Aug. 29, 1950 V. MILLS ET AL 2,520,423

PARTIAL HYDROGENATION OF UNSATURATED GLYCERIDE OILS

Filed May 2, 1947 2 Sheets-Sheet 1

FIG. 1.

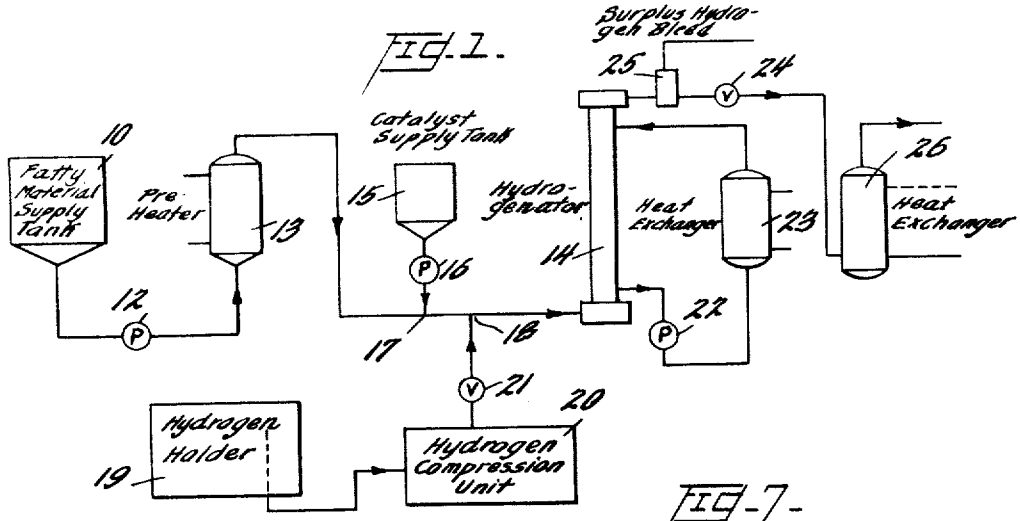


FIG. 4.

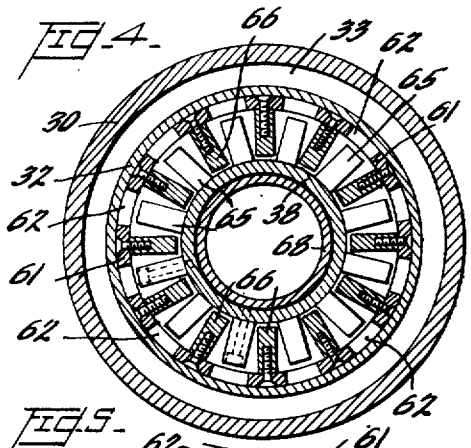


FIG. 5.

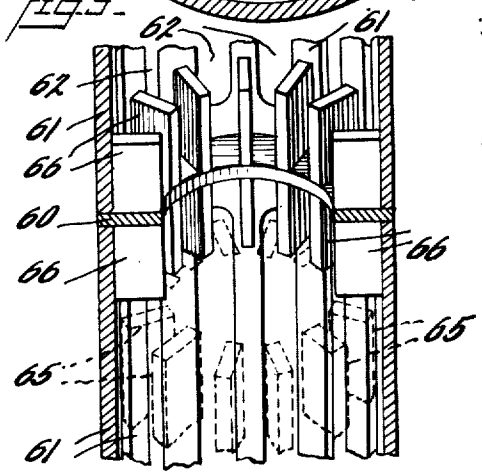
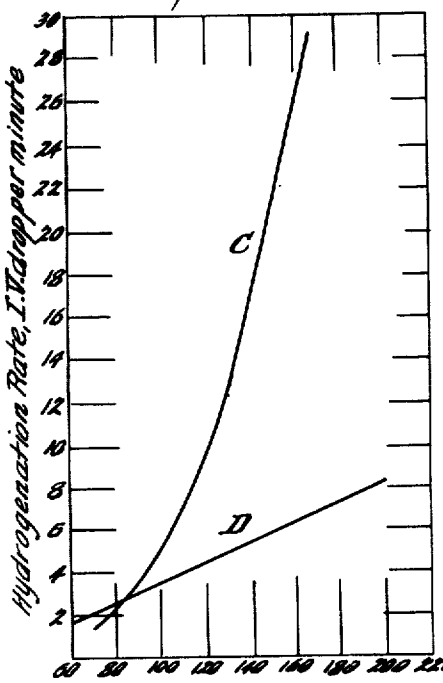


FIG. 7.



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PARTIAL HYDROGENATION OF UNSATURATED GLYCERIDE OILS

Filed May 2, 1947 2 Sheets-Sheet 2

FIG. 2.

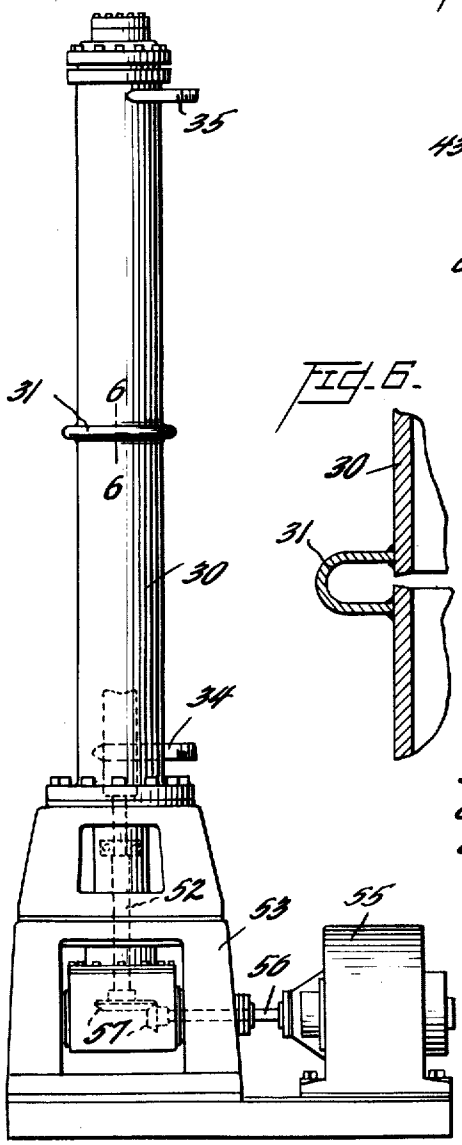
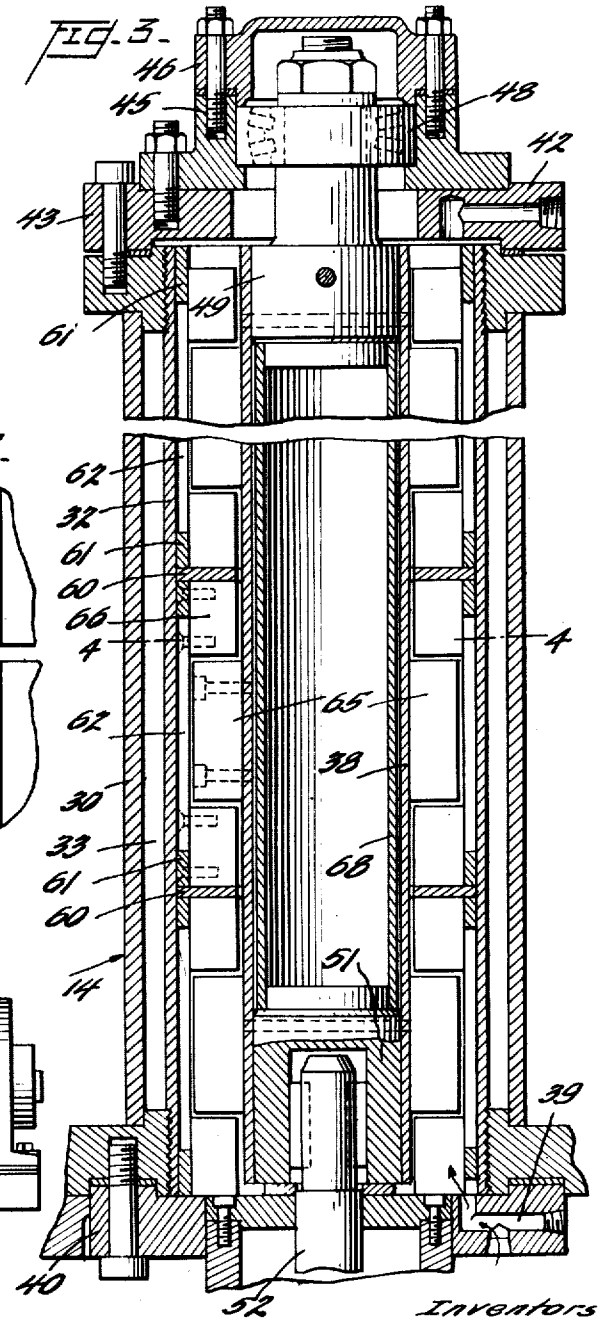


FIG. 6.

