybean phosphatides which comprises extracting the sludge with a solvent to remove the oil, treating the residue, containing some residual solvent, with water, evaporating the water and residual solvent, and incorporating another carrier such as a carbohydrate in an aqueous solution. Other processes, pertaining to the separation of soybean oil phosphatides, have been patented by Ginn,[82] Kraybill,[122] Thurman,[187, 188, 189] Beck and Klein,[22] and others. None of them is used commercially.

PROCESSING SOYBEAN OIL FOR FOOD USES

SOYBEAN oil, as produced by the various processes of pressing and solvent extraction, contains variable quantities of free fatty acids, coloring matter, phosphatides, albuminous or mucilaginous substances, aldehydic, ketonic, and other odorous constituents which render it unsuited, in the crude state, for many purposes. It is necessary, therefore, to subject the oil to various refining operations for the reduction, or more or less complete removal, of these objectionable products. Since soybean oil, unlike most vegetable oils, finds use in both the edible and the drying oil fields, the necessary degree of refining may depend on the ultimate use to which it is destined. For use in the paint industry, it may be subjected to so-called mechanical refining only, whereas for use in varnishes and enamels, it is ordinarily alkali-refined in a manner similar to that employed for the production of an edible oil.

When mechanically refined, for use in the drying oil industry, the phosphatides and mucilaginous substances are removed by emulsifying the oil with hot water or steam, or sometimes with water, containing a small percentage of alkali or alkali salts, and subjecting the emulsion to centrifuging to separate the so-called "break" material.[168]

Neutralizing and Washing

For production of an edible oil, and for use in the production of certain products for the drying oil industry, soybean oil requires more drastic refining. This is usually effected by treatment of the oil with caustic soda. When first introduced into the United States, crude soybean oil from Manchuria was refined exactly as was cottonseed oil. The product was inferior and was not readily accepted by the food industry. About 1930, when domestic soybeans became available in considerable quantities, the methods used in refining corn oil were applied to soybean oil with marked improvement in the quality of the oil. Improvements in both equipment and the various operations of neutralization, washing, bleaching, winterizing, and deodorization followed rapidly with a constant improvement in the quality of the finished oil.[58]

The neutralization of the crude soybean oil is effected by both batch and continuous methods.[169, 130] In the former method, the neutralization is carried out by means of treatment with alkali in large, open-top, cylindrical tanks called refining kettles, which are equipped with variable-speed, controlled agitators, heating coils or steam jacket, sprays for introducing the alkali solutions, and a jacketed settling cone. Refining kettles, holding 20,000 pounds of oil, are not uncommon. The oil, maintained at 20 to 25° C., is emulsified with 12 to 14° Bé. caustic soda, in slight excess above that required to neutralize the free fatty acids. Heating is carried out with moderate stirring until the so-called "break" appears. The break consists of small particles of soap derived from the free fatty acids originally present in the crude oil, excess caustic soda, unsaponifiable matter, and other impurities. With continued heating and slow stirring, the small particles coalesce, and when a temperature of 65 to 70° C. is reached, they become fluid and tend to settle. Heating and stirring are discontinued at this point, and the soap stock is permitted to settle below the neutral oil. After settling in the refining kettle for 18 to 20 hours, the supernatant oil is drawn off. The neutralized oil is washed by stirring with 8 to 10 per cent of water, heated nearly to the boiling point, and again allowed to settle. After washing and drying, the oil is ready for bleaching or storage as may be desired. The soap stock is used for the production of free fatty acids or for various products of the detergent industry.

The batch process of neutralization has been superseded, to a great extent, by the continuous centrifugal method, especially in the United States where it is claimed that 80 to 90 per cent of the oil is refined by the latter method. In this process, crude oil is pumped to a feed tank, equipped with an agitator to insure thorough mixing and to avoid the introduction of large quantities of settlings to the refining apparatus, at any time. Caustic soda solution of requisite strength is contained in a separate tank. Oil, from the feed tank, is withdrawn and passed through a proportionometer, adjusted to deliver the proper ratio of oil to caustic soda. The oil and caustic soda, properly proportioned, leave the proportionometer by separate lines and are introduced into a high-speed mixer. The resulting emulsion is forced through a tubular steam heater where the temperature is raised to 60 to 65° C. The time of contact between the oil and lye, in the mixer, is less than a minute, and in the heater about two minutes, after which, the oil and soap stock are continuously separated in a high-speed centrifuge of the Sharples, DeLaval, or National Acme type. Figures 34 and 35 show installation of several such centrifuges.

