PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Improvements in and relating to the Purification of Methanol and other Alcohols of Boiling Point below 100° C.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a Company registered under the laws of Great Britain, of Imperial Chemical House, Millbank, London, S.W.1, and JAMES WILSON ARMIT, a subject of the King of Great Britain and Ireland, of "Ebbacroft", 18, Woodcote Park Road, Epsom, in the County of Surrey, do hereby declare the nature of this invention to be as follows:—

This invention relates to the purification of methanol and other alcohols of boiling point below 100° C. and more specifically to the purification of methanol produced by the combination of carbon monoxide and hydrogen in the presence of a catalyst.

The by-products in the series of reactions involved in this and like processes may be fatty acids, esters, unsaturated hydrocarbons, aldehydes, acetals, ketones, ethers, mercaptans and alkyl sulphides. The free and combined acid, part of the mercaptans and much of the free aldehyde can be removed by treatment with alkali. In the lowest boiling fraction of methanol, mercaptans alkyl sulphides, low boiling ethers (for example dimethyl ether), and unsaturated bodies are objectionable impurities, and render the methanol unsuitable for various technical applications.

The principal object of the invention is to provide a process for purifying methanol and other alcohols of boiling point below 100° C. so that it is free of the disadvantages referred to above.

The invention in brief consists in the process which comprises the treatment of impure methanol or other alcohols of boiling point below 100° C. such as that referred to above with a halogen for example chlorine or bromine preferably in amount not less than that required to satisfy the unsaturated value of the methanol as determined by the Wijs or other suitable methods, the methanol or other alcohols of boiling point below 100° C. then preferably being fractionated and the vapours then preferably being scrubbed free from halogen acid by passing through hot alkali.

[*Price* 1/-]

The invention also consists in processes for the purification of methanol and other alcohols of boiling point below 100° C. especially methanol produced by the combination of carbon monoxide and hydrogen in the presence of a catalyst substantially as herein described and in products when made by these processes or by the obvious chemical equivalents thereof.

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

EXAMPLE 1.

1000 parts of crude anhydrous methanol of iodine value of 6.35 as determined by the Wijs method has chlorine passed into it until the weight has increased by about 1.8 to 2 parts.

The methanol is then distilled from a hot water bath, the vapours being passed through a bubbler containing caustic soda solution before passing to the fractionating column, the product being collected in the temperature range about 64.5° C. to 65° C. at a pressure of 760 mm.

EXAMPLE 2.

1000 parts of unpurified methanol with an iodine value of 12.7 by the Wijs method are treated with 8 parts of bromine and then fractionally distilled, the product distilling between about 64.5° C. and 65° C. being collected.

GENERAL.

By working as described above crude methanol of bad odour may be converted into methanol of good odour and substantial purity. Apparently the halogen combines with the alkyl sulphides giving dihalogen compounds, and also adds on to the other unsaturated bodies; other impurities are also apparently chlorinated or brominated with liberation of the corresponding halogen acid.

As regards fractionation, the halogenated bodies are apparently separated thereby. If the alcohol be anhydrous, these remain in the still. If a little water be present part at least of the halogenated hydrocarbons comes over in the first fraction as an azeotropic mixture with the

water, but the dihalides of the alkyl sulphide remain in the still.

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

COMPLETE SPECIFICATION.

Improvements in and relating to the Purification of Methanol and other Alcohols of Boiling Point below 100° C.

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, a Company registered under the laws of Great Britain, of Imperial Chemical House, Millbank, London, S.W.1, and JAMES WILSON ARMIT, a subject of the King of Great Britain and Ireland, of "Ebbacroft", 18, Woodcote Park Road, Epsom, in the County of Surrey, 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 methanol and other alcohols of boiling point below 100° C. and more specifically to the purification of methanol produced by the combination of carbon monoxide and hydrogen in the presence of a catalyst.

