PATENT SPECIFICATION

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791,044

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COMPLETE SPECIFICATION

Purification of Aliphatic Acids

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh 3, Scotland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the treatment of lower aliphatic acids formed by the liquid phase oxidation of paraffinic hydrocarbons, and in particular to the purification of such acids.

The production of lower aliphatic acids, such as acetic acid, propionic acid and butyric acid, by the oxidation of a paraffinic hydrocarbon of four to eight carbon atoms in the liquid phase at an elevated temperature with molecular oxygen has already been described in British Patents 743,989 and 743,990.

The components of the liquid oxidation product obtained may be classified as (a) volatile non-acidic oxidation products boiling up to 99° C. in the presence of water, hereinafter referred to as "light ends" (b) water, (c) aliphatic monocarboxylic acids of 1 to 4 carbon atoms and (d) higher boiling residues including higher acids. The relative proportions of these components (a) to (d) may vary widely, depending on the oxidation feedstock and conditions. This oxidation product may be distilled to separate off the light ends, and then subjected to fractionation to remove the water and formic acid and to obtain the aliphatic acids of 2 to 4 carbon atoms namely acetic, propionic and butyric acids as one or more fractions. While the C_2 to C_4 acids can be purified to a great extent by further fractionation steps so that the acid product passes the tests laid down in the British Standard Specifications, for instance B.S.S. 576, 1950 for acetic acid, it has not hitherto been possible to free the product completely from traces of odorous impurities and materials of a reducing nature which we have found exist in accordance with our invention. The presence of these latter impurities in the oxidation product is, in fact, highly surprising, in as much as compounds of a reducing character would have been expected to be completely removed during the oxidation reaction.

It is an object of the present invention to provide a process for the purification of aliphatic acids of 2 to 4 carbon atoms produced by the liquid phase oxidation of paraffinic hydrocarbons of 4 to 8 carbon atoms.

According to the present invention the process for the purification of impure aliphatic monocarboxylic acids of 2 to 4 carbon atoms produced by the liquid phase oxidation of paraffinic hydrocarbons of 4 to 8 carbon atoms and containing as impurities certain odorous substances and materials of a reducing nature comprises subjecting the acids to hydrogenation in the presence of a hydrogenation catalyst.

The hydrogenation reaction of the present invention is preferably carried out on fractions of the oxidation product containing acetic, propionic, or butyric acids, or mixtures of these acids, which have been substantially freed from formic acid. In a preferred embodiment the starting material for the process of the invention consists of acetic acid which has been recovered from the oxidation product of a paraffinic hydrocarbon by means of the process described in copending British Application No. 17600/53, Serial No. 771,992.

In this application is described a process for the recovery of acetic acid from the product of the liquid phase oxidation of aliphatic hydrocarbons containing light ends, as hereinbefore defined water, aliphatic monocarboxylic acids of 1 to 4 carbon atoms and higher boiling residues which comprises distilling the product to separate as distillate a mixture containing water and the

[*Price 3s. 6d.*]

aliphatic monocarboxylic acids of 1 to 4 carbon atoms and thereafter fractionally distilling this mixture to recover the acetic acid. The acetic acid recovered by this process passes the tests for acetic acid laid down in British Standard Specification 576, 1950. It has now surprisingly been discovered that this acid may be further improved in quality so that it passes the specification laid down in the British Pharmacopœia, 1953, page 11, which includes tests not included in the B.S. Specification, by subjecting it to the hydrogenating process of the present invention, which removes not only odorous impurities but also those materials which are themselves of a reducing nature.

The hydrogenation may be carried out in the liquid or vapour phase, liquid phase hydrogenation being preferred. The temperatures and pressures employed may be varied within wide limits, but in general room temperature and atmospheric pressure are suitable.

The catalysts which may be used include all the commonly recognised hydrogenation catalysts, but it is preferred to use a noble metal catalyst of the platinum or palladium group, which are especially efficient.

After treatment according to the process of the present invention the acid product may be recovered by the conventional methods, for instance by filtration or distillation.

The improvements effected by the hydrogenation step are measured by the reaction with aqueous potassium permanganate in tests of "permanganate index" and "permanganate time" described below and by the tests for odorous impurities given in the British Pharmacopœia, 1953, at page 12.