FIG. 3.



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PARTIAL HYDROGENATION OF UNSATURATED GLYCERIDE OILS

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Application May 2, 1947, Serial No. 745,661

10 Claims. (Cl. 260—409)

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This invention relates to the partial hydrogenation of unsaturated glyceride oils containing polyethylenic double bonds, for use in the manufacture of plastic shortening.

The vegetable oils of primary commercial interest in this connection in the United States are cottonseed oil and soybean oil, both of which are used in enormous quantities for the purpose. After being partially hydrogenated, and then deodorized, the fatty material is "plasticized" by chilling it rapidly to about 50° to 65° F. and whipping it until the super-cooled material has largely given up its heat of crystallization and has acquired a creamy texture. Upon standing for a short time at room temperature to complete its "setting up," the shortening acquires a soft plastic consistency which makes it suitable for working into doughs and batters for the making of various baked goods.

A shortening made in this way, entirely from partially hydrogenated oil, tends to become inconveniently soft when its temperature is warmed a few degrees, and tends to become inconveniently firm when its temperature is lowered a few degrees. It is thus said to have a narrow plastic range. A shortening having a broader plastic range, i. e. a wider range of temperatures within which it has a desirable plasticity, is produced by hydrogenating the oil slightly less and blending with this partially hydrogenated "base stock," before plasticizing, a minor proportion of trisaturated glyceride, known as "hard stock." Best results, from the standpoint of plasticity of such blended shortening, are achieved when normal oleic acid radicals predominate in the partially hydrogenated base stock of the shortening; saturated acid radicals are unnecessary in the base stock, requisite stiffness of the finished shortening being insured by the addition of sufficient hard stock. Again, the polyethylenic fatty acid radicals (principally the di-ethylenic radical, linoleic) are susceptible to oxidative rancidity, and the stability of the shortening is greatly enhanced by hydrogenation of such radicals.

Thus the ideal process of partially hydrogenating oils such as cottonseed or soybean would convert all of their polyethylenic fatty acid radicals to normal oleic acid radicals, with the conversion of few if any unsaturated acid radicals to saturated acid radicals.

In practice this ideal is never reached, partly because some of the unsaturated acid radicals are unavoidably saturated during the hydrogenation, but principally because of the inadvertent creation of glycerides containing isooleic acid radicals. Many of these isooleic glycerides are

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(1) solid at normal room temperature, and (2) melt at slightly above this temperature. Because of the first of these properties they add to the firming effect of the saturated radicals, frequently to such an extent that the desired plasticity is reached before the conversion of all of the polyethylenic radicals is complete, with the result that the finished shortening is insufficiently resistant to rancidity. Because of the second of the properties possessed by isooleic glycerides the finished shortening softens unduly when it is held at temperatures in the neighborhood of 90° to 100° F., and then when again brought to normal room temperature it becomes undesirably firm and "ribby" (uneven in consistency) because of the knitting or interlacing of the reformed crystals of isooleic esters, such shortening thus having what is known as an unstable plasticity.

To state the situation differently, besides the principal desired reaction:

(1) Polyethylenic acid radicals→normal oleic acid radicals, several undesired "side reactions" simultaneously occur, including:
(2) Polyethylenic acid radicals→isomeric oleic acid radicals
(3) Normal oleic acid radicals→isomeric oleic acid radicals
(4) Monoethylenic acid radicals→saturated acid radicals

Reactions (2), (3) and (4) all result (sometimes to an undesirable extent) in a firming of the final shortening which is produced from the hydrogenated oil. Reactions (2) and (3) tend to impart unstable plasticity to the product. Reactions (1) and (2) increase the product's resistance to rancidity, i. e. improve its keeping qualities.

No means has as yet been discovered for totally suppressing reactions (2), (3) and/or (4) while causing reaction (1) to proceed. Some control can be exercised, however, over the relative rates of these several reactions, the normal desire being to promote reaction (1) while impeding (or promoting to a lesser extent) reactions (2), (3) and (4). The principal difficulty standing in the way of accomplishing this desire is that reaction conditions which tend to suppress reactions (2) and (3) normally tend to stimulate reaction (4), and vice versa.

The general practice in partially hydrogenating an oil such as cottonseed oil or soybean oil, for use as a base stock in plastic shortening, is to choose reaction conditions best calculated to favor reaction (1) more than reactions (2), (3)

and/or (4), and to choose an endpoint which corresponds as nearly as possible to the complete elimination of polyethylenic radicals while not entailing the production of any more of the products of reactions (2), (3) and (4) than can be helped. A compromise between these desirable and undesirable results is thus necessary in order to produce a shortening having at least reasonably good keeping qualities together with at least reasonably good plastic properties.

During the years since the advent of hydrogenated vegetable shortening, a numebr of suggestions have been made, chiefly in the realm of improved catalysts and in the choice of favorable temperature and pressure range for the hydrogenation, with the object of obtaining either improved "selection" (i. e. the tendency to favor the hydrogenation of the more unsaturated acid radicals before the hydrogenation of the less unsaturated radicals), or a repression of isooleic formation. The present invention marks a definite advance in both of these directions, and thus permits one to produce a shortening having better keeping qualities for a given consistency, or a more desirable consistency for a given keeping quality, or some combination of these two advantages.

Prior investigators have found that "selectivity" is favored by high temperatures, hydrogenation in the neighborhood of 165° C., for example, being much more favorable to the preferential hydrogenation of linoleic to oleic than hydrogenation at 125° C. and below. The higher temperatures which favor "selectivity" are, however, objectionable in that they are known to favor the formation of isooleic glycerides. Increasing hydrogen pressure and increased agitation have in the past been found to be detrimental to "selectivity."

In the past, the time required to hydrogenate cottonseed oil and/or soybean oil to a consistency suitable for use as a base stock in plastic shortening has normally ranged from about an hour to two hours, at best half an hour or thereabouts when the hydrogenation temperature has been sufficiently high and the catalyst sufficiently active.

We have found that when the hydrogenation reaction is greatly speeded up, so that the desired endpoint is reached in a matter of a very few minutes, by the employment of adequate amounts of highly active nickel-containing catalysts, violent agitation, and superatmospheric hydrogen pressure, an unexpected degree of repression of the formation of isooleic acid radicals (reaction 2 and possibly 3) occurs, the extent of this being so beneficial as to more than offset those aspects of the process which are unfavorable from the point of view of obtaining "selectivity." This unprecedented speeding up of the reaction was impractical in batch type hydrogenation apparatus heretofore used, because accurate end point control is not feasible in such apparatus when the reaction must be terminated within a few minutes of its start, and also because of serious inadequacies of agitation and of heat removal. We therefore have developed a novel form of continuous process, and in this process we employ a special expedient which makes it possible to maintain a constant reaction rate and therefore to attain accurate end point control, this expedient being the continuous removal of the heat of reaction as it is liberated thus keeping the temperature of the oil practically constant during its hydrogenation.

The process herein described and claimed is generally applicable to the treatment of those vegetable oils which have iodine values between about 90 and 140, such as cottonseed oil, peanut oil, sesame oil, and soybean oil, to produce partially hydrogenated fats having iodine values between about 60 and about 90, for use either alone or blended with "hard stock" and/or with unhydrogenated oil in the manufacture of plastic shortenings. It will also find application in the partial hydrogenation of lard, particularly to improve its keeping qualities, and in the partial hydrogenation of marine oils. Mixtures of any of these oils with one another or with other glyceride oils such as palm oil are also suitable for treatment by our process.

