Solexol Fractionation of Menhaden Oil[1]

N. L. DICKINSON, The M. W. Kellogg Company, New York City,
J. M. MEYERS, J. Howard Smith Inc., Port Monmouth, N. J.

IN November, 1946, the M. W. Kellogg Company, engineers and contractors of petroleum and chemical plants, announced to the industry a solvent process for treating glyceride oils. Given the name "Solexol," it was a development of a process used extensively throughout the world to fractionate lubricating oils from crude petroleum residues. The solvent used in the process is ordinary propane, familiar as LPG (liquefied petroleum gas) or "bottled gas."

The separations performed in Solexol pilot plants, some of which were described in an article by H. J. Passino (1) are, in many instances, little short of amazing, not only of themselves but in the infinite variety of things which have been done with a single solvent and in a single tower. However in the almost five years since the announcement there has been a scarcity of information on the extent to which sound commercial operations have borne out the promise of pilot plant explorations. The only article on the subject published in this country, an excellent paper by E. B. Moore, describing the tallow decolorizing installation at Lever Bros. Baltimore plant, was presented before the Society at the 1949 fall meeting (2).

At this writing there are five commercial Solexol plants in regular service, and a sixth is under construction. Furthermore two of the Solexol units are supplemented by a continuous fractional crystallization (or winterizing) process, not heretofore announced, which goes by the name of "Propane Destearinizing." As the name suggests, it also employs versatile propane as solvent.

By way of brief resumé, the Baltimore Solexol installation comprises a single-tower decolorizing unit which processes more than 200,000 pounds per day of crude tallows, raising their color to 7-10 Lovibond red (5¼-inch column) at the expense of about 2% of "foots."

There is a three-tower Solexol plant at Simonstown, Union of South Africa, operated by Marine Oil Refiners Ltd., which concentrates vitamin A from fish liver oils to a potency of 300-400,000 Int. units per gram. About 5,000 lbs. of the liver oils, having a potency of 10-12,000 units per gram, are charged daily. The vitamin oil is winterized by Propane Destearinizing but, because of the small volume of the concentrate, the destearinizing equipment is not of the latest, continuous type. Currently this plant is being expanded to permit simultaneous fractionation of 40,000 lbs./day of pilchard oil to produce a high-quality, fast drying paint oil. Two articles dealing with the design of the plant and the commercial significance of vitamin and pilchard operations have been published in South Africa (3, 4).

At Cincinnati, Ohio, there is a single-tower Solexol plant which was built by Refinol Inc. to decolorize 120,000 pounds per day of crude tallows and which has been operated on a number of stocks, including tall oil and acid foots.

A major packing concern operates both Solexol and Propane Destearinizing in the midwest. The single-tower Solexol section is equipped alternately to decolorize or fractionate from 130,000 to 200,000 pounds per day of a variety of glycerides and low grade fatty acids. The destearinizing section has likewise processed both glycerides and fatty acids, continuously separating between stearin and olein or lard oil on the one hand, and between stearic and oleic acids or red oil on the other. Propane is the common and sole solvent for both sections.

Under construction in a European country is a two-tower Solexol plant which, when completed, will decolorize 154,000 pounds per day of acid whale oil or, alternately, decolorize and fractionate 121,000 pounds per day of herring oil to produce a premium quality drying oil and an improved edible fraction.

The fifth operating Solexol plant is located on the shores of New York's outer harbor at Port Monmouth, New Jersey. The operations conducted there have been chosen as the subject of this paper because they illustrate well several of the types of separations which liquid propane makes with ease and efficiency. Designed for 95,000 pounds per day of crude menhaden oil, this plant is equipped to decolorize it and to segregate by Solexol fractionation a concentrate of vitamins A and D, a "Standard Fraction" and a fast-drying "High Fraction." All three of the decolorized stocks may be winterized in the Propane Destearinizing section.

THE production of menhaden oil in the United States has for several years exceeded the production of sardine oil, and it has thus become the largest volume domestic fish oil. About 65 million pounds are pressed annually, about equal to sardine and herring oil combined (5). Menhaden fishing is confined to the Atlantic and Gulf coasts with the bulk of the catch concentrated in the four months of June through September.

Like other fish oils, crude menhaden oil has (in glyceride form) a high content of highly unsaturated C_{20} and C_{22} fatty acids (about 31%). It also contains about 45% of unsaturated C_{16} and C_{18} acids and about 24% of saturated acids. The latter is sufficient to interfere with the formation of hard, dry films (6).

