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INTRODUCTION

The world's waters annually produce a tremendous harvest of fish, being in 1962 40.4 million tons (Chapman 1965), close to 90% of which came from the oceans. The catch has doubled in the past 24 years and is increasing at the rate of 8% each year. The herring-like fishes, including anchoveta and sardines, made up 41% of the total in 1962 and an estimated 50% + in 1964. About one-third of the total catch is used for industrial purposes, mainly as fish meal for animal feeding, and the rest as fresh, frozen, dried, or canned for food.

The bulk of the fish oils of commerce are obtained as by-products from fish-meal production or from food fish wastes. World fish-oil production was an estimated 865,000 tons in 1966. Production has increased 25.5% since 1961. All other oils have increased enormously also so that fish still is only 2.5% of the total edible fats and oils produced and 13.4% of the inedible ones.

The energy needs of the approximately three billion world population and the normally lower price of fish oils versus the major edible oils and fats such as soybean, peanut, sunflower, cottonseed, palm, butter, and lard have steered the flow into food uses. They are used overseas for shortening, margarine, and compound cooking-fat manufacture. Probably over 75% is used for edible purposes, except in the United States. Outside the United States, the fish oils are refined, selectively hydrogenated, and deodorized for these applications. Fish oils in food products were discontinued in the United States very shortly after the new Food, Drug, and Cosmetic Act was enacted in 1938 (Culbertson 1963). They were considered adulterated products because the fish raw materials used in their manufacture were not all edible. Among the non-edible oils and fats, fish oils rank about 8th in volume, below tallow and grease, coconut, soybean, linseed, castor, sperm, and tall oil.

Supplies of fish oil could increase several fold if edible fish protein concentrates now being developed by the U.S. Bureau of Commercial Fisheries, Peru, and others become commercial on a big scale. An isopropanol extraction process is being developed at Beltsville, Maryland, by the Bureau (Anon. 1966B). There is currently also a great waste, through spoilage and scrapping, of fish that could be prevented and converted into still larger oil and meal supplies.

TABLE 18

WORLD OCEAN FISH CATCH 1962

Species	Volume of Catch Millions of Metric Tons
Herring & anchovy	14.6[1]
Cod, haddock, & hake	5.51
Horse mackerel & sea perch	4.27
Tuna and mackerel	2.38
Flat fish (halibut, sole, flounder)	1.2
Salmon & smelt	0.55
Sharks & rays	0.37
Others	6.77
	35.65

[1] Includes 1.1 MM tons of U.S. menhaden.

The composition of the world fish catch in 1962 is illustrated in Table 18.

Industrial uses (Anon. 1965B) today are mainly for protective coatings on wood, metal, fiber, and concrete; lubricants, medicinals; and some soap. The last use has declined so greatly that it is only a minor one. In the United Kingdom, for example, fish oils were only 0.3% of the total fatty raw materials used in soap. In protective coatings, fish oils compete mainly with linseed, soybean, castor, safflower, tung, and tall oils. It is the relatively low fish-oil cost contrasted to that of all other drying oils (except tall oil) as well as the high degree of unsaturation that make fish oils so useful in this field. The unique mixture of fatty acid chain lengths makes fish oils valuable also in lubricants, greases, paper sizes, buffing agents and textile auxiliaries.

TABLE 19

WORLD OIL PRICES IN 1964

Oil	Price Cents per Lb.
Tung	22.0
Peanut	14.3
Safflower, non-break	14.0[1]
Castor	12.4
Sunflower	11.5
Lard, prime	11.4
Linseed	10.8
Soybean	10.4
Peru fish oil	9.2
Menhaden	9.0[2]
Tallow, bleachable, fancy	7.6
Tall oil	7.5

[1] FOB San Francisco, Tanks, Dec. 20, 1965. Safflower has become an important high-quality oil for protective coatings in the U.S.
[2] The highest price in 14 years. The low in recent years was 4.6¢ in 1962.

World oil prices as of January-December 1964, CIF European ports, illustrate the relative market positions of fish oils and their major competitors (Table 19).

Food demand, including salad and cooking oils, margarine and shortening, controls prices for most of the oils, including fish. Peruvian fish oil, tallow, lard, and tall oil are obtained as by-products, complicating the pricing structure and supply still further. There exists considerable interplay and substitution of one oil for another, depending on relative prices and availability in the world markets.

