

EXPERIMENTAL STUDIES TO EXTEND USES OF FISH OILS IN THE LEATHER INDUSTRY

Part 1 - Experiments with Menhaden Oil ^{1/}

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ABSTRACT

The work reported here indicates that a satisfactory fat liquor can be made with menhaden oil. In the course of this work, a new technique for sulfating menhaden oil was developed. A public-service patent is being sought for this process.

INTRODUCTION

The leather industry requires large quantities of oils, greases, and waxes in the tanning and dressing of various kinds of leathers. Cod oil, an imported indus-

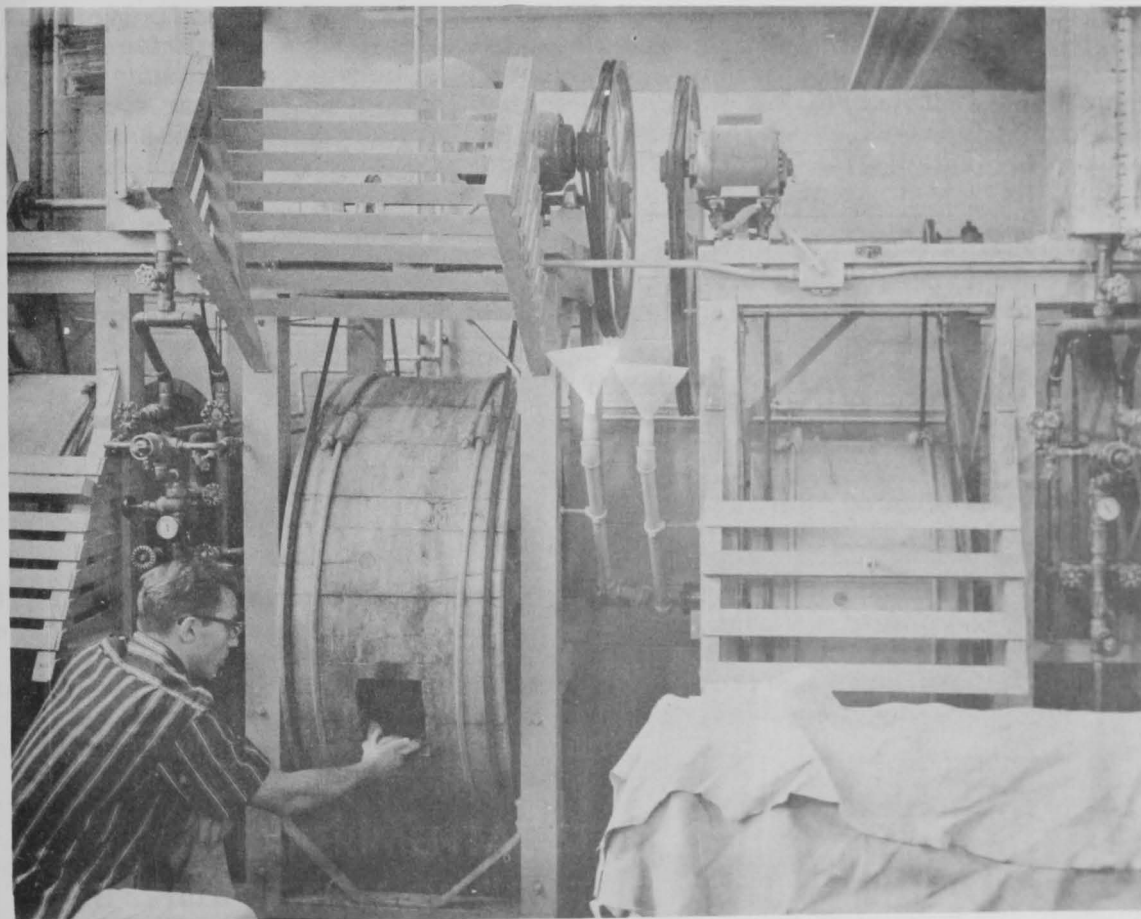


Fig. 1 - Pilot plant drums are used for fat-liquoring leather.

trial cod-liver oil not produced in this country, is the only fish oil that is being used at present in any quantity. Other oils have been tried experimentally but have not

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been considered satisfactory for one reason or another. A research program was developed to determine possible value of menhaden oil, at present available in large quantities, on fat-liquoring leather. Normally, both raw and sulfated oils are used for fat-liquoring so the research was mostly concerned with sulfating menhaden oil to reduce the rate of oxidation and polymerization which have previously caused difficulties in the use of the oil. The results obtained thus far are summarized in this report.

FAT-LIQUORING

Fat-liquoring consists of treating tanned wet skins or hides with an oil-in-water emulsion. The emulsion is taken up by the fibrous leather matrix, and the emulsion breaks and deposits oil, mainly within a certain thickness in the outer portion of the leather. During the drying of the leather, the deposited oil forms a film around the fibers, giving the finished product flexibility and serviceability.

