## EFFECT OF COLD-PRESSING COD LIVER OIL ON ITS CHEMICAL AND PHYSICAL CHARACTERISTICS

By ARTHUR D. HOLMES and MADELINE G. PIGOTT

Research Laboratories, E. L. Patch Co., Boston, Mass.

EDICINAL cod liver oil is prepared by cold-pressing, high quality, crude cod liver oil. This type of crude cod liver oil is obtained from fresh cod livers and contains stearin which will cause the oil to become cloudy or semi-solid if it is stored at low temperatures. Since the cod liver oil consumer prefers an oil that will remain clear at all temperatures, the crude cod liver oil is chilled to freezing or lower - frequently to about 26° F. It is then allowed to stand at this temperature until the stearin has crystallized. Subse-quently the semi-solid mixture of oil and hardened stearin is pressed to remove a sufficient amount of stearin so that the oil will remain clear at any temperature above about 32° F. The clear sparkling oil that is obtained is known in the trade as "non-freezing oil."

The United States Pharmacopeia<sup>1</sup> specifies that medicinal cod liver oil shall have the following chemical and physical characteristics, specific gravity 0.918 to 0.927 at 25° C.; saponification value 180 to 192; iodine value 145 to 180; free fatty acid not over 1.4%, and unsaponifiable matter not more than 1.3%. One hundred eleven samples of American medicinal oil<sup>2</sup> which were obtained from various sources were analyzed. The average values obtained for the chemical and physical characteristics were: specific gravity 0.923; refractive index 1.478; saponification value 186.8; iodine number 164.6; free fatty acid 0.546; and unsaponifiable matter 1.164 per cent.

While these values very satisfactorily meet the United States Pharmacopeia specifications, they do not necessarily represent the chemical and physical characteristics of commercial medicinal cod liver oil. In fact, there was considerable variation in the characteristics of the 111 samples under discussion. The specific gravity ranged from 0.9220 to 0.9227; the saponification value from 180.8 to 190.8; the iodine number from 147.6 to 183.1; the crude oil, the pressed oil and the stearin (press-cake) were analyzed for their chemical and physical characteristics by the methods outlined in the United States Pharmacopeia. The results of these analyses are reported in Table 1. Since the

TABLE 1—A COMPARISON OF THE CHEMICAL AND PHYSICAL CHARACTER-ISTICS OF CRUDE COD LIVER OIL, MEDICINAL COD LIVER OIL, AND COD LIVER "STEARIN"

COD DIVER STEARIN										
Sample No.	Nature of Sample	Sp. Grav. at 25°	Ref. Ind. at 20°	Sapon. Value	Iodine Number	F. F. A. Per Cent				
1	Crude oil Med. oil Stearin		1.4780 1.4790 1.4654 (40°)	184.8 185.8 191.1	$159.3 \\ 170.1 \\ 109.4$	$1.52 \\ 1.47 \\ 0.40$				
2	Crude oil Med. oil	0.9234	1.4780 1.4790 1.4730 (40°)	184.6 183.9 192.4	$146.2 \\ 159.9 \\ 125.3$	0.91 0.84 0.64				
3	Crude oil Med. oil	0.9242 0.9252	1.4785 1.4790	$197.6 \\ 196.0$	159.9	0.55 0,59				
4	Crude oil Med. oil	0.9245	1.4665 (40°) 1.4770 1.4780	$201.0 \\ 198.5 \\ 196.7$	$\substack{125.3\\155.8\\162.0}$	0.44 0.73 0.84				
5	Crude oil Med. oil	0.9240	1.4665 (40°) 1.4770 1.4779	203.3 188.3 199.2	$114.3 \\ 156.3 \\ 160.2 \\ 110.$	0.69 0.88 0.82				
6	Crude oil Med. oil	0.9237	1.4660 (40°) 1.4770 1.4783	$186.5 \\ 188.1 \\ 186.6 \\$	$118.9 \\ 148.7 \\ 155.8 \\ 155.$	$   \begin{array}{c}     0.66 \\     0.78 \\     1.03 \\   \end{array} $				
7	Crude oil Med. oil	0.9216	1.4651 (40°) 1.4780 1.4790	$197.3 \\183.5 \\183.4 \\$	$119.4 \\ 154.5 \\ 154.5 \\ 114.$	$   \begin{array}{c}     0.74 \\     0.50 \\     0.32 \\     0.52   \end{array} $				
8	Crude oil Med. oil		1.4649 (40°) 1.4785 1.4790 1.4650 (40°)	$186.5 \\ 185.0 \\ 185.5 \\ 188.2$	$113.0 \\ 151.5 \\ 145.8 \\ 114.5$	0.53 0.68 0.68 0.56				