The principal outlets for menhaden oil have been in the paint and varnish industry and in soaps and edible products. The animal feeding industry also consumes sizable quantities as a source and carrier for vitamins A and D. In order to be useful as a drying oil it must be winterized and refined; for soaps and edible products it must be hydrogenated. Although fish oils have long been processed and used in protective coatings for the improvement of adhesion, elasticity, and durability, the necessity for one or another form of processing, the sometimes variable quality and lack of experience in handling the oil, combined with trade prejudice, have reduced the marketability and limited the outlets for the crude fish oil.

SOON after the announcement of the Solexol process it became apparent to J. Howard Smith Inc., major producers of menhaden oil, that this new proc-

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[1] Presented at the 25th fall meeting, American Oil Chemists' Society, Chicago, Ill., Oct. 8-10, 1951.

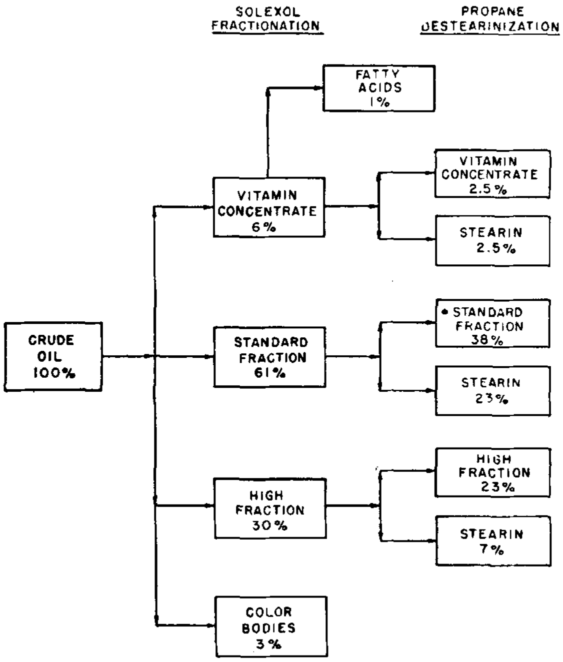

Fig. 1. Solexol fractionation of menhaden oil, processing sequence and yields.

ess offered a means of segregating the crude oil into fractions with improved properties more suitable for particular uses. Thus the plant was designed to produce a vitamin concentrate for the feeding oil industry, stearin for the soap and edible trade, and drying oils for the paint and varnish maker.

A typical yield distribution is shown in Figure 1, which illustrates both the distribution of products from Solexol fractionation of the crude and from subsequent Propane Destearinization of the intermediate fractions. These yields correspond to current specifications and an average grade of crude oil. A strong practical advantage of the process however lies in its ability to vary the yield of one or more fractions, by simple adjustment of automatic control instruments, to accommodate a change in market requirements or in the composition of the crude oil charge.

In order to make it easier for the reader unfamiliar with the literature on the solvent properties of propane to follow the menhaden oil flow sheet, it may be noted that liquid propane dissolves nearly all oily substances more or less completely at room temperature. When such solutions are heated moderately, progressively increasing amounts of an oil phase (containing much less propane than the original solution) are precipitated. If heating is continued until about 207°F., which is the critical temperature of propane, essentially nothing remains in solution. This decrease in solubility with increasing temperature is the reverse of the relationship observed with common solvents and occurs because the temperatures used in the Solexol process, while notably low by most comparisons, are above the temperature of maximum solubility, in an area known as the "paracritical region," for this particular solvent.

It is observed that the different constituents of the various oils are precipitated from solution at different temperatures, and thus we have a property capable of forming the basis for commercial separation of oils into their component compounds. In practice the sharpness of the separations are enhanced by carrying them out in countercurrent towers, with "stripping" and "reflux," very much as is done in distillation.

Having demonstrated such remarkable properties as a selective solvent in the Solexol process at temperatures in the range of 150° to 200°F., it is surprising that propane should also prove to be an ideal medium for fractional crystallization at temperatures of zero to —40°F. However this versatility had been forecast by the experience of the petroleum industry, which employs propane as a selective solvent for deasphalting and fractionation of lubricating oils into cuts of different viscosity and then uses the same solvent for dewaxing at subzero temperatures to meet pour point specifications.