The refined oil, from the centrifuge, contains less than 0.10 per cent of soap and less than 0.20 per cent of moisture, both of which must be removed by washing and drying in order to produce a stable oil of high quality. The refined oil, from the centrifuge, runs into a large receiving tank of 200 to 500 gallons capacity. The tank is equipped with steam coils and a temperature regulator to maintain the temperature of the contents at 70 to 80° C., as desired. As the

FIGURE 34

Battery of Sharples Super-Centrifuges, Soybean Oil Refinery, A. E. Staley Manufacturing Company, Decatur, Illinois (Courtesy of H. H. LaMent, The Sharples Corporation, Philadelphia, Pennsylvania)

neutral oil flows into the wash tank, hot water is continuously sprayed on its surface. The amount of water is maintained between 10 and 15 per cent of the weight of the neutral oil. The wash tank, which is either of the cone or dish-bottom type, is provided with an outlet, at the bottom, and a pipe line leading to a circulating pump of a capacity approximately three times as great as the net oil throughput. The pump circulates the hot oil and water mixture through a small elevated feed tank and back, through an overflow line, to the wash tank. The elevated feed tank is connected, by a feed header, to a battery of supercentrifuges. The feed line contains a float valve which opens only when the level in the wash tank has reached such a height that any unit volume of oil, which enters it, will remain in the system, in contact with the water for approximately ten minutes. Rapid circulation and mixing are maintained by the over-capacity

FIGURE 35

Battery of National Acme Centrifuges for continuous refining of soybean oil (Courtesy of The National Acme Company, Cleveland, Ohio) pump, since two-thirds of the mixture of oil and water, withdrawn from the bottom of the wash tank, are always returned through the overflow, the balance being withdrawn through the float valve to the supercentrifuge.

The oil and water mixture is continuously separated in the supercentrifuge, and the separated water, containing the soap, is run to the sewer. The oil is generally washed a second time by the same process, but at a higher temperature, usually 80 to 95° C. The discharged oil contains 0.4 to 0.5 per cent moisture which must be removed, as rapidly as possible, to prevent hydrolysis of the glycerides and destruction of antioxidants, during subsequent bleaching.

The removal of the moisture is effected by a process of continuous drying. The washed oil is run to a constant-level feed tank, from which, it is continuously fed in the form of a spray through a series of nozzles into the side of the vacuum chamber. A vacuum of about 28 inches is maintained in the chamber by means of a two-stage steam ejector and a barometric condenser. The oil spray is further broken up by a series of baffles to prevent entrainment, and the water vapor is exhausted by the ejectors. The washed and dried oil, containing 0.002 per cent soap and 0.05 per cent moisture, is continuously pumped from the drier and run to the bleach tanks or directly to storage, as desired.

Several methods are under investigation, especially in the United States, which have for their objective the refining of soybean oil by means of activated adsorbents, the process being a continuous, regenerative one. In common with all percolation processes, it possesses the following fundamental characteristics. The time of contact, between the oil and the adsorbent, is directly proportional to the depth of the bed and inversely proportional to the flow of oil through a bed of fixed cross section. The flow, in turn, is directly proportional to the cross sectional area of the column of adsorbent, and increases, although not in simple proportionality, with increasing pressure, increasing particle size, and decreasing depth of adsorbent. Decreasing particle size gives a more complete adsorption. Increasing temperature increases the flow by reducing the viscosity of the oil, but decreases the completeness of adsorption.

The Victor Chemical Works, Chicago, Illinois, have extensively investigated the adsorption refining of soybean oil by the use of activated tricalcium phosphate. Certain variables, mentioned above, have been fixed as a result of this work. For example, it has been determined that five times as much phosphatides are removed in the same column at 25° C. as can be removed at 65° C.

The optimum particle size of the adsorbent was found to be 20 to 30 mesh. Phosphatides and free fatty acids were found to be almost completely removed under optimum operating conditions, but the color was not greatly improved, since tricalcium phosphate has a low adsorption capacity for carotenoid pigments. When hexane was used as a carrier solvent for the oil, no appreciable effect was observed in the removal of phosphatides, but the flow of oil was considerably increased. The spent adsorbent, which holds approximately its own weight of oil and ten per cent of its weight of phosphatides, can be regenerated by extraction with a series of four solvents. The adsorbent is first washed with acetone to remove the oil, then with benzol-methanol (90 to 10) to remove the phosphatides, one per cent caustic soda in methanol to remove the fatty acids, and finally with methanol.