The determinations of permanganate index and permanganate time are carried out as follows:—

Permanganate Index—A 5 ml. sample of the acid is diluted with 5% weight/weight sulphuric acid (50 ml.) and maintained at 20°C. Potassium permanganate solution (0.1%) is then added dropwise until the rose pink colour just persists for one minute. The permanganate index is then 20 times the volume (in mls.) of permanganate solution used.

Permanganate Time—A 2 ml. sample of the acid is diluted with distilled water (20 mls.) and 0.1N potassium permanganate (0.5 ml.) is added. The time taken for the complete discharge of the pink colour is then noted up to a maximum of 2 hours.

The following examples are given further to illustrate the process of the invention. In the examples the parts by weight and parts by volume bear the same relation to each other as do kilograms to litres.

EXAMPLE 1.

An oxidation product, obtained by the liquid phase oxidation at 170°C. and at a pressure of 600 pounds per square inch gauge, of a paraffinic hydrocarbon fraction of boiling range 15 to 95°C. containing aqueous C_1—C_4 aliphatic acids, including formic, acetic, propionic and butyric acids, as well as volatile light ends, was introduced into a continuous still operated at a head temperature of about 60°—65°C. From the head of the still the volatile light ends were removed and from the base of the still, the base product comprising the aqueous acids was passed to a continuous still of 5 to 7 theoretical plates wherein the base product was fractionally distilled to separate the crude aqueous mixture of acids from the higher boiling material, the column being operated at a head temperature of about 100—110°C. The distillate comprising the aqueous aliphatic acids was fed to a continuous distillation column of approximately 15 theoretical plates, the reflux ratio being about 9:1 and the head temperature 90 to 95°C., the total distillate being about 10% of the feed. The distillate comprising subsidiary light ends, was passed to a phase separator where the distillate separated into two phases, all or part of the upper liquid phase being removed, any remainder being returned to the still as reflux; and all or part of the lower liquid phase being returned to the still as reflux, any remainder being removed. The base product, comprising the aqueous acids, was removed and passed to a continuous dehydrating still using isopropyl ether as entrainer. The overheads from the column were taken to a phase separator, the separated isopropyl ether layer returned to the column and the water removed. The still base product, comprising the dried acids, was passed to a continuous still using toluene as entrainer. The overheads from the column were taken to a phase separator, the lower layer comprising formic acid being taken off and the upper layer comprising toluene being returned to the column. The still base product was passed to a continuous fractionation still to separate as the overheads acetic acid, which was finally distilled to remove traces of toluene and formic acid. The still base product comprised the higher aliphatic acids and may be batch distilled to produce a propionic fraction which may be hydrogenated as described in Example 4 below. Butyric acid may be similarly obtained and hydrogenated.

The acetic acid obtained as above was completely colourless, contained no detectable amounts of esters or ketonic compounds and completely satisfied the requirements of British Standard Specification, B.S. No. 576, 1950. The acid had a permanganate index of 18 and permanganate time of more than 30 minutes and less than 120 minutes.

100 parts by weight of the acetic acid was hydrogenated in the liquid phase at atmospheric pressure and room temperature over 0.1 part by weight of Adams platinum oxide

catalyst when about 150 parts by volume of hydrogen (at N.T.P.) were absorbed. The product was filtered to remove catalyst and was found to have a permanganate index of 1 and a permanganate time of more than 120 minutes.

EXAMPLE 2.

Acetic acid satisfying the requirements of British Standard Specification 576, 1950, and prepared as described in Example 1, was found to have a permanganate index of 42 and a permanganate time of more than 30 minutes and less than 120 minutes. 100 parts by weight of the acid were hydrogenated in the liquid phase at atmospheric pressure and room temperature over 0.5 parts by weight of a catalyst consisting of 3.0% palladium on charcoal. The hydrogenated acid had a permanganate index of 6 and a permanganate time of more than 120 minutes.

EXAMPLE 3.

A sample of acetic acid which satisfied the requirements of British Standard Specification 576, 1950, and which had been obtained as described in Example 1, had a slightly musty odour in the odorous impurities test given in the British Pharmacopœia 1953, page 12. After hydrogenation over Adams platinum oxide catalyst as described in Example 1 the acid was odourless in the same test.

EXAMPLE 4.