Fractionating towers and other equipment for Solexol and Propane Destearinizing bear a marked similarity to those for Propane Deasphalting and Dewaxing. In fact, even on close inspection, it is easy to mistake the Port Monmouth menhaden oil refinery for one of the modern petroleum oil plants.

It is interesting to compare in a general way the commercial progress of Solexol in the oils and fats industry with the much older Propane Deasphalting and related processes for petroleum oils and resins which have had a commercial history extending over a period of about 17 years. There are in the neighborhood of 20 Propane Deasphalting Plants in service; only about half of them are of the modern tower type. The balance employ simple settling drums to effect separations. Nearly all of the petroleum installations are simple single-function units, i.e., they merely separate between asphalt and heavy lube oil. Two comparatively new units have towers for two different functions.

THE oils and fats industry traditionally moves with caution in accepting radically new processes and products. Yet in five years it has contracted for six Solexol plants and, of more technical significance, it is already operating more highly developed and complex installations than any in the petroleum industry. The Port Monmouth plant has solvent fractionating towers for three separate functions, and Marine Oil

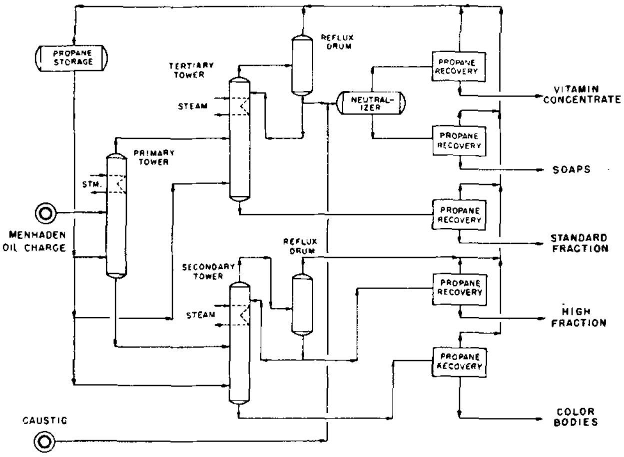

Fig. 2. Simplified flow diagram, Solexol Fractionation of menhaden oil.

Refiners, upon completion of their current expansion program, will have four solvent towers.

Figure 2 is a simplified flow diagram of the Solexol section of the Port Monmouth plant. Crude menhaden oil is charged from storage tanks into a primary tower in which treating conditions are maintained such that a separation is performed on the basis of unsaturation. Relatively saturated glycerides go overhead in solution in the bulk of the treating propane while relatively unsaturated constituents leave the bottom of the tower in an oily phase containing about an equal volume of propane. In this primary fractionation the vitamins A and D and the free fatty acids contained in the charge accompany the relatively saturated "standard fraction" in the overhead stream, while color bodies, oxidized fatty acids, and other extraneous substances go with the unsaturated bottoms product.

The overhead solution from the primary tower flows to a tertiary tower to be refractionated in the presence of additional propane and at higher temperatures. Here conditions are chosen to concentrate vitamins and free fatty acids in the overhead solution and to precipitate as bottoms phase the standard menhaden oil product. The tertiary overhead is neutralized in propane solution with dilute caustic soda to effect complete removal of free fatty acids as a soap solution. The neutralized solution of vitamin concentrate is freed of propane and sent to intermediate storage. The solvent contained in the aqueous soaps and in the standard fraction from the bottom of the tertiary tower are also recovered for reuse before these products go to field storage tanks.

The bottoms from the primary tower flow to the secondary tower in which they are treated at reduced temperature and solvent ratio. In this tower conditions are regulated so that the highly unsaturated "high fraction" (which had been precipitated under conditions existing in the primary tower) leaves the tower top in propane solution, and only color bodies and associated extraneous matter remain as lower phase to be withdrawn from the bottom. Solvent is recovered from both of these product streams before they leave the unit.

As indicated on the diagram of Figure 2, each Solexol tower has a series of steam coils in its upper section. These coils not only maintain a temperature such that the overhead solution carries only the intended oil components but serve to precipitate out of solution a portion of oily phase which runs back down the tower as "reflux." Similarly, propane is introduced into the bottom of the tower in such amount and at a temperature which causes more oil to dissolve than is ultimately carried out of the top of the tower. This excess solvent power effectively "strips" the bottoms product. Readers familiar with distillation theory will appreciate that these functions are quite analogous to those performed by reflux and stripping vapor in a modern distilling column.

