PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Improvements in and relating to the Purification of Alcohols.

We, Imperial Chemical Industries Limited, a Company registered under the laws of Great Britain, of Imperial Chemical House, Millbank, London, S.W.1, James Wilson Armit, of "Ebbacroft", 18, Woodcote Park Road, Epsom, in the County of Surrey, and George Edwin Wainwright, of Norton Hall, The Green, Norton-on-Tees, in the County of Durham, both subjects of the King of Great Britain and Ireland, do hereby declare the nature of this invention to be as follows:—

This invention relates to the purification of alcohols.

The object of the invention is to provide a method for the purification of alcohols and in particular the purification of methyl alcohol and higher alcohols produced by the combination of carbon monoxide and hydrogen in the presence of a catalyst.

In the reaction in the presence of a catalyst between carbon monoxide and hydrogen, methyl, ethyl, propyl and higher alcohols are produced. At the same time fatty acids, esters, unsaturated hydrocarbons, aldehydes, acetals, ketones, ethers, mercaptans and alkyl sulphides are formed as by-products. The separation of these from any particular fraction of alcohol, particularly methyl alcohol, by fractionation may be considered as impracticable.

The invention in brief consists in treating alcohols, especially alcoholic fractions such as those referred to above by a preliminary distillation for example with caustic alkali or a mixture of brine and caustic alkali followed by the addition of small quantities of aniline or derivatives of aniline containing acidic substituents in the nucleus, or other primary amines of comparatively high boiling point and phosphoric acid or sulphuric acid to the distillate and subsequent refractionation.

The invention also consists in a modification of the process according to the preceding paragraph according to which the two operations referred to as preliminary distillation and aniline and acid treatment are carried out consecutively and continuously, for example, in a plant in which the hot vapours from the alkali scrubbing column are passed directly into the boiling, alkali scrubbed, alcohol containing the required aniline and acid in a still fitted with a rectifying column.

The invention also consists in processes for the purification of methyl alcohol and higher alcohols especially those produced in the presence of a catalyst by the combination of carbon monoxide and hydrogen substantially as described.

The invention also consists in products when made by processes subtantially as described or by the obvious chemical equivalents thereof.

The following examples illustrate how the invention may be carried into effect references to parts being by volume and to percentages being by weight:—

Example 1.

To the crude methanol fraction of the product of the catalysed reaction between carbon monoxide and hydrogen are added half its bulk of saturated brine and a similar volume of 16—20% caustic soda solution. The oily top layer consisting of higher alcohols, hydrocarbons and the like, is separated off. The residue is distilled and the vapours scrubbed in the still head by a descending spray of 15—20% caustic soda solution. The quantity of soda required for efficient scrubbing will depend upon a number of factors for example design of still but in general not more than a volume equal to the volume of methanol will be required. The first fractions of the distillate may contain oily impurities (hydrocarbons, higher alcohols or the like) which are separated off by running into brine and returning the brine layer to the still. To the distillate free from oily impurities are added 5 parts of aniline and 5 parts of syrupy phosphoric acid (or 5 parts of concentrated sulphuric acid) per 1000 parts by volume and the whole is refractionated. These two operations may be carried out consecutively and continuously in a suitable still without condensation of the methanol after the soda treatment, for example, by means of a plant in which the hot vapours from the alkali scrubbing column are passed directly into the boiling, alkali scrubbed, alcohol containing the required aniline and acid in a still fitted with a rectifying column.

The methanol thus obtained is of pleasant odour, gives a colourless solution with an equal volume of concentrated sulphuric acid and only very slowly decolourises N/30 potassium permanganate solution.

EXAMPLE 2.

The crude isobutanol fraction from the product of the interaction of carbon monoxide and hydrogen in presence of a suitable catalyst is fractionated after addition of aniline and phosphoric acid or aniline and concentrated sulphuric acid to the extent of 5 parts by volume of each reagent per 1000 parts by volume of isobutanol. The distillate is free from objectionable odour.

GENERAL.