More specifically, our process comprises conducting the catalytic partial hydrogenation of natural glyceride oils containing polyethylenic fatty acid radicals in a continuous manner and within certain temperature and pressure ranges in the presence of an adequate amount of highly active catalyst, and under sufficiently violent mechanically induced agitation to cause the chemical addition of hydrogen to the ethylenic carbon atoms to proceed at exceptionally rapid rates, an important feature of the process being the continuous removal of reaction heat, whereby superior product characteristics and uniformity of product quality are obtained.

Objects of the invention include the aforementioned principal objectives of obtaining improved keeping quality for a given plasticity, and improved plasticity characteristics for a given keeping quality, and also the following:

To provide a method of producing hydrogenated oil of improved quality as a result of its very short exposure to high temperature.

To produce partially hydrogenated vegetable oil containing fewer isooleic acid esters than in comparable products made by commonly used processes heretofore available.

To produce partially hydrogenated vegetable oils having lower iodine values for a given degree of plasticity as compared with similar oils produced by prior hydrogenation practices.

To produce base stock for hydrogenated plastic shortenings having a wider temperature range of desirable plasticities than the range obtainable in similar shortenings made from the same oil by prior hydrogenation practices.

To produce base stocks for hydrogenated plastic shortenings having excellent stability of plastic properties when subjected to storage temperatures in the neighborhood of 90° F. and when subsequently used at normal room temperatures.

To provide a process for the partial hydrogenation of vegetable oils for use in plastic shortenings which permits obtaining superior uniformity of product composition, as a result of precise temperature and pressure control and endpoint control.

To provide a process having economies in operation resulting from the rapidity and uniformity of the reaction rate, including greater re-use value of catalyst, decreased cost of maintaining re-use hydrogen free from catalyst poisons, and improved operating efficiency of hydrogen generating plant and hydrogenating plant due to uniform production scheduling.

A suitable form of apparatus for carrying out our process is illustrated in the accompanying drawing, in which:

Figure 1 is a schematic flow chart showing the

principal elements of a typical continuous hydrogenation system;

Figure 2 is a side elevation of mechanically agitated continuous hydrogenator vessel;

Figure 3 is a vertical section of the vessel shown in Figure 2;

Figure 4 is a horizontal section of the vessel, taken on the line 4—4 of Figure 3;

Figure 5 is a fragmentary vertical section of the inner chamber of this same vessel, showing in perspective some of the hold-back baffles, or stators, and one of the horizontal baffles;

Figure 6 is a fragmentary sectional view taken on the line 6—6 of Figure 2; and

Figure 7 is a graph indicating reaction rates versus temperatures.

The detailed structure of the apparatus illustrated in these drawings forms no part of the present invention, and very favorable results have been obtained with apparatus of quite different design.

Referring to Figure 1, the unsaturated liquid material to be hydrogenated is delivered from supply tank 10 by means of pump 12 through a tubular preheater 13 to and through the hydrogenator 14. A suitable hydrogenation catalyst suspended in a small quantity of a suitable liquid (which may often be a portion of the material to be hydrogenated) is delivered from catalyst supply tank 15 by means of pump 16 either directly into the hydrogenator, or (as shown) into the pipeline which is delivering the main supply of material to be hydrogenated from the preheater to the hydrogenator, for example, at point 17. A continuous supply of hydrogen, or a suitable hydrogen-containing gas, is introduced into the same pipeline at another point ahead of the hydrogenator, for example at point 18, the hydrogen supply being drawn from a suitable reservoir or supply, as illustrated at 19, by means of compressor 20 through a pressure regulating valve 21. While flowing through the hydrogenator 14, the mixture of the liquid material to be hydrogenated, the catalyst, and the hydrogen is subjected to violent agitation to bring these three materials into intimate contact with one another and to bring about a rapid movement of the individual particles of each of the non-liquid phases in contact with the particles of the liquid phase, thus promoting a high velocity of the hydrogenation reactions which occur in this vessel. The heat of reaction which is liberated is preferably (especially when only partially hydrogenating an unsaturated material) completely, or at least for the most part, removed continuously by circulating a cooling medium through a jacket surrounding the reaction space in the hydrogenator, the cooling medium being circulated by means of pump 22, and the heat being removed from the cooling medium in heat exchanger 23. The reaction mixture passing through hydrogenator 14 is maintained at superatmospheric pressure, and this pressure may conveniently be regulated by means of the adjustable relief valve 24 in the outlet line leading from the hydrogenator. If a surplus of hydrogen is used, over that which reacts with the oil and that which remains dissolved in the liquid leaving the hydrogenator, this surplus may be separated and bled off through the top of small tank 25. The hydrogenated material leaving the hydrogenator is cooled by means of heat exchanger 26, and any remaining gas which has come out of solution subsequent to the drop in pressure at valve 24 is then separated from the hydrogenated material, and the catalyst is removed by filtration or by any other convenient method in apparatus not illustrated in the drawing.

The hydrogenator 14 of the system just described may be constructed as shown more particularly in Figures 2 to 6, inclusive, in which is illustrated a preferred type of hydrogenating apparatus. Thus the hydrogenator may comprise an outer jacket 30, provided with an expansion coupling 31 to relieve strains caused by temperature changes, and an inner cylinder 32, the jacket and cylinder defining an annular space 33 within which is circulated a fluid coolant, the inlet and outlet conduits for the coolant being shown in Figure 2 at 34 and 35 respectively. A hollow shaft 38, of substantially less diameter than cylinder 32, is disposed coaxially within the cylinder and supported for rotation about its vertical axis, shaft 38 and cylinder 32 defining an annular reaction passage in which the mixture of the liquid fatty material, the hydrogen, and the catalytic agent, is intensely agitated while flowing in an upward direction, being introduced through an inlet passage 39 formed in an annular plate 40 at the lower end of cylinder 32, and discharging through an outlet passage 42 in an annular plate 43 at the upper end of cylinder 32.

The hydrogenator is closed at its upper end by a cap structure comprising plate 43 and closure members 45 and 46, the several parts being bolted together as shown more particularly in Figure 3. A radial thrust bearing 48, seated in member 45 and retained in position by member 46 engages and supports a shaft 49 which extends within and is secured to the hollow shaft 38, whereby the latter is journaled for rotation. Received within and secured to shaft 38 at its lower end is a coupling element 51; a drive shaft 52, disposed coaxially of shaft 38, extends within and is secured for rotation with coupling element 51. Drive shaft 52 is journaled for rotation in the supporting base structure indicated generally at 53, the hydrogenator being suitably mounted on this base structure. A motor 55 having a shaft 56 drives shaft 52 through bevel gearing 57, whereby the hollow shaft 38 is rotated rapidly. It will be appreciated that the details of this construction form no part of the instant invention and may be varied widely.

The annular reaction passage between shaft 38 and cylinder 32 is divided into a series of compartments or reaction zones by means of a plurality of horizontally disposed annular disks or baffles 60, the baffles being spaced longitudinally of the hydrogenator. The outer diameter of each baffle 60 is such that the baffles fit snugly within cylinder 32, the inner diameter being slightly larger than the outer diameter of shaft 38, so as to afford slight mechanical clearance therebetween. The reacting materials owing upwardly are thus caused to flow through the restricted annular passages defined between shaft 38 and baffles 60 in moving from each compartment or reaction zone to the next higher zone, retention of the materials in each zone for a substantial length of time being assured. "Channeling," or too rapid movement of insufficiently reacted materials through and out of the hydrogenator, is thereby avoided. The baffles 60 may be retained in proper spaced relation by a series of spacing sleeves, the several sleeves fitting snugly within cylinder 32, so that each of the baffles is clamped between an adjacent pair of sleeves 61. Each of

the sleeves 61 may be formed with longitudinally extending slots 62, as shown more particularly in Figures 3 and 5, to reduce the weight of the sleeves and to increase the heat transfer surface and the volume and capacity of the several reacting zones. An efficient hydrogenator may be provided with as many as 11 baffles, or even more, so as to provide 12 or more reacting zones, but the number of zones may be varied widely.

