

EXPERIMENTAL PRODUCTION OF BLOWN MENHADEN OIL

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ABSTRACT

Tests were conducted on the production of blown menhaden oil to determine the effects of:

1. Pretreatment of the oil
2. Temperature of blowing
3. Blowing with dry air and with oxygen
4. The use of certain additives

A refined and bleached menhaden oil produces a lighter-colored blown oil of a higher viscosity in a shorter time and temperature than an oil which is not so treated. Low temperatures of blowing produce a lighter-colored blown oil but the time of processing to an equal degree of viscosity is longer. Oxygen is more effective than dry air for blowing. Certain additives accelerate the reaction producing a high viscosity oil in a shorter time.

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INTRODUCTION

In the commercial production of blown oil from menhaden (Brevoortia tyrannus) for certain industrial purposes, air is passed through cold-pressed oil until the viscosity of the oil is raised to the desired level. This increase in viscosity is attributed to oxidative polymerization, although little is definitely known of the exact mechanism involved.

The commercial blowers of menhaden oil generally want to produce oils light in color and with as high a viscosity as possible. Surveys have indicated that improvement of finished oil is desirable, but have brought out little information concerning present practices of commercial production. In the work reported herein the following factors have been considered: the effects of pretreatment, temperature, blowing with dry air and with oxygen, and the use of certain additives.

Brocklesby (1941) mentioned that fish oils were blown with air at 120° C. and warned against the use of higher temperatures since darkening of oil results. According to Bailey (1945), oils are blown at 200° to 250° F. (93° to 121° C.) for "several hours." Joachim (1934) indicated that blown fish oils were paler in color in the year 1934 than those previously produced, but he did not give specific color readings or data concerning processing conditions.

The National Paint, Varnish and Lacquer Association published a Drying Oils Index (1939) which currently lists a number of blown fish oils. Specifications are listed which include color and viscosity values on the Gardner^{1/} scale. These specifications have been used as a guide to possible improvements of blown menhaden oil in this study.

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^{1/}Gardner Color Standards for Liquids, The H. A. Gardner Laboratory, Inc., Bethesda, Maryland.

Oxidative polymerization of oils is undoubtedly involved in the production of blown oils. In this reaction, peroxides are formed which facilitate the coupling of glyceride molecules to form polymers. Increase in temperature speeds the production of peroxides and the polymerization, but it also decomposes the peroxides. It is believed that when peroxides decompose, that is, before the polymerization takes place, they tend to darken the oil and at the same time the acidity of the oil is increased. It is also known that high acidity of oil slows up polymerization. Temperature of blowing is therefore a prime factor which affects the final composition of the blown oil.

Alkali refining of the oil is advantageous because high acidity tends to slow the rate of polymerization. Such refining also improves the original color of the oil and at the same time removes natural antioxidants and other substances that may inhibit polymerization. Bleaching with activated carbon further improves the original color and possibly removes substances capable of subsequently producing undesirable color in the blown oil.

Blowing with oxygen, as compared to blowing with dry air, may possibly be advantageous because there is a higher concentration of oxygen at the bubble surface during the process. Metallic driers have long been known to catalyze the oxidation of oils.

EXPERIMENTAL

A glass apparatus was designed in which heating of the oil was accomplished by surrounding a glass tube reaction vessel with vapors from a boiling solvent (Figure 1). The temperature of the reaction vessel was controlled by the boiling point of the particular solvent used. This apparatus eliminated the need of an oil bath and a thermostat. Air was bubbled through the oil by means of a small pump. The oxygen used was that commonly used for welding and was released directly from the cylinder. The rate of flow was regulated so that the bubbles followed one another closely. Actual volume of gas per minute depended largely upon the viscosity of the oil.

The oil used was a commercial sample of light-colored, cold-pressed menhaden oil with 2.4 percent of free fatty acids, an iodine number of 120, and color value of 11 on the Gardner scale.^{1/} Some of the oil was alkali refined to a free fatty acid content of less than 0.1 percent and a color value of 9. Part of this oil was bleached with activated carbon to a color value of 6.5.

^{1/}Gardner Color Standards for Liquids, The H. A. Gardner Laboratory, Inc., Bethesda, Maryland.