The regenerated adsorbent is identical, in behavior, to freshly prepared material, and the loss in adsorbent is negligible. For continuous refining, four towers are required.

The use of a "solid silicic acid foam," for mechanically removing phosphatides, mucilages, sterols, pigments, etc., from crude oils, has been proposed by Brewer and Kraybill.[48] The adsorbent is produced by treating an aqueous sodium silicate solution with carbon dioxide to produce a rigid gel which is broken into small granules, treating the product with hydrochloric acid in water to liberate carbon dioxide within the mass, and then washing and drying the resulting "solid foam."

The high loss of oil, resulting from conventional methods of alkali refining, has led to the investigation of numerous other processes for removing the free acids and other impurities from crude glyceride oils. Although there appear to be no commercial installations, at present, the method of extracting the impurities, by means of solvents, has attracted considerable interest. A liquid, which is immiscible with the oil, but in which the free fatty acids and other undesirable substances are soluble, can be passed through a liquid-liquid extraction apparatus, in counterflow to the oil, in order to effect a continuous purification. Various patents have covered the use of amines,[65, 123] furfural,[74, 190] alcohols,[30] and other substances for this purpose.

Another refining method, used to some extent in Europe, is the removal of free fatty acids and other volatile substances from the oil by vacuum steam distillation. The apparatus and procedure are not radically different from those described under deodorization, the essential operation being the passing of hot oil (200 to 280° C.), in thin films, over baffles or other surfaces, under vacuum, flowing countercurrently to a stream of superheated steam.

Bleaching

After the soybean oil is refined, washed, and dried, whether by the batch or continuous method, it is then bleached to remove most of the coloring matter.[170] To accomplish this, the washed and dried oil is run to a closed tank, equipped for vacuum operation and fitted with a heating coil and agitator. Since soybean oil is somewhat difficult to bleach, a mixture of acid-activated bleaching clay and activated carbon is added to the oil, when the temperature reaches 75 to 80° C. Heating and agitation, either at atmospheric pressure or under vacuum, are continued until the temperature reaches approximately 110° C., and these conditions are maintained for an interval of 15 to 30 minutes. A siliceous filter aid may be added to assist in the filtration. At the end of the bleaching period, the mixture is pumped through a filter press which retains the bleaching agent and adsorbed materials.

A number of the factors, affecting the bleaching characteristics of soybean oil, have been described by Robertson, Munsberg, and Gudheim.[157] The possible advantages of employing a countercurrent system of multiple contact bleaching were pointed out by Hassler and Hagberg.[95]

In plants, handling large volumes of soybean oil, the spent bleaching earth may be extracted to recover the oil which it retains.[176] Because of its content of semi-drying oil, the spent bleaching material is a distinct fire hazard. The bleached oil, from the presses, is collected and further processed for use in the food trade or used per se for certain non-edible products.

Hydrogenation

In general, the processing of crude soybean oil, into finished oils, consists of five steps: neutralization, washing, bleaching, hydrogenation, and deodorizing. The hydrogenation step is omitted in favor of winterizing, in the production of salad oils, but when the finished oil is to be converted into shortening, margarine, or similar products, it is ordinarily hardened after being bleached. The process is carried out by bubbling hydrogen gas through the hot oil, in the presence of a nickel catalyst, either in batches or by continuous operation, in order to saturate a substantial portion of the double bonds occurring in the fatty acid chains.

The complete hydrogenation process comprises a number of operations, the principal ones being:

1. Preparation of the catalyst
2. Manufacture of the hydrogen
3. Hydrogenation
4. Catalyst recovery

The methods, for carrying out the steps in the process, vary a great deal from one refinery to another, but the procedures for soybean oil are generally the same as those used on other edible oils. Since the general theory and technological applications of hydrogenation have been described in great detail, in the literature,[172, 66] the various steps in the hardening process will be mentioned only briefly.

Certain of the rare metals, such as platinum and palladium, are satisfactory hydrogenation catalysts, but practically all the commercial hardening, which is carried out by batch methods, is catalyzed by less expensive, colloidal nickel. The metallic catalyst can be prepared by either "wet" or "dry" methods, the former being the more commonly employed. In the wet method, a finely ground nickel salt, such as nickel formate or nickel carbonate, is added to the oil, and it is reduced to metallic nickel in colloidal form by passing a stream of hydrogen into the heated mixture. Since the temperature, at which the reduction is carried out, approximately 460° F., is injurious to the oil, it is customary to prepare "catalyst concentrates" by filtering the reduced nickel, washing it with fresh oil, and resuspending it in a small amount of fresh oil for addition to the large batches of oil in the hydrogenation converters. It is possible to reduce some mixed catalysts, such as 20 per cent copper and 80 per cent nickel, at lower temperatures so that the catalyst can be prepared directly in the oil to be hardened. The amount of catalyst required varies somewhat with the manner of preparation and the operating conditions, but it is generally between 0.1 and 0.5 per cent of the weight of oil.

