The Present and Future of Drying Oils

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THERE are a large number of naturally occurring oils which in the raw state without the aid of added chemicals are capable of absorbing oxygen from the air and becoming solid. Such oils are termed drying oils, and a number are used in protective and decorative coatings. In discussing the present and future of drying oils, our problem would be greatly simplified if we could restrict the discussion to this single group of fats and oils. However the problem is quite complex, and the effects of a typhoon reducing the size of the Philippine Islands coconut crop or unseasonable weather reducing the harvestable output of palm nuts in the Belgian Congo or, to come closer to home, the effect of the late wet spring this year in reducing the corn crop in Iowa, all have a decided effect on available supplies of our drying oils.

S. O. Sorensen

Today, as in the past, fats and oils are among the most important commodities affecting various nations, both from the edible and the industrial viewpoint. These two uses overlap and partially depend upon one another. Factors tending to decrease our edible oil supplies or limiting the available quantity of soap stocks affect the broad picture of drying oil availability. This is becoming increasingly important now that the application of drying oils is no longer really the application of linseed oil. We are constantly striving for interchangeability of raw materials for protective coatings applications. The technological advances we have made, particularly in the last decade, toward applying a variety of oils in paints, linoleum, and printing inks have been such that on the worldwide front various fats and oils influence one another over a broader front than most people realize.

Although literally hundreds of oils from various vegetable, animal, and marine sources have been tried and sometimes used as drying oils, a relatively small number constitute the bulk of the commercially important oils used in protective coatings. Linseed, tung, dehydrated castor, fish, soybean, and tall oils make up a large proportion of the oils used in the paint and varnish industry and the closely allied linoleum and printing ink industries. Other oils such as perilla and oiticica are of secondary importance, and a number of minor drying oils including chia, hemp seed, poppy seed, safflower seed, sunflower, and walnut are used in small quantities.

The pattern of oil usage by the coatings industries has changed in the last 10 years. Soybean oil, dehydrated castor oil, and tall oil which were relatively inconsequential factors in the overall picture of drying oil use in the later '30's have assumed a position of real significance. Simultaneously, linseed consumption has dropped as methods of upgrading of relatively poorer drying oils have been improved. To illustrate how the pattern of drying oils use has changed, observe the following:

During the five-year pre-war period from 1937 to 1941, linseed oil accounted for 71% of all drying oils used industrially. Tung oil was used to the extent of 12%, and fish oil accounted for another 10% of the drying oils consumed. Three per cent each of soybean oil and dehydrated castor oil were used, with the remaining 2-3% of consumption being divided among the group of minor drying oils.

At the time we discussed the subject of availability of drying oils during the Drying Oils Symposium held here at the University of Minnesota during the spring of 1947 a distinct change in the consumption of drying oils had taken place. Flax and linseed oil imports from the Argentine which normally accounted for approximately half of our total supply of linseed oil decreased to a mere trickle. A vigorous program fostering flax production in the United States and Canada made up for a large part of the deficit produced by lack of Argentine flax. However linseed oil in 1947 dropped to 56% of the total drying oil consumption. Soybean oil which, on the average, accounted for only 3% of the total of drying oils used during the period from 1937 to 1941, has soared to second rank among drying oils at 16% of the total. Dehydrated castor oil, which was first introduced to the paint and varnish industry in the middle '30's proved to be a valuable product with a permanent industrial outlet, especially for flexible finishes of good color retentive properties. The volume jumped from under 2% of the total in 1937-41 to over 10% in 1947. During the war a newcomer made its appearance in the drying oil field. Tall oil, produced as a by-product of paper pulp production from wood, found a market for the preparation of low cost products where color was not of paramount importance.

