COMMERCIAL USES FOR MENHADEN OIL

Epoxidation of winterized, deodorized menhaden oil should produce a commercially-attractive plasticizer suitable for blending with other materials into resins, e.g. polyvinyl chloride.

The hydroxylation and epoxidation of menhaden oil as a source of new materials suitable for commercial development were studied by Arthur D. Little, Inc., as part of the over-all Service program to develop new uses for fish oils. Three possible uses for hydroxylated oil were investigated: (1) polyisocyanate adhesives, (2) alkyd resins, and (3) isocyanate foams. Epoxidized oil was investigated as a possible plasticizer for polyvinyl chloride.

Hydroxylated oils showed some possibility for use in adhesive formulations. Hydroxylation converts the double bonds to vicinal glycol structures, the degree of hydroxylation being readily controllable. A typical hydroxylation procedure is given: 288 grams of winterized and deodorized oil was mixed into 123 grams of acetic acid with 6 grams of sulfuric acid. The mixture was heated to 60° C., and 44.8 grams of 50 percent hydrogen peroxide was added slowly, keeping the temperature at 65° ± 5° C. The mixture was held at 65° C. for 4 hours with constant stirring. The reaction mixture was then washed with water, and with a 5-percent sodium carbonate solution. The product was extracted from the mixture with ether. After extraction, the ether solution was dried with magnesium sulfate, and the ether was evaporated from the product. The iodine number dropped from 179 in the raw oil to 127 in the product, indicating a loss of 28.8 percent unsaturation. It was later found that a 20-percent sodium chloride solution in place of plain water and eliminating the alkaline wash speeded up the washing.

The hydroxylated oil was tried in various adhesive formulations, with one using 1-chloro-2, 4-phenylene di-isocyanate (Mondur C) showing some promise. However, though the tensile strength of this adhesive was good, as measured by the sugar-maple block ASTM test D897-49, the impact and shear resistance was poor.

The use of hydroxylated menhaden oils in the formation of alkyd resins and isocyanate foams showed very little promise. The more expensive hydroxylated menhaden oils, due to the added expense of hydroxylation, did not produce better alkyd resins than did the cheaper dehydroxylated vegetable oils used in the resin industry. Hydroxylated menhaden oils formed poor isocyanate foams, having foamed (due to the entrapping of gases within the liquid resin as it sets into the rigid plastic) to only about twice the original volume. A commercially-successful foam will expand 10 to 30 times its original volume.

The most promising results were obtained with epoxidized oils made from winterized and deodorized menhaden oils. Epoxidation was carried out by adding, with agitation, oil to a 10-percent solution of preformed peracetic acid at 20° C. The temperature was allowed to rise to 50° C., and the product was extracted in the same manner as the hydroxylated oil. The report states that peracetic acid for commercial epoxidation of menhaden oil would be formed cheaper in situ--through the action of hydrogen peroxide on acetic acid in the presence of a mineral acid catalyst. (A recent development in epoxidation technique utilizes a cation-exchange resin catalyst.) The chemical cost of epoxidizing menhaden oil using peracetic acid in situ was calculated to be around 12 cents a pound. Acetylated monoglycerides (prepared by transesterification with glycerine and acetylated with acetic anhydride and sodium acetate) were also epoxidized. Acetylation of partially hydroxylated menhaden oil using systems of acetic acid with sodium acetate and acetyl chloride in pyridine proved unsuccessful.

NOTE: ABSTRACT OF FINAL REPORT SUBMITTED BY ARTHUR D. LITTLE, INC., CAMBRIDGE, MASS. THIS FIRM WAS AWARDED A CONTRACT BY THE UNITED STATES FISH AND WILDLIFE SERVICE TO STUDY THE HYDROXYLATION AND EPOXIDATION OF MENHADEN OIL AS A SOURCE OF NEW MATERIALS SUITABLE FOR COMMERCIAL DEVELOPMENT. FUNDS PROVIDED BY THE SALTONSTALL-KENNEDY ACT OF 1954 FINANCED THIS RESEARCH CONTRACT.

Analytical methods employed to measure the degree of hydroxylation and epoxidation are given. The report points out that the iodine number determinations were used as an indirect estimation of the degree of the above reactions. The iodine value gave a measure of the decrease in unsaturation and could not be used as an accurate method of determining the degree of reaction, since cross-linking occurred in the oxidation processes. Therefore, the oxirane or epoxy oxygen and the hydroxyl content was determined. The procedures for these last two determinations are given.

Some important considerations using epoxidized menhaden oil as a plasticizer are as follows: (1) it does not bleed (the tendency of the plasticizer to "bleed" to the surface of the film, thus producing an oily coating); (2) it has low volatility (the length of time a plasticizer remains in the compounded resin without evaporating); (3) it has some decomposition on heating; (4) it appears to be stable towards ultraviolet light; (5) it has no fire-retarding action; (6) its water extraction should be low (the degree of extractibility of the plasticizer from the polymer by water); (7) it has a fishy odor in some samples. Substantially odorless plasticizers were prepared using winterized steam-blown oil. The tendency of creep was not determined. (The lack of "creep" is a property of the plasticizer of imparting flexibility without permitting permanent distortion under stress.)

The report contains 5 tables and 21 references.

NOTE: THIS IS AN ABSTRACT PREPARED BY JOSEPH CARVER, CHEMIST, FISHERY TECHNOLOGICAL LABORATORY, BOSTON, MASS.

WHAT DO WHALES EAT?

The diet of the different kinds of whales is extremely varied, according to the anatomical difference of the various species. The toothed whales (such as the sperm whales, beaked whales, bottlenose dolphin, and killer whale) feed largely upon fishes, squids, and cuttlefish. The killer whale also eat any other mammal found swimming in the water. Bottlenosed dolphins feed upon mullet, sea trout, certain croakers, and even catfish. They have also been reported to eat shrimp. Some of the fresh-water dolphins evidently feed on plant material to some extent.

The baleen whales, of which the blue whale or sulphur bottom (the largest of living animals) is an example, feed upon great masses of very small animals called plankton. In the mouth of this type of whale are suspended the closely set plates of whalebone through the frayed ends of which water is passed while the plankton, such as the shrimplike krill and other forms, are filtered out. The baleen whales feed by cruising with their large mouths wide open, taking in the krill, among others, and occasionally schools of small fishes are also engulfed. One baleen whale was found to contain two tons of plankton in its stomach. Other types of baleen whales are the finback, piked whale, sei whale, and humpback whale.

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