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PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Improvements in the Manufacture of Higher Alcohols.

We, WILLIAM GARETH DAVIS, a British Subject, of Norton Hall, The Green, Norton-on-Tees, County Durham, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Broadway Buildings, Broadway, Westminster, London, S.W. 1, do hereby declare the nature of this invention to be as follows:—

In the synthetic manufacture of higher alcohols, such as isobutanol, by passing mixtures of carbon monoxide and hydrogen under pressure over catalysts at elevated temperatures, a reaction product is obtained which contains besides higher alcohols certain amounts of methanol and of water. The separation of the higher alcohols, chiefly isobutanol, from this mixture is however a matter of difficulty, and if a distillation of the crude reaction product is carried out a distillate containing methanol and water is obtained, although the greater part of the methanol may be removed in this way. The oil obtained by such a distillation may contain 75 per cent., higher alcohols, 15 per cent. methanol and 10 per cent. water, and from such a mixture anhydrous higher alcohols cannot be obtained in good yield by distillation alone owing to the existence of a pseudo azeotropic vapour mixture of higher alcohols, methanol and water, these three substances distilling together in practically constant proportion. We have found however that if a product rich in higher alcohols such as the aforesaid distillation residue be treated with a salting-out solution, the higher alcohol layer obtained contains only small amounts of water and of methanol, e.g. 3 per cent. of each, and from this mixture anhydrous higher alcohols can readily be isolated by distillation.

The present invention therefore consists in performing a salting-out operation on the mixture of higher alcohols, methanol and a relatively small proportion of water such as results from a primary distillation of the crude product of the synthetic process. The invention further consists in a combination of steps in the treatment of synthetic higher alcohols, including the sequence of operations of salting-out and distillation, with return of the first runnings to the salting-out operation.

[*Price* 1*s*.]

The principal object of the invention is to provide a continuous process for the isolation of anhydrous higher alcohols while avoiding the use of chemical dehydrating agents such as calcium chloride, potassium carbonate etc.

EXAMPLE.

Crude liquor containing 25 per cent. of higher alcohols, 60 per cent. of methanol, 15 per cent. of water and traces of other substances, was distilled until 90 per cent. of the methanol had been driven off and a liquor containing about 75 per cent. higher alcohols, 15 per cent. methanol and 10 per cent. water was left. Further distillation of a sample of this liquor resulted in a distillate containing enhanced proportions of methanol and water compared with higher alcohols, and the yield of anhydrous fusel oil was only about 10—20 per cent. of the original amount in the sample. However, when the main quantity of distillation residue containing 75 per cent. higher alcohols was extracted with saturated brine, a layer containing 92 per cent. higher alcohols, 3 per cent. of methanol and 5 per cent. of water was obtained. By distillation of this mixture a large yield of anhydrous higher alcohol was obtained, the first distillates containing water and methanol being returned to the brine extractor. The brine solution was distilled to recover the methanol and after saturation was returned to the extractor.

On an industrial scale the process would be carried out continuously by employing a continuous still, taking off methanol from the top of the still column and the 75 per cent. higher alcohol liquor from an intermediate plate of the column. The extraction with brine would also be rendered continuous by passing the alcoholic liquor in fine drops upwards through a body of brine contained in a tower, the upper layer of enriched higher alcohols being taken off at an overflow and a continuous withdrawal of brine being effected at the base of the tower.

Dated this 20th day of March, 1928.

W. P. THOMPSON & Co.,
12, Church Street, Liverpool,
Chartered & Registered Patent Agents.

COMPLETE SPECIFICATION.

Improvements in the Manufacture of Higher Alcohols.