Menhaden is protected in the United States at present by tariffs which prevent encroachment by the tremendous amount of Peruvian anchovy oil exported into the world market.

SOURCES

The major fish-oil-producing countries are Peru, Chile, Iceland, Norway, South Africa, Canada, and the United States. China and Japan are also big producers but do not engage in world trade. Peru and Chile are late comers, but have experienced a meteoric increase in production. Peru has become the largest exporter in the world—295 million pounds in 1964, mostly anchovy, and an estimated 298 million pounds in 1965. Norway and Iceland are the chief sources of herring on the world scene. The South African countries have an annual production of approximately 132 million pounds of sardine (pilchard) oil. The fish catch is increasingly of the "oily" type—the Peruvian anchovy, American menhaden, South African pilchard, and North Atlantic herring.

The United States in 1964 produced 172 million pounds of menhaden oil, an estimated 185.3 million pounds total of all fish oils. In the last ten years, the total fish oils produced ranged from 165 million in 1957 to 266 million in 1961. Menhaden was 90% of the total, the remainder being mainly herring, Pacific sardine, and a little tuna and mackerel (Anon. 1966 A). The menhaden catch of the United States is used entirely for industrial oil and meal production, none for edible fish use. Menhaden are indigenous to the United States. Approximately two-thirds of the catch is from the Gulf Coast, one-third from the North Atlantic. Alaska and western Canada are the chief sources of domestic herring, with Maine being the least prolific. In addition to the domestic sources, the United States imported 3.9 million pounds of herring oil in 1964, mainly from Peru,[1] 7.7 million pounds of cod, and 7.2 of cod liver oils. However, the actual consumption of all fish oils is lower than the production figures indicate since the U.S. exports much of its oil—151.5 million pounds in 1964, mainly

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[1] The Peruvian herring oil may actually have been anchovy.

menhaden. U.S. consumption ranged from a low of 83 million pounds in 1954 to a high of 168 million pounds in 1961.

It is interesting to note that preliminary gross results from a study by the Bureau of Commercial Fisheries (Chapman 1965) indicate roughly a standing crop of 4–6 million tons of anchovy off southern California and northern Mexico, about 3 million tons of hake, and about 11 million tons for all types (maximum sustainable yield) off the U.S. coasts. Thus, a tremendous potential for oil exists but has still to be confirmed or proven economically feasible. The total actual catch was 2.26 million tons in 1964. The size of the catch hasn't changed much in the last thirty years, but the composition has greatly. This is a complicated study and not too much is yet known reliably.

COMPOSITION

There is still much to learn about fish oils even though progress has been considerable. Research interest in these oils remains high since they are the best known natural sources of long-chain, polyunsaturated fatty acids, although from a food point of view they are very low in the normal "essential fatty acids." There is much work being done to determine the functionality of the fish acids in human nutrition.

Commercially, the composition of the oils sold is not as clearly standardized by trading, association, ASTM, AOCS, and Federal rules and specifications as are other industrial oils such as soybean, cottonseed, linseed, dehydrated castor, and tung. Table 20 lists representative values.

Corresponding values for industrial vegetable oils with which the fish oils are competitive are shown in Table 21.

TABLE 20

RANGES OF FISH-OIL CONSTANTS

Constant	Menhaden Gulf	Menhaden Atlantic	Herring	Sardine (Pilchard)	Anchovy[1]
Iodine value	145–170	150–185 175–190[2]	120–150	160–194	180 minimum 196–198.5[3]
Saponification value	4	185–190	185–195	185–195	191–193.5[3]
Free fatty acid, %	4	3 maximum	0.2–5.0	0.1–13	1 maximum 0.2[3]
Moisture and insolubles, %	4	1 maximum	1 maximum	4	0.5 maximum
Gardner color, #	4	4	4	4	9 maximum
Unsaponifiables, %	4	0.6–1.6	2–3	0.5–2	3 maximum
Titer, °C	4	30–34	23–27	28–32	3.9 10[1]

[1] Peruvian semi-refined, industry practice.
[2] NPVI. Association raw material index, October 1965.
[3] Representative samples entering U.S in 1962 and 1964—courtesy of Archer-Daniels-Midland Company.
[4] Reliable data unavailable.

The differences most apparent from Tables 20 and 21 are in titer and iodine value.