The by-products in the series of reactions involved in this and like processes may be fatty acids, esters, unsaturated hydrocarbons, aldehydes, acetals, ketones, ethers, mercaptans and alkyl sulphides. The free and combined acid, part of the mercaptans and much of the free aldehyde can be removed by treatment with alkali. In the lowest boiling fraction of methanol, mercaptans, alkyl sulphides, low boiling ethers (for example dimethyl ether), and unsaturated bodies are objectionable impurities, and render the methanol unsuitable for various technical applications.

The principal object of the invention is to provide an improved or modified process for purifying methanol and other alcohols of boiling point below 100° C. so that they are free of the disadvantages referred to above.

The invention in brief consists in a process for the purification of alcohols of boiling point below 100° C., for example, methanol, especially methanol as produced by the combination of carbon monoxide and hydrogen in the presence of a catalyst which consists in treating the impure alcohol with a halogen, in amount not less than that required to satisfy the unsaturated value of the alcohol as determined by the Wijs or like method, distilling the product and then removing free halogen acid from it by means of alkali and then fractionating.

The invention also consists in a process according to the preceding paragraph, in which the distilled but still uncondensed halogenated alcohol vapour is passed through hot alkali, and the thus scrubbed vapour fractionally condensed.

The invention also consists in a modification of the process according to the preceding paragraph, in which the distillate from the halogenated product is condensed, alkali added thereto, and the mixture fractionally distilled.

The invention also consists in processes for the purification of methanol and other alcohols of boiling point below 100° C. especially methanol produced by the combination of carbon monoxide and hydrogen in the presence of a catalyst substantially as herein described and in products when made by these processes or by the obvious chemical equivalents thereof.

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

EXAMPLE 1.

100 parts of crude anhydrous methanol of iodine value of 6.35 grammes per 100 grammes as determined by the Wijs method has chlorine passed into it until the weight has increased by about 1.8 to 2 parts.

The methanol is then distilled from a hot water bath, the vapours being passed through a bubbler containing caustic soda solution before passing to the fractionating column, the product being collected in the temperature range about 64.5° C. to 65.5° C. at a pressure of 760 mm.

EXAMPLE 2.

100 parts of unpurified methanol with an iodine value of 12.7 grammes per 100 grammes by the Wijs method are treated with 8 parts of bromine and then fractionally distilled, the product distilling between about 64.5° C. and 65.5° C. being collected, the fractionated and condensed product being then treated for the removal of halogen acid by means of alkali, and being again fractionated.

GENERAL.

By working as described above crude methanol of bad odour may be converted

into methanol of good odour and substantial purity. The invention is not, however, limited to the purification of methanol or 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 impurities of the type referred to above and of boiling point below 100° C. no matter what the manner of synthesis or manufacture may be.

Apparently the halogen combines with the alkyl sulphides giving dihalogen compounds, and also adds on to the other unsaturated bodies; other impurities are also apparently chlorinated or brominated with liberation of the corresponding halogen acid.

As regards fractionation, the halogenated bodies are apparently separated thereby. If the alcohol be anhydrous, these remain for the most part in the still. If a little water be present part at least of the halogenated hydrocarbons comes over in the first fraction as an azeotropic mixture with the water, but the dihalides of the alkyl sulphide remain in the still.

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 of boiling point below 100° C., which consists in treating the impure alcohol with a halogen, in amount not less than that required to satisfy the unsaturated value of the alcohol as determined by the Wijs or like method, distilling the product and then removing free halogen acid from it by means of alkali and then fractionating.

2. A process as claimed in Claim 1, in which the distilled but still uncondensed halogenated alcohol vapour is passed through hot alkali, and the thus scrubbed vapour fractionally condensed.

3. A process as claimed in Claim 1, in which the distillate from the halogenated product is condensed, alkali added thereto, and the mixture fractionally distilled.

4. A process as claimed in any of the above claims applied to the purification of methanol.

5. A process as claimed in any of Claims 1 to 3 applied to the purification of methanol produced by the combination of carbon monoxide and hydrogen in the presence of a catalyst.

6. Processes for the purification of alcohols of boiling point below 100° C. substantially as described.

7. Purified alcohols of boiling point below 100° C. when prepared by processes as herein described and claimed or by the obvious chemical equivalents of those processes.

Dated this 21st day of July, 1930.

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