When the catalyst is prepared by the dry reduction method, an insoluble nickel salt is precipitated upon an inert carrier. For example, nickel carbonate can be precipitated upon fuller's earth, by adding sodium carbonate to a suspension of the finely ground carrier, in a solution of nickel sulphate. The product is washed, dried, and reduced by heating it in a stream of hydrogen. It is preferable to carry out the reduction at the lowest practicable temperature in order to obtain a very active catalyst, 550 to 650° F. being typical operating temperatures. The catalyst thus formed is added to the oil with care to prevent exposure to the air.

In batch hydrogenation, the oil is charged into tall steel tanks which vary a great deal in details of construction. They are equipped with heating coils and with a "spider" or similar device for spraying hydrogen into the bottom of the tank. The hydrogen gas, in most refineries, is generated either electrolytically or by reducing steam by means of iron. The hydrogenators, or converters, are also often equipped with a stirrer. Purified hydrogen is passed through the oil, and unabsorbed gas is withdrawn from the top, recompressed to the appropriate pressure, and again injected into the converter. A wide range of temperatures and pressures is employed, although 270 to 300° F. and 20 to 30 pounds per square inch might be considered typical operating conditions. The hydrogenation is continued until samples, which are withdrawn, exhibit the proper melting point or iodine number, approximately 100° F. and 60 to 70, respectively, in the cases where the ultimate product is shortening. The catalyst is filtered out of the hydrogenated product, and the residual nickel is reclaimed. The hardened oil is then deodorized, often after treatment with additional bleaching earth, to bring about a final decolorizing.

Hydrogenation is also effected, to some extent, by continuous methods. In continuous installations, the catalyst chamber is a cylindrical cage in which there are packed nickel turnings or similar forms of nickel. The oil and hydrogen are pumped through the catalyst mass, under appropriate pressure and temperature conditions, and the hardening occurs while the oil is flowing through a series of these chambers. The spent catalyst is regenerated by anodic oxidation, followed by reduction with hydrogen, at a temperature of 250° C. The operation of continuous hydrogenation plants has been described by Manderstam.[129] The process is said to result in the formation of a higher proportion of isoöleic acid than is usually obtained in well regulated batch operations, and there is, consequently, less opportunity for its immediate introduction in this country.

The processes and derived products of hydrogenation of soybean oil have been the subject of numerous investigations, and a fairly voluminous literature has resulted therefrom. The effects of catalysts, temperature, and pressure have been principally investigated, especially with respect to the degree of hydrogenation, and the type of products formed. Low pressures and moderate temperatures ordinarily have been employed for the production of semi-hardened products for use in the edible oil industry, and high pressures and temperatures for the production of more completely hydrogenated products for other uses. For production of shortening, it is desirable to obtain as low an iodine number as possible, without hardening beyond the optimum consistency. Partial hydrogenation of linoleic acid, as an example, results in some products which are harder than others, i.e., isoöleic and oleic acids, respectively. It is advisable to employ a catalyst and conditions which are selective to the formation of oleic rather than isoöleic acid, since it is then possible to hydrogenate to a lower iodine value to obtain a given consistency or degree of hardness, and a more stable product results.

The selective or controlled hydrogenation of soybean oil, at 180° C., in the presence of nickel, was investigated by Hilditch and Moore[105] who found that the amount of saturated derivatives did not increase until the amount of linoleic acid fell to 10 per cent or less. Similar results were found by Richardson, Knuth, and Milligan.[152] Ueno and coworkers[198] investigated the nutritive value of soybean oil, hydrogenated at 120° C., especially with respect to the effect on vitamin A activity. Mazume[134] investigated the formation of isoöleic acid, during the low-temperature hydrogenation of soybean oil, and found that the greater the amount of catalyst used, the greater was the formation of isoöleic acid. The presence of a small amount of copper (0.3 per cent) resulted in the formation of large amounts of isoöleic acid, whereas larger quantities (4.0 per cent) gave only small amounts of the iso-acid. Exposure of the reduced nickel catalyst to air, prior to use, also resulted in increased production of isoöleic acid.