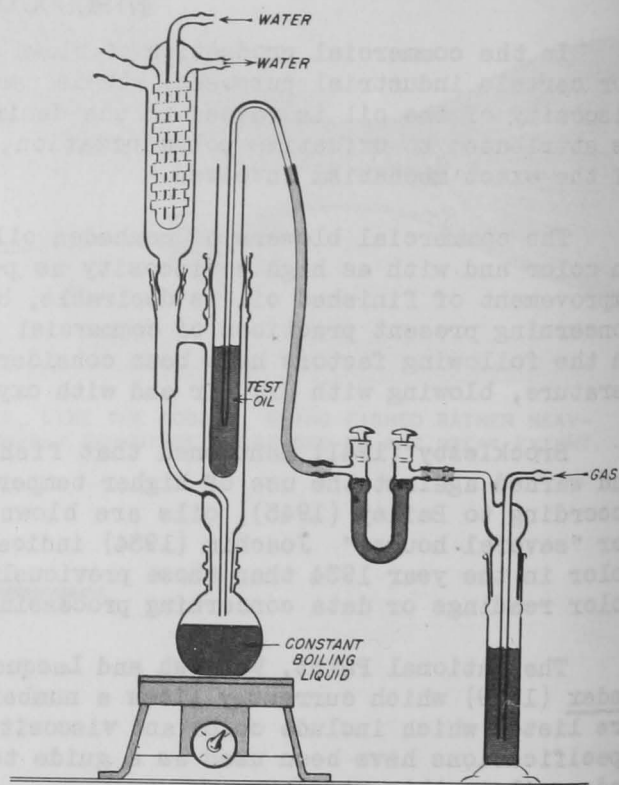
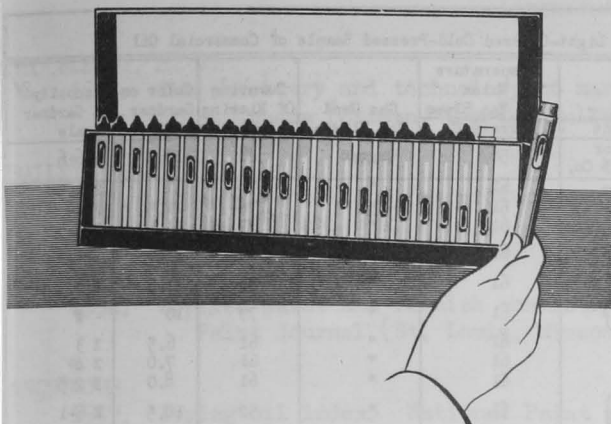


FIGURE 1 - APPARATUS USED IN THE EXPERIMENTAL BLOWING OF MENHADEN OILS.



A BUBBLE VISCOSIMETER

The metallic driers used were "Uversol Driers" except for the cobalt and manganese soaps, which were prepared in this laboratory from fish oil acids. The benzoyl and lauroyl peroxides used were granular commercial products. Samples of the prepared oils were then blown at 58°, 61°, 82°, 95°, and 111° C.

Since a Gardner viscosimeter^{2/} was available only after the oils were blown, the samples could not be blown to a predetermined viscosity. The blowing was, therefore, stopped when the oil appeared sufficiently viscous, when undesirable color developed, or when an abnormally long blowing time had elapsed.

DISCUSSION

The data in Table 1 show that a number of oils were produced with a viscosity of Z6 (Gardner scale) or higher and with Gardner color values ranging from 10.5 to 15. A number of oils of lower viscosities were also produced with color values well within the range of the oils listed in the Drying Oils Index of 1944. The lightest color value listed in the Index for blown fish oils of viscosity Z6 or higher is 10-11. One other oil is listed of viscosity Z6 with a color of 9-10. The specifications do not mention whether any of these oils were produced from menhaden oil. Some of the heavier blown oils are described as being produced from sardine oil. It would appear from the data here presented that a blown menhaden oil can be prepared which will meet the specifications listed in the Drying Oils Index.

SUMMARY OF RESULTS

1. An alkali-refined and bleached, light-colored, cold-pressed menhaden oil will produce a lighter blown oil of higher viscosity in a shorter time at a given temperature than an oil which is not so treated.
2. Comparatively low temperatures maintained during the blowing process generally result in oils of lighter color than those produced at the higher temperatures.
3. The time of processing to an equal degree of viscosity is longer at the lower temperature.
4. Oxygen is more effective than air as a blowing gas for menhaden oil.
5. The addition of cobalt driers to the oil decreases the blowing time at all temperatures. These driers can be used to produce a light-colored oil at low temperatures in a short time. The driers cause excessive darkening of the oil if comparatively high temperatures are used.

^{2/}The Gardner Bubble Viscometer, H. A. Gardner Laboratory, Inc., Bethesda, Maryland.

Table 1 - Data on the Production of Blown Oil from a Light-Colored Cold-Pressed Sample of Commercial Oil