An examination of the monthly summaries of factory consumption of fats and oils in the Commerce Department's Facts for Industries Series indicates that the total consumption of drying oils in the manufacture of paints and varnish and the closely allied linoleum, oil cloth, core oil, and printing ink industries totalled 740 million pounds during 1949. Breaking the total down into percentage consumption of the various oils, we find the following: linseed 47.8%, soybean oil 20.1%, tung oil 12.9%, tall oil 6.0%, castor oil 5.9%, and fish oil 4.6% with the remaining 2% accounted for by other oils such as oiticica, safflower, walnut, etc. These figures are, to a certain extent unrealistic in that they include oils processed by manufactured establishments only. The oil (chiefly linseed) used for thinning of paste paints, mixing with house paints and other non-manufacturing use is not included. During 1949 the total domestic disappearance of linseed oil exceeded the factory consumption by 225 million pounds. If we take into account that large non-manufacturing consumption of linseed oil for paint mixing, wood sealing, etc., the actual figures for linseed consumption in protective coatings rise to 60% of the total drying oils consumption, other oils diminishing proportionately percentagewise.

To those who are interested in reading a detailed position as far as fats and oils are concerned, I would suggest that you refer to the "Industry Report on Fats and Oils," Annual Review 1949, issued in March 1950 by the U. S. Department of Commerce. In the following summary I will borrow from this and other governmental statistical reports for the picture regarding the present situation on drying oils.

THE world production, trade, and consumption of fats and oils have increased materially during the past four decades. Expansion and demand have been caused in part by increased population and in part by technological developments resulting in increased per capita utilization of oil, particularly of vegetable oil. During World War II blockades and occupation of producing areas, together with inadequate shipping, seriously curtailed production and consumption with a resultant depletion of fat stocks. The low period in 1946 has been followed by years of unusually large domestic production of both animal and vegetable oils. New records were established in fats and oils in 1949. The production of primary fats and oils from domestic materials of 11.6 billion pounds was 1.3 billion larger than in 1948 and was the largest output in history. Extremely favorable production resulted in a volume of exports which was also the largest ever recorded. Shipments of 2.3 billion pounds were equal to 2½ times the 1943 figure and nearly five times the pre-war average. At the same time imports of 1.1 billion pounds were 155 million pounds smaller than received in 1948. Thus the United States was on a net export basis by more than 1 billion pounds of fats and oils in contrast to net imports of 353 million pounds in 1948 and an average of 1½ billion pounds before the war.

While the production and exports reached new highs during 1949, the apparent domestic disappearance of 10.3 billion pounds was somewhat less than that of 1948. Per capita consumption is indicated at 66 pounds, which is two and a half pounds less than the 1948 figure and four pounds lower than the prewar average. Per capita disappearance of edibles of 43 pounds was half a pound larger than in 1948 whereas the consumption of inedibles dropped three pounds to 23 pounds.

Factory and warehouse stocks of primary fats and oils rose to 2.1 billion pounds by the end of 1949, which is approximately half a billion more than the closing 1948 stocks. However when government holdings of linseed oil, butter, and the stock pile items are considered, commercial stocks are smaller than a year ago and substantially below the pre-war average of 2.2 billion.

The domestic production of fats and oils will continue to be large in 1950. Cottonseed oil production will be smaller, but the production of lard, butter, and soybean oil probably will be larger. Soap stock oils such as inedible tallow and grease are expected to rise somewhat above the 1949 level. In the drying oil field the incoming flow of imported oils may continue to be low, but the availability of linseed oil and soybean oil should aid in meeting the requirements of the drying oil industry.

The United States foreign trade of fats and oils in 1949 showed the largest net exports in history. Net shipments of 1,130,000,000 pounds contrast with net imports of 353,000,000 pounds in 1948 and pre-war net imports of one and a half billion pounds. Even in the previous peak year of 1944, when our exports were swelled by lend-lease shipments, net exports were less than 700,000,000 pounds. Although total imports of fats and oils in 1949 were lower than in the previous years, the change in our trade position was caused primarily by a record shattering volume of exports. The total shipments of fats, oils, and oil-bearing materials in terms of oil in 1949 amounted to 2,274,000,000 pounds, which is two and a half times the 1948 figure and nearly five times the pre-war average. In contrast, total imports in terms of oil of 1,145,000,000 pounds were 155,000,000 less than received in 1948 and little more than half of the average pre-war receipts.

Before the war the United States produced around 8,000,000,000 pounds of fats and oils from domestic materials and augmented the domestic production with imports of one and a half billion pounds. In the last year the output of domestic materials was nearly four billion pounds larger than pre-war figure. Thus, even with the extremely large net exports of over one billion pounds in 1949, the aggregate net supplies available for domestic consumption by our expanded population were larger than pre-war.

