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PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION.

Improvements in the Recovery of Methanol.

We, WILLIAM JOSEPH VICTOR WARD, 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 in addition to higher alcohols, substantial quantities of methanol and also small quantities of unsaturated compounds of an unpleasant odour. When an attempt is made to isolate by distillation the higher alcohols and methanol from the crude reaction product, unpleasant bodies come off with the methanol fraction and it is impossible to effect a satisfactory purification of the methanol from these substances by further distillation. We have now found, however, that by treating the impure methanol with a salting-out solution and a a solvent for hydrocarbons, especially a hydrocarbon such as benzol, that the obnoxious impurities are taken up by the hydrocarbon solvent and the methanol subsequently distilled from the salt solution, after separation from the solvent layer, furnishes methanol of good quality and substantially free from unsaturated bodies.

EXAMPLE.

The crude reaction product obtained by passing a mixture of 50 per cent. carbon monoxide and 50 per cent. hydrogen under a pressure of 200 atmospheres over a catalyst comprising 27 per cent. zinc oxide, 50 per cent. chromium oxide and 23 per cent. manganese oxide, at a temperature of 410° C. and a space velocity of 12,000 was distilled and the methanol fraction collected. It was of obnoxious smelling character and on dilution with water produced a turbidity. Its bromine value was 1.4 (grams of bromine absorbed per 100 c.c. of sample).

300 c.c. of this impure methanol were shaken with 600 c.c. of saturated brine solution and 50 c.c. of benzene. The benzene layer was removed and the extraction repeated with 20 c.c. of fresh benzene to remove fine droplets not separated at first. The brine solution was then distilled and successive fractions of 20, 20 and 200 c.c. were collected. Their bromine numbers were 1.85, 0.64 and 0.1 respectively. The last fraction produced no turbidity on dilution with water. Accordingly, the main fraction of the methanol, after rejection of "tops" represented high-grade methanol.

A blank experiment in which crude methanol, obtained in the manner described above, was distilled and the bromine values of the various fractions noted, gave the following results:—

First 10 c.c. -	- Bromine No.	1.74
Second 10 c.c. -	,, ,,	1.77
Next 30 c.c. -	,, ,,	1.60
Next 200 c.c. -	,, ,,	1.2

It is therefore evident that very little improvement in the quality of the methanol is effected by distillation alone.

The impurities taken up by the hydrocarbon solvent may be separated by distillation and the purified solvent used again.

Dated this 20th day of March, 1928.
W. P. THOMPSON & Co.,
12, Church Street, Liverpool,
Chartered & Registered Patent Agents.

COMPLETE SPECIFICATION.

Improvements in the Recovery of Methanol.

We, WILLIAM JOSEPH VICTOR WARD, a British Subject, of Norton Hall, The Green, Norton-on-Tees, County Durham, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, a British Company, of Broadway Buildings, 50—60, Broadway, Westminster, London, S.W. 1, do hereby declare the nature of this invention and

[*Price* 1/-]

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 in addition to higher alcohols, substantial quantities of methanol and also small quantities of compounds of an unpleasant odour, e.g. unsaturated hydrocarbons. When an attempt is made to isolate by distillation the higher alcohols and methanol from the crude reaction product, unpleasant bodies come off with the methanol fraction and it is impossible to effect a satisfactory purification of the methanol from these substances by further distillation. We have now found, however, that by treating the impure methanol with a salting-out solution and a solvent for hydrocarbons which is substantially immiscible with the mixture of crude methanol and the salting-out solution especially a hydrocarbon such as benzene, the obnoxious impurities are taken up by the hydrocarbon solvent and the methanol subsequently distilled from the salt solution, after separation from the solvent layer, furnishes methanol of good quality and substantially free from impurities.

Example 1.

The crude reaction product obtained by passing a mixture of 50 per cent. carbon monoxide and 50 per cent. hydrogen under a pressure of 200 atmospheres over a catalyst comprising 27 per cent. zinc oxide, 50 per cent. chromium oxide and 23 per cent. manganese oxide, at a temperature of 410° C. and a space velocity of 12,000 was distilled and the methanol fraction collected. It was of obnoxious smelling character and on dilution with water produced a turbidity. Its bromine value was 1.4 grams of bromine absorbed per 100 c.c. of sample.

800 c.c. of this impure methanol were shaken with 600 c.c. of saturated brine and 50 c.c. of benzene. The benzene layer was removed and the extraction repeated with 20 c.c. of fresh benzene to remove fine droplets not separated at first. The brine solution was then distilled and successive fractions of 20, 20 and 200 c.c. were collected. Their bromine numbers were 1.85, 0.64 and 0.1 respectively. The last fraction produced no turbidity on dilution with water. Accordingly, the main fraction of the methanol, after rejection of "tops" represented high-grade methanol.

A blank experiment in which crude methanol, obtained in the manner described above, was distilled and the bromine values of the various fractions noted, gave the following results:

First 10 c.c.	-	Bromine No.	1.74
Second 10 c.c.	-	,, ,,	1.77
Next 30 c.c.	-	,, ,,	1.60
Next 200 c.c.	-	,, ,,	1.2

It is therefore evident that very little improvement in the quality of the methanol is effected by distillation alone.

The impurities taken up by the hydrocarbon solvent may be separated by distillation and the purified solvent used again.

Example 2.

A mixture of methanol obtained along with other alcohols, by the catalyst hydrogenation of the oxides of carbon with 15—20 per cent. of its volume of benzene was supplied to the base of a column containing brine (70—80 per cent. saturated solution). The impure benzene was taken off at the head of the column and the brine/methanol mixture at the base. The brine/methanol mixture was distilled so that about 20 per cent. of the methanol was removed, together with the small quantities of benzene and impurities associated with the crude mixture. The residue was then transferred to another still, from which pure methanol was collected. The bromine number of the pure methanol was 0.1; that of the first distillate from the crude mixture was 2.0. The benzene taken off at the top of the extraction column was purified by distillation, the impurities being taken off at the top of the still column and the pure benzene at an intermediate plate. The impurities for the most part, consisting of higher-boiling hydrocarbons, remained 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. Process for the purification of synthetic methanol obtained simultaneously with higher alcohols by the catalytic hydrogenation of oxides of carbon, which consists in treating it with a salting-out solution and a solvent for hydrocarbons which is substantially immiscible with the mixture of crude methanol and the salting-out solution.

2. Process as claimed in claim 1 in which a hydrocarbon is used as the solvent for hydrocarbons.

3. Process as claimed in Claim 2 in which benzene is used as the solvent for hydrocarbons.

4. Process for the production of purified

synthetic methanol as claimed in claim 1 in which the mixture of methanol and the salting-out solution, after separation from the solvent, is distilled and the main body of pure distillate collected separately from the first runnings.

5. Process as claimed in claims 1, 2 and 3 in which the solvent, after separation from the mixture of methanol and salting-out solution, is purified by distillation, the main body of purified distillate being collected separately from the more volatile impurities.

6. Process as claimed in claims 1, 2 and 3 in which brine is used as the salting-out solution.

7. Process as claimed in claim 6 in which unsaturated brine is used, preferably of strength equal to 70—80 per cent. of the saturated solution.

8. Process for the purification of methanol substantially as described.

9. Synthetic methanol whenever purified by the processes above described and claimed.

Dated this 20th day of December, 1928.

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

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