In order to effect intense agitation of the material, each zone may be provided with a series of agitator blades 65, and with cooperating stator blades or stationary baffles 66 located above and below the agitator blades. The agitator blades 65 are disposed radially of and are bolted securely to the hollow shaft 38 in circumferentially spaced relation, one such series of agitator blades being shown in dotted lines in Figure 5. In order to prevent leakage of the reacting materials past the securing bolts to the interior of the shaft 38, a sleeve 68 extending within and over the major portion of the length of shaft 38, is welded to the latter at each end. The circumferentially spaced stator blades 66 are likewise disposed radially of the axis of shaft 38, and are bolted or are otherwise secured to the sleeves 61 adjacent to each of the annular disks 60, preferably intermediate the slots 62 formed in sleeve 61, as shown in Figure 5. It will be observed that each reaction zone is provided with one series of agitator blades 65 and two series of cooperating stator blades 66, the latter acting to resist continuous swirling movement of the reacting materials about shaft 38 and otherwise serving to increase the degree of agitation imparted to the materials. Preferably, blades 65 and 66 in adjacent series are so dimensioned as to afford only the necessary mechanical clearance between each other; similarly, only mechanical clearance is afforded between the stator blades 66 and the shaft 38 and between the agitator blades 65 and the sleeves 61.

In the particular hydrogenator illustrated, we effectively avoid undue contamination of the finished product with raw oil or with insufficiently hydrogenated oil by a combination of two provisions: first, the relatively long passage between the walls of cylinder 32 and the central shaft 38 through which the reaction mixture passes on its way from the entrance to the exit of the hydrogenator, the flow through this passage being interrupted repeatedly by a series of transverse agitators separated from one another by a corresponding series of stator blades tending to break up swirling induced by the agitators; and second, the horizontal circular baffles, elements 60, which subdivide the reaction zone into a plurality of lesser zones each communicating with the adjoining one by means of a passage of greatly restricted cross-sectional area. The importance of these factors will be pointed out later on.

When the process of the present invention is in operation under typical conditions, with the flow of oily liquid, suspended catalyst, and hydrogen passing at uniform rates in contact with one another through the reaction vessel under conditions of extreme turbulence, the temperature of the liquid is established at a chosen value (as hereinafter discussed) by adjusting the pressure of the steam or the temperature and rate of flow of other heating medium through the jacket of the oil preheater, and this temperature is maintained with but little or no rise as the oil passes through the hydrogenator by controlling the temperature or rate of flow of the water or other cooling medium through the jacket surrounding the hydrogenator.

The degree of reaction, or completeness of hydrogenation (as measured from time to time by determining the iodine value, or the refractive index, or the congeal point, or the titer, or other index, of samples of the hydrogenated liquid withdrawn from the system after the reaction has ceased) may conveniently be controlled by regulating the rate of introduction of the liquid to be hydrogenated. As this liquid rate is varied one may simultaneously and correspondingly vary the rates of feed of the catalyst slurry and the hydrogen, thus maintaining constant proportions of catalyst and hydrogen in relation to the liquid feed rate, or one may alternatively keep one or both of these secondary feed rates constant, or vary it independently of the liquid feed rate, thus gaining an independent or supplementary control over the extent of the hydrogenation which occurs. The amount of hydrogen which is supplied to the hydrogenator should of course be adequate for the degree of hydrogenation desired, and may conveniently be somewhat in excess of this amount in order to insure utilizing the maximum hydrogenating capacity of the hydrogenator.

An outstanding aspect of our invention is the discovery of surprising improvements in product quality which result directly or indirectly from the very high reaction rates which it employs, even when other operating variables of the process are within undesirable ranges from the standpoint of "selection," as contrasted with the corresponding product characteristics produced by the slower hydrogenation rates (at corresponding temperatures) which characterize prior practices. Advantage of these quality improvements may be taken in several different ways, depending largely upon the correlation of the reaction temperature and hydrogen pressure. We will discuss this subject in the next four paragraphs in terms of cottonseed oil hydrogenated to an iodine value in the neighborhood of 70 to 78, this hydrogenated product then being blended with 6% to 6.5% of "hard stock" and plasticized to produce plastic shortening having a consistency at room temperature in the general range of that of the commercial hydrogenated vegetable oil shortening "Crisco" and/or of that of some of the best grades of edible lard. This discussion (except as concerns the fourth preferred region described below) is equally applicable to the similar treatment of soybean oil hydrogenated to the same consistency value (corresponding to a somewhat higher iodine value than with cottonseed oil), or to blends of cottonseed oil and soybean oil, and to other similar unsaturated glyceride oils and fats suitable for use in the manufacture of shortening. It is also applicable, although with less pronounced benefits, to such oils hydrogenated to end points outside of the preferred limits, 70 to 78, but usually not beyond the wider limts, 60 to 90.

Preferred region 1.—We have found that by employing moderately high reaction temperatures, from about 150° C. to about 180° C., and by elevating the hydrogen pressure to within an especially advantageous range which extends from about 20 to about 60 pounds per square inch, our process produces shortenings having materially superior keeping qualities to those shortenings of equal consistency value produced by slower processes. Example 1 is typical of this use of our invention. Pressures substantially below 20

pounds do not produce a fast enough reaction to gain this outstanding benefit, and pressures substantially above 60 pounds tend to be too seriously detrimental to selectivity. Within this critical combination of temperature and pressure ranges the injurious effect of pressure upon selectivity and the stimulating effect of the relatively high temperature upon isooleic formation are found to be more than offset by what appears to be a suppression of the formation of isooleic acid radicals due directly or indirectly to the pressure employed coupled with the other favorable conditions inherent in our process, with the net result that the hydrogenation is carried to a substantially lower iodine value than would be normal to attain a given consistency, and a shortening having superior keeping qualities is thereby obtained. This result could not be predicted from information hitherto available. One could, of course, stop the hydrogenation at a point which gives a normal keeping quality, and thus obtain an abnormally soft product if this should be desired.

Preferred region 2.—Another preferred way which we have discovered of taking advantage of the quality improvements which depend upon the extreme rapidity of our process is in the employment of relatively low temperatures, from about 90° C. to about 120° C., at correspondingly higher pressures, within a range which extends upwards from about 100 pounds per square inch. Within this especially advantageous combination of low temperature range and high pressure, the suppression of the formation of isooleic acid radicals is so great that it offsets the injuries effects upon selectivity of both the low temperature and the high pressure, with the net results that when the hydrogenation is carried to a given consistency value, as compared with corresponding prior shortenings, a product having keeping qualities about equal to those of the corresponding prior shortenings and having superior plastic characteristics is produced. Of the glycerides in the hydrogenated oil which are solid at room temperature (i. e. glycerides of saturated acids and of isooleic acids) and which impart body and a degree of firmness to the shortening, a greater proportion in this case—as compared with more slowly hydrogenated oils—are saturated glycerides and a lesser proportion are isooleic glycerides. This shift in proportions of these two solid types of glycerides imparts to the shortening a wider plasticity range (i. e. a wider range of temperatures in which desirable plasticity values exist), a better texture, and an excellent stability of plasticity following storage at summer temperatures in the neighborhood of 90° F. Example 2 is typical of this use of our invention.

Preferred region 3.—A third preferred temperature-pressure region of our process lies between temperatures of 110° C. to 150° C., with hydrogen pressure increasing with temperature. In this region the preferred pressure is 120 p. s. i. or above for 110° C. hydrogenation temperature, 160 p. s. i. or above for 130° C., 300 p. s. i. or above for 150° C. This region (3) is adjacent to region (2) and accomplishes similar benefits The increasingly bad influence of increasing temperature upon "isooleic" formation is compensated in this region by the increasingly beneficial influence of short hydrogenating time, a combined result of higher temperature and higher pressure, and the bad influence of increasing pressure on "selection" is compensated by the good influence upon this factor of increasing temperature. Within this preferred region the hydrogenation conditions should be so chosen as to obtain a rate equivalent to an iodine value drop per minute of at least 5 units at 110° C., at least 14 units at 130° C., and at least 35 units at 150° C., with minimum rates for intermediate temperatures lying on a smooth curve connecting these three points. Example 10 is typical of operation within this region.