THE following is a summary on the outlook for the drying and semi-drying oils. No attempt will be made to consider in detail the situation with respect to edible oils, but we must keep in mind at all times that our drying oil products are very definitely tied in with the edibles and that the two must be considered together in order to obtain an accurate overall picture.

Flax is the source of the world's most important drying oil, linseed oil. The 1949 domestic flaxseed crop of 43.7 million bushels was 20% smaller than the record of 54.5 million bushels produced in 1948. However the 1949 crop was the third largest on record and was 45% above the 10-year (1938-47) average of 30.1 million bushels. The decline in last year's crop is directly attributable to a poor yield induced by dry weather during the growing season. The harvested acreage of 4.9 million acres was approximately the same as in 1948, but the yield of 8.9 bushels per acre compared unfavorably with the high 1948 yield of 11.2 bushels and the 10-year average of 9.2 bushels. Linseed oil production in 1949 amounted to 745 million pounds, somewhat higher than the 1948 figure of 726 million and the largest since the peak of 937 million pounds obtained in 1944 when one-third of the production was shipped to Russia under the lend lease program.

The extremely large crops of flax obtained in 1947, 1948, and 1949 have brought the flaxseed stocks on hand at the beginning of 1950 up to a peak level. Stocks in all positions totalled 42 million bushels on January 1, 1950, and were about 6% larger than the previous January 1 high of 39.7 million bushels attained in the preceding year. Reflecting the surplus position in this country, the United States was on a net export basis with respect to both flaxseed and linseed oil. Traditionally we have been on a net import basis with regard to flaxseed, and in the years

1944-1947 we also imported substantial quantities of linseed oil. The imports of flaxseed in 1949, practically all of which were received from Canada and Mexico, amounted to only 147 thousand bushels whereas exports, principally going to France, Italy, and Benelux, amounted to 3.1 million bushels.

The 1950 flaxseed crop will be supported at 60% of the farm parity price as of April 1, 1950, in contrast with 90% of parity price for the 1949 crop. Sixty per cent of the modernized parity price of February 15, 1950, is $2.54/bushel as compared with a support price of $3.99/bushel, Minneapolis basis, for the 1949 crop and $6.00 for the 1948 crop which was equivalent to 136% of parity. In establishing the lower level of support for the 1950 crop, Department of Agriculture cited the large supplies of flaxseed and linseed oils available for the 1949-1950 season, the equivalent of two years of normal domestic requirement. The March 1 growers' intentions point to a planted flaxseed acreage of four million acres, 23% less than in 1949. The acreage actually planted will be governed largely by price relationship and moisture conditions at the time of planting. However if the intended acreage is planted and the average yield obtained, a crop of 36 million bushels will be produced, 17% less than last year's crop but still above the normal average period.

In Argentina the acreage planted to flaxseed for harvest in 1949-1950 is estimated at three million acres as compared with three and a half million in 1948-49 and 3.9 million in 1947-48. Despite the reduction in acreage the new crop is forecast at 24.6 million bushels, 25% greater than last year's crop. The crop last year in the Argentine was reduced by low yield and heavy abandonment whereas favorable growing weather this season will probably result in considerably better yield. Despite the upturn in production the current Argentine flax crop is still substantially below the pre-war 1935-39 average of 60 million bushels when Argentine ranked first among world producers of flaxseed. In the past few years Argentina has lost its position to the United States.

The entire 1949-50 flax crop will add to the export surplus already on hand from previous Argentine harvests. As of November 30, unsold flaxseed stocks held by the Argentine Trade Promotion Institute were estimated at 9.4 million bushels while holdings of linseed oil amounted to 600,000 pounds. No export price for flaxseed has yet been announced by the Argentine Trade Promotion Institute, but the linseed oil price has been established at a price equivalent to 15½c/lb. f.o.b. Buenos Aires.

In Uruguay unfavorable growing weather has reduced the 1949-50 flax crop to an estimated 2.8 bushels. There were no stocks on hand from the 1948-49 crop, thus after deduction of flax for domestic seed requirement there will be an exportable surplus equivalent to only 34 million pounds of linseed oil.