Gill and Ma[81] studied the effect of temperature, pressure, agitation, and amount of catalyst on the hydrogenation of soybean oil, and concluded that an increase in any one of these factors increased the rate of hydrogenation. However, at stirring rates of 320 revolutions per minute and above, a temperature change of 10°, between the limits of 150 and 180° C., produced little or no effect on the rate of reaction. One per cent of catalyst was found to be the maximum amount required for successful hydrogenation.

Waterman and Bertram[201] investigated the hydrogenation of soybean oil, with respect to the decrease in thiocyanogen and iodine numbers, and found that the two characteristics differed widely in their respective rates of decrease. Waterman and van Vlodrop[203] investigated the hydrogenation of soybean oil with colloidal nickel catalyst, prepared from nickel carbonyl, and obtained a product melting at 60° C., when the hydrogenation was carried out at a temperature of 60° C. and at atmospheric pressure, for one and three quarter hours.

Yamaguchi and coworkers[206] investigated the preparation of nickel and copper catalysts, from the corresponding formates, in the presence of soybean oil, and the effect of time and temperature on the hydrogenation of the oil by those catalysts.

Botkovskaya [46] concluded from an investigation of the effect of the presence of phosphatides and peroxides on the hydrogenation of soybean oil that the former were without effect, whereas the latter were chiefly responsible for retarding the rate of reaction. Sato and Ozaki [166] claim that the use of a high-tension electric discharge increases the catalytic hydrogenation of soybean oil, without affecting the quality of the reaction.

More recently, considerable attention has been given to the effect of high temperatures and pressures on the course of the hydrogenation reaction of soybean oil. Waterman, van Tussenbroek, and van Dijk [202] investigated the hardening of soybean oil, at pressures varying from 130 to 146 atmospheres at 32, 50, and 55° C., using 3 per cent nickel-kieselguhr catalyst, and also at atmospheric pressure and a temperature of 175 to 180° C. Analysis of the hardened fats indicated that the formation of glycerides, containing one or more saturated fatty acid residues, was more pronounced in hardening at high pressures and low temperatures.

Shinozaki and Kubo [174] extensively investigated the high temperature and pressure hydrogenation of soybean oil, especially with respect to the formation of non-glyceride products. At temperatures below 250° C., hydrogenation with a copper-bearing catalyst resulted principally in the saturation of the various double bonds in the glyceride molecule, whereas between 300 and 325° C., considerable production of fatty acids occurred. The latter reaction reached a maximum at 350° C., when alcohols began to form, and ceased abruptly at about 375° C. with the formation of hydrocarbons. Octadecyl stearate, melting at 58.5° C., was isolated from the reaction mixture, formed at 350° C. When copper-chromium catalyst was employed at 390° C., the wax ester, formed at 325 to 350° C., was completely decomposed with the formation of higher hydrocarbons (octadecane), and between 410 and 450° C., gasoline-like oils of specific gravity 0.74 were formed in seventy per cent yield. This last reaction was extensively studied by Shinozaki and coworkers,[175] under various conditions. High pressures and a sixty-minute reaction time resulted in a maximum yield of hydrocarbon oil. Temperatures below 430° C. were ineffective, and of the various catalysts examined, nickel salts gave the best results. With about 3 per cent of this catalyst, the oil obtained was colorless, had a specific gravity less than 0.7, and contained 1.1 per cent unsaturated compounds, 7.6 per cent naphthenic hydrocarbons, and 91.3 per cent saturated compounds. Kino [116] investigated the production of ketones which were formed by heating hydrogenated soybean oils with magnesium powder at 300 to 350° C. The melting points of the resulting ketones were found to increase with the increase of the amount of saturated acids in the hardened oil. Koyama [121] studied the high-pressure hydrogenation of soybean oil, in the presence of a series of copper-bearing catalysts and concluded that a 70:30 copper-nickel mixture, which was not pretreated with hydrogen, was the most effective of the catalysts investigated.

The literature, pertaining to the mechanism of hydrogenation reactions, has been reviewed by McCutcheon.[127]

Deodorization

Following the various treatments of neutralization, washing, bleaching, and hydrogenation, soybean oil still retains its characteristic taste and odor because of the presence of difficultly volatile substances. The removal of these substances is effected in the final step of the purification process. This deodorization is generally carried out by the batch method, although continuous deodorizers are used to a limited extent. In the batch method, the oil is maintained at a temperature of 180 to 210° C., under a vacuum of 5 to 12 mm, for 6 to 8 hours or longer, during which time, it is subjected to treatment with superheated steam.