Preferred region 4.—A fourth manner of obtaining improved product characteristics by means of our process is in the hydrogenation of cottonseed oil (or cottonseed oil-soybean oil blends) to produce that special type of plastic shortening which has exceptionally good keeping qualities even when incorporated in baked goods which undergo extreme exposure to high temperature, as in the making of crackers and biscuits which may then be kept for a long time before being consumed. It is preferred to hydrogenate the oil for such a shortening until substantially all linoleic glycerides have been converted to a less unsaturated condition, which with cottonseed oil usually requires going to an iodine value below 70. This also calls for the employment of a temperature which produces good "selection," preferably within the range 150° C. to 180° C., and also for a pressure which is not detrimental to "selection," preferably a superatmospheric pressure not higher than 20 pounds per square inch. Although such low pressures do not produce reaction rates as fast as are otherwise obtainable, the employment of extremely violent agitation and adequate amounts of active catalyst nevertheless result in hydrogenation rates within these temperature and pressure ranges of over 5 iodine value units drop per minute, and as a consequence the formation of isooleic glycerides is minimized. Thus we are able to produce a product having esceptional keeping qualities and a consistency more suitable for effective working in bakery mixing machines than similar shortenings made by slower hydrogenation processes. Example 7 typifies this application of our process.

One may if he desires employ our process with temperature and/or pressure conditions intermediate between the four sets of conditions just discussed, for example temperatures between 120° C. and 150° C. with hydrogen pressures between 40 and 100 p. s. i., thus achieving those general benefits which accompany our process, particularly freedom from hydrolysis and thermal decomposition, because of the very short time the oil is held at elevated temperature, and uniformity of product composition and characteristics, because of the close and uniform control of hydrogenating conditions. Example 9 illustrates this method of employing our invention.

To facilitate an understanding of the invention, including its several special aspects, its employment in a number of typical hydrogenations will be described.

Example 1.—Refined and bleached prime cottonseed oil containing 0.04% of its weight of nickel, in the form of a suspension of a finely divided promoted nickel catalyst having an activity of 5.7 units (as hereinafter explained), was pumped at a rate of 2.44 pounds per minute through a preheater, in which its temperature was raised to 166° C., and thence into and through a small sized continuous hydrogenator resembling the one shown in Figures 2 to 6 except that it had only three circular baffles, elements 60. The internal dimensions of this hy-

drogenator were a diameter (element 32) of 4 inches, a height of 60 inches, and a free space volume of 353 cubic inches (of which about 78% is occupied by oil and 22% by gas under average operating conditions); and the speed of its agitator was 1000 R. P. M. The arrangement of the equipment was like that shown in Fig. 1, except that the catalyst feed tank 15 was dispensed with, the catalyst being added to the oil in supply tank 10 which was provided with a mechanical agitator. A stream of electrolytic hydrogen, amounting to about 1.45 cubic feet per minute under standard conditions (all gas volumes will be expressed in terms of standard conditions unless otherwise stated), was introduced at a pressure of 50 pounds per square inch (all pressures are superatmospheric gauge pressures) into the oil feed line at a point near its point of entry into the hydrogenator. A sufficient flow of cooling water was passed through the jacket of the hydrogenator to keep the outlet hydrogenated oil temperature at 168° ± 1° C. A bleed of 0.25 cubic foot per minute of surplus hydrogen was withdrawn from the oil just beyond its outlet from the hydrogenator, the oil was then reduced in pressure to a few pounds above atmospheric, was then passed through a tubular cooler in which its temperature was reduced to about 60° C., was then passed through another vented tank from the top of which a small amount of unconsumed gas was withdrawn, and the substantially gas-free oil was then passed through a filter press for the removal of catalyst.

By this process the cottonseed oil was reduced in iodine value from about 110 to 75.7 in 3.4 minutes, the average hardening rate being 10.2 iodine value units drop per minute. A one gram sample of this hydrogenated oil when subjected to a standard oxygen absorption test absorbed 3 c. c. of oxygen in 24 hours. The consistency of the product of this example, when made into plastic shortening, was determined by blending 6 parts of substantially fully hydrogenated cottonseed oil, called "hard stock," with 94 parts of the 75.7 I. V. product, plasticizing this blend by chilling and agitating in a known manner under standardized conditions and measuring the consistency of the resulting plastic shortening by means of a standardized penetration test.

For purposes of comparison another portion of the same cottonseed oil and catalyst slurry was hydrogenated by the conventional batch method at 165° C., atmospheric pressure, with moderate mechanical agitation, to the same degree of consistency, similarly determined. The time required in the batch method to reach this common consistency value, which occurred when the iodine value reached 81.0 (over 5 I. V. higher than in the case of the continuous process), was 35 minutes. When subjected to the same oxygen absorption test a one gram sample of the batch-hydrogenated oil absorbed the 3 c. c. of oxygen in 18 hours.

Thus the fat processed by our rapid continuous process had an indicated keeping quality about 33 per cent better than that of the fat of comparable consistency made from the same oil by a conventional batch method, this being due to a lower linoleic content in the former. It was possible to reach this lower linoleic content in our process by minimizing isooleic formation, with its attendant firming effect.

Another conventional (though abnormally rapid) comparative batch run was made on another portion of the same oil, the temperature again being 165° C. but the pressure being 50 lbs. (the same as in the continuous run). To reach the same consistency value (adjusting all actual results to this comparable basis by applying well established correction factors) the time required was 9 minutes, the iodine value of the hydrogenated oil was 80.0 and its 3 cc. oxygen absorption time was 19 hours. This product thus was also inferior to the one made by our process.

Example 2.—With the same apparatus as in Example 1, except that the agitator speed was 580 R. P. M., another lot of refined and bleached cottonseed oil was hydrogenated to an iodine value of 74.5, under the following conditions:

Oil and catalyst supply rate pounds per minute	1.76
Amount of Ni in the oil—percent by weight	0.1
Activity of catalyst—units	5.4
Hydrogen inlet rate—C. F. M.	1.2
Surplus hydrogen outlet rate—C. F. M.	0.3
Hydrogen pressure—p. s. i.	150
Oil inlet temperature—° C.	110
Oil outlet temperature—± 1° C.	112
Av. time of oil in hydrogenator—minutes	4.8
Total I. V. drop	35.5
I. V. drop per minute, average	7.4

When blended with 6.25% of its weight of substantially fully hydrogenated cottonseed oil (iodine value about 8) and plasticized as explained in the fourth from last paragraph of Example 1, the product thus produced had a penetration value of 232 units at 70° F. and this value increased (i. e. the product softened) 78 units when warmed to 90° F.

For comparison another portion of the same oil and catalyst was subjected to rapid batch hydrogenation at a temperature of 110° to 113° C., at a pressure of 150 p. s. i., employing mechanical agitation, to substantially the same iodine value as in the continuous process (specifically, to 74.1 iodine value), the time required being 19 minutes, and was blended with enough hard stock (7%. to produce a plasticized shortening having the same 70° F. penetration value (232 units) as that produced from the continuously hydrogenated material. The penetration value of this second lot of batch-hardened shortening increased 97 units upon warming from 70° F. to 90° F. and it was undesirably "ribby" or uneven in consistency due mainly to a higher content of isooleic acid esters (5.7% isooleic in combined fatty acids in continuous product as compared with 8.6% in the batch product).

The oxygen absorption time of the continuously hardened oil was 14 hours, and that of the batch-hardened oil was also 14 hours.

Thus the shortening produced from continuously hydrogenated oil had a smoother consistency than that made by the batch process, and a uniformity of consistency over a range of temperatures commonly encountered in kitchen and bakery practice such that it varied only 80 per cent as much as the batch-hardened lot.