I would like to comment at this time on the work being carried out by the Flax Development Institute. This organization has worked for many years on the improvements of the quality of the various strains of flax, following which they have carried their message to the farmer advising him regarding proper agricultural practices and, in general, sponsoring the continued and increasing planting of flaxseed in the flax producing areas. This organization is made up of crushers, consumer industries, agronomists at the agricultural colleges, and other agricultural research leaders. Through publicity sponsored by the institute in the form of bulletins, pamphlets, and brochures, together with the holding of local meetings featuring addresses by top-flight agricultural experts, the institute has done much to increase the total acreage devoted to flax culture and also to increase the yield of flax obtained per cultivated acre. The work has been important and the results have been decidedly worthwhile.

The primary consumption of soybean oil is in the edible field. However in the last four to five years the use of soybean oil by the drying oil industry has advanced remarkably so that soybean oil is now our second most important drying oil accounting for one pound out of every five pounds of drying oil consumed during 1949. The 1949 production of soybeans of 222,000,000 bushels came close to equalling the record of 223,000,000 bushels harvested in 1948 and exceeded the 1938-47 average production of 148,000,000 bushels by 50%. Before the war the United States produced an average of only 77,000,000 bushels annually whereas the large crops harvested in recent years have elevated this country to the position of the world's leading soybean producer. Soybean oil has become our most important vegetable oil, leading the erstwhile king, cottonseed oil, in each of the last six years. Production during 1949 attained the amazing total of 1,860,000,000 pounds, the largest on record. The 1949 production topped the 1948 output by 225,000,000 pounds and was equal to four and a half times the average of 419,000,000 pounds produced in the 1937-41 pre-war period.

A new peak was also established in the United States for the export of soybean oil and soybeans. Combined exports of crude and refined soybean oil amounted to 359,000,000 pounds, more than four times as much as were shipped out in 1948, more than three times the previous peak obtained in 1947. Soybean exports of 23.4 million bushels contrasted with 6.5 million bushels reported in 1948 and the previous record of 10.5 million bushels in 1939 when many European countries bought heavily in anticipation of war. As in both 1948 and 1947 most of the export volume of soybean oils went to Europe, which accounted for approximately 90% of the total. Leading European outlets were Germany, Italy, Spain, Greece, Austria, and the Netherlands. The substantial quantities shipped to Mediterranean countries helped to supplement short supplies resulting from reduced olive oil production.

Growers' intentions on planting of soybeans as of March 1 totalled 13.5 million acres. For the 1950 crop year this represents an increase of 12% over the average for the past several years. If about the same proportion of total acreage is harvested for beans as in recent years, and average yields are obtained, the soybean crop will be in the neighborhood of 10 to 20 million bushels above the previous record set in 1948.

Castor oil has found a permanent place in the drying oil field, architecturally. The imports of castor beans and castor oil amounted to 141 million pounds on an oil basis in 1949, placing this item second behind coconut oil and copra among imported oils. Brazil furnished 95% of the beans and 99% of the oil which was imported with Haiti, Ecuador, and

Thailand furnishing the balance of the castor bean receipts. The production of castor beans in Brazil in 1949 was somewhat smaller than the production in 1948 but was still the second largest on record. Because of lower drying oil prices, it is considered likely that there will be a decrease of perhaps 5% in this year's production.

Tung oil for many years ranked as the second most important drying oil, being of particular value in varnish cooking. The tung oil imports during 1949 were disappointing to the drying oil trade. Incoming shipments of 65 million pounds were less than half of the 133 million received in 1948 and were 35 million pounds smaller than the 1937-41 average. Of the total, China was the source of 43 million pounds as against 130 million pounds in 1948 while Argentina emerged as a supplier of tung oil to the United States, furnishing 17 million pounds. The remainder was received almost entirely from Hong Kong. Although it was estimated that China's exportable surplus of tung oil at the end of 1949 could equal the heavy shipment made in 1947-48, exports of the current season will be substantially less than potentially available. The extremely unsettled conditions in China with subsequent disruption of transportation has impeded the movement of the tung oil from the interior producing areas to ports of shipment. Arrival of tung oil at Shanghai, the principal port of shipment for China's vegetable oils and oil seeds, is limited because of the effect of the Nationalist blockade. The present tendency to increase exports to the USSR may also reduce the availability of tung oil in the United States, which before the war accounted for approximately 75% of the Chinese tung oil export.

