UNITED STATES PATENT OFFICE.

JAMES DEWAR, OF LONDON, AND ADOLF LIEBMANN, OF WEYBRIDGE, ENGLAND, ASSIGNORS TO THE PROCTER AND GAMBLE COMPANY, OF CINCINNATI, OHIO, A CORPORATION OF OHIO.

HYDROGENATION OF FATS AND OILS.

1,275,405. Specification of Letters Patent. Patented Aug. 13, 1918.

No Drawing. Application filed June 2, 1914. Serial No. 842,538.

To all whom it may concern:

Be it known that we, Sir JAMES DEWAR, of 21 Albemarle street, London, England, and ADOLF LIEBMANN, of the Whim, Weybridge, in the county of Surrey, England, both subjects of the King of Great Britain, have invented new and useful Improvements in the Hydrogenation of Fats and Oils, of which the following is a specification.

It is known that the hydrogenation of unsaturated fats and oils can be effected in the liquid state by the treatment of such fats and oils with hydrogen in the presence of catalysts such as platinum, palladium, iron, copper, cobalt, and especially nickel. This process involves two operations, the production of the catalyst and the subsequent hydrogenation of the fat or oil.

The use of a finely divided metallic oxid in the presence of the fat or oil has also been suggested for the purpose of carrying out the operation of producing catalyst and hydrogenation of the fats and oils in one step. The temperature required is however very high and may lead to the formation of deleterious by-products.

Furthermore the use of organic salts such as formates, acetates, lactates of iron, nickel, copper and cobalt has been proposed as a source for the catalyst and a mixture of one of these compounds with the fat or oil has been described to yield on treatment with hydrogen saturation of the fat or oil. The results of the last mentioned process are however at the temperature described as suitable for the hydrogenation namely, 170° to 200° centigrade highly unsatisfactory.

We have already invented a process which is the subject of our application of even date herewith Serial No. 842,537 for the production of metallic catalysts from their oxygen compounds by reduction with hydrogen at a lower relative temperature than could hitherto be accomplished.

The last mentioned process can be applied with great advantage to the hydrogenation of unsaturated fats and oils inasmuch as it can be carried out with great rapidity and at a comparatively low temperature in the presence of an unsaturated fat or oil.

According to our present invention which consists in the hydrogenation of unsaturated fats and oils in the liquid state we produce the catalyst and the hydrogenation of the fats or oils in one and the same operation and at the same relatively low temperature by mixing the fats or oils with a mixture of the oxids (either hydrated or anhydrous) or the carbonates of two or more of the catalytic metals viz:—nickel, cobalt, or copper, or with a mixture of the oxids or carbonates of one or more of the said catalytic metals with palladium, platinum or silver, in a fine state of division, or with a mixture of the oxids or carbonates of one or more of the said catalytic metals with silver oxid, passing hydrogen through the mixture while it is being stirred and heating the mixture to a temperature at which the reduction takes place. Hydrogenation proceeds concurrently with the production of the catalyst and the conversion of the unsaturated body by the addition of hydrogen to the molecule is very rapid.

This invention is of importance in the hydrogenation of fats and oils as by its use the production of the catalyst and the hydrogenation of the oil can be carried out as aforesaid in one operation at such a relatively low temperature that the fats or oils undergo practically no decomposition and the saturation proceeds with extreme rapidity.

We classify our invention according to the following types—

A. Hydrogenation of fats and oils in a liquid state by treatment with hydrogen of an unsaturated fat or oil in the presence of mixtures of hydroxids, oxids, or carbonates of two or more of the catalytic metals viz:—nickel, cobalt, or copper.

B. Hydrogenation of fats and oils in a liquid state by treatment with hydrogen of an unsaturated fat or oil in the presence of a mixture of one or more of the metallic compounds as defined in "A" with finely divided palladium, platinum, or silver.

C. Hydrogenation of fats and oils in a liquid state by treatment with hydrogen of an unsaturated fat or oil in the presence of a mixture of a metallic compound as defined in "A" and silver oxid.