Various designs of deodorizers are in use, and although differing somewhat in construction details, they consist essentially of a tank of 15,000 to 30,000 pounds capacity which is provided with an elaborate system of baffles to prevent carrying over of the oil with the steam, a multiple-stage, steam-jet vacuum pump, steam compressor, or other means of superheating the steam, a thermo-compressor to compress the vapors from the deodorizer, and a barometric condenser. The steam enters at the bottom of the column of oil, 8 to 10 feet, or more, in height, and passes upward and out, through the condensing system. The proper temperature and flow of steam through the oil, as well as the length of time, required to effect the maximum degree of deodorization, commensurate with the production of the highest quality in the finished product, depend on the characteristics of the oil and on the skill and past experience of the operator. When, in the judgment of the operator, the oil has been properly deodorized, it is dropped to a vacuum tank, equipped with cooling coils, in which it is cooled before being further processed into edible products, or before loading into tank cars, drums, or cans preparatory to shipment. Freshly deodorized soybean oil is bland, contains less than 0.02 per cent fatty acids, and has a Lovibond color reading of 10 to 15 yellow and 1 to 1.5 red in a 133 mm cell.

The disadvantages of the batch system of deodorization of soybean oil are the length of time which the oil must be heated, the poor contact between the oil and steam, and the hydrostatic pressure which increases from the surface to the bottom of the oil layer. Consequently, a number of continuous deodorization systems have been devised both in Europe[171] and in the United States which are intended to eliminate these disadvantages. The systems are all somewhat similar in principle and depend, for their action, on flowing a thin film of preheated oil downward, over bubbling caps, plates, or a packing material, against a rising current of superheated steam. Deodorization of the oil is carried out in a high vacuum, in 4 to 6 minutes, following which, the oil is rapidly cooled by being circulated through cooling coils. The Elliott Company, Pittsburgh, Pennsylvania, furnishes continuous deodorizing units in standard sizes, ranging from 500 to 5,000 pounds per hour, and the Foster Wheeler Corporation, New York, New York, furnishes similar equipment,[53, 54] capable of handling 24,000 to 144,000 pounds of oil daily. The Blaw-Knox Company of Pittsburgh, Pennsylvania, also offers a continuous deodorizing system.

Winterizing

Winterizing is an operation which originated in the cottonseed oil industry. In order to obtain a salad oil, which would remain clear in cool climates, the practice was adopted of allowing tanks of "summer" oil to stand out of doors during cold weather. The so-called "stearine" crystallized and settled out, leaving a supernatant "winter" oil, suitable for use in the preparation of salad oils, mayonnaise, and similar products. The methods and equipment, used in most of the large refineries, have passed through several stages of development during evolution into their modern forms, although it is universally admitted that even present-day practice is extremely awkward in most respects. The development of winterizing technology has been described by Lee.[126] Highly refined soybean oil will normally remain clear for an indefinite time, when kept at 0° C., but most commercial oil will begin to freeze at —4° C. and remelt at about —3° C. The material, which separates from refined soybean oil, at low temperatures, apparently does not consist of so-called stearines which are obtained from cottonseed oil under the same conditions. Earle and Detwiler [59] examined a wax obtained by solvent extracting the filter aid and precipitate remaining in the filter presses of a commercial soybean oil winterizing installation. They found the average chain length of the acids to be 22 carbon atoms, and the principal alcohols were found to have chain lengths of 28 to 32 carbon atoms. On the assumption that 50 pounds of filter aid are used for each 15,000 pounds of winterized oil, these authors concluded that the wax, containing about 10 per cent of free alcohols, comprised 0.001 to 0.002 per cent of the original oil.

In winterizing an oil, it is important that the rate of cooling and circulation of the oil should be controlled in a manner conducive to proper coalescence of the solid particles into easily filterable precipitates. The usual practice is to charge the oil into large horizontal tanks which are fitted with internal cooling coils. Although the usual heat-transfer medium is brine which has been chilled by an ammonia refrigeration system, some of the recent installations perform the cooling by direct expansion of the refrigerant into the coils, within the tanks. The oil is rather rapidly cooled to a temperature of 40 to 45° F., and it is allowed to stand for two or three days while the solid materials settle. The oil is then clarified by forcing it through precoated plate-aid-frame filter presses which are installed in a refrigerated room.

