PATENT SPECIFICATION

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1518

PROVISIONAL SPECIFICATION

Improvements in the Purification of Alcohols

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany) to be as follows :—

Aliphatic alcohols obtained by synthesis, by fermentation or by carbonisation of wood frequently contain carbonyl compounds, such as aldehydes or ketones, which greatly restrict the employment of the alcohols by reason of their chemical reactivity and their unpleasant odour. These impurities cannot be separated by simple distillation. It has been proposed, *inter alia*, to distill the alcohols in the presence of amines, as for example aniline, if desired in the presence of small amounts of mineral acid, whereby the aldehydes and ketones are converted into high molecular weight products so that the pure alcohol is then capable of being separated by distillation. This process can, however, only be used when the alcohols are free from water or highly concentrated. In the presence of large amounts of water in the initial product, it is impossible by the said process, even with most careful rectification, to obtain products free from carbonyl compounds.

My foreign correspondents have now found that pure alcohols can also be obtained from their aqueous solutions or mixtures containing carbonyl compounds as impurities in a simple manner by treating them with primary amines in the liquid phase under increased pressure at a temperature lying appreciably above the boiling point of the alcohol to be purified. The proportion of water to alcohol which is present in the initial mixture has no influence on the efficiency of the purification. Similarly the content of carbonyl compounds in the aqueous alcohol to be purified may be of any height.

In most cases it is a question of removing the carbonyl compounds contained in mixtures of methyl or ethyl alcohol and water, but aqueous higher alcohols, such as propyl, isopropyl and isobutyl alcohols, may also be purified by the said process.

It is especially suitable to use amines of high boiling point, such as isohexylamine, isoheptylamine or octylamine, or even amines of higher boiling point, such as dodecylamine, because these, in the form of their reaction products with the carbonyl compounds, are to a great extent insoluble in the mixture of alcohol and water and may be separated therefrom together with the major portion of the unconverted amine as a liquid of lower specific gravity and then worked up.

The purification may be carried out at temperatures up to more than 200° Centigrade ; it is most favourable, however, to work at from 170° to 190° Centigrade.

The process may be carried out for example by adding an excess of amine to the crude aqueous alcohol, and, advantageously after separating any layer of lower specific gravity formed which contains the reaction product formed from the amine with a part of the carbonyl compounds present, heating in a well filled pressure-tight container for the necessary time, on an average from 30 to 60 minutes, at the said temperature and then subjecting to rectifying distillation at atmospheric pressure.

It has been found to be specially advantageous to introduce the amine and the aqueous alcohol separately and continuously under a pressure at which the reaction still takes place in the liquid phase into a pressure-tight vessel heated to the said temperature and then to release the product from pressure directly in a distilling column.

In every case there is obtained after distillation of the aqueous crude alcohol treated in the said manner a distillate in which no aldehydes can be detected even with sensitive reagents, such as metaphenylenediamine hydrochloride.

The following Examples will further illustrate the nature of this invention but the invention is not restricted to these Examples. The parts are by weight.

EXAMPLE 1.

3800 parts of a mixture of methanol and

[*Price* 1/-]

Price 2d

water having a specific gravity of 0.950 and having an aldehyde content of 0.3 per cent. calculated as butyraldehyde, such as is obtained by the working up of a crude product obtained by catalytic reduction of carbon monoxide under pressure, are shaken for 15 minutes with 200 parts of iso-hexylamine. The whole is then allowed to stand until formation of layers has taken place. (From the layer of lower specific gravity there may be obtained by distillation from acid solution, a mixture of aldehydes consisting mainly of isobutyraldehyde).

The lower layer is heated in an autoclave to 180° Centigrade in the course of two hours. After cooling, the original unitary solution has again separated into two layers. The layer of lower specific gravity contains the impurities in the form of insoluble amine reaction products. The lower layer yields, by rectifying distillation, 750 parts of a methyl alcohol which no longer becomes yellow in colour with 1 per cent. meta-phenylene diamine hydrochloride solution.

EXAMPLE 2.