Sample No. of Menhaden Oil/	Additional Treatment of Menhaden Oil	"Drier" Used		Temperature At Which Oil Was Blown Degrees C.	Gas Used For Blowing	Duration Of Blowing in Hours	Color on Gardner Scale	Viscosity ^{2/} on Gardner Scale
		Type	Percent					
1	-	Cobalt Oleate	{0.15 or 0.014% Co.	58	Oxygen	48	10.5	Z 6+6
2	-	-	-	61	"	78	11	Z 1.5
3	-	Lauroyl Peroxide	0.1	61	"	76	11.5	Z 4
4	-	Benzoyl Peroxide	0.1	61	"	77	11.5	Z 4.5
5	-	{Lauroyl Peroxide Co-6}	{0.1 0.005}	61	"	56	11.5	Z 1.5
6	-	Co-6	0.01	61	"	37	11.5	Z 4.5
7	-	{Lauroyl Peroxide Co-6}	{0.01 0.001}	61	"	79	10	W
8	Refined and bleached	-	-	61	"	61	6.5	Z 3
9	" " "	Benzoyl Peroxide	0.1	61	"	61	7.0	Z 4
10	" " "	Lauroyl Peroxide	0.1	61	"	61	8.0	Z 2.5
11	" " "	{Lauroyl Peroxide Co-6}	{0.1 0.005}	61	"	52	10.5	Z 6+1
12	-	-	-	82	"	48	11.5	Z 2
13	Refined and bleached	-	-	82	"	48	9.5	Z 5
14	-	Lauroyl Peroxide	0.5	82	"	48	11.5	Z 1
15	-	{Lauroyl Peroxide Co-6}	{0.1 0.005}	82	"	38	13	Z 6+4
16	-	-	-	82	Air	48	9.5	< U
17	-	Pb-24 ^{3/}	0.05	82	"	48	10.5	< U
18	-	{Lauroyl Peroxide Co-6}	{0.1 0.005}	82	"	48	13	Z 2
19	-	Mn-6 ^{3/}	0.01	82	"	48	11.5	< U
20	-	-	-	95	"	72	12.5	Z 4
21	Refined and bleached	-	-	95	"	35	11.5	Z 5.5
22	Cold-pressed to Iodine No. 183.7	-	-	95	"	66	12.5	Z 5
23	25% by weight of re-esterified oil of Iodine No. 228 added (final Iodine No. 192)	-	-	95	"	59 ^{1/2}	12.0	Z 6+5
24	-	-	-	95	"	77	13-	Z 6+5
25	25% by weight of re-esterified pentaerythritol oil added (final Iodine No. 187)	-	-	95	"	74	14.5	Z 6+6
26	-	Co-6	0.005	95	"	44	15	Z 6+1
27	-	Cobalt Oleate	0.15	95	"	35	16.5	Z 5.5
28	Refined and bleached	Manganese Oleate	0.05	95	"	48	12.5	Z 6+5
29	" " "	Manganese Oleate	0.05	95	"	63	-	gelled
30	-	-	-	111	Oxygen	23 ^{1/2}	13.5	Z 5.5
31	-	Benzoyl Peroxide	0.2	111	Air	35	13.5	Z 2
32	-	Benzoyl Peroxide	0.2	111	"	33	12	< U
33	Refined	-	-	111	Oxygen	42 ^{1/2}	12.5	Z 6+1
34	Refined and bleached	-	-	111	Air	55 ^{1/2}	11.5	Z 1
35	25% by weight of re-esterified oil added (final Iodine No. 192)	-	-	111	Oxygen	44	13.5	Z 4.5
36	-	Cobalt-Manganese fish oil acid soaps	0.1	111	"	19 ^{1/2}	14	Z 6+4
37	-	{Lauroyl Peroxide Benzoyl Peroxide Co-6}	{0.1 0.5 0.005}	111	Air	42	<18	Z 6+7

^{1/}The menhaden oil was a light-colored, cold-pressed oil with 2.4 percent free fatty acid, an Iodine No. of 120, and a color value of 11 on the Gardner scale.

^{2/}Viscosities over Z 6 are indicated arbitrarily as Z 6 with +1, +2, etc., denoting viscosities over the scale.

^{3/}"Universal Driers" -- Co-6 = Cobalt as 6 percent liquid; Pb-24 = Lead as 24 percent liquid; Mn-6 = Manganese as 6 percent liquid.

6. The addition of benzoyl and lauroyl peroxides increases the rate of viscosity change only slightly.

7. An increase in the iodine value of the menhaden oil by the addition of esters resynthesized from highly unsaturated acids from fish oils increased the rate of viscosity change, but not sufficiently to compensate for the increased cost.

8. The addition of 0.1 percent of a mixture of cobalt and manganese soaps (1 to 1 ratio of cobalt to manganese) of menhaden oil acids to oil blown at 111° C. produced a high viscosity oil in only 19.5 hours.

LITERATURE CITED

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REFRIGERATED LOCKER STORAGE OF FISH AND SHELLFISH

Shellfish present a problem quite different from fin fish in that more preparation is necessary before they can be frozen. Since some shellfish are available for only short periods of the year, it may be especially advantageous to freeze them for later home use.

Oysters, scallops, and clams can be successfully frozen. Since considerable practice is required in order to open the shells satisfactorily, an inexperienced person will do better to obtain the shucked products, which are readily available in season.

The commercial pack of frozen shrimp exceeds those of all other frozen shellfish packs combined. For locker storage, raw shrimp are most successfully frozen after breaking off the heads and appendages but without removing the shell from the tail or edible portion. Cooked crab meat and lobster meat should be packed in jars with $2\frac{1}{2}$ percent brine.

In most cases it is best to use frozen shellfish within a period of three or four months; however, a storage life of six months may be attained where storage accommodations are especially good, and the temperature is as low as -10° F.

--Fishery Leaflet 128