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HYDROGENATION OF MARINE OILS

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This invention relates to the hydrogenation of marine oils such as whale oil, for example, to prepare shortening, margarine and the like and, more particularly, relates to the hydrogenation of marine oils using a palladium metal catalyst.

Marine oils are distinguished by their considerable content of fatty acids having variable chain length, ranging both above and below C_{18} , and by the presence of highly unsaturated acids, having four or more double bonds, together with a considerable quantity of saturated acids, i.e. the latter may comprise as much as 25 percent of the total acids. They are generally the cheapest of all fats and oils, and commercially important members of this group are derived from the whale, and from small oily fishes such as the sardine, menhaden and herring. Sperm whale oils are actually liquid waxes to a large degree, and are valuable when sulfurized as lubricants for extreme high pressure conditions. They are not suitable for hydrogenation to shortening and margarine.

Hydrogenated oil from whales other than the sperm whale is a valuable product, widely used throughout the world, except in the United States, as a constituent of fat mixtures employed in the manufacture of margarine. Whale oil constitutes 20-40 percent of all the fats used for this purpose. Heretofore, plant-hydrogenation of whale oil has been effected using only nickel catalysts, and the hydrogenated product is usually satisfactory if the hydrogenation is carried out only to a low iodine number. Products having higher iodine numbers, however, in the range of 73-75 for example, and correspondingly lower melting points in the range of 33-35° C. for example, frequently are unsatisfactory as they have poor oxidation stability and easily revert to an unpleasant fishy odor. Whale oil hydrogenated to an I.N.=73-75 (M.P.=33-35° C.) is an especially important component of winter-margarine produced in many countries throughout the world.

Whale oil is an extremely complex mixture and presents certain problems not encountered in the treatment of vegetable oils, i.e. whale oil contains saturated acids having 14-20 carbon atoms, unsaturated acids having 14-22 carbon atoms and 1-6 double bonds, together with 1.5 to 3 percent of unsaponifiable matter. Sulfur and nitrogen compounds may also be present. The particular problems presented in the treatment of whale oil result from the large amount of multiple unsaturation. Oils containing more than one double bond are known to be especially unstable to oxidation, i.e. in the formation of hydroperoxides in the oxidation of oils, the hydroperoxides are produced much more rapidly from linoleic than from oleic glycerides. The same is also true of compounds having more than two double bonds, but to a greater degree.

Thus, the problem in preparing a satisfactory hydrogenated whale oil is one of preferentially removing the compounds having multiple unsaturation. When the oil is reduced to a low iodine number, the problem is less acute, since most of the double bonds, multiple or other-

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wise, are removed. In this connection, it was found that comparable products are obtained when whale oil is reduced to an iodine number of about 55, or to an iodine number of about 35, melting points 40-42° C. and 46-48° C., respectively, using either nickel or palladium catalysts. However, in the preparation of products having higher iodine numbers, palladium is definitely a superior catalyst and produces a completely satisfactory product, whereas the product produced using nickel, is a less stable one. Such higher iodine numbers, typically those in the range of 65-80 for shortenings and margarines, are found in the desirable soft fats as contrasted to the less useful hard fats having iodine numbers in the range of 35-55.

The superiority of palladium may be attributed to two causes: (1) it is selective, i.e. it preferentially hydrogenates multiple double bonds, thereby contributing to oxidation stability; and (2) it results in a product having more trans isomers, which is the higher melting form of product and contributes to a desirable consistency. The higher trans content in products produced by palladium hydrogenation also contributes to the oxidation stability of the products, since trans olefins are more stable to oxidation than are cis olefins. At room temperature, the product produced by nickel hydrogenation is mostly oil, whereas the product produced from palladium hydrogenation is semi-solid, and in this connection, note the solid fat index of Table I below.

In the preparation of the palladium catalyst of the invention, any conventional method may be employed, such as suspending a catalyst support in water and adding a solution of a compound of palladium thereto, after which a precipitating agent is added and stirring of the suspension at a temperature in the range of 20° C. to 100° C., continued for a period of 20 to 60 minutes. The hot suspension is then filtered, washed and the precipitate is dried.

In the catalyst of the invention, the palladium may be present on a suitable support in a quantity equivalent to about 0.01 to 10 percent by weight of the total catalyst, including the support, preferably 0.1 to 5 percent by weight. Among the catalyst supports which may be employed to prepare the catalyst of the present invention are carbon, alumina, including activated alumina, silica gel, kieselguhr, asbestos, and the like, but carbon is the preferred support for a number of reasons, including ease of recovery of the catalytic metal. The form of the catalyst may be granular, extruded, or pelleted if used as a stationary catalyst, as in a continuous process, or preferably powdered if used in batch processes.

In the hydrogenation of marine oils, the hydrogenations may be performed in an ordinary hydrogenator in which hydrogen is added in the conventional manner, i.e. it may be pressured in over the oil, or bubbled up therethrough. Hydrogenations performed using the catalyst of the present invention, generally are performed at a temperature in the range of 50 to 200° C., hydrogenation time in the range of 40 to 400 minutes, a hydrogen pressure in the range of atmospheric to 100 p.s.i.g., preferably atmospheric to about 50 p.s.i.g., and using a catalytic metal concentration, based upon the weight of oil hydrogenated, in the range of 0.002 to 0.005 percent.