PROBLEMS IN THE USE OF MENHADEN OIL FOR FAT-LIQUORING

Many oils are capable of reducing the cohesion of the fibers, but all oils do not produce the requisite feel, temper, and firmness in the leather. Tanners considered menhaden oil undesirable because of the high rate of oxidation and polymerization. They have felt that such properties might tend to harden the surface of the leather and unduly increase firmness. Furthermore, because of the susceptibility to oxidation, the filmed raw oil on chrome-tanned leather might cause spontaneous combustion. Gummy-spew might also be formed by oxidation. The possible yellowing of leather surfaces treated with fish oil might make the use of it undesirable in the manufacture of white or pastel leathers.

Since most of these hypothetically undesirable properties of the oil are associated with its chemically-unsaturated portion, the indicated approach was to reduce the amount of unsaturation. Two possible ways of doing this are by epoxidation and sulfation.

EPOXIDATION

The work on epoxidation was suggested by staff members of the Bureau's Fishery Technological Laboratory, College Park, Md. They pointed out that by partially lowering the iodine number of the oil, the product probably would be less reactive and more desirable for use in fat-liquoring.

Epoxidized menhaden oils with iodine numbers of 156 and 117 were supplied by the Bureau of Commercial Fisheries. These products have not been completely evaluated at the present time. A British Patent (1958) describes the use of epoxidized oils for oiling and waterproofing leather, indicating that possible uses exist for epoxidized menhaden and other fish oils.

SULFATION

Generally, the content of oil in a fat-liquored leather is about 5 to 6 percent, calculated on a dry basis. In fat-liquoring, sulfated oils are mixed with sufficiently large proportions of raw oils to modify the properties of the mixture. Since large quantities of sulfated oils are employed in the leather industry, the use of sulfated menhaden oil would enhance the chance of our finding new markets.

The work on the sulfation of menhaden oil first was carried out in the laboratory. The procedures developed in the laboratory then were tested on a larger scale in the pilot plant.

LABORATORY STUDIES

The laboratory studies were designed to compare, before and after 9 months' storage, the properties of leathers fat-liquored with menhaden oil, cod oil, and

neatsfoot oil. The aging of fat-liquored leather was considered necessary because of the oxidation and polymerization properties of an oil such as menhaden. The oil properties mentioned could produce a stiff leather with time as well as causing a decrease in extractable grease. This could adversely change the physical properties of the fat-liquored leathers necessitating the evaluation at the end of nine months' shelf storage. Both cod-oil and neatsfoot-oil fat liquors are presently used in the leather industry (but for different types of leather). The oxidation and polymerization properties of neatsfoot oil are different from those of cod and menhaden oil, and the characteristics of the leather produced also differ. The danger of spontaneous combustion, formation of gummy spew at high concentration of oil, and yellowing of leather surfaces exists with cod oil, though possibly to a lesser extent than with menhaden oil. For these reasons, evaluation of menhaden-oil fat-liquored leather as compared to cod-oil and neatsfoot-oil fat-liquored leathers should indicate whether menhaden oil is satisfactory for use in fat-liquoring.

SULFATION OF MENHADEN OIL: Although a sulfated menhaden oil would be a desirable product, industry personnel stated that this oil is difficult to sulfate by regular plant procedures. They pointed out that special precautions must be taken in order to prevent an extremely rapid reaction accompanied by excessive oxidation. At the Tanners' Council Laboratory, a procedure was developed for sulfating menhaden oil that reduced the hazards involved. A public-service patent is now being sought for this process.

PROCEDURE IN LABORATORY STUDIES: Chrome-tanned leather samples were fat-liquored to a 6-percent fat content on the basis of dry weight of leather. The fat-liquors consisted of mixtures of 60 parts sulfated oil and 40 parts raw oil (by weight) prepared from menhaden, cod, and neatsfoot oils.

RESULTS OF LABORATORY STUDY: The results of the laboratory study for the new and aged leathers indicated that neatsfoot-oil fat-liquored leather produced a leather that was softer to the feel^{2/}, was less firm, did not yellow on the surface, and showed less decrease in extractable grease after aging than did the leathers treated with either cod oil or menhaden oil. The same tests for leather quality when applied on a comparative basis between cod-oil and menhaden-oil fat-liquored leathers indicated that no large differences existed between them. No important differences were found in the strength properties of the differently fat-liquored leathers. None of the three fat-liquored test leathers produced spews. On the basis of these encouraging results, pilot-plant fat-liquoring studies were conducted to verify the laboratory findings.

PILOT-PLANT STUDIES

The pilot-plant fat-liquoring work was conducted at a commercial tannery. Four 100-pound batches of chrome-tanned hides were dyed black and fat-liquored, with the following combinations:

- Test I. 60-40 mixture of sulfated menhaden oil and raw menhaden oil.
- Test II. 60-40 mixture of sulfated cod oil and raw cod oil.
- Test III. 60-40 mixture of sulfated menhaden oil and raw cod oil.
- Test IV. Tannery control (neatsfoot-oil fat liquor).