We, WILLIAM GARETH DAVIS, a British Subject, of Norton Hall, The Green, Norton-on-Tees, County Durham, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Imperial Chemical House Millbank, London, S.W. 1, formerly of Broadway Buildings, 50—60, Broadway Westminster, London, S.W. 1, 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:—

In the synthetic manufacture of higher alcohols, such as isobutanol, by passing mixtures of carbon monoxide and hydrogen under pressure over catalysts at elevated temperatures, a reaction product is obtained which contains besides higher alcohols certain amounts of methanol and of water. The separation of the higher alcohols, chiefly isobutanol, from this mixture is however a matter of difficulty, and if a distillation of the crude reaction product is carried out a distillate containing methanol and water is obtained, although the greater part of the methanol may be removed in this way. The oil obtained by such a distillation may contain 75 per cent. higher alcohols, 15 per cent. methanol and 10 per cent. water, and from such a mixture anhydrous higher alcohols cannot be obtained in good yield by distillation alone owing to the existence of a pseudo azeotropic vapour mixture of higher alcohols, methanol and water, these three substances distilling together in practically constant proportion. We have found however that if a product rich in higher alcohols such as the aforesaid distillation residue be treated with a salting-out solution, the higher alcohol layer obtained contains only small amounts of water and of methanol, e.g. 3 per cent. of each, and from this mixture anhydrous higher alcohols can readily be isolated by distillation.

The present invention therefore consists in performing a salting-out operation on the mixture of higher alcohols, methanol and a relatively small proportion of water such as results from a primary distillation of the crude product of the synthetic process. The invention further consists in a combination of steps in the treatment of synthetic higher alcohols, including the sequence of operations of salting-out and distillation, with return of the first runnings to the salting-out operation.

The principal object of the invention is to provide a continuous process for the isolation of anhydrous higher alcohols while avoiding the use of chemical dehydrating agents such as calcium chloride, potassium carbonate etc.

EXAMPLE.

Crude liquor containing 25 per cent. of higher alcohols, 60 per cent. of methanol, 15 per cent. of water and traces of other substances, was distilled until 90 per cent. of the methanol had been driven off and a liquor containing about 75 per cent. higher alcohols, 15 per cent. methanol and 10 per cent. water was left. Further distillation of a sample of this liquor resulted in a distillate containing enhanced proportions of methanol and water compared with higher alcohols, and the yield of anhydrous fusel oil was only about 10—20 per cent. of the original amount in the sample. However, when the main quantity of distillation residue containing 75 per cent. higher alcohols was extracted with saturated brine, a layer containing 92 per cent. higher alcohols, 3 per cent. of methanol and 5 per cent. of water was obtained. By distillation of this mixture a large yield of anhydrous higher alcohol was obtained, the first distillates containing water and methanol being returned to the brine extractor. The brine solution was distilled to recover the methanol and after saturation was returned to the extractor.

On an industrial scale the process would be carried out continuously by employing a continuous still, taking off methanol from the top of the still column and the 75 per cent. higher alcohol liquor from an intermediate plate of the column. The extraction with brine would also be rendered continuous by passing the alcoholic liquor in fine drops upwards through a body of brine contained in a tower, the upper layer of enriched higher alcohols being taken off at an overflow and a continuous withdrawal of brine being effected at the base of the tower.

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. Process for the separation of higher alcohols from the crude product of the catalytic hydrogenation of oxides of carbon, which consists in distilling the crude product to remove the bulk of the

methanol and to isolate a fraction rich in higher alcohols, and treating the said fraction with a salting-out solution.

2. Process as claimed in Claim 1 in which the higher alcohol fraction after the salting-out operation is distilled, the first runnings containing water and methanol are returned to the salting-out step, and the higher alcohols are recovered in a substantially anhydrous state.

3. Process as claimed in Claim 1 or 2 in which brine is used as the salting out solution.

4. Process as claimed in Claims 1, 2 or 3 in which the salting out solution is distilled to recover methanol therefrom.

5. Continuous process for the separation of higher alcohols substantially as described.

6. Higher alcohols whenever prepared or produced by the method described and claimed above.

Dated this 20th day of December, 1928.

W. P. THOMPSON & Co.,
12, Church Street, Liverpool,
Chartered & Registered Patent Agents.

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[Wt. 51A.—125/9/1929.]