free fatty acid from 0.2% to 1.65%and the unsaponifiable material from 0.97% to 1.40%. These results obviously raise a question as to the cause for these variations. It is believed that the nature of the ration that the fish had been eating and the conditions of manufacture and storage of the oil influence the chemical and physical characteristics. Accordingly it seemed desirable to obtain some data concerning the possible influence of one phase of the manufacturing process, cold-pressing, upon the characteristics of cod liver oil.

For the purpose of this study, eight samples of crude cod liver oil were obtained on the open market. They were chilled to 26°-28° C. and allowed to stand several hours to permit the stearin to crystallize Subsequently the semi-solid, chilled oil was pressed. The "stearin" that resulted was completely liquid at 40° C., but it was not true stearin since it contained some non-freezing oil which remained in the presscake even after long pressing. The stearin was cloudy or semi-solid at room temperature it was necessary to warm it to 40° C. in order to make the specific gravity and refractive index determinations. It will be noted from a comparison of the values reported above that the specific gravity of the medicinal oils Nos. 1, 2, 3, 4, 6 and 7 is higher than that of the corresponding crude oils. The specific gravity of crude oils Nos. 5 and 8 is essentially the same as that of the corresponding medicinal oils. The refractive index is higher for all eight medicinal oils than for the crude oils. The saponification values are higher for medicinal oils Nos. 1, 5 and 8 than for the corresponding crude oils but the saponification values are higher for crude oils Nos. 2, 3, 4, 6 and 7 than for the medicinal oils. The iodine number was higher for medicinal than for crude oils Nos. 1, 2, 4, 5 and 6, but the iodine number was higher for crude oil No. 8. The free fatty acid was higher for crude than for medicinal oils Nos. 1, 2, 5 and 7 but the acidity was

<sup>&</sup>lt;sup>1</sup>Pharmacopeia of the United States, XI Edition, Mack Printing Company, Easton, Pennsylvania, 1936.

<sup>&</sup>lt;sup>9</sup>The Chemical and Physical Characteristics of Cod Liver Oil. Arthur D. Holmes and Walter Z. Clough, Oil and Fat Industries, Vol. 4, December, 1927, page 403.

higher for medicinal than for crude oils Nos. 3, 4, 6 and 8.

It is impossible to make a close comparison of the values for specific gravity and refractive index of the crude and medicinal oils with the values for the stearin since these values for the latter were determined at 40° C. instead of 25° C.

These results substantiate those included in an earlier report<sup>3</sup> of the

<sup>\*</sup>Vitamin Potency of Cod Liver Oils XVIII, Effect on Vitamin Potency of Cold-Pressing Cod Liver Oils. Arthur D. Holmes and Madeleine G. Pigott. Ind. Eng. Chem., Vol. 18, February, 1926, page 188. effect on vitamin potency of coldpressing cod liver oils. In the earlier study the average values obtained were for the crude cod liver oils specific gravity 0.9194, refractive index 1.4756, saponification value 190.8, iodine number 147.5, and free fatty acid 0.50% and for the medicinal oils specific gravity 0.9197, refractive index 1.4766, saponification value 193.7, iodine number 154.3, and free fatty acid 0.58%. It was also found from biological assays that cold-pressing did not produce any significant difference in the vitamin potency of the crude and pressed oils.