D. Hydrogenation of fats and oils in a liquid state by treatment with hydrogen of an unsaturated fat or oil in the presence

of the mixtures mentioned in "A", "B", and "C" produced on the surfaces of porous substances.

Although silver and silver compounds have hitherto not been considered as catalysts, for the purpose of this invention they seem to exercise catalytic action.

The mixtures produced according to the types "A", "B", "C", and "D" may be used in varied proportions of the catalytic constituents and in different total proportions to the fat or oil to be hydrogenated.

For the purposes of this specification the expression "mixed catalyst" is a generic term which we apply to the catalyst products resulting from the operations and substances mentioned in paragraphs A, B, C, and D.

The process of hydrogenation according to our invention can be considerably accelerated by bringing hydrogen of increased density into intimate contact with the oil and catalyst and this can be very readily accomplished by working under a pressure which may be ten times or more than that of the atmosphere and the duration of the process is considerably reduced thereby.

The following examples will serve to illustrate further how the invention can be carried into effect but the invention is not confined to these examples—the parts are by weight.

Example I.

A solution of 89.2 parts of nickel nitrate (crystals) and of 9.3 parts of copper nitrate (crystals) is poured into a hot solution containing 46 parts of potassium carbonate. The precipitate is collected on a filter, washed thoroughly until free from soluble salts and then dried on the water bath; it is then heated to a temperature below red heat until the weight is constant. 100 parts of cottonseed oil are then stirred with a quantity of the oxid thus prepared the metal contents of which correspond to two per cent. of the weight of the oil. A very strong current of hydrogen is passed through the mixture which is then heated for 2 hours at about 190° centigrade while being continuously stirred. On cooling the oil is found to be hard and very nearly saturated, the iodin number which is the measure of saturation, being reduced from 110.6 of the original oil to 20.4.

A similar experiment carried out with the same mixture of oxids and whale oil shows after an hour a reduction of the iodin value from 114.8 to 20.6 and after two hours to 1.9.

Example II.

100 parts of whale oil are mixed with a quantity of nickel and copper hydrates (containing ninety per cent. of metallic nickel and ten per cent. of copper) in proportion of about two per cent. of the metals to the weight of the oil and a very strong current of hydrogen is passed through the mixture while it is being continuously stirred and heated for one hour at about 185° centigrade. The iodin value of the whale oil is thus reduced from 128.8 to 32.3 and the oil is quite hard.

Example III.

Nickel and copper carbonates are prepared in molecular proportions in the manner described in Example I hereof and a quantity of the carbonate the metal contents of which amount to about two per cent. of the weight of the oil used is mixed with cottonseed oil and a very strong current of hydrogen is passed through the mixture, while it is being continuously stirred and heated for two hours to about 185° centigrade. The iodin value is reduced from 113 to 38.6, and the oil is hard.

Example IV.

44.6 parts of nickel nitrate (crystals) and .2 parts of palladium chlorid are dissolved in water with the addition of a little hydrochloric acid. The solution is warmed and added to a hot aqueous solution containing 15 parts of caustic soda and two parts by volume of 40 per cent. formalin. A dark gray precipitate is obtained, collected on a filter and dried on the water bath.

100 parts of whale oil are mixed in an autoclave with 3 parts of the product thus prepared (about two per cent. of metal contents) the autoclave closed and the mixture being well stirred and heated while hydrogen is passed through, to about 180° to 190° centigrade, the outlet of the hydrogen being so regulated that the pressure in the autoclave is about 140 lbs. After half an hour the oil after cooling is quite hard, the iodin number being reduced from 128.8 to 36.1.

Example V.

Whale oil is mixed with nickel hydrate and silver oxid (ninety per cent. nickel and ten per cent. silver) in proportion of about two per cent. of the combined metals to the weight of the oil used. A very strong current of hydrogen is passed through the mixture for two hours while it is being continuously stirred and heated up to about 195° centrigrade. The iodin value of the oil is reduced from 114.8 to 62.1, which is the measure of saturation of the oil.

Example VI.

