or where they specify the yellow and/or red to be used in determining given grades."

The question may reasonably be raised as to the wisdom of leaving a fixed yellow, and yellow-red ratio in our methods for an oil on which experience now provides so little support for the justification for the values designated. While the Committee does not favor these values, it believes them to have been put into the method as a result of a considerable experience and prefers at this time to make only the changes in wording recommended above, with the thought that in the coming year a considerable experience in reading bleached refined colors on soybean oil will be accumulated by which we will be in a better position after another year to judge further the wisdom of abolishing altogether any fixed yellow or yellow ratio.

Finally, the Committee would like to recommend to the Uniform Methods and Planning Committee two minor additions of an editorial nature to the method under "Color," (1) that the section heading, page 16f, now reading, Refined Oils—Color be changed to read, Refined and Bleached Oils—Color; (2) in the second paragraph under the sub-heading, (b) Determination—let this paragraph have a sub-heading in appropriate type as follows: *Refined Oils.* Let the paragraph following this then be given the sub-heading, *Refined and Bleached Oils.* The Chairman came to the conclusion that these heading changes and additions would help clarify the meaning of the various paragraphs in the method on Color, as a result of puzzling back and forth through the method seeking out the exact meaning and intent in respect to the immediate question concerned in this report.

Egbert Freyer, Chairman

G. Worthen Agee
Lamar Kishlar
N. F. Kruse
Ralph Marmor
J. H. Sanders
D. H. Wheeler

Fish Oil in the Protective Coating Field

W. H. MATTIL
The Werner G. Smith Company (Division of Archer-Daniels-Midland Co.)
Cleveland, Ohio

A SEARCH of the records of history for the birth or inception of fish oil reveals that it really never had one, and it may be assumed that, like Topsy, it "just grew." At least, there is no record of its discovery and no eminent sponsor to proclaim its virtue. Early records indicate that the fish caught along the coasts of France and Spain, and later along our Atlantic Coast, were used as food. The by-products, heads, scrap, and excess fish were converted into fertilizer. Lewkowitsch summarizes the background of fish oil in a single statement in which he writes, "and it is owing to the demand for fertilizer that the fish oil industry has assumed such large dimensions." Actually, the industry is relatively new, and again Lewkowitsch may be quoted as saying, in 1914, "The employment of sardine oil in the varnish industry can only be looked upon as an experiment which, doubtless, has led to failure."

During the past 30 to 40 years, the industry has grown tremendously and, in 1925, the following opinion is reported in Toch's Chemistry and Technology of Paints, "Results obtained from proper grades of fish oil warrant the use of fish oil in the hands of an intelligent manufacturer." While this statement, made 20 years ago, could not be referred to as enthusiastic, it is definitely an indication of progress. Practically all earlier references on fish oil were in error because the fish caught consisted of a mixed variety of low oil content. They were also improperly processed and partially putrefied in transportation. Therefore, we cannot attach too much significance to the reports of the earliest investigators, nor should we continue to retard the data they compiled as conforming to present day practice.

This global war has increased the incentive in research to almost a fever pitch. Most of us, layman and chemist alike, entertained ideas on replacements for critical materials far from our own field of endeavor. Perhaps a few of us were specific or practical in our thinking. Washington authorities and civilians, as well, overtaxed themselves in advancing the determined stand that we were not to be defeated by shortages.

The outcome of this mad scramble to avoid the use of critical materials will be evident in the years that follow the war. However, the most cautious result that we may forecast is that it helped immeasurably in the obliteration of credulous thinking, fixed ideas, and unconfirmed opinions. In short, it brought us up-to-date. No one needs to be told that this war created a whole new set of values; they are self-evident and affect our daily lives. Perhaps, one of the most impressive changes that has been fundamental and necessary is the conversion from imported drying oils such as tung oil, oiticica, and perilla to oils of a domestic source.

Sponsored by consumer-demand and the progressive incentive of oil processors, fractionated fish oil products were developed that are sufficiently capable of replacing wood oil. Solvent segregated fish oil products, introduced in 1940, have been used to replace wood oil in finishes for landing boats, plywood gliders, metal food closures, marine and harbor installations, aircraft, and numerous other items.