Table 1 - Analytical Data on Sulfated Oils Used in Pilot-Plant Fat-liquoring Tests

Oil Tested	Water (Percent)	Total Alkali	Acid Value	pH	Combined SO ₃
					Percent
Sulfated menhaden oil of Test I.	25	0.52	12.7	6.2	5.6
Sulfated cod oil of Test II	25	1.3	41.0	6.5	4.7
Sulfated menhaden oil of Test III.	25	1.2	46.0	6.2	4.7

^{2/}Neatsfoot oil is purposely used by tanners to produce a soft leather.

The sulfated menhaden oils employed in this study were prepared on a pilot-plant scale by a cooperating chemical company, using the procedure developed at the Tanners' Council Laboratory. The sulfated menhaden oil of Test III differed from that of Test I in that it was prepared to meet the specifications for the sulfated cod oil used in Test II. The analytical data on the oils are presented in table 1.

RESULTS OF PILOT-PLANT STUDY: The purpose of the pilot-plant study was to determine if a menhaden-oil fat-liquor produced a desirable leather in comparison to leather fat-liquored with the neatsfoot oil or with the cod oil now in common use. Plant evaluation showed no significant difference between cod-oil and menhaden-oil fat-liquored leathers, thus indicating that they have similar properties. As was expected, the neatsfoot-oil fat-liquored leather was less firm than were the test leathers fat-liquored with either cod-oil or menhaden-oil fat-liquors. Differences in firmness between the two test leathers treated with the fish oils were not noticeable. None of the fat-liquored leathers produced spew. The menhaden-oil fat-liquored leather had a fishy odor in the crust state, but this odor was not present in the finished leathers.

The results of the pilot-plant study confirm the earlier observation made in the laboratory that menhaden-oil fat-liquor is similar in properties to the fat-liquor of cod oil and that menhaden oil therefore will make a satisfactory fat liquor.

SUMMARY

1. The leather industry offers a potential expanded use of fish oils, particularly in fat-liquoring.
2. The process of fat-liquoring consists of treating tanned wet skins or hides with an oil-in-water emulsion, which after the leather is dried, gives the finished product flexibility and serviceability.
3. Although menhaden oil is the fish oil produced in largest quantity, the ease of oxidation and polymerization poses certain problems for fat-liquoring.
4. Two possible ways of reducing the tendency of menhaden oil to oxidize and polymerize are to epoxidize and to sulfate the oil.
5. The studies on epoxidation have not been completed, but the patent literature indicates that epoxidized oil can be used for oiling and waterproofing leather.
6. Sulfation of menhaden oil presents difficulties. The reaction is extremely rapid by regular procedures and is accompanied by excessive oxidation. A procedure developed during the present work and for which a public-service patent is being sought, however, reduces the hazards involved.
7. In laboratory studies, chrome-tanned leather was fat-liquored with mixtures of 60 parts sulfated oil and 40 parts raw oil prepared from menhaden, cod, and neatsfoot oils.
8. Results of the laboratory study indicated, as was expected, that the neatsfoot-oil fat-liquored leather produced a softer leather. There was also less decrease in extractable grease on aging than when either cod oil or menhaden oil were used. No important differences were found in the strength properties of the differently fat-liquored leathers, and none of the leathers produced spew. No significant differences were found between the cod-oil and menhaden-oil fat-liquored leathers.
9. To check on the favorable results obtained in these laboratory studies, the experiments were repeated on a pilot-plant scale. The results were the same as in the laboratory tests.

10. It is concluded that a satisfactory fat liquor can be made from menhaden oil.

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FISH OIL RESEARCH MAY SHED LIGHT ON HEART DISEASES

A research project to study the relationship of fish oil in the diet to cholesterol deposits in the circulatory system of the body has been authorized by the U. S. Department of the Interior, Bureau of Commercial Fisheries. The research is expected to contribute to the fund of information being compiled on various phases of arteriosclerosis, particularly the coronary types.

It is the unsaturated fatty acids (unstable and susceptible to chemical change) which abound in fish oil that are the center of attention. Studies already made under the Saltonstall-Kennedy Act for the improvement of domestic commercial fisheries have shown that fish oils contain a greater amount and a greater diversity of these unsaturated fatty acids than do many other food fats. The current investigations are also being made under the Saltonstall-Kennedy program.

In one experiment miniature pigs are being used to determine the deposition of cholesterol in the body. Fish oil fatty acids of known degrees of unsaturation will be fed to the test animals. Ultimately the animal will be killed and the arteries examined to evaluate the effects of the several diets employed.

Another test will be made on rats to determine which of the many fish oil fatty acids are essential to physiological welfare. One objective is attempting to determine the relationship of fish oils to metabolism and fat transport in the body, while still another is probing the properties of fish oil that may have pharmaceutical applications.

The nutritive qualities of fish in reference to heart disease and current related dietary research is explored in some detail in the July 1958 issue of the Commercial Fisheries Review, published monthly by the Bureau of Commercial Fisheries. Reprints of this article--Separate 515--are available through the Office of Information, U. S. Fish and Wildlife Service, Department of the Interior, Washington 25, D. C.