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HYDROGENATION OF OILS

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This invention relates to the hydrogenation of organic materials and more particularly to the selective or partial and controlled hydrogenation of oils or similar compounds containing unsaturated organic compounds.

It has been known to hydrogenate oils containing unsaturated fatty materials by contacting the oil with hydrogen gas in the presence of metallic catalysts. Such procedures, however, have been directed to the complete saturation of the unsaturated or open bonds in the fatty materials of the oil and the production of completely saturated compounds, such as stearine, in the oil, or to the uncontrolled hydrogenation of oils, and not to the regulated absorption of hydrogen atoms over the various unsaturated molecules within the oil.

The present invention is particularly concerned with the selective or partial hydrogenation of the unsaturated fatty materials in vegetable, animal or fish oils to produce materials of desired characteristics, such as melting point, setting point and iodin number. It is an object of the invention to provide an improved process whereby hydrogenation may be accurately controlled to produce the desired product. Another object is to provide a method whereby the unsaturated compounds having more than one open-bond may be selectively hydrogenated to saturate some of the open or unsaturated bonds without saturating all of them. It is also an object to provide a method whereby cotton seed oil may be selectively hydrogenated to provide a product having improved characteristics for use in the preparation of butter substitutes and similar compounds. Other objects will become apparent.

I have found that by subjecting an oil containing unsaturated glycerides, at a suitable temperature, to a properly proportioned mixture of hydrogen and an inert gas, such as nitrogen, in the presence of a catalyst, the unsaturated glycerides containing two double bonds, such, for example, as the glycerides of linoleic acid, may be hydrogenated to produce glycerides containing only a single unsaturated bond, such, for example, as the glycerides of oleic or isooleic acid. By this procedure the partial absorption of hydrogen by many fatty molecules is accomplished rather than the complete saturation of some of the molecules without hydrogenation of the others.

Because of the dilution of the gas in following this procedure it is possible to obtain a greater pressure within the vessel with a small quantity of gas. Also because of the dilution, fewer of the active gas atoms are available as the absorption starts in the molecule. Furthermore the dissemination of the active gas throughout an atmosphere of the inert gas makes it necessary for the open bonds of the liquid molecules to overcome the slight adhesive resistance of the atoms of the mixed gases in absorbing the active gas. These three possible explanations of the principle of the selective absorption are given because any one or more of them may be responsible for the improved effect. It is not intended, however, that the invention should be limited by any explanation as to its theory of operation.

In describing the invention reference will be made to its use in the hydrogenation of cottonseed oil to produce a product having a suitable melting point, setting point and iodin number to make it particularly adapted for use in the preparation of butter substitutes. It is not intended, however, to restrict the invention to this particular use, since it may also be applied to the selective hydrogenation of other grades of vegetable, animal and fish oils containing open-bonds and susceptible to hydrogenation, for example, linseed oil, corn oil, peanut oil, sun-flower oil, soya bean oil or to mixtures of these oils or to mixtures of these oils with other more completely saturated oils, such as cocoanut oil, palm kernel nut oil or palm oil. By hydrogenation of a mixture of even a small quantity of a highly unsaturated oil such as cottonseed oil with a more completely saturated oil such as cocoanut oil, the melting point of the mixture may be raised to considerably above that obtainable by hydrogenation of the cocoanut oil alone. My invention may also be used in the selective hydrogenation of mineral oils containing unsaturated hydrocarbons or in other reactions between unsaturated compounds and gases which react therewith (for example, oxygen, chlorine, sulphur trioxide, etc.,) with or without a catalyst, for example in the oxidation of drying oils in the preparation of paints and varnishes or in the sulphonation of oils.