However, when the component fatty acids are compared, as in Tables 22 and 23, the uniqueness of the fish oils becomes obvious as well as the reasons for their usefulness. The variation in values reflects the difficulties in the analyses and also different sources of oil.

TABLE 21

RANGES OF SOME NON-FISH OIL CONSTANTS

	Linseed[1]	Soya	Sunflower	Tung[2]	Rapeseed[2]	Tall[3]
Iodine value	170–200[4] 177, min.[1] 188, min.	120–141	120–135[4] 125–136[2]	160–175	97–108	127–132
Sap value	189–195	189–195	188–194	189–195	170–180	—
FFA, %	2 max.	⁵	⁵	⁵	⁵	ca. 100
Unsap, %	1 max.	1.5 max.	1.5 max.	1	1.5 max.	—
Titer, C.	19–21		16–20	36–37	11.5–15.0	—
Rosin acids	⁵	⁵	⁵		⁵	0.6

[1] ASTM, D 23 4-48 for raw oil.
[2] AOCS standards.
[3] Distilled fatty acids only—Bauer (1961).
[4] Maas et al. 1962.
[5] Reliable data unavailable.

TABLE 22

RANGES OF FATTY ACIDS FROM FISH OILS[1]

	Per cent Composition			
	Menhaden	Herring	Sardine (Pilchard)	Anchovy[3]
Extent of unsaturation				
Saturated acids	29.1–43.3	19.3–29.8	23–26	33–35
Monoenes	23.9–32.2	46.2–62.0		26–29
			35–48[4]	
Dienes	2.4–7.6	2.6–4.3		3.4–7.5
Trienes	0.9–1.4	0.6–4.1	[2]	0.3–3.2
Tetraenes	3.2–3.8	0.9–3.2		
Pentaenes	11.8–15.8	2.0–9.9	29–36[5]	28–30[5]
Hexaenes	5.4–17.7	7.6		
Acid chain length				
C₁₄	6.2–12.3	7.6–11.4	5.1–8.6	11
C₁₅ and C₁₇	1.5	0.8–2.2	[2]	3
C₁₆	29.6–40.0	13.8–27.6	26–32	29
C₁₈	19.7–29.4	19.4–24.1	21–22	21–24
C₂₀	12.4–23.0	12.6–19.6	18–26	20–21
C₂₂	16.8–21.7	20.5–27.3	11–14	11–15
C₂₄	0.1–0.9	0.9	15.4	0.6

[1] Data from Maas et al. 1962; Jart 1965; Peifer et al. 1960; Lane et al. 1963; Iverson 1958 and 1965; Gruger et al. 1964.
[2] Reliable data unavailable.
[3] Data from Archer-Daniels-Midland: private communication.
[4] Figures are for combined monoenes and dienes.
[5] Figures are for combined tetraenes, pentaenes, and hexaenes.

TABLE 23

RANGES OF UNSATURATION OF SOME NON-MARINE OILS[1]

	Per cent Composition					
	Linseed	Soy	Sunflower	Tung	Rapeseed	Tall[2]
Extent of unsaturation						
Saturated	10-11.5	12.3-15	13.3	3.6-4.9	0.1-2	3
Monoenes	19-22	18.2-35	19.7-23.7	8.7	69.7-72	51-57.3
Dienes	14.5-18.3	44.5-57.2	60.2-69.8	14.8	14-16	35-46
Trienes	47.4-58.9	5.0-9	0.8	—	8-9.6	0-1.5
Trienes, conjugated	—	—	—	71.6	—	2.5
Acid chain length						
C_{12}	—	0.2	—	—	—	—
C_{14}	—	0-0.2	—	—	—	—
C_{16}	6.2-7.0	8-14.9	11	4	0-4	3.5
C_{18}	93.0-93.8	89-92	89-90	96	43	96.5
C_{20}	—	0-1	0-1	—	13	—
C_{22}	—	—	—	—	40	—
C_{24}	—	—	—	—	2	—

[1] Data from Mills 1964; Anon. 1959.
[2] Distilled tall oil fatty acids only.

The polyenoic acids are predominately found in the C_{20} and C_{22} chain lengths; the saturated acids in the C_{14} and C_{16} chain lengths; the monoenoics are scattered through the C_{16}, C_{18}, C_{20}, and C_{22} chain lengths.