An alternate method of refluxing the tertiary and secondary towers is provided. Overhead product from either of these towers (partially stripped of solvent) may be pumped back to the top tray. As a general thing, equally good results are obtained with either method of refluxing, and occasionally both methods are used.

Because of propane's low boiling point its separation from product streams is simple and complete and does not require temperatures high enough to damage even the sensitive vitamin concentrate. In general, recovery comprises heating the solutions with steam in an evaporator or flash drum at sufficient pressure so that the vapors evolved can be condensed with plant cooling water, followed by steam stripping at essentially atmospheric pressure. Only the traces of propane removed in the final stripping require compression. For a thorough description of typical propane recovery equipment the reader is referred to the article of E. B. Moore (2). Solvent losses at Port Monmouth are normally about 0.05% of the circulating rate.

All of the products of the Solexol section, with the exception of the color bodies, are winterized by propane destearinizing. Since the destearinizing section is a single unit, only one of the three fractionated stocks can be winterized at a time. Runs are made successively on each stock in accordance with inventory requirements. A diagramatic flow sheet of the destearinizing section is shown in Figure 3.

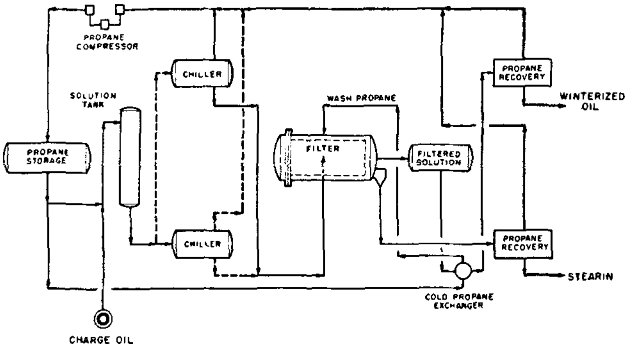

FIG. 3. Simplified flow diagram, propane destearinization of fractionated menhaden oil.

Charge oil (which may be vitamin concentrate, standard fraction, or high fraction) is mixed with liquid propane and held briefly in a solution tank. Leaving this tank, it is cooled by heat exchange and discharged into one of two chillers. When a chiller is filled, the incoming stream is switched to the second chiller and the first one enters its refrigeration cycle.

In both Propane Dewaxing and Propane Destearinizing chilling is accomplished by "auto-refrigeration," that is by evaporation of the solvent itself. It is merely necessary to lower the pressure imposed on the chiller, and the temperature of the solution falls a corresponding amount. Should the pressure be reduced to zero, the temperature would be —44°F., the atmospheric boiling point of propane. However this is a lower temperature than ordinarily required.

As the temperature in a chiller drops, the higher melting compounds in the oil form small solid crystals which remain suspended in the propane solution. Chilling is continued until all the stearin components are solidified and the individual crystals have grown large enough to filter readily. At this point the contents of the chiller comprises a fairly thick slurry.

Chillers are alternated so that there is always a supply of chilled slurry ready to charge to the filter. The continuous rotary filter separates between solid stearin and liquid propane-oil solution. The stearin cake is continuously washed with cold liquid propane

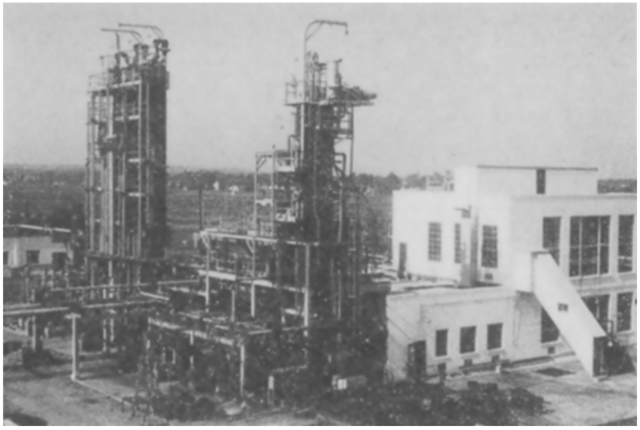

FIG. 4. View of Solexol Section. On the left are the Primary, Secondary, and Tertiary Towers. Strippers and Product Coolers for both sections are in the center. The building at the right houses pumps, compressors, and control room (first floor) and destearinizing filter on the second floor.

to remove solution which adheres to the solid particles. Since the vapor pressure of propane at filtering temperatures is ordinarily above atmospheric, the entire filter is enclosed in a pressure shell.