In the preparation of cotton seed oil for use in producing butter substitutes, it is desirable to increase the melting point of the oil to slightly below the normal body temperature and to provide an oil having its melting point and setting point as close together as possible. It is also important, however, to avoid complete saturation of the glycerides in such oil in such a manner as to produce glycerides of the saturated fatty acids, such as stearine. The melting points referred to herein are measured according to the Wiley melting point determination method, which is the official melting point determination method of the Asso-

ciation of Official Agricultural Chemists. The iodin number determinations are measured according to the Wijs iodin number method, based upon a one hour absorption. This is also the official iodin number method of the above association. The setting point determinations are made by a method similar to that used in determining the titre of fatty acids and are carried out as follows:

The setting point apparatus consists of an accurate titre test thermometer graduated in tenths of a degree, a hard glass test tube 6 inches long and one inch in diameter having a mark positioned 3 inches from the bottom. A brass rod bent at the bottom to form a horizontal loop which will encircle the stem of the thermometer and fit loosely to the wall of the test tube; a 4 ounce wide mouth bottle about 4½ inches long and 2 inches in diameter, which serves as an air jacket for the test tube. A cork stopper bored to hold the test tube in the bottle. Another cork stopper bored at its center to hold the thermometer in the test tube and notched at the edge for the stirring rod; two 600 cc. beakers are provided for water baths. In making the test the liquefied oil is brought to a temperature of not less than 50° C. and enough of it is poured into the test tube to fill the latter to the 3'' mark. The thermometer and stirring rod are then adjusted in the tube which is then placed in a water bath at 10° C. The oil is stirred by a vertical motion of the stirring rod until its temperature drops to 35° C. The tube is then lifted from the bath and the oil agitated while the tube is held in the air until the temperature reaches 30° C., after which the tube is replaced in a water bath at 10° C. and the agitation continued until the temperature drops to 25° C. The tube is then quickly placed in the bottle serving as an air jacket, after which the said bottle is placed in a water bath maintained at a temperature of 15° C. The cork should be held in place by suitable means. The oil is agitated slowly and uniformly until the temperature reaches its lowest point and comes to rest for about 30 seconds. The thermometer is then pulled up so that its lower end is 1½'' from the bottom of the tube and the stirring rod is raised out of the oil. The temperature is then read at frequent time intervals and the maximum temperature reached before the mercury column starts to drop, is recorded. This maximum temperature is taken as the setting point. This point is also sometimes referred to as the congealed point of the fat.

In carrying out the selective hydrogenation of the oil about 8000 pounds of whole neutral cottonseed oil having a melting point of about 36° F. and an iodin number of about 106–110 may be introduced into an enclosed tank provided with a suitable agitator, the size of the tank being such that the oil will occupy about ½ of its volume. The remaining space in the tank is filled with pure nitrogen gas. The oil is then heated to about 280° F. and about .1% of nickel catalyst (produced by reducing nickel hydrate) is added to and thoroughly mixed with the oil. More nitrogen may be then introduced into the space above the oil to increase the pressure in the container to about 80 pounds per square inch. Hydrogen gas is then introduced into the nitrogen atmosphere, the temperature of the oil being maintained at about 280° F. by means of a cooling coil and the pressure within the container being maintained at not over about 100 pounds per square inch. The hydrogenation is carried on for about 3 hours, the oil being stirred throughout that period. The hydrogen gas absorbed during the treatment (an important index) under these conditions would be about 621 cubic feet to each thousand pounds of oil. By this treatment an oil having a melting point of about 96.8° F., an iodin number of about 67.1 and a setting point of about 25.1° C., may be produced.

The above example is merely given as illustrative and it is not intended to restrict the invention to the particular temperatures, time, concentrations, etc., described therein since it is obvious that in starting with various materials and in producing various products, it will be necessary to alter the conditions of the hydrogenation. The temperature of hydrogenation may vary from about 200 to 400° F. although it is preferred to maintain the temperature during this period at about 275 to 300° F. The catalyst may be added before or when the oil is at this temperature but it is preferred to add it after the oil is heated to above about 210° F. The pressure may be varied from those given; for example, pressures from below atmospheric pressure to very high pressures may be used. Other gases or gaseous mixture which are technically pure and are inert to the ingredients used may be substituted for nitrogen. For example, carbon dioxide, other fully oxidized and inert gaseous oxides, or the rare gaseous elements or steam may be used, alone or with nitrogen or other gases, as the inert diluent. Such gases or gaseous mixtures should not contain foreign gas impurities or substances which would poison any catalysts that might be used or would give an undesirable odor or flavor to the product. Other catalysts may also be used, for example, reduced nickel prepared from other bases or other metallic catalysts, such as copper, iron, aluminum, palladium, platinum, cobalt, chromium, manganese, titanium, molybdenum, vanadium and the like may be used. These may be present in finely divided suspension within the oil or may be deposited upon an inert carrier such as "filtercel" and suspended in the oil. The quantity of catalyst required may vary, for example, from about .1% to 1% depending upon the catalyst used and the degree of fineness to which it is subdivided or the surface exposed.