The average values for the eight samples show that the specific gravity, refractive index, saponification value, iodine number and free fatty acid content of the medicinal oils are higher than those of the crude oils from which they were prepared. From these results it appears that cold pressing raises slightly the chemical and physical characteristics for medicinal cod liver oil above those of the crude oil from which it is prepared.

## FISH OIL AS A PAINT MEDIUM

M ORE than 30 years ago I investigated the use of Fish Oil as a paint medium and at that time the only oil available for the purpose was the Menhaden Oil gathered on the Eastern Coast of the United States.

Since that time I published various articles on the use of Fish Oil as a paint material. The last one published in "The Chemistry and Technology of Paint," page Nos. 237 to 247, describes Herring Oil, Whale Oil, Porpoise Body Oil, etc. Lately there has appeared a Fish Oil on the market made from sardines collected on the West Coast of the United States and this oil is superior to Pilchard and Herring Oil previously collected on the same Coast.\* The specifications of the Sardine Oil are as follows:

## By MAXIMILIAN TOCH

The drying of these oils is best achieved by the addition of a 5 per cent liquid drier containing lead manganese and cobalt and the oil when used alone and mixed with a pigment ground in linseed oil apparently dries in the open air at 70° over night. Months afterwards when the humidity arises above normal, the paint becomes tacky, even when as little as 30 per cent is used, the balance being Linseed or Perilla.

All of the Fish Oils that I have ever used, including those under discussion after, yellow much more than any of the other drying oils. Raw or Refined Fish Oils mixed with any white pigment turn a light amber color when placed in the dark for four weeks in the presence of moisture. My test for after-yellowing has always been to

Alkali refined sardine oil	Acid No. 0.25	Sapon. Value 190 193	Iodine Value 180 190	Spec. Gravity @ 60° F. .930 .938	Cold Test 32° F. 2 hrs.
Spec. varnish grade sardine oil	0.5	over 190	190 200	.935	24°F. 2 hrs.
Crystol K light	2	190 200	116 118	.961) .965) @ 15.5	
Crystol K medium Crystol K heavy	3.5 5	190 190 200	110 104 106	.9685 @ 15.5 .9723 @ 15.5	° Ċ.

All of the foregoing oils excepting the Refined have no fishy odor whatever and the Crystol K Heavy, which is very much like a Stand Oil, has an odor analogous to Poppy Oil. paint a sample, allow it to dry in normal light and then place it in a box with the painted side upward but underneath the sample a piece of blotting paper saturated with water is placed. This is the quickest after-yellowing test that I know of. The film of all fish oils never gets as hard as other drying oils and therefore in a brittle varnish a small percentage of Refined or Heavy Bodied Fish Oil increases the desired elasticity.

Sardine Oil has one quality possessed, to my knowledge, by no other oil. It is admirably suited for making Smokestack Paints where dark colors are desired.

In the usual China Wood Oil Spar Varnish which is used as a medium with aluminum for exterior purposes, the addition up to 30 per cent of a suitable Fish Oil like Sardine increases the life and the resistance to heat of the Aluminum Paint. A slight discoloration may take place, which is not always a detriment.

Smokestacks and boiler fronts which are painted black are suitable surfaces for the use of Fish Oil. This, however, does not refer to an unlined stack where the base frequently reaches a temperature of 500° C. or more.

Fish Oil is unsuited for paints under water, but for painting the steel decks of ships when mixed with Lamp Black and drier, dries sufficiently hard and elastic in 24 hours and does not track. For this purpose half of the Heavy Bodied Oil and half Benzine or Petroleum Thinner which flashes above 100, mixed with a suitable pigment, is of considerable value and when scraped by anchor chains or cargo of any kind, abrasion occurs but no splintering.

<sup>•</sup>I am indebted to the Werner G. Smith Company for five samples of oils which they sent me which I personally examined.