Example 3.—With the same apparatus as in Example 2, a lot of refined and bleached soybean oil was hydrogenated to an iodine value of 82.8, under the following conditions:

Oil and catalyst supply rate pounds per minute	2.14
Amount of Ni in the oil—percent by weight	0.1
Activity of catalyst—units	4.5
Hydrogen inlet rate—C. F. M.	1.89
Surplus hydrogen outlet rate—C. F. M.	0.3

Hydrogen pressure, p. s. i.	25
Oil inlet temperature, ° C.	165
Oil outlet temperature, ° C.	168
Av. time of oil in hydrogenator, minutes	4
Total I. V. drop	52.2
I. V. drop per minute, average	13

For comparison another lot of the same oil was hydrogenated with the same catalyst (but with the amount reduced to 0.04% Ni) under typical factory conditions for batch operation. The temperature was 165° C., the hydrogen pressure just above atmospheric, the agitation was that provided by vigorous gas flow, the time of hydrogenation was 48 minutes, and the final iodine value was 81.9.

The blended, plasticized shortening of the continuous process had a penetration value of 235 units at 70° F., whereas the comparable batch product was firmer by 40 penetration units. (If the iodine values of the two had been the same, the batch product would still have been firmer by about 34 units.)

Example 4.—In a large hydrogenator similar to that illustrated in Figs. 2 to 6, having an internal diameter of 8 inches, an internal height of 97 inches, a free space of 2164 cubic inches[1], and an agitator speed of 200 R. P. M. operated in the general manner of Example 1 except that the catalyst (slurried in oil) was fed separately into the hydrogenator and that purified hydrogen made by the steam iron process was used, a lot of refined and bleached cottonseed oil was hydrogenated under the following conditions:

Oil supply rate, pounds per hour	350
Catalyst slurry rate, do	7.56
Percent Ni in catalyst slurry	5.0
Amount of Ni addition, percent of wt. of oil	0.11
Activity of catalyst, units	5.4
Hydrogen inlet rate, cubic ft./hr.	204
Surplus hydrogen outlet rate, cubic ft./hr.	30
Hydrogen pressure, p. s. i.	150
Oil inlet temperature, ° C.	89
Oil outlet temperature, ° C.	92
Av. time of oil in hydrogenator, minutes	8.6
Initial I. V.	112
Final I. V.	77
I. V. drop per minute, average	4.1

Example 5.—In the same hydrogenator as in Example 4, operated in the same general manner, a lot of refined and bleached cottonseed oil was hydrogenated under the following conditions:

Oil supply rate, pounds per hour	1000
Catalyst slurry rate, do	17.6
Percent Ni in catalyst slurry	2.5
Amount of nickel addition, percent of wt. of oil	.044
Activity of catalyst, units	5.0
Hydrogen inlet rate, C. F. H.	634
Surplus hydrogen outlet rate, C. F. H.	30
Hydrogen pressure, p. s. i.	50
Oil inlet temperature, ° C.	160
Oil outlet temperature, ° C.	167
Av. time of oil in hydrogenator, minutes	3
Initial I. V.	112.0
Final I. V.	69.5
I. V. drop per minute, average	14.2

Example 6.—In the same hydrogenator as in

[1]About 78% of which is occupied by oil under average operating conditions.

Example 4, operated in the same general manner except that there was no bleed of surplus hydrogen, a lot of refined and bleached cottonseed oil was hydrogenated under the following conditions:

Oil supply rate, pounds per hour	505
Catalyst slurry rate, do	8.8
Percent Ni in catalyst slurry	5.0
Amount of nickel addition, percent of wt. of oil	.087
Activity of catalyst	4.7
Hydrogen inlet rate, C. F. H.	297
Hydrogen pressure, p. s. i.	100
Oil inlet temperature, ° C.	106
Oil outlet temperature, ° C.	103
Av. time of oil in hydrogenator, minutes	5.94
Initial I. V.	112.0
Final I. V.	70.6
I. V. drop per minute, average	7.0

The hydrogenated products of Examples 4, 5 and 6, when mixed with minor proportions of "hard stock," deodorized, and plasticized, produced shortenings having excellent plastic properties and good keeping qualities. Whereas conventional batch hydrogenation causes a partial hydrolysis amounting to an increase of about .03% to 0.10% in the free fatty acid content of refined cottonseed oil hydrogenated to about 75 I. V., our continuous process causes scarcely any hydrolysis, raising the free fatty acid content only about 0.01%.

In place of the cottonseed oil employed in Examples 4, 5, and 6, one may employ any other refined and bleached oil or fat containing polyethylenic double bonds which is suitable for making base stock for hydrogenated shortening, the only substantial difference being that the initial and final iodine values will vary depending upon the individual characteristics of each oil.

Example 7.—In the same hydrogenator as in Example 4, operated in the same general manner, two equal portions, A and B, of a mixture of equal parts of refined and bleached cottonseed and soybean oils were hydrogenated under the following conditions:

	A	B
Oil supply rate, lbs./hr.	390	410
Catalyst slurry rate, lbs./hr.	7.64	7.64
Ni in catalyst slurry	5.89	5.89
Amount of Ni addition, percent of wt. of oil	.115	.110
Activity of catalyst	4.6	4.6
Hydrogen inlet rate, cu. ft./minute	5.9	5.6
Surplus hydrogen outlet rate, cu. ft./minute	0.6	0.6
Hydrogen pressure, lbs./sq. in.	19	19
Oil inlet temperature, °C.	166	165
Oil outlet temperature, °C.	168	168
Av. time of oil in hydrogenator, minutes	7.7	7.3
Initial I. V.	124.2	124.2
Final I. V.	67.6	71.8
I. V. drop per minute, average	7.5	7.5

For comparison a third portion, C, of this mixture of oils was hydrogenated by a typical factory batch procedure, at 162–168° C., under about 10 pounds pressure, in 65 minutes to an iodine value of 71.3.

Each of the three hydrogenated products was blended with 2% of "hard stock," deodorized, and plasticized under comparable conditions. The time required for a one gram sample of each to absorb 3 c. c. of oxygen under the same standardized test conditions as those employed in testing the products of Examples 1 and 2, and the pene-

tration values of each at 70° F. were as follows:

	A	B	C
Oxygen absorption time, hours	156	112	136
Penetration value	153	217	161

By interpolation between A and B, one would expect that a product having an oxygen absorption time of 136 hours would have a penetration value of 182. The batch hardened product having this oxygen absorption time was actually, and undesirably, much firmer, having a penetration value of 161.

Example 8.—In the same hydrogenator as in Example 4, operated in the same general manner, a mixture of equal parts of refined and bleached cottonseed and soybean oils was hydrogenated under the following conditions:

Oil supply rate—lbs. per hour	310
Catalyst slurry rate—do	8.57
Per cent Ni in catalyst slurry	5.0
Amount of Ni addition—per cent	.135
Activity of catalyst	5.0
Hydrogen inlet rate—C. F. H.	266
Surplus hydrogen outlet rate—C. F. H.	36
Hydrogen pressure—lbs./sq. in.	100
Oil inlet temperature—°C.	111
Oil outlet temperature—°C.	112
Av. time of oil in hydrogenator—minutes	9.7
Initial I. V.	124.8
Final I. V.	72.6
I. V. drop per minute, average	5.4

We have found that when cottonseed oil and at least an equal amount of soybean oil are hydrogenated in our process as mixtures, a product having a better keeping quality is obtained for a given penetration value than would be the case if the same oils were hydrogenated separately and then blended in the same proportions. The following table illustrates this:

Oil Proportions		Oxygen absorption time for shortening having 70° F. penetration value of 250	
Cottonseed	Soybean	Actual	Expected
100	0	19.5	--------
50	50	35	32
25	75	46	38
0	100	44	--------

Exceptionally good shortenings may be made by employing in their composition at least two thirds of such a continuously hydrogenated mixture of 50 to 90% soybean oil and 50 to 10% cottonseed oil.