It appears that by the alkali treatment referred to above the free and combined acids are removed and a considerable proportion of the free aldehydes is polymerised to non-volatile bodies. In the aniline and acid treatment anilides of the ketonic bodies appear to be formed, the acetals, which are not readily hydrolysed by alkalies, are decomposed by the free acid and then condense with the aniline, and the unsaturated bodies combine with the excess of acid. The quantity of brine and alkali and of aniline and sulphuric acid or phosphoric acid employed should be chosen with regard to the proportion in which the impurities are present in the alcohols. We have found convenient quantities to be 50% brine and 100—150% of 15—20% caustic soda solution calculated on the volume of alcohol treated. Of this caustic soda 66% or thereabouts is used as a scrubbing agent in the still head. The quantity of soda required for efficient scrubbing will depend upon a number of factors for example design of still and still head. The residue in the still may be reused for treating fresh batches after skimming off the oily and tarry condensation products. We have also found a convenient quantity of aniline and concentrated sulphuric acid or aniline and syrupy phosphoric acid to be about 5 parts by volume of each per 1000 parts by volume of alcohol treated.

The invention is not limited to the examples or to the quantities referred to above.

In place of aniline we may use homologues or derivatives of aniline containing acidic substituents in the nucleus, or other primary amines of comparatively high boiling point. In place of phosphoric acid sulphuric acid may be used.

Dated this 13th day of December, 1929.
MARKS & CLERK.

COMPLETE SPECIFICATION.

Improvements in and relating to the Purification of Alcohols.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a Company registered under the laws of Great Britain, of Imperial Chemical House, Millbank, London, S.W.1, JAMES WILSON ARMIT, of "Ebbacroft", 18, Woodcote Park Road, Epsom, in the County of Surrey, and GEORGE EDWIN WAINWRIGHT, of Norton Hall, The Green, Norton-on-Tees, in the County of Durham, both subjects of the King of Great Britain and Ireland, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the purification of alcohols.

The object of the invention is to provide a method for the purification of alcohols and in particular the purification of methyl alcohol and higher alcohols produced by the combination of carbon monoxide and hydrogen in the presence of a catalyst.

In the reaction in the presence of a catalyst between carbon monoxide and hydrogen, methyl, ethyl, propyl and higher alcohols are produced. At the same time fatty acids, esters, unsaturated hydrocarbons, aldehydes, acetals, ketones, ethers, mercaptans and alkyl sulphides are formed as by-products. The separation of these from any particular fraction of alcohol, particularly methyl alcohol, by fractionation may be considered as impracticable.

The invention consists in a process for the purification of alcohols which comprises submitting the alcohol to a preliminary distillation with caustic alkali, then mixing with the distillate small quantities of a primary amine of boiling point above the temperature of distilation of the alcohol mixture, together with phosphoric acid or sulphuric acid and fractionating the mixture.

The invention also consists in a process according to the preceding paragraph in which the primary amine is selected from aryl amines such as aniline or homologues of aniline or derivatives of aniline containing negative substituents in the nucleus, for example, sulphanilic acid.

The invention also consists in a process according to either of the preceding two paragraphs in which the caustic alkali addition contains brine.

The invention also consists in a modification of the process according to any of the preceding three paragraphs in which the two operations referred to as preliminary distillation and amine and acid treatment are carried out consecutively and continuously, for example, in a plant in which the hot vapours from the alkali scrubbing column are passed directly into a still fitted with a rectifying column and containing the required amine and acid, together with some of the boiling, alkali scrubbed, alcohol.

The invention also consists in a process according to any the preceding four paragraphs applied to the purification of alcohols produced by the combination of carbon monoxide and hydrogen in the presence of a catalyst.

The invention further consists in processes for the purification of alcohols substantially as hereinbefore described, and in purified alcohols when made by those processes or by the obvious chemical equivalents thereof.

The following examples illustrate how the invention may be carried into effect references to parts being by volume and to percentages being by weight:—

EXAMPLE 1.