TOTAL production of fish oil in 1949 amounted to 129 million pounds, down slightly from the 131 million pounds produced in the previous year and substantially below the pre-war average of more than 200 million pounds. An increase in sardine oil output offset a drop in the Alaskan herring oil production and a small decrease in menhaden. Sardine oil production of 46 million pounds represented an increase of 28 million pounds over 1948. Menhaden oil production of 52 million pounds was 6 million pounds lower while Alaska herring oil production of 5 million pounds was only 18% as large as in 1948. Although the menhaden catch was the largest ever recorded, lower oil content resulted in the decline in output. The virtual failure of the Alaska herring catch was attributable to curtailed operations arising from price disagreement between fisher and processor. The domestic disappearance of 159 million pounds of fish oils in 1949 was 20 million greater than 1948, but otherwise was the lowest in recent years. An increase in the Alaska herring total during 1950 could result in distinctly higher levels of fish oil availability during 1950.

Imports of oiticica oil in 1949 were only 8.9 million pounds, one-half as large as in 1948 and only 45% of the average pre-war receipts. As in the case of castor oil, Brazil is virtually our sole source for this drying oil. This sharp reduction in our imports reflected a drastic cut in production of oiticica seed in Brazil in 1949. The output of 3,000 tons, oil basis, was equal to only 15% of the 1948 crop and was equivalent to approximately 18,000 tons of oil. Although it is still somewhat early accurately to estimate the 1950 oiticica crop, trade circles are anticipating a crop equivalent to approximately 13,500 tons of oil.

Perilla oil has been virtually nonobtainable for several years. The world production of perilla seed is concentrated in Asia, with Manchuria alone contributing over two-thirds of the total, and China, India, and Korea accounting for most of the remainder. The major producing areas are under Communist domination, and it appears probable that virtually the entire perilla output eventually will go into Russian hands.

In the foregoing summary an attempt has been made to review the drying oils situation as it exists today. Attempting to glance into the future is extremely difficult. It appears probable that cottonseed production will decrease in 1950 from the near record output of 1949. The decrease in cottonseed output should be counterbalanced by a record soybean oil crop in 1950. Barring disastrously low yields of these two items for edible purposes, there should be as much soybean oil available for drying oil use in 1950 as there was in 1949. The lowering of the support on flax for 1950 will probably result in some reduction of the crop. However stock piles in government hands total two years of normal linseed oil consumption so no pinch should be observed in the availability of linseed oil. The occupation of increasingly larger portions of China by Communist forces will probably render the tung oil situation more chaotic in 1950 than it has been in the past year. Tung oil receipts during 1950 may very well be lower than those of 1949. On the average, wholly adequate supplies of drying oils should be available for the protective coating industries during 1950 although the relative proportions of the individual oils may be different from the past several years.

During the war years there was intensive research on the use of soybean oil in the manufacture of paint, varnish, and linoleum. However actual use by the industries was curtailed during the war and the immediate post war period because of the allocation of fats and oils for specific uses. The pattern of war research has been continued in the post war period, and drying oil chemists are constantly striving to attain interchangeability of our base raw materials so that fats and oils which are in plentiful supply can be used in place of those which are in short supply. For instance, modified soybean oils have been produced which to all intents and purposes are equivalent to linseed oil for the manufacture of house paint. Dehydrated castor oil and maleic treated soybean oils have been developed as varnish cooking oils of excellent quality, and some products have been produced which approach the tung oil in cooking speed and quality in the finished varnish. The upgrading of soybean and linseed oil by removal of the saturated fractions has attained limited commercial significance. As drying oil modification in this way is more thoroughly understood and practical production problems are solved, it is to be anticipated that segregated soybean oils might be produced to be directly competitive with linseed, and segregated linseed to be functional replacements for perilla. It is particularly important and necessary that such a program of research on the interchangeability of fats and oils be continued so that we can to a reasonable extent be independent of world supplies under emergency conditions. I believe the future of such research is virtually limitless.