Example 9.—In the same hydrogenator as in Example 2, operated in the same general manner, a lot of refined and bleached soybean oil was hydrogenated to an iodine value of 81.3 under the following conditions:

Oil and catalyst supply rate—lbs./min.	1.65
Amount of Ni in the oil—per cent	.06
Activity of catalyst	5.0
Hydrogen inlet rate—C. F. M.	1.56
Surplus hydrogen outlet rate—cu. ft./min.	0.3
Hydrogen pressure—lbs./sq. in.	50
Oil inlet temperature—°C.	140
Oil outlet temperature—°C.	141
Av. time of oil in hydrogenator—minutes	5.1

Total I. V. drop	53.7
I. V. drop per min., average	10.5

Example 10.—In the same hydrogenator as in Example 1, but equipped with 11 circular baffles, element 60, and with the catalyst added as a separate slurry, a mixture of equal parts of cottonseed oil and soybean oil was hydrogenated as follows:

Oil supply rate—lbs./hr.	203
Catalyst slurry rate—lbs./hr.	4.99
Per cent Ni in catalyst slurry	3.0
Amount of Ni addition per cent of wt. of oil	0.074
Activity of catalyst	6.9
Hydrogen inlet rate—C. F. M.	2.78
Surplus hydrogen outlet rate—C. F. M.	0.50
Hydrogen pressure—P. S. I.	200
Oil inlet temperature—°C.	124
Oil outlet temperature—°C.	127
Avg. time of oil in hydrogenator—minutes	2.5
Initial I. V.	125.0
Final I. V.	77.7
I. V. drop per minute, avg.	18.8

The resulting product had excellent keeping qualities combined with good consistency, and was substantially equivalent in these respects to the product of Example 8.

It is understood that the material to be hydrogenated and the hydrogen supply will normally be as free as is practicable from such impurities as would hinder the reaction. Freedom from compounds of sulfur is especially important, within limits readily attainable in current commercial practice.

Broadly speaking, the temperature to be employed in hydrogenating oils for use in plastic shortening by our process may be selected within the range from about 60° C. to about 180° C. Below 60° the rate is undesirably slow, and above 180° C. the product quality tends to suffer due to thermal breakdown. The choice of a particular range between these broad extremes is of importance depending upon the particular product characteristics desired, as previously indicated. Higher temperatures, within the broad range of our process, very definitely speed up the reaction when other controls are held constant. This effect is illustrated in a typical case by curve C of Fig. 7, as later explained.

The pressure of the gas phase in the present process when substantially pure hydrogen is employed, or the partial pressure of the hydrogen in the gas phase when a hydrogen-containing gas is used, will preferably be a superatmospheric pressure not exceeding about 500 pounds per square inch, measured at the gas inlet to the hydrogenation zone. We have already indicated the manner in which different pressures within these extremes influence the resulting product characteristics. At a hydrogenation temperature of 165° C. for example, the rate of hydrogenation in our process may be increased at least threefold by increasing the hydrogen pressure from atmospheric to 30 pounds per square inch above atmospheric, and the rate at a pressure of 150 pounds should be two to three times the rate at 30 pounds, all other controls being constant.

One of the factors which we have found to be essential for our abnormally rapid reaction rate is a catalyst of high activity. We prefer a catalyst having an activity of at least four units on the scale of values which is explained in the next paragraph, and we have normally employed

a catalyst having an activity of about five units. Catalysts composed principally of nickel, promoted if desired by metals (or their oxides) such as copper, chromium, cobalt, zirconium, thorium, or other known catalyst promoters, are preferred. High activity catalysts made from noble metals, such as platinum and palladium, may be employed although their high cost makes them commercially unattractive. Metal sulfide catalysts have been found unsatisfactory for use in our process.

To determine the activity of nickel-containing hydrogenation catalysts in comparable numerical terms, a representative sample of the catalyst is employed to hydrogenate cottonseed oil under carefully standardized conditions and the resulting drop in the butyro-refractive index of the oil is reported as the activity value of the catalyst. For this test a long-neck flat-bottom glass flask of 260 milliliter body capacity may be employed as the hydrogenation vessel, this flask being fitted with a cork through which pass the stem of a thermometer whose bulb is immersed in the oil in the flask, a close fitting bearing for an agitator shaft, a metallic tube for the introduction of hydrogen leading down and around the agitator and terminating directly under and pointing upward towards the center of the agitator, and a metallic tube to serve as an outlet for excess hydrogen. The agitator consists of a horizontal one-inch length of steel tubing having a one-eighth inch bore, welded at its mid point to the lower extremity of a vertical steel agitator shaft and having a one-eighth inch hole drilled through its wall at a point diametrically opposite and below its point of attachment to this shaft. The agitator clears the bottom of the flask by about one and one-fourth inches, and its shaft is directly connected to a motor which operates at 3500+200 R. P. M. A vertical baffle may be employed if needed to prevent a vortex effect such as might reduce the effectiveness of the agitation. The hydrogen outlet tube leads to the lower portion of a small bottle which is about three-fourths filled with cottonseed oil. For the purposes of this test one needs a cylinder of compressed electrolytic hydrogen, a supply of kieselguhr equivalent in quality to Johns-Manville's Celite guhr, grade FC (or other good grade guhr known to be acceptable in glyceride oil hydrogenation) and a supply of good grade recently refined and bleached cottonseed oil. This oil should be fully refined with caustic, and preferably rebleached in the laboratory for 5 minutes with 6% of a good grade of fuller's earth (such as General Reduction Company's Carlton or Pike's Peak earth) at 105° C., followed by filtration. The flask is charged with 200 grams of this oil, and to this are added an amount of the catalyst which contains just 0.20 gram of nickel, and 0.80 gram of the guhr. The contents of the flask are mixed and a few grams are filtered and the refractive index of the filtrate is measured. The flask is then placed in an oil bath which entirely surrounds its body and extends at least an inch below the flask bottom, and the cork and accompanying assembly of tubes, agitator, and thermometer is inserted in the neck of the flask. The flask and its contents are then heated to 100° C. with no agitation except for a slow stream of hydrogen bubbling through the oil. When 100° C. is reached the agitator is started and the hydrogen flow is increased to 0.08 cubic foot per minute, measured at standard conditions. These hydrogenating conditions are maintained for exactly 30 minutes, whereupon the source of heat is removed, the agitator shut off, and the hydrogen flow stopped. A refractive index measurement is made on a small filtered sample of the hydrogenated oil. The difference between the two refractive index measurements, in butyro refractometer units, is reported as the activity value of the catalyst. Scrupulous cleanliness of the equipment used in this test, and avoidance of the use of rubber in any contact with the oil, are recommended. A preliminary run under the conditions of the test, but without refractive index measurements, is found to be a good means of conditioning the equipment for use in the test in order to insure reproducible results.

It is well known that, up to a certain point, the overall rate of absorption of hydrogen during the hydrogenation reaction depends on the amount of catalyst surface exposed to the liquid being hydrogenated, provided an adequate hydrogen supply is maintained (and we believe that this calls for maintaining an adequate supply of hydrogen dissolved in the liquid being hydrogenated). We find that for many practical purposes an amount of catalyst equivalent to a weight of nickel amounting to from 0.03 per cent to 0.10 per cent of the weight of the liquid to be hydrogenated is sufficient when using a catalyst having an activity of about 4 to 6 units. Under most practical conditions there is not much advantage in exceeding 0.20 per cent of nickel with a catalyst of this activity range because other factors, such as available dissolved hydrogen supply, then tend to become limiting.

A very high degree of agitation is of paramount importance in obtaining the full benefits from the present process. We have found that the use of even large amounts of very active catalyst together with high temperatures and high pressures do not enable one to obtain desirably high reaction rates unless one also provides violent mechanically induced agitation. We prefer direct mechanical agitation by means of moving agitator blades, although an equivalent result may be obtained in a reaction vessel which contains no moving mechanical parts but which is provided with means for introducing a fluid reactant, either the gas or the liquid, or both, in one or more high velocity jets. It is our belief that the agitation should be so violent as to cause rapid movement of the liquid interface relative to the solid interface at the surface of each catalyst particle, as contrasted with a condition in which the liquid interface on the solid particle is relatively stationary or stagnant, and also that the agitation should be such as to break up the gas bubbles to such a great extent as to facilitate continuous renewal of the supply of hydrogen dissolved in the liquid as this supply is rapidly used up in the course of the reaction. Good agitation of this sort is provided in the apparatus illustrated in the drawings when the clearance between the rotors and the stators does not exceed about three sixteenths or one fourth of an inch and when the peripheral speed of the outer edges of the rotors is of the order of six feet per second. The use of stators to retard the swirling action of the liquid, which would otherwise be induced by the rotating agitators, is important particularly in order to avoid a centrifugal effect which would tend to move the suspended catalyst towards the outer walls of the vessel and would simultaneously tend to move the gas bubbles towards the center of the vessel.