Let us reflect upon this transition. In 1914, Lewkowitsch reported fish oil to be a failure in varnishes; in 1940, we find fractionated fish oils accepted as a wood oil replacement. Prior to 1940, fish oil products consisted of blown oils, kettle-bodied oils, and a few products treated with resin, other oils, lime, etc. All of these oils were used extensively in coatings that were designed to serve a specific purpose.

Blown oils were, and are at present, being used to contribute to the flow and leveling characteristics of

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This paper was given in a symposium on drying oils at the New Orleans meeting on October 7, 1943.

Acid	Empirical Formula	Mol. Weight	Acid No.	Boiling Pt. °C at 10 m.m.	Melting Pt. °C	Double Bonds	Babassu	Butter	Castor	Chinese Tallow	Coconut	Cod	Corn	Cottonseed	Dogfish	Hempseed	Herring	Kapok	Lard	
Caproic	$C_6H_{12}O_2$	116.16	483	99	-8	0		1.4			0.2									
Caprylic	$C_8H_{16}O_2$	144.21	389	124	16.5	0	6.5	1.5			8.0									
Capric	$C_{10}H_{20}O_2$	172.26	326	152	31.3	0	2.7	2.7			7.0									
Lauric	$C_{12}H_{24}O_2$	200.31	280	170	43.6	0	45.8	3.7		1.9	48.0									
Myristic	$C_{14}H_{28}O_2$	228.37	246	190	53.8	0	19.9	12.1		3.7	17.5			0.5			7.0		1.0	
Palmitic	$C_{16}H_{32}O_2$	256.42	219	210	62.9	0	6.9	25.3		66.3	8.8		7.5	21.0		}10.1	8.0	10.0	26.0	5.
Stearic	$C_{18}H_{36}O_2$	284.47	197.5	226	69.9	0		9.2	0.3	1.2	2.0		3.5	2.0				8.5	11.5	3.
Arachidic	$C_{20}H_{40}O_2$	312.52	179	240	75.2	0		1.3					0.5					1.3		
Behenic	$C_{22}H_{44}O_2$	340.58	164.5	257	80.2	0														
Lignoceric	$C_{24}H_{48}O_2$	368.63	152	272	84.2	0							0.2							
Lauroleic	$C_{12}H_{22}O_2$	198.3	285			1		0.4												
Myristoleic	$C_{14}H_{26}O_2$	226.35	248			1		1.6												
Palmitoleic	$C_{16}H_{30}O_2$	254.4	221		-1.5	1		4.0									18.0			
Oleic	$C_{18}H_{34}O_2$	282.46	198.5		14	1	18.1	29.6	8.0	26.9	6.0		46.3	33.0		12.6	9.0	46.1	58.0	5.
Gadoleic	$C_{20}H_{38}O_2$	310.5	180.5		24.5	1														
Erucic	$C_{22}H_{42}O_2$	338.56	165.5		33.5	1														
Ricinoleic	$C_{18}H_{34}O_3$	298.46	187.5		17	1			87.8											
Linoleic	$C_{18}H_{32}O_2$	280.44	200		-11	2		3.6	3.6		2.5		42.0	43.5		53.0	13.0	33.6	3.5	61.
Linolenic	$C_{18}H_{30}O_2$	278.42	201		-30	3										24.3				25
Elaeostearic	$C_{18}H_{30}O_2$	278.42	201		44	3														
Licanic	$C_{18}H_{28}O_3$	292.4	192			3														
Arachidonic	$C_{20}H_{32}O_2$	304.5*	185*			3-5											20.0			
Clupanodonic	$C_{22}H_{36}O_2$	332.5*	169*			3-5											25.0			
	* Average Characteristics							Butyric 3.0												
Iodine Number							15	30	85	20 29	10	130 150	123	110	120 150	165	123 142	85	55	18
Saponification Value of the Oils							247 250	216 240	177 187	200 207	252 260	170 180	189 193	192 200	170 225	190 193	179 193	189 195	196 200	19 19
Solidifying Point in °C							22 26	28 33	-12 -10	45 50	23		-12 -10	-2 +2		-22		30	27 30	-2
Titre in °C							23			45 53	20 23		18 20	32 38		15 17	23 27	27 32	36 43	[illegible] 2

interior finishes. Also, these oils have been used in caulking compounds and are well known for the properties they impart in maintaining durability, elasticity, and package stability.