The high iodine value (unsaturation) of menhaden oil is produced by the unique combination of mono-, tetra-, penta-, and hexaenoics as distinct from the vegetable oils that predominate in mono-, di-, or tri-enoics.

The polyenoic acids, from the most recent data (Ackman 1964), are predominately *cis* rather than *trans* in configuration, non-conjugated, and attached to the 2-position in the triglycerides. This is essentially the same as in most of the vegetable and animal oils.

Except for rapeseed oil, none of the industrial vegetable oils have carbon chain lengths over C_{18} in contrast to fish oils.

For further details on fatty acid composition of fish oils see Chapter 1.

INDUSTRIAL UTILIZATION OF FISH OILS

The major industrial uses take advantage either of the unique type and high degree of unsaturation of the fish oils to produce elastic durable polymers or of the long and diverse mixture of chain lengths to add lubricity, detergency, and plasticity functionalities. Currently fish oils are consumed mostly as the natural or crudely separated triglyceride mixtures or in hydrogenated form, neither of which fully utilizes the potential of the unique components. For drying oil purposes, some of the saturated glycerides, "stearines," and odor bodies are first removed. Alkali refining and bleaching are used to remove the minor amounts of free fatty acids,

TABLE 24

MAJOR USE AREAS FOR MENHADEN OIL

Year	Menhaden Oil Production	Domestic Use	Drying Oils	Lubri- cants	Feeds	Fatty Acids	Others
	MM lb.	MM lb.	MM lb.	MM lb.	MM lb.	MM lb.	MM lb.
1962	233	156	70	25	36	19	6
1963	168	104	24	27	23	12	18
1964	175²	82²	58	4	4	15.26+³	
1965	175²	75²	4	4	4	4	4

¹ MM lb. = millions of lb.
² Estimates.
³ A minimum estimate for hydrogenated acids only from the Fatty Acid Producers' Council.
⁴ Reliable data unavailable.

phospholipids, sterols, hydrocarbons, protein degradation products, and pigments that contribute to color and odor.

U.S. statistics (Anon. 1965C) on U.S. consumption indicate fish oils to be seventh highest among industrial fats and oils. About the same ranking occurs for world usage. More than one-half of the domestic production is exported, mainly for consumption in foods. Drying oil uses—paints, varnishes, lacquers, resins, caulks, sealants, inks, putty—are the major outlets, with lubricants, animal feeds, and fatty acids consuming the remainder about equally (see Table 24).

The classification used below is based on whether the natural unsaturated triglycerides, the natural saturated or hydrogenated glycerides, or the hydrolyzed acids are the major starting raw materials for the products described.

Natural Unsaturated Triglycerides

Most of the products below utilize the high reactivity of the carbon to carbon double bonds for polymerization, copolymerization, oxidation, isomerization, sulfation, and epoxidation.

Protective Coatings.—The amount of fish oil used varies from year to year as shown above, mainly due to price fluctuations relative to other oils. Normally fish oils are an attractive raw material for this purpose due both to the price and the high quality coatings produced. In all drying oil uses, the quantity of fish oils used ranks below that of tall oil but ahead of tung. Linseed, soy, and castor are the top-ranking oils in decreasing order. Fish oils are consumed in alkyds, varnishes, and per se in paints. Heat-bodied oils, mixed with raw linseed oil, go into exterior house paints. Air-blown oils are valuable in nitrocellulose plasticizers, barn and roof paints, and as rust-proofing coatings. Copolymerized with dicyclopentadiene, the oils make good primers. Bodied oils are mixed with tung oil to lower the costs of varnish manufacture.

However, synthetic resins and polymers—mainly derived from petrochemicals—have cut heavily into the market. This is true for all drying oils.