In spite of the potentialities of fat interchangeability as indicated above, we must still consider the world fat situation as a whole in calculating our future course. What the future holds on the political and economic front is anyone's guess. The tense international situation has actually forced the nation to maintain a partial war economy. The stock piling of supplies and the subsidizing of planting of critical materials characteristic of our own economy are reflected on the whole world-wide front. When I asked my pet crystal ball what the drying oil situation would be next year, it grimaced and shuddered, and when I followed with a question as to what the world-wide fat situation would be in 1950, it groaned and broke into large and small pieces. If my crystal ball breaks down under such a simple question, who am I to try and give you the answer?

The Chemistry of Drying Oils

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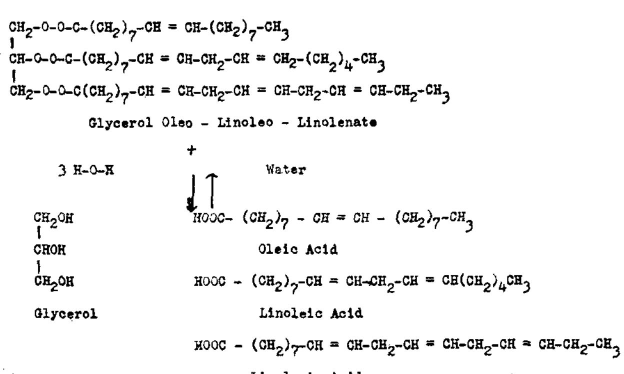
A DRYING oil is so-called because it dries, that is, it changes from an oily film to a tough insoluble film when exposed to air. This ability to polymerize by the action of the oxygen of the air is perhaps the most important chemical property of the drying oils (and the most difficult to completely explain chemically). Polymerization by heat is also important in making bodied oils for varnishes or for paints where the greater viscosity of the bodied oils controls penetration into porous surfaces. A discussion of the chemistry of the polymerization of drying oils by oxygen and heat will therefore be the principal object of this paper.

D. H. Wheeler

Other chemical properties of the drying oils and the drying oil acids are interesting as means of analysis, for making derivatives and modifications of the oils or acids. These chemical properties will also be discussed.

Drying oils, as they will be considered here, are the esters of naturally occurring unsaturated or drying fatty acids with polyhydric alcohols, or closely related compounds. Obviously then there are two parts to a drying oil, the unsaturated acid and the polyhydric alcohol.



These parts will be considered separately at first, and then the effect of their combination will be discussed with application of the concept of functionality to the drying and bodying properties of the drying oils.

The Unsaturated Acids

The unsaturated acids of greatest importance in drying oils are those containing 18 carbon atoms and two or more double bonds. These C_{18} polyethenoid acids occur as mixed glycerides in the common drying and semi-drying oils, such as linseed, perilla, tung, oiticica, dehydrated castor, safflower, soy, sunflower, corn, and cottonseed oils. The 20 and 22 carbon polyethenoid acids present in fish oils such as herring, menhaden, and sardine are also of considerable importance. In natural drying oils these acids always occur as mixed glycerides, esters of the trihydric alcohol, or glycerol.

Unsaturation of the polyethenoid acids may vary in two important respects:

1. The number of double bonds present.
2. The arrangement of the double bonds in relation to one another.

It is remarkable that the commercially important unsaturated acids have a double bond between carbon atoms 9 and 10, and no other double bonds closer to the carboxylic acid group.

Oleic acid has only one double bond and has very little activity as a drying oil component.

$$CH_3(CH_2)_7-CH=CH-(CH_2)_7-COOH$$

Oleic Acid

Linoleic acid has two double bonds separated by a methylene carbon atom and two single bonds.

$$CH_3(CH_2)_4CH=CH-CH_2-CH=CH-(CH_2)_7-COOH$$

Linoleic Acid

It is fairly active in its ability to polymerize by the action of oxygen or heat and is remarkable for its non-after-yellowing properties in alkyds and other protective coatings.

Linolenic acid, with three double bonds similarly separated, is much more rapid in its ability to polymerize by oxidation or heat.

$$CH_3CH_2-CH=CH-CH_2-CH=CH-CH_2-CH=CH(CH_2)_7-COOH$$

Linolenic Acid