The invention will be further illustrated by reference to the following specific example:

EXAMPLE I

In Table I below, the conditions employed in the hydrogenation of whale oil and the properties of the product are given. Inspection of the table will establish the superiority of palladium, i.e. comparison of Experiments 1 and 6 establishes the more desirable plastic

properties of the product obtained from palladium hydrogenation as seen in the solid fat index, this index being a measure of the solids in the fat at various temperatures. This method of measuring plastic properties by dilatation is the Official Method of the American Oil Chemists Society—Cd-10-57. These much more desirable plastic properties in the product resulting from the palladium hydrogenation, are probably due to the higher trans content, i.e. 62 percent from palladium hydrogenation, and only 44.3 percent from nickel hydrogenation.

The product produced by palladium hydrogenation also has superior oxidation stability, as will be seen by

3-pound batches of whale oil. The hydrogenations were performed using the agitation, temperature, pressure, reaction time, and catalyst conditions indicated in Table I below. It was found that the reaction rate increased appreciably with increased agitation. Processing was controlled by measurement of the refractive index, and iodine numbers were determined at a constant temperature of 24° C., using the method of Hanus. Determination of capillary melting points and thiocyanogen numbers was made by Official Methods of the American Oil Chemists Society. The trans content was determined by infrared absorption at 10.36 μ . The conditions and results are as follows:

Table I.—Hydrogenation of whale oil

Exp.	Catalyst	Kg./Ton Oil	Percent Metal in Oil	T.° C.	Pressure, p.s.i.g.	Agit., r.p.m.	Time, Mins.	Iodine Numbers	Thiocyanogen Number	Linoleic Acid, ¹ Percent	Trans Content, Percent
1-----	1% Pd/C.	2.5-----	0.0025	160	30-----	290	210	75.2	72.6	2.7	61.4
2-----	1% Pd/C.	2.5-----	0.0025	175	atm-----	290	400	79.1	-----	-----	63.0
3-----	5% Pd/C.	0.66-----	0.0033	175	atm.→20	290	400	78.0	74.8	3.4	62.0
4-----	2% Pd/C.	1.2-----	0.0024	175	atm-----	290	200	79.5	-----	-----	63.5
5-----	2% Pd/C.	1.4-----	0.0028	175	atm-----	290	180	76.9	75.0	2.0	61.5
6-----	Ni cat.	2 Kg. nickel metal.	0.2	175	atm-----	290	150	76.9	72.9	4.5	44.3
7-----	Ni cat.	do-----	0.2	175	atm-----	290	340	72.2	-----	-----	39.0

¹ Multiple unsaturation calculated as linoleic acid.

Exp.	Cap. M. P.	Congeal Point	Solid Fat Index				Oxidation Stability						
							Peroxide Number				Aldehyde Value		
			20°	26.7°	36°	42°	Start	8 hrs.	13 hrs	19 hrs.	Start	13 hrs.	Increase
1-----	34.4	26.9	25.2	16.4	neg.	neg.	-----	-----	-----	-----	-----	-----	-----
2-----	33.0	24.2	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
3-----	34.4	24.6	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
4-----	33.8	24.9	-----	-----	-----	-----	4	4.7	6.6	168	3	8.4	5.4
5-----	34.7	25.4	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
6-----	33.7	22.3	12.4	7	neg.	neg.	-----	-----	-----	-----	-----	-----	-----
7-----	37.2	24.3	-----	-----	-----	-----	2.9	4.7	11	252	2	10.4	8.4

comparison of the peroxide numbers and aldehyde values in Experiments 4 and 7. The peroxide number was determined by the Official Method of the American Oil Chemists Society—Cd-8-53, and the larger the peroxide number obtained in a given period, the more unstable is the product to oxidation. It will be seen from the table that although the palladium product initially had a higher peroxide number, because it was older when analyzed, it gave a much smaller peroxide number than did the product produced by nickel hydrogenation at the termination of the test. The peroxide build-up is exponential because of the auto-catalytic nature of the oxidation.

Aldehydes are also formed when an oil is oxidized and the aldehyde is probably a decomposition product of a peroxide. Hence, a measure of the aldehyde value (milliequivalents of aldehyde per 10,000 grams of oil) formed after aeration, is a measure of the stability of the oil to oxidation; the smaller the aldehyde value, the more stable the oil. From Experiments 4 and 7 in Table I below, it will be seen that, although the palladium product initially had a higher aldehyde value, because it was older when it was analyzed, after 13 hours aeration the increase in aldehyde value was smaller than with the sample hydrogenated in the presence of nickel. These values further establish that hydrogenation of whale oil with palladium produces a product of exceptional oxidation stability. The aldehyde content was determined by measuring by optical density, the absorption at 350 μ on a Beckman DU Spectrophotometer.

The hydrogenations were all performed in a stainless steel hydrogenator, which was successively charged with

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and the invention includes all such modifications.

What is claimed is:

1. A method for hydrogenating marine oils which comprises treating the oil to be hydrogenated with hydrogen in the presence of a palladium metal catalyst to produce a hydrogenate product having an iodine number in the range of about 60-85.
2. A method according to claim 1 in which the oil is a whale oil other than sperm whale oil.
3. A method according to claim 1 in which the palladium metal is supported on carbon.
4. A method according to claim 1 in which the hydrogenated oil has a solid fat index greater than 15 at 20° C. and greater than 10 at 26.7° C.
5. A method according to claim 1 in which the hydrogenated oil has a peroxide number less than 10 after standing for 13 hours and less than 200 after standing for 19 hours.
6. A method according to claim 1 in which the hydrogenated oil has an aldehyde value less than 10 after standing for 13 hours.
7. A method according to claim 1 in which the hydrogenate product has an iodine number between about 72-80.

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