A propionic acid fraction, boiling point 140°C./760 mm., was obtained by batch distillation of the residues remaining after recovery of acetic acid from the oxidation product as described in Example 1 and had a permanganate index of more than 200. 100 parts by weight were hydrogenated in the liquid phase at atmospheric pressure and room temperature over 0.1 part by weight of Adams platinum oxide catalyst. As a result of this treatment the permanganate index of the propionic acid was reduced to 2.

EXAMPLE 5.

Acetic acid prepared as described in Example 1 and having a permanganate index of 12 was caused to flow at atmospheric pressure and temperature at 2.5 volumes per hour down a 30 centimetre by 2 cms. cylindrical bed of 4—8 mesh granular carbon impregnated with 1% by weight of palladium, countercurrent to a stream of hydrogen at 20 volumes per hour. The hydrogenated acid had a permanganate index of 2.4.

When the same feedstock was passed down the catalyst at double the rate (i.e. at 5.0 volumes per hour) the permanganate index of the product was 3.6.

Another feedstock, having a permanganate index of 36, was also passed down this catalyst under the same conditions as stated in paragraph 1 of this Example and the product had a permanganate index likewise of 3.6.

EXAMPLE 6.

Acetic acid prepared as described in Example 1 and having an initial permanganate index of 29 was passed at atmospheric pressure and temperature at 1 volume per hour through an apparatus in which hydrogen was dispersed through a sintered glass disc into a column containing 100—200 mesh "Celite" (Registered Trade Mark) a commercial grade of silica impregnated with 1% palladium and suspended in acetic acid. The apparatus was so arranged that acetic acid could be fed in at one point and withdrawn at another by way of a settling tank, from the bottom of which the catalyst was fed back to the reaction zone.

The permanganate index of the product was 4.0.

What we claim is:—

1. The process for the purification of impure aliphatic monocarboxylic acids of 2—4 carbon atoms, produced by the liquid phase oxidation of paraffinic hydrocarbons of 4—8 carbon atoms and containing as impurities certain odorous substances and materials of a reducing nature, which comprises subjecting the acids to hydrogenation in the presence of a hydrogenation catalyst.

2. The process as claimed in claim 1 wherein the acids are substantially free from formic acid.

3. The process as claimed in either of the preceding claims wherein the liquid phase oxidation product is distilled to separate as distillate a mixture containing water and the aliphatic monocarboxylic acids of 1—4 carbon atoms and thereafter this mixture is fractionally distilled to recover the acetic acid which is used as the starting material in the process of the present invention.

4. The process as claimed in any of the preceding claims where the hydrogenation is carried out in the liquid phase.

5. The process as claimed in any of the preceding claims wherein the hydrogenation catalyst is a member of the platinum group of metals.

6. The process for the purification of aliphatic monocarboxylic acids substantially as described herein with reference to the examples.

7. Aliphatic monocarboxylic acids of 2—4 carbon atoms when purified by the process of any of the preceding claims.

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catalyst when about 150 parts by volume of hydrogen (at N.T.P.) were absorbed. The product was filtered to remove catalyst and was found to have a permanganate index of 1 and a permanganate time of more than 120 minutes.

EXAMPLE 2.

Acetic acid satisfying the requirements of British Standard Specification 576, 1950, and prepared as described in Example 1, was found to have a permanganate index of 42 and a permanganate time of more than 30 minutes and less than 120 minutes. 100 parts by weight of the acid were hydrogenated in the liquid phase at atmospheric pressure and room temperature over 0.5 parts by weight of a catalyst consisting of 3.0% palladium on charcoal. The hydrogenated acid had a permanganate index of 6 and a permanganate time of more than 120 minutes.

EXAMPLE 3.

A sample of acetic acid which satisfied the requirements of British Standard Specification 576, 1950, and which had been obtained as described in Example 1, had a slightly musty odour in the odorous impurities test given in the British Pharmacopoeia 1953, page 12. After hydrogenation over Adams platinum oxide catalyst as described in Example 1 the acid was odourless in the same test.

EXAMPLE 4.