It is appropriate at this point to consider several important features in the design of hydrogenation vessels suitable for use in our process. Our requirements of a continuous and simultaneous inflow and outflow of the oil being treated, under the conditions of extreme turbulence caused by the violent agitation, would surely result in serious contamination of the finished hydrogenated product with raw material or only partially processed material if one used hydrogenation vessels resembling many of those heretofore used or proposed. It has been found that this highly objectionable result may be satisfactorily avoided by either of two alternative expedients—and preferably by a combination of both of them—each tending to retard movement of insufficiently hydrogenated material through and out of the hydrogenator.

The first expedient is to employ a reaction chamber which is relatively quite long, from entrance to exit, and which thus permits the employment of a relatively large number of successive sets of transverse agitators, interspersed with successive sets of stator blades, whereby the flow of material from inlet to outlet is repeatedly interrupted.

The second expedient is to subdivide the reaction zone into a series of interconnecting lesser zones, the interconnecting passages being so greatly restricted in cross sectional area that the agitation occurring in one of these zones is not felt to an appreciable extent in the adjoining zone. Our circular baffles, **60**, which leave an annular passage around the shaft just one eighth of an inch wide in a hydrogenator having an internal diameter of 8 inches and a shaft diameter of 4 inches, accomplish this purpose.

The horizontal circular baffles, elements **60**, although preferred features of the hydrogenation vessel, may if desired be omitted entirely. In this event "channeling" of insufficiently hydrogenated material to the outlet is to a large extent avoided, although not to the full extent preferred for some purposes, when the length of the chamber from inlet to outlet is such as to permit the employment of at least 10 to 15 separate sets of agitators, each set separated from the next by a cooperating set of stator blades.

By providing the mechanical agitation in a direction which is predominantly transverse (preferably perpendicular or even somewhat counter) to the main direction of flow of the liquid being hydrogenated, the agitator-impelled transfer of unprocessed raw material towards the outlet of the vessel is minimized. This may be accomplished by aligning the pressure resisting surfaces of the agitator blades and of the stator blades so that they face in a direction generally transverse to, and not tending towards, the general direction of liquid flow. While the blade surfaces thus define planes substantially parallel to the general direction of liquid flow, slight inclination is of course permissible, and inclination tending to retard axial flow may in some cases be desirable.

When the chief reliance for the avoidance of "channeling" is placed in horizontal baffles such as elements **60**, with a minimum of agitator blades—i. e. when each of the lesser zones between two horizontal baffles is provided with just one set of transverse agitators—"channeling" is to a large extent avoided, although perhaps not to the full extent preferred for some purposes, by thus subdividing the hydrogenation space into at least six lesser zones.

The hydrogenator used in our process is designed to provide for efficient removal from the reactants of large quantities of heat, since the heat generated by the reaction amounts to about 2 B. t. u. per pound of oil hydrogenated per unit of iodine value drop. Thus the rate of heat development in Example 5, wherein 1015 pounds of oil are hydrogenated per hour to a 42.5 I. V. drop, amounts to about 86,000 B. t. u. per hour. In the hydrogenator illustrated in the drawings, the heat transfer surface is large in relation to the cubical contents of the vessel, and the heat transfer coefficient is high because of the violent agitation.

A single minimum limit for the reaction rate to be expected from our process cannot be established, because of the wide ranges of operable conditions as set forth above, particularly in temperature and pressure. Nevertheless it is distinctly desirable to provide some guide to indicate the minimum rate of hydrogenation that should be attained for preferred results when operating our process with different materials and at different temperature levels.

In general, the amount and activity of the catalyst, the purity of the oily liquid and the gas, the hydrogen pressure, and the effectiveness of the agitation should be such as to produce at least as high a reaction rate as that indicated by line D of Figure 7 for the particular temperature employed, an exception being those cases wherein pressures but slightly above atmospheric are employed in the interest of securing maximum "selectivity," in which event the rate should still exceed 67 per cent of the values of line D.

Curve C of Figure 7 represents the attainable hydrogenation rate with purified triglyceride oils in the iodine value range from 110 to 70, at a hydrogen gauge pressure of 150 pounds per square inch, using 0.1 per cent of nickel in promoted catalyst having an activity value of 5.

Having thus described our invention, what we claim and desire to secure by Letters Patent is:

1. The continuous process of partially hydrogenating unsaturated glycerine oils containing polyolefinic double bonds and having initial iodine values above 90 to produce fats having iodine values between about 60 and about 90, suitable for use in the manufacture of shortening, which comprises: (1) flowing said oil at a temperature between about 60° C. and about 180° C. into, through, and (at a point remote from the inlet) out of confined hydrogenation zone, and continuously introducing hydrogen gas into said zone under a controlled and substantially uniform superatmospheric pressure not exceeding about 500 pounds per square inch; (2) maintaining mechanically induced violent agitation of a turbulent character in each of at least four separated adjoining localities along the path of said oil within said zone, thereby promoting highly effective contacting of all reactants while simultaneously restricting movement of the oil intermediate said localities and thus retarding movement of insufficiently hydrogenated oil through and out of said zone; (3) establishing, with the aid of a continuously introduced supply of highly active finely divided nickel-containing catalyst, a hydrogenation rate averaging at least as great as that represented by the point on line D of Figure 7 which corresponds to the hydrogenation temperature employed; (4) continuously removing from the reaction mixture substantially all of the heat liberated by the hydrogenation reaction, thereby facilitating effective and con-

stant control of the desired end point of the reaction; and (5) continuously removing the hydrogenated oil from the hydrogenation zone at an iodine value between 90 and about 60.

2. The process of claim 1, in which the unsaturated oil is vegetable oil having an iodine value between about 90 and about 140, and the activity of the catalyst as herein defined is at least about 4 units.

3. The process of claim 2, in which the hydrogenation temperature is between about 150° C. and about 180° C., the hydrogen pressure is between about 20 pounds and about 60 pounds per square inch, and the hydrogenation rate corresponds to an average iodine value drop of at least 6 units per minute: thereby producing base stock for plastic shortening having superior keeping qualities and desirable consistencies.

4. The process of claim 2, in which the hydrogenation temperature is between about 90° C. and about 110° C., the hydrogen pressure is above about 100 pounds per square inch, and hydrogenation rate corresponds to an average iodine value drop of at least 3 units per minute; thereby producing base stock for plastic shortening having superior plastic properties and desirable keeping qualities.

5. The process of claim 2, in which the hydrogenation temperature is between about 110° C. and 150° C., the hydrogen pressure is at least about 120 pounds per square inch, and the hydrogenation rate corresponds to an average iodine value drop of not less than 5 units per minute at 110° C. hydrogenation temperature, not less than 14 units at 130° C., not less than 35 units at 150° C., the minimum rate for intermediate temperatures lying on a smooth curve connecting the said 110° C., 130° C., and 150° C. minimum values; thereby producing base stock for plastic shortening having a superior combination of keeping qualities and plastic properties.

6. The process of claim 2, in which the hydrogenation temperature is between about 150° C. and about 180° C., the hydrogen pressure does not exceed about 20 pounds per square inch, and the hydrogenation rate corresponds to an average iodine value drop of at least 5 units per minute, and the partially hydrogenated oil is retained in the hydrogenation zone until its iodine value drops below about 70, thereby producing base stock for hydrogenated shortening having exceptionally good keeping qualities.

7. The process of claim 1, in which the average time required to hydrogenate each portion of the oil does not exceed ten minutes.

8. The process of claim 2, in which the oil is cottonseed oil.

9. The process of claim 2, in which the oil is soybean oil.

10. The process of claim 2, in which the oil is a mixture containing between 10 and 50 percent of cottonseed oil and between 50 and 90 percent of soybean oil.

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