The stearin is pumped away from the filter as a propane slurry, and both stearin and filtrate (winterized oil) are freed from propane in the same manner as in the solvent recovery equipment of the Solexol section.

Propane vapors from the chillers are compressed to sufficient pressure so that they can be condensed with plant cooling water. The same compressors also handle low pressure vapors from the strippers of both Solexol and Destearinizing sections. The use of a common solvent permits many other items of solvent handling equipment to be common to the two sections.

Just as adjustment of temperature and solvent ratio permit control of color, iodine number, etc., in the Solexol section, the titer and cold test of the stearin and winterized oil may be controlled in the Destearinizing section by adjustment of solvent ratio, chilling temperature, and filter wash.

Temperatures, pressures, and flow rates throughout the plant are under the automatic regulation of control instruments grouped in a single control room. Five operators per shift adequately supervise all of the equipment. In keeping with modern practice in process construction towers, drums, heat exchangers, etc., and many of the pumps are located out-of-doors. The filter, compressors, and some of the pumps are housed.

TABLE I

Solexol Fractionation of Crude Menhaden Oil, Properties of Charge and Products (Before Propane Destearinizing)

	Crude	Vitamin Concentrate	Standard Fraction	High Fraction	Color Bodies
Yield, vol. %	100	6	61	30	3
Color (Gardner)	12	4	4	7	Dark
Iodine No. (Wijs)	175	105	158	201	230
Acid No	3.0	12	3.8	1.3	4.0
Saponification No	190	200	197	193	185
Unsaponifiables, wt. %	1.2	2.3	0.7	0.9	1.0
Saturated Acids, wt. %	28	55	30	24	19
Vitamin A, I.U./gm	30	140	....	....	....
Vitamin D, USP/gm	35	270	....	....	....

Table I compares the properties of a typical crude menhaden oil with those of four oils produced from it by commercial Solexol fractionation. The fractions are arranged from left to right in order of decreasing solubility in propane. It is apparent from the tests that saturates and vitamins are preferentially extracted into the more soluble cuts while unsaturated glycerides are less soluble and highly colored compounds least soluble of all.

TABLE II

Propane Destearinization of Vitamin Concentrate from Solexol Fractionation of Menhaden Oil, Properties of Charge and Products

	Charge	Winterized Vitamin Concentrate	V.C. Stearin
Yield, vol. %	100	50	50
Vitamin A, I.U./gm	140	270	....
Vitamin D, USP/gm	270	530	80
Iodine No. (Wijs)	105	150	75
Saponification No	200	196	204
Unsaponifiables, wt. %	2.3	3.0	1.5
Cold Test, hrs. at 32°F	....	5	....
Titer, °C	....	....	43

Table II illustrates the effect of Propane Destearinizing on the properties of the vitamin concentrate. The most significant factor is the increase in vitamin potencies which are almost doubled since there is little loss in the stearin.

Under the present market structure vitamin oils of the low order of potency obtainable from fish body oils are not a profitable product. Therefore this portion of the stock is being left with the standard fraction.

TABLE III

Propane Destearinization of Standard Fraction from Solexol Fractionation of Menhaden Oil, Properties of Charge and Products

	Charge[a]	Winterized Standard Fraction	Standard Stearin
Yield, vol. %	100	61	39
Color (Gardner)	4	5	4
Iodine No. (Wijs)	154	185	105
Acid No	4.5	5	3.6
Saponification No	197	193	203
Unsaponifiables, wt. %	0.9	1.1	0.5
Saturated Acids, wt. %	32	21	50
Cold Test, hrs. at 32°F	....	Indefinite	....
Titer, °C	....	....	41

[a] Composite of standard fraction and vitamin concentrate.

Table III furnishes typical analyses corresponding to the destearinizing of the standard fraction, from which, in this case, the vitamin concentrate has not been removed. Destearinizing results in a substantial increase in iodine number and a corresponding

TABLE IV

Propane Destearinization of High Fraction from Solexol Fractionation of Menhaden Oil, Properties of Charge and Products

	Charge	Winterized High Fraction	High Stearin
Yield, vol. %	100	77	23
Color (Gardner)	7	7	7
Iodine No. (Wijs)	201	220	135
Acid No	1.3	1.4	1.0
Saponification No	193	192	195
Unsaponifiables, wt. %	0.9	1.0	0.5
Saturated Acids, wt. %	24	18	45
Cold Test, hrs. at 32°F	....	Indefinite	....
Titer, °C	....	....	37

decrease in content of saturated acids. The finished standard fraction, it should be noted, is higher in iodine number than the original crude oil and is also of light color and comparatively low in saturated constituents. The standard stearin is also of excellent quality, having a light color, high titer, and high saturated acid content.