For practically all surface coatings, the high percentage of saturated fatty acids is a serious disadvantage and reduction to lower levels is necessary. "Winterizing" by cold pressing is the major process used in the U.S. Solvent fractionation—mainly propane (the Solexol process)—has been used commercially. Liquid sulfur dioxide, furfural, molecular distillation, and urea complexing have been described in the literature (Schlenk and Ebner 1959; Gruger 1960; Freeman 1940; Hixon and Miller 1953). The iodine values of the menhaden oils so treated are raised to as high as 200, which increases their value as drying oils—faster drying and harder, less tacky films are obtained. Oils such as cod-liver, having only 20% saturated acids initially have an advantage in this respect. Semi-refined anchovy with its high iodine value "dries" quite rapidly. Oils classed as drying oils usually have over 130 I.V., semi-drying oils 100–130, and non-drying oils 100. However, the desirable properties are not characterized solely by I.V. There are considerable variations in properties even among oils with the same iodine values. Anchovy versus "winterized" menhaden is an example of this. "Winterized" menhaden is reported to penetrate and adhere to rusty surfaces better than some of the other drying oils (DeSesa 1959).

The commercial "winterized" oils, known as L.C.P. (light cold pressed) or L.P. (light pressed) oils, do not give sufficiently hard films to compete with linseed oil. However, converted into alkyd resins with phthalic anhydride, isophthalic acid, or maleic anhydride, fish oils can be used to increase durability and hardness and become valuable performers. The U.S. Department of Commerce reported, for instance, that 4.7 million lb. fish oil were used in resins in 1964, and 4.0 in 1963 (Anon. 1965A). Maleic anhydride acting as a trifunctional component increases cross-linking, and is especially helpful. Pentaerythritol or other polyhydroxy alcohols are included to esterify the acids, and compatibility with nitrocellulose is increased. The "maleinized" oils, when neutralized with ammonia, become water dispersible and useful in water-based coatings. A tendency for these alkyds to yellow on exposure to ultraviolet light, however, restricts their usefulness. Most of the highly polyunsaturated oils have the same defect.

Maleinized oils for heat resistant finishes have been reported (Troupe et al. 1957). A broad range of industrial products from isophthalic acid alkyds have been described (DeSesa, 1959). Phthalic-based alkyds of 60% oil length show superb drying speed and hardness, exceeded only by dehydrated castor oil (DeSesa 1963).

An outstanding class of products are the copolymers made from cyclopentadiene or dicyclopentadiene. These are designed for applications in industrial enamels, varnishes, rust inhibitive paints, and primers (Anon. 1964). These copolymers have less tendency to yellow and possess less odor. Several U.S. companies produce them commercially.

Styrene is also used as a comonomer with both the oils and the oil-alkyds. Faster drying times, increased hardness, and improved water and alkali resistance are obtained. Films from methyl divinyl acetylene copolymers are claimed to give impact-stability, hardness, flexibility, and good adhesion (Marsel 1959).

Some work has been done overseas to convert the normally unconjugated carbon to carbon double bonds to conjugated systems (Reed 1965). This gives them some tung-like properties, useful in varnishes and makes copolymerization with vinyl toluene, divinyl benzene, methyl methacrylate, and acrylonitrile possible with better colors and films (Kooy 1964).

Heat-bodied fish oils are important commercial products. The stability, odor, viscosity, solubility, compatibility, and water and alkali resistance are improved. Contributions to gloss and leveling characteristics also result. Exclusion of air during the bodying process (polymerization) was an advance of modern vintage resulting in the production of a superior quality bodied fish oil.

Blown oils (air-oxidized) are also standard products with some of the same advantages as the heat-bodied ones. The surface activity is increased through the formation of oxygenated molecules, which is an advantage in some uses, such as pigment grinding. However, for the same reason, solubility in mineral spirits is decreased, and water resistance is lowered. Blown oils are also reported to be valuable in making foundry cores. In 1961, the Department of Commerce reported 1.9 million pounds were consumed in making core oils, as against 8.3 million pounds of tall oil.

The unsaturated alcohols, both conjugated and unconjugated, made by the sodium reduction route—have been reported for drying oil uses. Esterified with maleic, pyro-mellitic, and phthalic anhydride improved speed of drying to tack-free films, and high-temperature polymerization properties were obtained (Ayres 1958; Rizzo 1957).

In recent years, interest in fish oils as air entrainment agents for the protection of concrete against winter damage has been renewed.

See Chapter 17 for more details on use of fish oils in protective coatings.

Lubricants.—Most of the lubricant and grease applications use derivatives of fish oils, rather than the oils themselves. These derivatives are described later on in the chapter in the section on hydrogenated glycerides.