The present methods, for winterizing vegetable oils, are thought by many to be unnecessarily time-consuming and to involve the tying up of excessive amounts of oil while the process is being completed. It is also quite generally appreciated that a continuous winterizing method is hardly possible if carried out in a manner at all similar to the present practice, because of the length of time necessary for proper conditioning of the precipitate. However, analogous problems have been solved in the petroleum industry with the result that extremely large-scale dewaxing of lubricants is now quite commonly performed by continuous operations, involving no appreciable hold-up of the product. The successful introduction of such methods into the vegetable oil industry would go a long way toward improving plant efficiencies and lowering processing costs.

Shortening

Usual types of shortening, made from soybean oil, are prepared by beating air or other gas into properly hydrogenated or hardened oil, the product being thoroughly emulsified. Such shortenings are made from pure soybean oil as well as from practically all other edible oils and from mixtures of various fats and oils. Approximately half of the soybean oil produced in this country is consumed in such products.

Ordinary vegetable oil shortening is made in either of two ways. The first method consists in hydrogenating an entire batch of oil until its iodine number is lowered to a given value, i.e., 60 to 70, or until it acquires the desired consistency at room temperatures. The sequence of operations is hydrogenation, deodorization, and solidification. Hydrogenation imparts a typical flavor which must be removed. The hardened material is then chilled, and air is whipped into it to produce the completed emulsion. Shortenings of this type are produced only in plants which have hydrogenation equipment, but they are generally considered to be the more stable type.

The other method of manufacturing comprises mixing unhardened oil with the proper amount of rather completely hydrogenated oil or oleostearine, the proportions being controlled to produce the desired degree of plasticity in the final product. The mixture is chilled and emulsified with air exactly as in the production of the completely hydrogenated type. Shortenings of this kind are made in many refineries which do not have hydrogenation equipment, since a relatively large amount of unhydrogenated oil can be sufficiently thickened by the addition of a small amount of completely hardened fat. The hardened components usually consist either of oleostearine or of fairly completely hydrogenated oil, shipped to the refinery from some plant having hydrogenation facilities.

In either process, the methods of chilling the fat and emulsifying it are the same, although there are several methods of accomplishing the desired results. Until recent years, it was standard practice to run the hardened oil over a chill roll, prior to the emulsification step. The roll is a horizontal, steel cylinder about 9 feet long and 4 feet in diameter. It revolves at 6 to 10 revolutions per minute and is cooled to —10 to +10° F. by means of circulated brine or direct expansion of refrigerant. Liquid fat, at 120 to 130° F., is fed onto the roll and congeals in a thin, somewhat translucent film which adheres to the roll surface for nearly a complete revolution, before being removed by a scraper knife. Final temperature of the fat depends upon the roll temperature and upon the speed of rotation.

The chilled fat, at a temperature of 50 to 70° F., falls into a trough, known as the "picker pan," in which it is beaten by pickers, extending from a longitudinal shaft, rotating at 80 to 180 revolutions per minute. The amount of air, whipped into the mixture, is governed by the speed and shape of the pickers and should be 8 to 12 per cent by volume. Too much air results in a "fluffy" product, and insufficient beating causes a greasy or oily texture. The air, introduced in the picker pan, is finely subdivided, and lumps are eliminated by forcing the mixture through screens, expansion valves, and other homogenizing devices, at pressures usually approximating 400 to 600 pounds per square inch. The product is a white, creamy emulsion which rapidly crystallizes, setting to the firm consistency of lard or other shortening agents.

A more recent development, in the production of shortening, is the use of closed system chilling units, more often referred to as internal chilling machines. These are jacketed, nickel or stainless steel cylinders, 6 to 8 inches in diameter and about 4 feet long, equipped with longitudinal scraper-stirrer blades. The blades are accurately mounted on a large-diameter mutator shaft which allows only about an inch of annular clearance between it and the cylinder wall. The scraper blades float in the cylinder and are made to bear lightly against its walls by centrifugal force and by the resistance of the fat to their rotation. The radial force thus developed is insufficient to cause metal-to-metal contact. Even microscopic films are scraped from the walls by the revolving blades, but no metal-to-metal contact occurs to afford opportunity for metallic contamination of the product. Cooling takes place by virtue of direct ammonia expansion in the jacket, and the liquid fat is forced through the cooling unit, at a rate commensurate with the amount of cooling required. A separate inlet is provided for admitting air or inert gas to produce the emulsion. It has been variously claimed that the use of nitrogen, for example, in place of air results in a more stable shortening.