Since fish oil is slower drying than linseed, it is often used as a drying control, and helps to provide a "wet edge" which eliminates brush marks, laps, or streaks in the finish. It provides a greater flexibility in paints and is especially desirable in those highly pigmented.

Oil processors are equipped today to kettle-body oil under high vacuum, a process which introduces an entirely new aspect over the old practice of bodying oils in an open kettle. Under high vacuum, an oil develops a maximum degree of polymerization with minimum oxidation. Oxidation, as can be evidenced in blown oils, limits solubility, color retention, and increases a condition known as polymer cloud. Polymer cloud can be developed in many oils by faulty bodying. It is apparent in poor film formation, cloudiness, uneven drying, and often results in the precipitation of drier, saturated material, etc.

The opinion expressed by the Los Angeles Production Club on this subject is that "the polymer cloud is a function of the heating rate and the temperature." However, the authors of "Chemistry and Technology of Marine Animal Oils" report that this explanation does not coincide with their own findings in which "the precipitated material proved to be saturated glycerides."

This condition may be nothing more than the usual decrease in solubility that takes place in an oil in proportion to the increase in oxidation. When an oil is kettle-bodied in the presence of air, a greater de-

Mustard	Neatsfoot	Oiticica	Olive	Ouri curi	Palm	Palm kernel	Peanut	Perilla	Poppyseed	Rape	Rubberseed	Safflower	Salmon	Sardine	Sesame	Soybean	Sperm-head	Sperm-body	Sunflower	Tallow-Beef	Tallow Mutton	Teaseed	Tung	Ucuhuba	Walnut	Whale	Pilchard
				9.8		3.0																					
				8.2		3.0											3.5										
				45.8		52.0											16.0	1.0						13.3			
				9.0	1.0	15.0				1.0		0.1	3.8	5.0			14.0	5.0		2.0	1.0	0.3		66.6	0.1	8.0	5.1
.5	18.0	5.0	6.0	7.7	42.5	7.5	7.0	7.5	4.8	1.0	7.4	3.9	15.0	14.0	7.8	6.5	8.0	6.5	3.5	32.5	21.0	7.6	4.0	8.9	4.4	12.1	14.4
	3.0	5.0	4.0	2.3	4.0	2.5	5.0		2.9	1.0	9.2	1.5	2.0	3.1	4.7	4.2	2.0		2.9	14.5	30.0	0.8	1.5	1.6	0.9	2.3	3.2
							4.0				0.3	0.4			0.4	0.7			0.6			0.6			0.1		
8										1.0																	
.1					0.1		3.0			1.0		0.1			0.1	0.1			0.4								
																	4.0										
													0.1	0.1			14.0	4.0								1.5	0.1
													10.6	11.8			15.0	26.5								15.0	11.8
.3	79.0	5.9	83.0	13.1	43.0	16.0	60.0	8.0	30.1	29.0	30.0	26.4	17.3	10.0	49.3	33.6	17.0	37.0	34.0	48.3	43.0	83.3	15.0	6.6	17.8	33.4	6.2
																	6.5	19.0									
1.5										50.0								1.0									
.1		10.0	7.0	2.2	9.5	1.0	21.0	38.0	62.2	15.0	33.4	67.4	11.5	15.0	37.7	52.6			58.6	2.7	5.0	7.4		3.0	73.1	9.0	11.5
.7								46.5		1.0	20.7	0.2				2.3									3.3		
																							79.5				
		74.1																									
													23.5	22.0												8.2	17.9
													16.2	19.0												10.5	13.8
																	65% Acids 35% Alcohols										C_{24} 15.2
																	Analysis on fatty acids										
00	70	180	85	15	50	25	90	195	135	100	140	145	130 160	160 190	110	133	70	90	133	40	40	85	165	13 16	160	110 150	184 200
6 4	194 193	188 192	190 195	255 260	196 206	244 255	189 193	189 197	189 196	170 180	186 195	188 194	183 186	189 193	188 193	190 194	140 144	122 130	189 194	196 200	193 195	190 195	190 194	218 228	189 197	192 196	186
6 5	-4		-3 0		32 38	25 27	-2 0		-20 -15	-9		-18 -13			-4 0	-20 -23			-18 -16	35 38	35 38	-9 -5					
		44 47			38 47		28 32	12 17	16 19		33	16		28 34	21 24	20 21				37 47			37 38	42 47	31 33	22 24	