The Department of Commerce reported five million pounds consumed in lubricants in 1964, 5.2 million in 1963 (Anon. 1965A). Specially oxidized heat polymers are effective lubricants in the presence of water and are used for propeller shafts and auxiliary marine steam driven engines. Sulfurized fish oils are one of the components of extreme pressure paraffin base oils (Mitacek and Greham 1965; Swensen 1942). Lead soaps of menhaden oil are used for the same purpose.

Caulks and Sealants.—Minor quantities of sealing compounds are designed around blown and heat polymerized fish oils. They are formulated to achieve prolonged elasticity, good slip, and binding properties. Oleo resinous binders for glazing putties and sealants, and building caulks are mainly prepared from soy and linseed oils. However, in many instances, formulations are interchanged between these vegetable oils and fish oils, depending on the relative costs of the oils.

Leather Treatment Agents.—Sulfated menhaden, herring, cod, and sperm oil are used extensively in fat liquoring compositions. They are usually medium SO_3 oils (4–6%) which are applied to the leather from aqueous emulsions after the tannage is completed. The oil confers internal lubricity which results in the familiar soft feel of leather.

Printing Inks.—Heat-bodied and blown fish oils mainly are used for printing ink formulations. Increased versatility for this application is often obtained from copolymerizing mixtures of these two. Menhaden, herring, and sardine oils are suitable for blending with or partial replacement of linseed oil. Printing ink manufacture has become highly complicated and the requirements quite stringent, with much of the market held by synthetic resins and polymers today. A good review of the subject was published by Dunning (1959).

Animal Feeds.—As noted in Table 24, a high percentage of the fish oils consumed in the United States ends up in animal feeds. The amount in a given feed mix is normally restricted to prevent the carryover of objectionable flavors and odors into the carcass of the animal. Sometimes hydrogenated sardine oil is added to the menhaden to raise the melting point of the mixture (Rosenberg 1963). Considerable research is being done by the U.S. Bureau of Commercial Fisheries on the nutritional effects of the oils and ways of removing the "fishy" flavors and odors. It is interesting to note that oils carefully prepared from fresh fish tissue are relatively bland (Chipault and McMeans 1965).

Insectides.—Fish oils are excellent stickers and useful defoliant aids for emulsion application of insecticides. Potassium soaps are preferred where no interference with the leaf breathing apparatus is desired. The ammonium soaps of menhaden and salmon oil are reported to be effective against nematodes (Sokoloff 1962).

Plasticizers and Surfactants.—Expoxidation with hydrogen peroxide introduces an oxirane oxygen atom into the carbon to carbon double bond positions. Several patents have appeared recently indicating some commercial interest in these products for plasticizers, special surface coatings, surfactants, and leather fat-liquoring agents. Menhaden, herring, anchovy, and other fish oils are mentioned. The epoxidized monoglycerides and acetylated monoglycerides as well as the oils are described (Ault and Feuge 1959; Findley 1962; Dazz 1962; Plapper and Dieckelmann 1963A and 1963B; Swift & Co. 1962; Wisnick et al. 1964).

Saturated Natural and Hydrogenated Glycerides

The reactivity of the carbon to carbon double bonds with hydrogen is utilized to saturate the fish oils. The hydrogenated glycerides, and the corresponding hydrogenated acids that result, make up probably the second biggest industrial market for fish oils. It is difficult to assess its exact size, but it is probably growing as fast or faster than any other outlet.

The hydrogenation processes use activated metal catalysts such as nickel and in general are similar to vegetable oil hydrogenations (see Chapter 18). The "fishy" odor is destroyed by hydrogenation. The melting point and titer (hardness) are raised considerably. These are among the most important effects of hydrogenation. Hydrogenation is probably the most widely used and most studied economic development in the fat field. Some 50% of the saturated fatty acids produced commercially are of the hydrogenated type.

At times, menhaden oil has been lower priced than, or equal priced with, inedible tallows (bleachable, fancy). This, as well as the wide range of carbon chain lengths and the high percentage of chain lengths over C_{18}, gives a great range of utility. The improved stability that results from the reduction of the unsaturation is valuable in applications where only the unusual chain length composition is needed.

Lubricants—Most lubricating greases consist of lubricating oils thickened with metal soaps. The bulk of the hydrogenated fish oil soaps are actually made from the acids rather than the fat. They are discussed together in this section.