The results of destearinizing the high fraction are shown in Table IV. As suggested by the iodine number of 220, the finished high fraction is a premium paint oil of unusual characteristics. It is very fast bodying and in alkyd and varnish formulations shortens cooking time and contributes film hardness. The stearin recovered from this operation is satisfactory, after hardening, for soap manufacture and has been used in edible products.

It might be expected that the small stream of concentrated color bodies segregated in the Solexol section would be a waste product, useful only as pitch or fuel. Actually, this oil is highly unsaturated and reactive, as indicated by its iodine number of 230, and it has found a number of successful applications in binders, core oils, and dark colored paints and varnishes.

TABLE V

Laboratory Heat Bodying Tests at 550°F.
Small Tubes in Oil Bath

	Time to Reach Z_2 Viscosity	Color at Z_2 Viscosity (Gardner)	Acid No. at Z_2 Viscosity
Solexol Fractions	*minutes*		
Wint. standard fraction	440	12	5.0
Wint. high fraction	180	10	4.0
Color bodies fraction	50	Dark	6.0
Alkali refined menhaden oil	400	12	4.2
Linseed oil	480	9	4.0

The heat bodying characteristics of standard, high and color bodies fractions produced at Port Monmouth are compared in Table V with reference samples of linseed oil and conventionally refined menhaden oil. The tests were conducted in glass tubes heated by an oil bath. While linseed has a slightly better color when bodied in the presence of air, the fish oils can be bodied to a color of 6-9 under an inert atmosphere.

Table VI compares standard alkyd resins of 35% phthalic anhydride content with the linseed reference oil. The menhaden alkyds cook faster and dry to a hard film faster than the linseed. While the standard fraction yields a resin with poor alkali resistance, that produced with the high fraction is equivalent to the reference oil in this respect.

TABLE VI

Evaluation of Oils as Alkyd Resin Bases
(Phthalic Anhydride Content 35%)

	Solexol Standard Fraction	Solexol High Fraction	Linseed Oil
Cooking time at 485°F., hrs	4	4	5
Solids, wt. %	50	50	50
Viscosity (Gardner)	Z	Y	Y
Color (Gardner)	8	6	6
Acid No	5.8	5.8	2.7
Film Tests			
Dust free, mins	20	20	20
Sward hardness at 72 hrs	12	14	8
Water resist. recov. time, mins	20	45	45
3% alkali resistance, 24 hrs	Failed	Whitened	Whitened

The winterized oils find their major application in varnish formulae. Table VII compares the properties of typical 50-gallon oil length glycerol ester varnishes produced in the laboratory from standard, high and color fractions with a corresponding linseed oil reference varnish. Both the high and color fractions cook much faster and give a harder, but slightly less flexible, film. The standard fraction cooks a little slower but forms a film of satisfactory hardness.

TABLE VII

Evaluation of Oils in Ester Gum Varnishes
(50-Gallon Oil Length Glycerol Ester)

	Solexol Standard Fraction	Solexol High Fraction	Color Bodies Fraction	Linseed Oil
Cooking Time at 570°F., mins	335	145	85	265
Solids, wt. %	50	50	50	50
Viscosity (Gardner)	C	B	C	E
Color (Gardner)	15	13	Dark	10
Film Tests				
Dust free, mins	120	120	85	150
Sward hardness at 200 hrs	8	12	16	4
Kauri reduction, max. pass. %	120	110	110	135

These oils may be blown, and the high fraction is suitable for calcicote vehicles.

In Tables V to VII we have tried to illustrate the drying character of these new industrial oils by comparing formulations of straight menhaden fractions with corresponding straight linseed oil formulae. It is to be understood that they are not usually used alone but rather are blended with linseed and other oils to provide a balanced combination of reaction rate, film hardness, and manufacturing economy.

In summary, Solexol and Propane Destearinization have brought to the producer of marine oils the capability of converting a crude fish oil into light-colored specialized fractions each better suited for its purpose than the original oil.

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