



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: PCT/US98/17989</p> <p>(22) International Filing Date: 2 September 1998 (02.09.98)</p> <p>(30) Priority Data: 08/925,811 5 September 1997 (05.09.97) US</p> <p>(71) Applicant: HENKEL CORPORATION [US/US]; Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US).</p> <p>(72) Inventors: KINSMAN, Donald, V.; 128 Manor Lane, Fort Thomas, KY 41075 (US). WHITE, J., Matthew; 8390 Whitegate Drive, Morrow, OH 45152 (US). ANNEKEN, David, J.; 5338 Thrasher Drive, Cincinnati, OH 45247 (US).</p> <p>(74) Agent: DRACH, John, E.; Henkel Corporation, Suite 200, 2500 Renaissance Boulevard, Gulph Mills, PA 19406 (US).</p>	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	
<p>(54) Title: METHOD OF MAKING HYDROGENATED ACIDS</p>		
<p>(57) Abstract</p> <p>A mixture of saturated and unsaturated carboxylic acids are hydrogenated with an effective amount of a hydrogenation catalyst and in the presence of an effective amount of an adsorbent to produce a hydrogenated product having less than about 200 ppm of oxygenated by-products.</p>		

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**TITLE OF THE INVENTION:**  
**Method of Making Hydrogenated Acids**

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**BACKGROUND OF THE INVENTION:**

10 Mixtures of saturated and unsaturated carboxylic acids are conveniently converted to products substantially free of unsaturation by means of catalytic hydrogenation. Such a process is particularly useful in the commercial production of fatty acids, compounds which are used to make base stocks for soap production, as intermediate raw materials for producing a wide range of surfactants, as foam control agents and precipitants in a variety of cleaning products, as superfatting agents in personal cleansing bars, as softener components, and for a number of other more specialized purposes. Fatty acids are obtained from fats and oils by a process the first step of which is referred to as splitting. Splitting is the hydrolysis of a fat or oil to form three molecules of fatty acid and one molecule of glycerine. The glycerine is separated and refined in a separate operation. The crude, split fatty acids are usually then distilled to remove color bodies and odoriferous materials. This sequence of splitting and distilling yields the most basic tallow and coconut fatty acids which are widely used for preparing bar soaps. This basic type of coconut fatty acids also finds use in the preparation of a variety of types of surfactants. While these simple split

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and distilled tallow and coconut fatty acids do have wide use, many in the soap and detergents industry prefer materials with improved colors, color stabilities and odors. These improvements are often effected by hydrogenation.

5 In the case of tallow the hydrogenation is a partial hydrogenation. It is generally controlled so as to reduce or totally eliminate the polyunsaturated acids which are inevitably present in split tallows. Reducing or eliminating the polyunsaturates can significantly improve the color stability of the fatty acids and many soap producers find that this carries through to improving the storage properties of their soap bars. The hydrogenation process also improves the initial  
10 color and odor of the partially hydrogenated fatty acids and this also is generally found to carry through to bar soaps. The typical catalyst used for hydrogenation is some type of nickel catalyst and it is a nonselective catalyst. That means that besides reducing polyunsaturated acids to monounsaturated acids - basically oleic acids - it also reduces some amount of unsaturated acid to saturated acid -  
15 basically stearic acid. During the hydrogenation step, oxygenated compounds such as alcohols, acids and lactones may be formed which can have a deleterious effect on products and/or processes utilizing such acids. For example, the presence of alcoholic impurities could interfere with the production of acid chlorides.

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#### BRIEF SUMMARY OF THE INVENTION:

Hydrogenated carboxylic acids are made by a process which comprises contacting a mixture of saturated and unsaturated carboxylic acids with a catalyst effective amount of a hydrogenation catalyst and in the presence of an effective amount of an adsorbent to produce a hydrogenated product having less than  
25 about 200 ppm of oxygenated by-products. The process may also be carried out by first contacting a mixture of saturated and unsaturated carboxylic acids with a catalyst effective amount of a hydrogenation catalyst to form a hydrogenated product containing oxygenated by-products and then contacting the hydrogenated product with an effective amount of an adsorbent to produce a  
30 hydrogenated product having less than about 200 ppm of oxygenated by-products.

## BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING:

Not Applicable.

## DETAILED DESCRIPTION OF THE INVENTION:

5 The process according to the invention can be applied to the production of any carboxylic acid made by the hydrogenation of a mixture of saturated and unsaturated carboxylic acids. The simplest example is the production of hydrogenated propionic acid having less than about 200 ppm of oxygenated compounds by the hydrogenation of a mixture of acrylic and propionic acids (propenoic and propanoic acids). The process according to the invention is particularly useful for the commercial production of hydrogenated fatty acids wherein the presence of oxygenated compounds could have a deleterious effect on products and/or processes utilizing such acids. For example, hydrogenated stearic acid made by fully hydrogenating mixtures of saturated and unsaturated tallow fatty acids. Hydrogenation converts these mixtures which contain C<sub>18</sub> 10 unsaturated acids to stearic acid. During the hydrogenation step, oxygenated compounds such as alcohols, acids and lactones may be formed. The reduction step is typically carried out by contacting the acid mixture with hydrogen in the presence of a catalyst. The typical catalyst used for hydrogenation is some type of nickel catalyst and it is a nonselective catalyst. That means that besides 20 reducing polyunsaturated acids to monounsaturated acids - basically oleic acids - it also reduces some amount of unsaturated acid to saturated acid - basically stearic acid. There is also some conversion of cis-unsaturated acids to trans-unsaturated acids.

25 The process according to the invention can be carried out in either of two ways. In one embodiment, a mixture of saturated and unsaturated carboxylic acids is contacted with a catalyst effective amount of a hydrogenation catalyst to produce a hydrogenated product which may contain oxygenated compounds. The hydrogenated product is then contacted with an effective amount of an adsorbent to decrease the amount of any oxygenated compounds to less than 30 about 200 ppm.

In another embodiment, a mixture of saturated and unsaturated carboxylic acids with a catalyst effective amount of a hydrogenation catalyst and in the

presence of an effective amount of an adsorbent to produce a hydrogenated product having less than about 200 ppm of oxygenated by-products. In this embodiment, the adsorbent can be present as part of the catalyst as, for example, the catalyst support or it can be added separately at the beginning of the hydrogenation.

The mixture of saturated and unsaturated carboxylic acids can be composed of any type of saturated and unsaturated carboxylic acids. Since the process according to the invention is particularly useful for the commercial production of hydrogenated fatty acids, it can be utilized with a fatty acid stream from the processing of any type of fat or oil. For example, the mixture of carboxylic acids can be a crude fatty acid stream following the splitting or hydrolysis of tallow or coconut oil. Tallow fatty acids will typically contain somewhere around 50 to 52% unsaturated acids of which all but a few percent, maybe 4% or less, are  $C_{18}$  unsaturated acids. Simple split coconut fatty acids contain around 15% of  $C_{8-10}$  acids. In one embodiment of the process according to the invention, the mixture of saturated and unsaturated carboxylic acids is solvent separated stearic acid. The mixture of saturated and unsaturated acids may also be obtained from the hydrolysis of sunflower oil, palm oil, tall oil, soybean oil and canola oil. Solvent separated stearic acids are obtained by dissolving tallow fatty acids in a solvent and then passing them through chilled crystallizers where the solid, saturated acids crystallize out to form a slurry which is then filtered. Not all the unsaturated acids are removed by filtration so the crude stearic is subjected to some combination of hydrogenation and distillation combination to produce single, double and triple pressed stearic.

The catalyst that can be used in the process according to the invention can be any catalyst useful for hydrogenating unsaturated compounds. Such catalysts include but are not limited to platinum, palladium and nickel. The preferred catalyst is nickel. The most preferred catalyst is nickel on acid clay, a commercially available example of which is E-428D from Calsicat; Mallinckrodt Inc., Calsicat Div., 1707 Gaskell Ave., Erie, PA, 16503.