Hydrogenated menhaden, herring, and sardine oils and acids are used. The 32 to 45% content of C_{20} and C_{22} acids helps solubilize the soaps in the mineral oils. The whole oil use is limited by the effects on solubility of the soaps in the lubricating oil. Aluminum soaps are particularly sensitive to this effect. A different-type gel or thickening effect is obtained if the by-product, glycerin, is left in the grease. The metal portion of the soap is almost invariably sodium, calcium, lithium, barium, aluminum, or lead,

predominantly the first two. Lithium and barium soaps are becoming more popular because of the combination of good heat and water resistance. The composition of the fatty acids used critically affects the properties of the greases. Grease manufacture has become complicated by the ever-increasing severity of the operating conditions imposed by modern machinery.

Lithium hydrogenated fish-oil greases are notable for their chemical stability, high water resistance, and high dropping points. Block sodium greases, high temperature mixed sodium-barium greases, and hydrated calcium greases employ hydrogenated fish oils. Aluminum greases made from herring-oil acids are claimed to have good working stability, to set well at high temperatures, and to be non-grainy (Lux and Parker 1958).

The total quantity of fatty acid soaps used in grease for 1960 was approximately 32.4 million pounds. In 1962, about 23 million pounds of hydrogenated fish oils or acids were used (Anon. 1963) in the manufacture of lubricating greases. Some of this was not in soap form. Methyl and butyl esters are used, for instance, the latter as additives to improve "oiliness."

The saturated glycerides are effective in lubricating textile yarns during processing. Part of the usage includes softening, wetting, emulsifying, and water-proofing agents. Partially hydrogenated and sulfated tri- and monoglycerides are useful in these applications. Significant tonnages go into this total market in one form or another.

Leather is "stuffed" with the hydrogenated oils to contribute softening and water-proofing functions and suppleness.

Buffing Compounds.—These materials consist essentially of an abrasive held together by a waxy lubricating material. The fish oils, with their broad ranges of carbon chain lengths and high percentages of C_{20} and C_{22} acids, work well as setting agents which strengthen the buffing bar, reduce shrinkage, and provide some wetting action. The fatty acids are also used in compounding buffing materials to control the amount of shrinkage.

Miscellaneous.—There are a number of proprietary uses scattered over a wide range of end products. Hot-melt adhesives, for example, are consumers of fish oils.

Fatty Acids

The third major area for the industrial uses of fish oils is the manufacture of fatty acids. Splitting or hydrolysis of the triglycerides produces the fatty acids and glycerin. Splitting is an old art that started with batch saponification with alkali, followed by acidulation of the resulting soap with acids. The modern methods are based on continuous, automated, high-pressure splitting with steam in stainless steel equipment with high

thermal efficiencies for economical operation. The fish oils are usually hydrogenated before splitting to minimize degradation. The mixtures of acids produced are either used as such or fractionally distilled, solvent separated, or crystallized into special products with segregated chain lengths. There are commercial products with 75% contents of C_{20} and C_{22} and 25% C_{18} chain lengths acids as well as 30% and 40% of C_{20} and C_{22} acids. The only other source of these chain lengths is rapeseed oil. Fish oils are the only common oils containing the C_{24} acid.

Normally only the acids in hydrogenated form are distilled commercially. Conventional fractional distillation requires such high temperatures that losses by degradation and polymerization are excessive if the unsaturated acids are the feed stock. Large-scale production of fractionated nonhardened fish oil acids is not practiced currently, although good separations of the unsaturated acids have been achieved commercially with sardine oil.

In the United States, fish oils have been an economical source of fatty acids and compete generally with the other natural fats and oils besides having their own unique applications. In 1964, there was an estimated 510.4 million pounds (Fatty Acid Producers' Council estimate) of saturated and unsaturated fatty acids produced plus approximately 266 million pounds of tall oil derived fatty acids (less than 10% rosin type only).

In addition to the above (Table 25), there are some unsaturated fish oil fatty acids included in the 10.1 million pounds of combined vegetable and marine acids reported by the council as produced in 1964. Some of the fatty acids are obtained from by-product soap stock from alkali refining. The history of production is shown in Table 26. If these Council estimates are used, production has not shown much variation over the years. Overseas production is undoubtedly as large or larger.