3800 parts of the mixture of methanol and water used in Example 1 are shaken with 100 parts of iso-hexylamine. After separating the layers, the lower layer is pressed continuously under a nitrogen pressure of 100 atmospheres into a tube heated to 180° Centigrade and provided with filler bodies. The reaction product, after releasing the pressure to atmospheric pressure, is subjected to rectifying distillation. 760 parts of a methanol entirely free from aldehyde are obtained.

EXAMPLE 3.

3800 parts of a mixture of methanol and water obtained from the synthetically-prepared crude product and having a specific gravity of 0.939 and an aldehyde content of 1.13 per cent. calculated as butyraldehyde have added thereto 276 parts of iso-heptylamine, the whole being heated to 180° Centigrade in an autoclave during the course of two hours without separating the layers formed. By cooling to room temperature, the formation of layers takes place. The upper layer is separated and methanol entirely free from aldehyde is obtained from the lower layer by rectifying distillation.

EXAMPLE 4.

The crude mixture of methanol and water and the iso-heptylamine used in Example 3 are pressed separately into a reaction tube heated to 180° Centigrade and under a pressure of 30 atmospheres which is filled with rings. The reaction mixture leaving the reaction tube is subjected to rectifying distillation, methyl alcohol free from aldehyde being obtained.

EXAMPLE 5.

4000 parts of a mixture of normal propyl alcohol and water obtained synthetically from carbon monoxide and hydrogen and having a specific gravity of 0.940 and an aldehyde content of 1.4 per cent. calculated as amyl aldehyde, are mixed with 250 parts of iso-octylamine and heated for 30 minutes at 180° Centigrade in an autoclave. After cooling, the upper layer is separated and the lower layer subjected to rectifying distillation.

The distillate obtained is entirely free from aldehyde.

Dated this 13th day of August, 1937.

J. Y. & G. W JOHNSON,
47, Lincoln's Inn Fields, London.
W.C.2.
Agents.

COMPLETE SPECIFICATION

Improvements in the Purification of Alcohols

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany) and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement :—

Aliphatic alcohols obtained by synthesis, by fermentation or by carbonisation of wood frequently contain carbonyl compounds, such as aldehydes or ketones, which greatly restrict the employment of the alcohols by reason of their chemical reactivity and their unpleasant odour. These impurities cannot be separated by simple distillation. It has been proposed, *inter alia*, to distill the alcohols in the presence of amines, as for example aniline, if desired in the presence of small amounts of mineral acid, whereby the aldehydes and ketones are converted into high molecular weight products so that the pure alcohol is then capable of being separated by distillation. This process can, however, only be used when the alcohols are free from water or highly concentrated. In the presence of large amounts of water in the initial products, it is impossible by the said process, even with most careful rectification, to obtain products free from carbonyl compounds.

My foreign correspondents have now found that pure alcohols can also be obtained from their aqueous solutions or mixtures containing carbonyl compounds as impurities in a simple manner by treating them with primary amines in the liquid phase under increased pressure at a temperature lying appreciably above the boiling point of the alcohol to be purified. The proportion of water to alcohol which is present in the initial mixture has no influence on the efficiency of the purification. Similarly the content of carbonyl compounds in the aqueous alcohol to be purified may be of any height.

In most cases it is a question of removing the carbonyl compounds contained in mixtures of methyl or ethyl alcohol and water, but aqueous higher alcohols, such as propyl, isopropyl and isobutyl alcohols, may also be purified by the said process.

It is especially suitable to use amines of high boiling point, such as isohexylamine, isoheptylamine or octylamine, or even amines of higher boiling point, such as dodecylamine, because these, in the form of their reaction products with the carbonyl compounds, are to a great extent insoluble in the mixture of alcohol and water and may be separated therefrom together with the major portion of the unconverted amine as a liquid of lower specific gravity and then worked up.

The purification may be carried out at temperatures up to more than 200° Centigrade; it is most favourable, however, to work at from 170° to 190° Centigrade.