Prepared by The Werner G. Smith Co. (Division of Archer-Daniels-Midland Co.)

gree of oxidation takes place, which limits solubility. Often that portion of an oil which is more saturated becomes less soluble in the oxidized unsaturated portion and either forms a cloud, or in extreme cases, is precipitated. However, in present production, the high vacuum kettle-bodied fish oils are odorless, provide excellent color retention and film forming properties, and do not exhibit excessive polymer cloud or precipitation of saturated materials.

Recently, following the trend to reduce the oil content of paints, the trade experienced the serious problem of providing flexibility, flow and proper drying speed at low oil content. It was found that fish oil could fulfill the necessary requirements and, in addition, provide an economy unmatched by other oils.

The economy of fish oil is a very essential consideration. When a manufacturer is forced to use less oil, such as the condition we have recently experienced, he cannot make as much paint—or profit. At the present time, fish oil happens to be lower in price than other oils and offers the attractive advantage of enabling a manufacturer to increase his profit by reducing his oil content, and still conform to the principles of sound paint formulation.

In the development of the "two-coat" house paint, fish oil is used because of its stability at extremely heavy viscosities. The oil bodies very rapidly and requires only one-half to one-third the time necessary to body linseed. It has a much lower progressive bodying action as a finished product and fulfills the requirement of common paint-making practice that a product be easy to handle and retain stability.

Leaders of our industry have endeavored through the years to raise the quality of their products. This consistent improvement led to the separation of the oil itself into various fractions. Perhaps this step was copied from the petroleum refiners.

The motorist of today would never consider the use of crude petroleum oil in his car and, following this thought, we may go a step further and reason that the paint formulator of tomorrow will not consider crude vegetable or marine oils in his finishes. It is now quite evident that special oils, fractionated and segregated products, will enjoy an expansion in the formulation of post-war finishes.

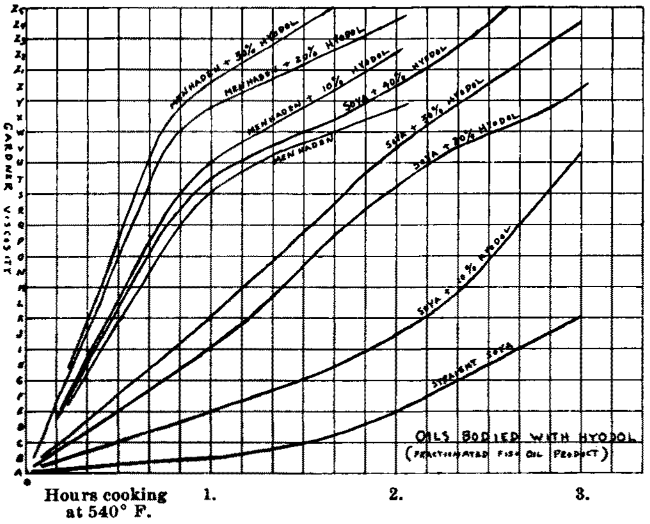
The intensified program of replacing critical materials, which has placed the spotlight upon special oils, has also placed fish oil in an enviable position from a standpoint of its composition. An analysis of the fatty acids of various oils indicates that fish oil alone contains C_{20} and C_{22} acids. These highly unsaturated acids permit the development of the wood oil replacement products previously mentioned. Clupanodonic acid has five double bonds in the 4, 8, 12, 15, and 19 position, and has a theoretical iodine value of 384. This degree of unsaturation is considerably greater than can be found in other oils and is a natural approach in replacing fast-drying imported materials.

Fractionated fish oil products available today are produced by several separate and distinct methods. The first and perhaps most satisfactory method is that of solvent segregation of bodied glycerides. Consider for a moment the action that takes place in kettle-bodying of an oil. Here, through heat treatment, the highly unsaturated oil molecules combine, oil molecule to oil molecule, thus forming a larger molecular structure. On the other hand, the saturated oil molecules, which are unreactive, remain relatively unchanged. Thus, in kettle-bodied oil, there are both large and small molecular structures. These can be segregated in a suitable solvent by selectivity and gravitational difference.