A propionic acid fraction, boiling point 140°C./760 mm., was obtained by batch distillation of the residues remaining after recovery of acetic acid from the oxidation product as described in Example 1 and had a permanganate index of more than 200. 100 parts by weight were hydrogenated in the liquid phase at atmospheric pressure and room temperature over 0.1 part by weight of Adams platinum oxide catalyst. As a result of this treatment the permanganate index of the propionic acid was reduced to 2.

EXAMPLE 5.

Acetic acid prepared as described in Example 1 and having a permanganate index of 12 was caused to flow at atmospheric pressure and temperature at 2.5 volumes per hour down a 30 centimetre by 2 cms. cylindrical bed of 4—8 mesh granular carbon impregnated with 1% by weight of palladium, countercurrent to a stream of hydrogen at 20 volumes per hour. The hydrogenated acid had a permanganate index of 2.4.

When the same feedstock was passed down the catalyst at double the rate (i.e. at 5.0 volumes per hour) the permanganate index of the product was 3.6.

Another feedstock, having a permanganate index of 36, was also passed down this catalyst under the same conditions as stated in paragraph 1 of this Example and the product had a permanganate index likewise of 3.6.

EXAMPLE 6.

Acetic acid prepared as described in Example 1 and having an initial permanganate index of 29 was passed at atmospheric pressure and temperature at 1 volume per hour through an apparatus in which hydrogen was dispersed through a sintered glass disc into a column containing 100—200 mesh "Celite" (Registered Trade Mark) a commercial grade of silica impregnated with 1% palladium and suspended in acetic acid. The apparatus was so arranged that acetic acid could be fed in at one point and withdrawn at another by way of a settling tank, from the bottom of which the catalyst was fed back to the reaction zone.

The permanganate index of the product was 4.0.

What we claim is:—

1. The process for the purification of impure aliphatic monocarboxylic acids of 2—4 carbon atoms, produced by the liquid phase oxidation of paraffinic hydrocarbons of 4—8 carbon atoms and containing as impurities certain odorous substances and materials of a reducing nature, which comprises subjecting the acids to hydrogenation in the presence of a hydrogenation catalyst.

2. The process as claimed in claim 1 wherein the acids are substantially free from formic acid.

3. The process as claimed in either of the preceding claims wherein the liquid phase oxidation product is distilled to separate as distillate a mixture containing water and the aliphatic monocarboxylic acids of 1—4 carbon atoms and thereafter this mixture is fractionally distilled to recover the acetic acid which is used as the starting material in the process of the present invention.

4. The process as claimed in any of the preceding claims where the hydrogenation is carried out in the liquid phase.

5. The process as claimed in any of the preceding claims wherein the hydrogenation catalyst is a member of the platinum group of metals.

6. The process for the purification of aliphatic monocarboxylic acids substantially as described herein with reference to the examples.

7. Aliphatic monocarboxylic acids of 2—4 carbon atoms when purified by the process of any of the preceding claims.

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* C L M S *

PROVISIONAL SPECIFICATION

Purification of Aliphatic Acids

We, THE DISTILLERS COMPANY LIMITED, a British Company, of 12, Torphichen Street, Edinburgh, 3, Scotland, do hereby declare this invention to be described in the following statement:—

The present invention relates to the production of lower aliphatic acids by the liquid phase oxidation of paraffinic hydrocarbons, and in particular to the purification of such acids.

The production of lower aliphatic acids, such as acetic acid, propionic acid and butyric acid, by the oxidation of a paraffinic hydrocarbon of four to eight carbon atoms in the liquid phase at an elevated temperature with molecular oxygen has already been described in our copending Applications Nos. 25789/52, 25792/52, 25794/52, 1051/53 and 11469/53 (Serial Nos. 743,989, 743,990, 743,991, 771,991 and 767,290). The components of the liquid oxidation product obtained may be classified as (a) volatile non-acidic oxidation products boiling up to 99° C. in the presence of water, hereinafter referred to as "light ends" (b) water, (c) aliphatic monocarboxylic acids of 1 to 4 carbon atoms and (d) higher boiling residues including higher acids. The relative proportions of these components (a) to (d) may vary widely, depending on the oxidation feedstock and conditions. This oxidation product may be distilled to separate off the light ends, and then subjected to fractionation to remove the water and formic acid and to obtain the aliphatic acids of 2 to 4 carbon atoms as one or more fractions. While the C_2 to C_4 acids can be purified to a great extent by further fractionation steps so that the acid product passes the tests laid down in the British Standard Specifications, for instance B.S.S 576, 1950 for acetic acid, it has not hitherto been possible to free the product completely from traces of odorous impurities and materials of a reducing nature. The presence of these latter impurities in the oxidation product is, in fact, highly surprising, in as much as compounds of a reducing character would have been expected to be completely removed during the oxidation reaction.