Asbestos is impregnated with a solution containing equal parts of nickel nitrate (crystals) and copper nitrate (crystals) in such strength that the metal contents of asbestos and oxids, after their production, amount to twenty per cent. of the combined

weight of the same. The impregnated asbestos is dried and heated to convert the nitrates into oxids. Seventy five parts of cottonseed oil are mixed in an autoclave with 5.5 parts of the asbestos thus prepared (the metal contents amounting to about one per cent. of the oil) the autoclave is closed and the mixture is heated while being well stirred and hydrogen being passed through at about 180° to 190° centigrade and the outlet of the hydrogen is so regulated that the pressure in the autoclave is about 140 lbs. After half an hour the oil after cooling is quite hard and practically converted into a saturated compound the iodin value being reduced from 113 to 2.7.

According to all the above examples the catalyst is separated from the oil at the end of the operation by filtration and can be used over again or reconverted by well known methods. In case some traces of the catalyst should remain in the oil the same can be removed in a manner well known to chemists.

In the foregoing examples we have described the use of the oxids in quantities the metal contents of which amount to about one or two per cent. of the weight of oil treated. We do not limit ourselves to these proportions as they may be considerably varied either lowered or increased.

We find that of the above mentioned mixed catalysts the one produced from nickel and copper compounds is the most economic.

It is well known that certain substances act as poisons to a catalyst and care has therefore to be taken that the hydrogen is pure and the oils to be hydrogenated are in a sufficient state of purity in order to avoid the destruction of the catalyst on this account.

We have found that electrolytic hydrogen is always of sufficient purity for the purpose of this invention.

There are sometimes certain substances in some oils capable of coagulation which are very detrimental to the process of hydrogenation and have therefore to be removed in the well known way.

For the purpose of the present invention we desire to exclude the use of oxygen compounds of iron mixed with other catalytic or non-catalytic metals or oxids thereof.

For simplicity and convenience, we designate the metals of group "A" above, viz., nickel, cobalt and copper, as "heavy metal catalysts"; and the metals of group "B", viz., palladium, platinum and silver, as "noble metal catalysts". It will be observed that the invention contemplates the preparation of mixed catalysts consisting either of a plurality of the heavy metal catalysts, or of one or more of these heavy metal catalysts in association with a noble metal catalyst. Whatever its components may be, the mixed catalyst may be used by itself, or applied to a porous support. The term "metal of the nickel group" is used to include nickel and cobalt.

What we claim is:—

1. For use in the hydrogenation of fats and oils, a mixture of compounds of different catalytic metals, one at least of which is a heavy metal catalyst, said mixture reducible by hydrogen in the hydrogenation process.

2. For use in the hydrogenation of fats and oils, a mixture of compounds of different catalytic metals, one at least of which is a heavy metal catalyst, said mixture reducible by hydrogen in the hydrogenation process at temperatures not exceeding 200° C.

3. The method of preparing a mixed catalyzer and hydrogenating fats or oils in one operation, which consists in treating the heated fat or oil with hydrogen in presence of a mixture of compounds of different catalytic metals, one at least of which is a heavy metal catalyst.

4. The method of preparing a mixed catalyzer and hydrogenating fats or oils in one operation, which consists in treating the fat or oil with hydrogen in presence of a mixture of compounds of different catalytic metals, one at least of which is a heavy metal catalyst, at a temperature not exceeding 200° C.

5. For use in the hydrogenation of fats and oils, a mixture of compounds of different catalytic metals, one at least of which belongs to the nickel group, said mixture reducible by hydrogen in the hydrogenation process.

6. For use in the hydrogenation of fats and oils, a mixture of a nickel compound with a compound of another catalytic metal, said mixture reducible by hydrogen in the hydrogenation process.

7. For use in the hydrogenation of fats and oils, a mixture of compounds of nickel and copper, said mixture reducible by hydrogen in the hydrogenation process.

In testimony whereof we have signed our names to this specification in the presence of two subscribing witnesses.

JAMES DEWAR.
ADOLF LIEBMANN.

Witnesses:
HERBERT D. JAMESON,
GILBERT F. TYSON.