To the crude methanol fraction of the product of the catalysed reaction between carbon monoxide and hydrogen are added half its bulk of saturated brine and a similar volume of 16—20% caustic soda solution. The oily top layer consisting of higher alcohols, hydrocarbons and the like, is separated off. The residue is distilled and the vapours scrubbed in the still head by a descending spray of 15—20% caustic soda solution. The quantity of soda required for efficient scrubbing will depend upon a number of factors for example design of still but in general not more than a volume equal to the volume of methanol will be required. The first fractions of the distillate may contain oily impurities (hydrocarbons, higher alcohols or the like) which are separated off by running into brine and returning the brine layer to the still. To the distillate free from oily impurities are added 5 parts of aniline and 5 parts of syrupy phosphoric acid (or 5 parts of concentrated sulphuric acid) per 1000 parts by volume and the whole is refractionated. These two operations may be carried out consecutively and continuously in a suitable still without condensation of the methanol after the soda treatment, for example, by means of a plant in which the hot vapours from the alkali scrubbing column are passed directly into a still fitted with a rectifying column and containing the required amine and acid together with some of the boiling, alkali scrubbed, alcohol.

The methanol thus obtained is of pleasant odour, gives a colourless solution with an equal volume of concentrated sulphuric acid and only very slowly decolourises N/30 potassium permanganate solution.

EXAMPLE 2.

The crude isobutanol fraction from the product of the interaction of carbon monoxide and hydrogen in presence of a suitable catalyst is distilled with alkali and then fractionated after addition of aniline and phosphoric acid or aniline and concentrated sulphuric acid to the extent of 5 parts by volume of each reagent per 1000 parts by volume of isobutanol. The distillate is free from objectionable odour.

GENERAL.

The invention is not limited to the purification of alcohols produced by the combination of carbon monoxide and hydrogen in the presence of a catalyst but the methods indicated herein apply to any alcohols containing the type of impurity of the character indicated no matter what the manner of synthesis or manufacture may be.

It appears that by the alkali treatment referred to above the free and combined acids are removed and a considerable proportion of the free aldehydes is polymerised to non-volatile bodies. In the aniline and acid treatment aniline condensation products of the ketonic and aldehydic bodies appear to be formed, the acetals, which are not readily hydrolysed by alkalis, are decomposed by the free acid and then condense with the aniline, and the unsaturated bodies combine with the excess of acid. The quantity of brine and alkali and of aniline and sulphuric acid or phosphoric acid employed should be chosen with regard to the proportion in which the impurities are present in the alcohols. We have found convenient quantities to be 50% brine and 100—150% of 15—20% caustic soda solution calculated on the volume of alcohol treated. Of this caustic soda 66% or thereabouts is used as a scrubbing agent in the still head. The quantity of soda required for efficient scrubbing will depend upon a number of factors for example design of still and still head. The residue in the still may be reused for treating fresh batches after skimming off the oily and tarry condensation products. We have also found a convenient quantity of aniline and concentrated sulphuric acid or aniline and syrupy phosphoric acid to be about 5 parts by volume of each per 1000 parts by volume of alcohol treated.

The invention is not limited to the examples or to the quantities referred to above.

In place of aniline we may use homologues of aniline or derivatives of aniline containing negative substituents in the nucleus, such as for example, sulphanilic acid. In place of phosphoric acid we may use sulphuric acid.

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

1. A process for the purification of alcohols which consists in submitting the alcohol to a preliminary distillation with caustic alkali, then mixing with the distillate small quantities of a primary amine of boiling point above the temperature of distillation of the alcohol mixture, together with phosphoric acid or sulphuric acid and fractionating the mixture.

2. A process as claimed in Claim 1 in which the primary amine is selected from aryl amines such as aniline or homologues of aniline or derivatives of aniline containing negative substituents in the nucleus, for example, sulphanilic acid.

3. A process as claimed in Claim 1 or Claim 2 in which the caustic alkali addition contains brine.

4. A modification of the process claimed in any of the above claims in which the two operations referred to as preliminary distillation and amine and acid treatment are carried out consecutively and continuously, for example, in a plant in which the hot vapours from the alkali scrubbing column are passed directly into a still fitted with a rectifying column and containing the required amine and acid, together with some of the boiling, alkali scrubbed, alcohol.

5. A process as claimed in any of the above claims applied to the purification of alcohols produced by the combination of carbon monoxide and hydrogen in the presence of a catalyst.

6. Processes for the purification of alcohols substantially as hereinbefore described.

7. Purified alcohols when made by the processes hereinbefore described and claimed or by the obvious chemical equivalents thereof.

Dated this 15th day of July, 1930.

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