It is an object of the present invention to provide a process for the purification of aliphatic acids of 2 to 4 carbon atoms produced by the liquid phase oxidation of paraffinic hydrocarbons of 4 to 8 carbon atoms.

According to the present invention the process for the purification of aliphatic monocarboxylic acids of 2 to 4 carbon atoms substantially free from formic acid produced by the liquid phase oxidation of paraffinic hydrocarbons of 4 to 8 carbon atoms comprises subjecting the acids to hydrogenation in the presence of a hydrogenation catalyst.

The hydrogenation reaction of the present invention is carried out on fractions of the oxidation product containing acetic, propionic, or butyric acids, or mixtures of these acids, which have been substantially freed from formic acid. In a preferred embodiment the starting material for the process of the invention consists of acetic acid which has been recovered from the oxidation product of a paraffinic hydrocarbon by means of the process described in our copending Application 17600/53 (Serial No. 771,992). In this application is described a process for the recovery of acetic acid from the product of the liquid phase oxidation of aliphatic hydrocarbons containing light ends, as hereinbefore defined, water, aliphatic monocarboxylic acids of 1 to 4 carbon atoms and higher boiling residues which comprises distilling the product to separate as distillate a mixture containing water and the aliphatic monocarboxylic acids of 1 to 4 carbon atoms and thereafter fractionally distilling this mixture to recover the acetic acid. The acetic acid recovered by this process passes the tests for acetic acid laid down in British Standard Specification 576, 1950. It has now surprisingly been discovered that this acid may be further improved in quality by subjecting it to the hydrogenating process of the present invention, which removes not only odorous impurities but also those materials which are themselves of a reducing nature, so that the acid product passes the specification laid down in the British Pharmacopœia, 1953, page 11.

The hydrogenation may be carried out in the liquid or vapour phase, liquid phase hydrogenation being preferred. The temperatures and pressures employed may be varied within wide limits, but in general room temperature and atmospheric pressure are suitable.

The catalysts which may be used include all the commonly recognised hydrogenation catalysts, but it is preferred to use a noble metal catalyst of the platinum or palladium group, which are especially efficient.

After treatment according to the process of the present invention the acid product may be recovered by the conventional methods, for instance by filtration or distillation.

The improvements effected by the hydrogenation step are measured by the reaction with aqueous potassium permanganate in tests of "permanganate index" and "permanganate time" described below and by the tests for odorous impurities given in the

British Pharmacopœia, 1953, at page 12.

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100 parts by weight of the acetic acid was hydrogenated in the liquid phase at atmospheric pressure and room temperature over 0.1 part by weight of Adams platinum oxide catalyst when about 150 parts by volume of hydrogen (at N.T.P.) were absorbed. The product was filtered to remove catalyst and was found to have a permanganate index of 1 and a permanganate time of more than 120 minutes.

EXAMPLE 2.

Acetic acid satisfying the requirements of British Standard Specification 576, 1950, and prepared as described in Example 1, was found to have a permanganate index of 42 and a permanganate time of more than 30 minutes and less than 120 minutes. 100 parts by weight of the acid were hydrogenated in the liquid phase at atmospheric pressure and room temperature over 0.5 parts by weight of a catalyst consisting of 3.0% palladium on charcoal. The hydrogenated acid had a permanganate index of 6 and a permanganate time of more than 120 minutes.

EXAMPLE 3.

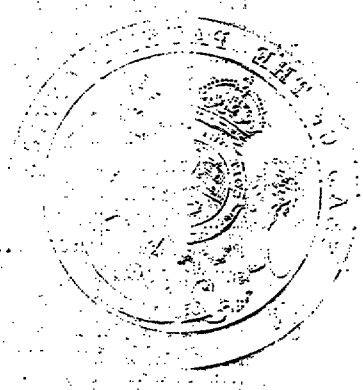
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EXAMPLE 4.

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N.F. Baker.