A considerable volume of solvent is necessary, since in the manufacture of a solvent segregated oil over 60% of the original oil is removed. This 60% which has been removed is considered detrimental to ideal drying principles and consists of oleic and palmitic glycerides. That these materials are detrimental cannot be held in doubt, but be assured, however, that fish oil, is not alone in its content of such substances. All natural drying oils contain large portions of harmful ingredients and the removal of these by simple and economic methods is another challenge to research.

There are three basic principles by which oils may be improved. First, a portion of an oil which is considered inferior may be removed; second, a material may be added to an oil to stimulate drying; third, a change in the chemical structure of the oil may be brought about by the proper use of catalytic or physical influences.

Fish oil lends itself admirably to the first method —that of separation or fractionation. Further, the use of additives is considered relatively simple and they can be employed by the varnish maker if he so desires. Changing the chemical structure of an oil often entails the use of chemicals which destroy properties that are highly beneficial.



As indicated previously, there are other methods of fractionating fish oil, so let us consider a second method—fractionation by distillation. Briefly, in the distillation method, the oil must first be converted into a distillable form, either by splitting and distilling acids, or by converting into a methyl or ethyl ester. The material is then subjected to vacuum distillation in which the saturated portion is separated from the unsaturated material. This process must be very carefully controlled, since several acids distill within a rather close range of each other at reduced pressure. The highly unsaturated acids which are separated by this method are re-esterified with glycerin, pentaerythritol or other poly alcohols, forming a suitable ester for the varnish industry. In the esterification process, which requires heating, a polymerization action will take place unless the esterification is stopped at an acid number of 8. For this reason, two products are usually furnished to the trade: One at a raw oil viscosity with an acid number of 8, and another completely esterified, but having a viscosity of Z-4 on the Gardner-Holdt scale. In addition to lowering the acid number of this latter product, complete deodorization of the oil has been achieved through heat treatment under vacuum.

In order to be most critical of this work, let us reflect upon the performance and properties of both fractionated and segregated oils from a comparison standpoint. While it is apparent that both of these processes endeavor to remove undesirable portions of the oil, it is here that the fundamental relationship ends and a marked influence on separate characteristics becomes obvious.

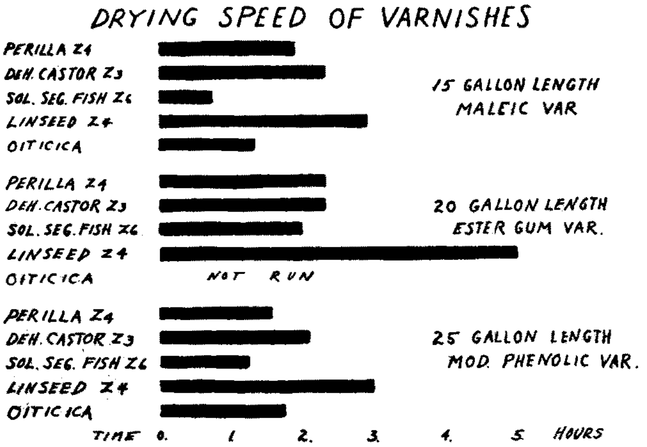
One may assume that the separation of such highly unsaturated materials as the clupanodonic portion would result in a product too hard and brittle for varnish making. This is not true. Actually, in the solvent segregation process previously discussed, the fast drying oil obtained consists of mixed-acid glycerides. By this statement, we mean that there are present in fish oil a number of acids of varying degrees of unsaturation. Three of these acids are connected to the same glycerin (usually three different acids) and the possibility of three of the same acids being connected to one glycerin is exceedingly small. There fore, this process selects not only the highly unsaturated material, but a portion of lesser unsaturated acids connected to the same glycerin.