Internal chilling machines offer other advantages. The scraper action is so effective in rapidly removing congealed fat from the cold cylinder walls that much more efficient heat transfer occurs than can be obtained with the conventional chill roll. The consequently more rapid crystallization results in formation of finer crystals, improving the consistency of the product, and insures a relatively high capacity. Feed rate, gas influx, temperature, and pressure are more readily controlled, and it is, therefore, possible to make a more uniform shortening. Total enclosure of the process also prevents condensation of moisture in the fat, during treatment.

The steps, in the internal chilling process, are approximately the same as those comprising the chill roll method.

Hydrogenated oil, from storage, runs into a work tank having a float-operated level controller. A positive displacement pump withdraws oil from the work tank, and an inlet, for air or inert gas, is provided in the suction line. The mixture of gas and fat is forced through a pressure-regulating valve into the chilling apparatus, or "A-unit," which usually consists of two cooling cylinders, Nos. 1 and 2, although some makes use only one cylinder. The warm oil-gas mixture enters at the bottom of the vertical cylinder No. 1 and leaves from the top. It is then forced through cylinder No. 2 in a similar manner, and is discharged in a super-cooled condition. The effluent is then gently mixed in a horizontal, cylindrical, water-jacketed chamber, known as a "B-unit," while crystallization rapidly takes place with consequent evolution of heat. The entire system is under pressure up to this point, but the pressure is released when the crystallized product is extruded from the blending unit for packaging. The release in pressure causes expansion of the minute air bubbles and thereby results in a whiter color in the finished shortening.

Margarine

Margarine or oleomargarine is an emulsion of fats and oils, milk, and salt. The fat and oil amount to 80 to 85 per cent, and the salt to 3 or 4 per cent. During recent years, 16 to 20 per cent of soybean oil consumption has been in the production of margarine. Soybean oil has composed 25 to 34 per cent of the total quantity of fats and oils thus consumed, compared to 40 to 50 per cent for cottonseed oil. The balance has consisted mainly of smaller amounts of coconut and oleo oils. Considerable quantities of margarine are made, using only hydrogenated soybean oil as the fatty ingredient, but it is more generally the practice to blend hydrogenated soybean oil with other fats.

Production methods have been modernized during the past few years. In older processes, milk, which has been soured to the proper acidity, is mixed with the fat in a large churn, having a cooling jacket. The milk is introduced first, at a definite temperature, and then the fat is added, with vigorous stirring. The mixture is cooled and gradually becomes thicker in consistency and less transparent. Finally, crystallization takes place, causing an abrupt rise in temperature, but the churning is continued until the temperature commences to fall once more. The agitation is then discontinued, and the thick mass is discharged into a powerful stream of ice water. A trough or vat collects the water and crumbly margarine chunks, and the latter are skimmed off to be kneaded in a butter worker. Salt is added during the working process.

Modern plants employ a different congealing and emulsification technique. First, the milk is inoculated with a mother culture and allowed to ripen for 10 to 12 hours, at 80 to 90° F., or until its acidity reaches approximately 10 per cent. Glass-lined or stainless steel, closed tanks, with agitators and temperature-control jackets, are used for this step of the process. Great care is taken, in the preparation of the mother culture, to prevent contamination, since the palatability of the finished product is dependent upon the specific action of the proper microörganisms in producing certain flavoring substances, mainly diacetyl. Meanwhile, the fat or fat blend is prepared. If only one oil is used, having been previously hardened to the proper consistency, it is simply withdrawn from storage and pumped into the blending tank where its temperature is properly adjusted. In other cases, a number of fats and oils are blended, the proper hardness of the blend being obtained by properly proportioning hardened and unhardened oils. A part of the milk, e.g., 25 per cent, may be added to the fat in the blender, with thorough stirring.

The fat is then withdrawn by a proportioning pump and forced, at high pressure, through ammonia-jacketed chilling tubes, or "A-units," similar to those used in the production of shortening. The balance of the milk, in which the proper amount of salt has been dissolved, is cooled to approximately 20° F. and pumped into the cold fat as it leaves the chilling tubes, and the mixture then passes through a blender. This is a horizontal tube with a central shaft having projecting mixing pins. The final setting to consistency, required for forming and cutting, takes place in the "B-unit" which is usually a series of three jacketed tubes. Screens, between the tubes, serve to break up any lumps, but there is no other mechanical stirring provided. Warm water is circulated through the jackets to keep material from sticking to the walls. In some cases, the chilling, crystallizing, working, and blending operations are all combined and carried out in a single chilling and agitating unit. In either case, the final product is extruded through a die in the form of a slab which is cut into proper sizes for packaging.

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