The amount of catalyst that can be used in the process according to the invention is an effective amount which is any amount necessary to bring about

the desired degree of hydrogenation. An effective amount will be readily determinable by one of ordinary skill in the art and may depend upon such factors as, for example, the composition of the starting material, the composition of the catalyst, and the hydrogenation temperature. When the process according to the invention is used to make hydrogenated fatty acids, the catalyst amount will typically vary from about 0.7 ppt to about 3.5 ppt (ppt is parts catalyst per thousand parts of carboxylic acid).

The mixture of saturated and unsaturated carboxylic acids can be contacted with a catalyst effective amount of a hydrogenation catalyst at a temperature in the range of from about 180°C to about 240°C, preferably from about 190°C to about 230°C, and most preferably from about 200°C to about 220°C.

The adsorbent that can be used in the process according to the invention can be carbon black, a commercially available example of which is DARCO® KB from Norit Americas, Inc., 1050 Crown Pointe Parkway, Suite 1500, Atlanta, GA, 30338; silica, alumina, or clay such as kaolinite, montmorillonite, bentonite, atapulgite, illite and halloysite, a commercially available example of which is FILTROL® Grade 13, Harshaw/Filtrol, 30100 Chagrin Boulevard, Cleveland, OH, 44124.

In each embodiment of the present invention as described above, an amount of the adsorbent is used. The effective amount is any amount necessary to decrease the amount of the oxygenated compounds to less than about 200 ppm as determined, for example, by integration of the methylene proton peaks in the 4.9-5.0  $\delta$  region of the H<sup>1</sup> NMR spectrum.

Any analytical method known to those of ordinary skill in the art useful for the determination of oxygenated by-products as identified herein can be used. The preferred method is by integration of the methylene proton peaks in the 4.9-5.0  $\delta$  region of the H<sup>1</sup> NMR spectrum as described in Example 2 below. A concentration of 200 ppm is the approximate threshold level for detection of oxygenated by-products in the PFT H<sup>1</sup> NMR spectrum.

The following examples are meant to illustrate but not to limit the invention.

## EXAMPLE 1

A sample of crude solvent separated stearic acid was hydrogenated to an iodine value of less than 1 with varying amounts of nickel on acid clay catalyst (E-428D) and a clay adsorbent (Filtrol 13) under the hydrogenation conditions of 205°C, 1 hour and 300 psi hydrogen. The samples were then filtered over dicalite and distilled under a vacuum of 1-3 torr, 1% top cut and a pot temperature of 250°C and their H<sup>1</sup> NMR spectra were taken.

In the control sample (1), the hydrogenation was accomplished using a low catalyst concentration and no added adsorbent. The catalyst and adsorbent were present as one component in that the nickel catalyst was deposited on acid clay which also functioned as the adsorbent. No additional adsorbent was added. Peaks were observed at 4.9-5.0  $\delta$  in the H<sup>1</sup> NMR spectrum indicating the presence of oxygenated by-products at a level equal to or greater than 200 ppm. In the case of sample (2), the hydrogenation was accomplished using an elevated catalyst level and a corresponding elevated adsorbent level as the catalyst support compared with the control but no separately added adsorbent. No peaks were observed at 4.9 -5.0  $\delta$  in the H<sup>1</sup> NMR spectrum indicating that the level of oxygenated by-products was less than 200 ppm. In the sample (3), the hydrogenation was accomplished using the low catalyst level of the control but in the presence of added adsorbent. No peaks were observed at 4.9 -5.0  $\delta$  in the H<sup>1</sup> NMR spectrum indicating that the level of oxygenated by-products was less than 200 ppm. The results as reported in Table 1 below. From Table 1 it is seen that when hydrogenations are carried out in the presence of an effective amount of an adsorbent (samples 2 and 3) which is present either as the catalyst support or added separately, the concentration of the oxygenated by-products is less than 200 ppm.