The process may be carried out for example by adding an excess of amine to the crude aqueous alcohol, and, advantageously after separating any layer of lower specific gravity formed which contains the reaction product formed from the amine with a part of the carbonyl compounds present, heating in a well filled pressure-tight container for the necessary time, on an average from 30 to 60 minutes, at the said temperature and then subjecting to rectifying distillation at atmospheric pressure.

It has been found to be specially advantageous to introduce the amine and the aqueous alcohol separately and continuously under a pressure at which the reaction still takes place in the liquid phase into a pressure-tight vessel heated to the said temperature and then to release the product from pressure directly in a distilling column.

In every case there is obtained after distillation of the aqueous crude alcohol treated in the said manner a distillate in which no aldehyde can be detected even with sensitive reagents, such as metaphenylenediamine hydrochloride.

The following Examples will further illustrate how the said invention may be carried out in practice but the invention is not restricted to these Examples. The parts are by weight.

EXAMPLE 1.

3800 parts of a mixture of methanol and water having a specific gravity of 0.950 and having an aldehyde content of 0.8 per cent. calculated as butyraldehyde, such as is obtained by the working up of a crude product obtained by catalytic reduction of carbon monoxide under pressure, are shaken for 15 minutes with 200 parts of iso-hexylamine. The whole is then allowed to stand until formation of layers has taken place. (From the layer of lower specific gravity there may be obtained by distillation from acid solution, a mixture of aldehydes consisting mainly of isobutyraldehyde).

The lower layer is heated in an autoclave to 180° Centigrade in the course of two hours. After cooling, the original unitary solution has again separated into two layers. The layer of lower specific gravity contains the impurities in the form of insoluble amine reaction products. The lower layer yields, by rectifying distillation, 750 parts of a methyl alcohol which no longer becomes yellow in colour with 1 per cent. metaphenylene diamine hydrochloride solution.

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3800 parts of the mixture of methanol and water used in Example 1 are shaken with 100 parts of iso-hexylamine. After separating the layers, the lower layer is pressed continuously under a nitrogen pressure of 100 atmospheres into a tube heated to 180° Centigrade and provided with filler bodies. The reaction product, after releasing the pressure to atmospheric pressure, is subjected to rectifying distillation. 760 parts of a methanol entirely free from aldehyde are obtained.

EXAMPLE 3.

3800 parts of a mixture of methanol and water obtained from the synthetically-prepared crude product and having a specific gravity of 0.939 and an aldehyde content of 1.13 per cent. calculated as butyraldehyde have added thereto 276 parts of iso-heptylamine, the whole being heated to 180° Centigrade in an autoclave during the course of two hours without separating the layers formed. By cooling to room temperature, the formation of layers takes place. The upper layer is separated and methanol entirely free from aldehyde is obtained from the lower layer by rectifying distillation.

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tube heated to 180° Centigrade and under a pressure of 30 atmospheres which is filled with rings. The reaction mixture leaving the reaction tube is subjected to rectifying distillation, methyl alcohol free from aldehyde being obtained.

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4000 parts of a mixture of normal propyl alcohol and water obtained synthetically from carbon monoxide and hydrogen and having a specific gravity of 0.940 and an aldehyde content of 1.4 per cent. calculated as amyl aldehyde, are mixed with 250 parts of iso-octylamine and heated for 30 minutes at 180° Centigrade in an autoclave. After cooling, the upper layer is separated and the lower layer subjected to rectifying distillation.

The distillate obtained is entirely free from aldehyde.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is :—

1. A process for the manufacture and production of pure alcohols from aqueous solutions or mixtures of aliphatic alcohols containing carbonyl compounds as impurities which consists in treating them with primary amines in the liquid phase under increased pressure at a temperature lying appreciably above the boiling point of the alcohols to be purified.

2. The process for the manufacture and production of pure alcohols substantially as described in each of the foregoing Examples.

3. Pure alcohols when obtained in accordance with the process particularly described and ascertained.

Dated this 2nd day of June, 1938.

J. Y. & G. W JOHNSON,
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Agents.

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