TABLE 25

U.S. SATURATED FATTY ACID PRODUCTION

Year	Hydrogenated Fish & Marine	Total Saturated
	Millions of Lb.	Millions of Lb.
1961	10.3	—
1962	12.5	259.8
1963	9.6	271.2
1964	10.3[1]	297.9

[1] Fatty Acid Producers' Council estimated 15.26 million pounds in 1964, probably a more correct figure.

The major industrial applications of the acids are based on the reactivity of the carboxyl group. Neutralization, esterification, hydrogenation, and ammonolysis are the major chemical reactions used.

TABLE 26

FISH AND MARINE FATTY ACIDS PRODUCTION

Year	Millions of Lb.
1955	20.22
1956	19.40
1957	16.55
1958	10.57
1959	8.33
1960	8.73

¹ Data from Anon. 1960.

Only the clearly identified segments of the market are discussed separately below. The acids are highly flexible chemical intermediates with many uses, some of which are very proprietary. Rubber compounding agents, brake blocks, cosmetics, pharmaceuticals, slushing compounds, wood preservatives, rust inhibitors, candles, water-dispersible paint vehicles, and paper-sizing agents have been mentioned.

Metal Soaps.—The metal soaps are products that contain carboxyl groups neutralized with metals. The sodium and calcium soaps specifically are actually made to a large extent by saponification of the hardened oil itself with caustic soda or hydrated lime. Others such as the aluminum and zinc soaps are made by double decomposition with the ammonium or sodium soaps and water-soluble salts of the metals.

The use in lubricating grease was described earlier. The aluminum HFA soap is valuable also in water-proofing and as a "flatting" agent in paints. At one time the zinc and lead soaps of the unsaturated acids were used as paint driers, but this has largely been discontinued. Various soaps —aluminum and calcium—are used in leather, textile, and paper waterproofing and sizing. The unique carbon chain lengths improve the solubility of the soaps in non-aqueous media.

Esters.—Many miscellaneous commercial products are made by esterification of the acids or interesterification of the oils themselves with alcohols. Methyl, ethyl, and butyl alcohols are used. Butyl esters of saturated acids are recommended as lubricants for rolling aluminum, die-casting plastics, textile spinning, and alloy metal-working. There has been some commercial interest in the esters for conversion to the alcohols by hydogenation.

Alcohols.—The fish oil alcohols are of minor commercial interest currently. Catalytic or sodium hydrogenation of the ester group in the methyl or ethyl esters or catalytic hydrogenation of the carboxyls of the free acids yields the alcohols. The industrial applications of high molecular weight alcohols in general are many, and very large tonnages are consumed in

biodegradable detergents. Fish oil-derived alcohols, however, are mainly
of research and development interest.

Nitrogen Derivatives.—An important family of products is made by
reacting the carboxyl group with ammonia. Amides are the primary reac-
tion products. These are then converted by dehydration to nitriles, the
latter by hydrogenation to primary, secondary, and tertiary amines. Qua-
ternary ammonium derivatives are obtained from the amines. Figures for
the volume of fish oils consumed this way are not available. The com-
mercial uses in general parallel those of the same products made from
other raw materials—textile and fabric softeners, ore beneficiation, plastic
film antiblocking agents, antistatic agents, bactericides, fungicides, corro-
sion inhibitors, cationic surfactants, waxes, paper coatings, petroleum ad-
ditives, grease thickeners, boiler treatment, fuel additives, and asphalt an-
tistrip agents. Textile, plastic, and petroleum applications predominate.
The polarity of the amine derivatives makes them particularly useful in
these fields.

Miscellaneous.—Studies have been made demonstrating that the unsatu-
rated fish oil fatty acids are efficient, powerful, and selective collectors for
the impurities in iron ores by froth flotation (Karrick 1965). The com-
mercial possibilities for iron ores have been studied. Patent claims have
been made for beryllium ore flotation (Havens 1963).

Monoglycerides, acetylated monoglycerides, and aldehydes have been
investigated using the unsaturated fatty acids from menhaden, herring,
tuna, and sardine oils (Karrick 1965).

The acid chlorides and the quaternary ammonium chlorides have been
described.

Halogenated derivatives have been made including those from bromina-
tion of the methylene carbon separating the double-bonded carbons.
Chlorinated fish oils have been examined for the fire-retarding of wood.

The sizing of hardboard with the C_{20} and C_{22} chain length fatty acids to
prevent the absorption of water was tested with good results (Sinclair
1964).

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