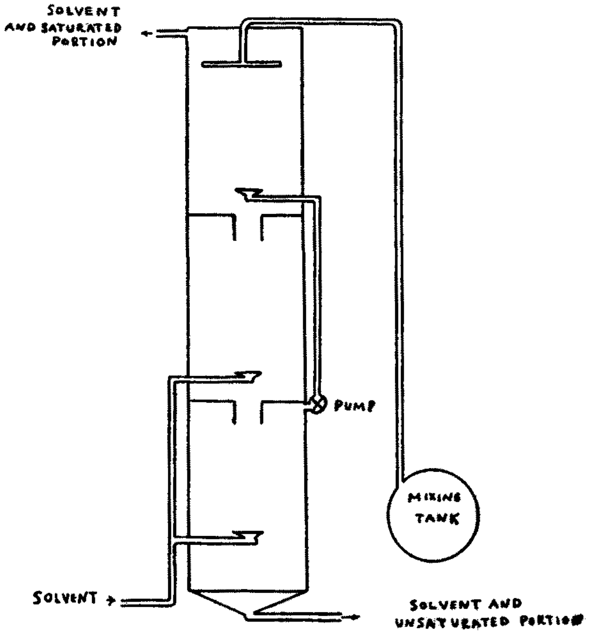
In the distilled type of product, where it is possible to fractionate acids with considerably more precision, almost pure esters may be formed. In the development of this product by the industry, tests revealed that certain pure esters were not desirable. They were definitely brittle. In consulting with the trade, it was found that, while optimum drying speeds were desirable, pure esters were not practicable and most manufacturers were not equipped to handle that type of material. In short, they desired a product with a greater balance of properties.

Acting upon such recommendations, fish oil processors mixed acids of varying degrees of unsaturations before final re-esterification, and developed products meeting the requirements of the trade. Therefore, in both solvent segregated and fractionated oils, the paint trade is assured a certain degree of flexibility. Both products are designed to meet specific requirements. The solvent segregated product has a kauri reduction value between wood oil and perilla and, in effect, is used to replace these oils. The distilled, re-esterified product is not used directly as a replacement, but as an additive to increase drying speed and hardness in softer oils such as linseed or dehydrated castor.

Another essential difference between a solvent segregated product and a distilled product as known today is the resistance to water, alkali, and natural weathering conditions. In this respect, the solvent segregated product is vastly superior. During the solvent washing process, virtually all the free fatty acids and decomposition products developed during the kettle-bodying stage have been removed. Also, all possible monoglycerides and diglycerides, all smaller molecular structures, have been removed, and, as a result, the film formation consists of large even molecular sizes that dry from the bottom of the film upward to a hard, extremely resistant coating. Such a solvent segregated product has a much better alkali and water resistance than perilla and is equal to wood oil in comparable phenolic varnishes under 30 gallon length.

As mentioned before, the distilled product does not have an alkali or water resistance that will permit its use as a wood oil replacement. The reason for this is that it is a re-esterified product and, as such, contains traces of monoglycerides and diglycerides, which, like acids, are detrimental to long film life. All re-esterified products (whether fish oil, linseed, synthetic, conjugated oils, or others) usually contain some reaction products of esterification. In production, the water and excess poly alcohol may be removed at higher temperatures, but free fatty acids, monoglycerides and diglycerides remain on esterification. These cannot exist in a solvent segregated product.





SOLVENT SEGREGATION OF BODIED OILS

However, in the fortification of linseed oil, where it is desirable to increase drying speed and hardness, a distilled re-esterified product may be used with prudence. Actually, the water and alkali resistance of such a product, while inferior to wood oil, is superior to linseed. The purpose involved may be to develop, as economically as possible, a definite increase in drying speed. Since the varnish formulator may desire to incorporate a large volume of linseed in order to achieve this economy, he cannot expect the best possible water resistance. In theory, as well as in practice, a distilled product offers its greatest advantage in economic utilization. On the other hand, the feasible and practical approach in the use of the solvent segregated product is to classify it between wood oil and perilla. This recommendation is based upon the sum of the physical characteristics of such oils, and is more apparent in short oil vehicles than in long ones.

In conclusion, we urge the oil chemist to keep in mind these fractionated and segregated products, for, in the gradual adoption of these fast drying oils by the coating trade, a new and increasingly important "by-product" in the form of saturated oils will be made available to the textile, leather, and petroleum industries. These new products offer to industry in general a wider latitude in the choice of raw materials, and are in line with the principle of sound technical design.