TABLE 1

<u>Sample No.</u>	<u>428D Catalyst Conc.*</u>	<u>Filtrol 13 Conc.*</u>	<u>Conc. 4.9-5.0 <math>\delta</math></u>
1	1.0 ppt	—	0.02%
2	1.7ppt	—	not detected
5 3	1.0ppt	0.7ppt	not detected

\*-ppt is parts per thousand parts of carboxylic acid

## EXAMPLE 2

The H<sup>1</sup> PFT NMR spectra of the samples in deuteriochloroform solvent from Example 1 were obtained using a Varian Unity 400 spectrometer. At least 1000 pulses were collected for each spectra. The spectra were expanded at least 1000 times in order to detect peaks in the 4.9-5.0  $\delta$  region. The concentration of the 4.9-5.0 peaks was estimated by comparing it to the -CH<sub>2</sub>CO<sub>2</sub>- peaks between 2.3 and 2.4  $\delta$ .

What is claimed is:

1. A process which comprises contacting a mixture of saturated and unsaturated carboxylic acids with an effective amount of a hydrogenation catalyst and in the presence of an effective amount of an adsorbent to produce a hydrogenated product having less than about 200 ppm of oxygenated by-products.
2. The process of claim 1 where the catalyst is nickel on acid clay.
3. The process of claim 1 wherein the amount of the catalyst is from about 0.7 to about 3.5 parts catalyst per thousand parts of carboxylic acid mixture.
4. The process of claim 1 wherein the process is carried out at a temperature of from about 180°C to about 240°C.
5. The process of claim 4 wherein the temperature is from about 190°C to about 230°C.
6. The process of claim 5 wherein the temperature is from about 200°C to about 220°C.
7. The process of claim 1 wherein the adsorbent is carbon black, silica, alumina or clay.
8. The process of claim 1 wherein the mixture of saturated and unsaturated carboxylic acids is comprised of fatty acids.
9. The process of claim 8 wherein the fatty acids are derived from tallow or coconut oil.
10. The process of claim 8 wherein the fatty acids are derived from sunflower

oil, palm oil, tall oil, soybean oil or canola oil.

11. A process comprising the steps of: (1) contacting a mixture of saturated and unsaturated carboxylic acids with an effective amount of a hydrogenation catalyst to produce a reduced product comprised of oxygenated by-products; (2)  
5 contacting said hydrogenated acid with an effective amount of an adsorbent to decrease the amount of said oxygenated compounds to less than about 200 ppm.

12. The process of claim 11 where the catalyst is nickel on acid clay.

13. The process of claim 11 wherein the amount of the catalyst is from about  
10 0.7 to about 3.5 parts catalyst per thousand parts of carboxylic acid mixture.

14. The process of claim 11 wherein the process is carried out at a temperature of from about 180°C to about 240°C.

15. The process of claim 14 wherein the temperature is from about 190°C to about 230°C.

16. The process of claim 15 wherein the temperature is from about 200°C to about 220°C.  
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17. The process of claim 11 wherein the adsorbent is carbon black, silica, alumina or clay.

18. The process of claim 11 wherein the mixture of saturated and unsaturated  
20 carboxylic acids is comprised of fatty acids.

19. The process of claim 18 wherein the fatty acids are derived from tallow or coconut oil.

20. The process of claim 18 wherein the fatty acids are derived from sunflower oil, palm oil, tall oil, soybean oil or canola oil.

INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/17989

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC(6) :C07C 51/36  
 US CL :554/ 141,147  
 According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**  
 Minimum documentation searched (classification system followed by classification symbols)  
 U.S. : 554/ 141,147

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
 Please See Extra Sheet.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	US 5,693,835 A (KONISHI et al.) 02 December 1997, entire document.	1-20

Further documents are listed in the continuation of Box C.  See patent family annex.

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Date of the actual completion of the international search 03 DECEMBER 1998	Date of mailing of the international search report <b>15 JAN 1999</b>
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**INTERNATIONAL SEARCH REPORT**

International application No.  
PCT/US98/17989

**B. FIELDS SEARCHED**

Electronic data bases consulted (Name of data base and where practicable terms used):

**APS, CAS ONLINE**

search terms: hydrogenation, adsorbent, fatty acids, fats, oil, clay, nickel catalyst, sunflower oil, tallow oil, coconut oil, carbon blk, silica, alumina, canola oil, palm oil