The relative volumes of oil and gas may be varied from those given above. Also, the ratio of hydrogen gas to nitrogen gas may be altered. By varying the proportion of hydrogen in the inert gas the selectivity of the hydrogenation may be controlled to any desired extent from practically no selectivity with substantially little nitrogen to maximum selectivity with high percentage of nitrogen. In the example given the quantity of hydrogen gas (determined by volume at atmospheric pressure) present during the hydrogenation did not exceed about 20% of the quantity of nitrogen present.

It is preferred to introduce the hydrogen gas into the volume of nitrogen gas above the oil while the latter is being agitated to expose new surfaces to the gas, although the invention may also be utilized by introducing into the body of the oil a suitable mixture of hydrogen and an inert gas, such as nitrogen, to give the desired selective hydrogenation. When this practice is followed, the mechanical agitation may be reduced or omitted. In following the latter practice, a gas circulating pump would draw from the gas area within the apparatus and would discharge through perforated distributors below the oil.

Hydrogen gas would be fed as needed into the circulating lines to provide the proper gas mixture before contacting the oil.

The oil produced in this manner is of particular value in the preparation of butter substitute or other food products in which it is desirable to use an oil having a melting point slightly below body temperature and a setting point as close to the melting point as possible. In producing butter substitute the oil prepared as described above may be emulsified with cultured milk, chilled and crystallized, worked, kneaded and seasoned with salt, as is the usual practice in the production of such products.

The terms used in describing and claiming the invention have been used in their descriptive sense and not as terms of limitation and it is intended that all equivalents of the terms used be included within the scope of the appended claims.

What I claim is:

1. A method for the controlled selective hydrogenation of an oil containing unsaturated fatty compounds, comprising heating the oil to 200–400° F., adding a finely divided catalyst to the oil, maintaining an inert gas in the space above the oil in a closed vessel to increase the pressure to above atmospheric pressure, and introducing hydrogen directly into the inert gas above the oil while the latter is being agitated.

2. A method for the controlled selective hydrogenation of an oil containing unsaturated fatty materials comprising heating the oil to about 275–300° F., adding a finely divided catalyst to the oil, maintaining nitrogen in the space above the oil in a closed vessel, and introducing hydrogen gas directly into the nitrogen while agitating the oil and maintaining it at a temperature of about 275–300° F.

3. A method for the controlled selective hydrogenation of cottonseed oil for use in producing a butter substitute comprising, heating the oil to about 275–300° F., introducing a finely divided nickel catalyzer into the oil, maintaining an inert gas in the space above the oil in a closed vessel, agitating the oil and introducing hydrogen directly into the inert gas while maintaining the oil at the elevated temperature.

4. A method for preparing cottonseed oil for use in producing a butter substitute comprising, heating the oil to about 200–400° F. in the presence of a finely divided nickel catalyzer, agitating the oil and subjecting it to a mixture of hydrogen and an inert gas until the melting point of the product reaches about 90–98° F. and the setting point of the product reaches about 22–27° C., the inert gas being maintained in the space above the oil and the hydrogen being introduced directly into the inert gas.

5. A method for the controlled selective hydrogenation of an oil containing unsaturated fatty compounds, comprising heating the oil at a temperature of 200 to 400° F. while agitating it with a catalyst and maintaining an inert gas in the space above the oil, and introducing hydrogen directly into the inert gas above the oil during the heating.

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