

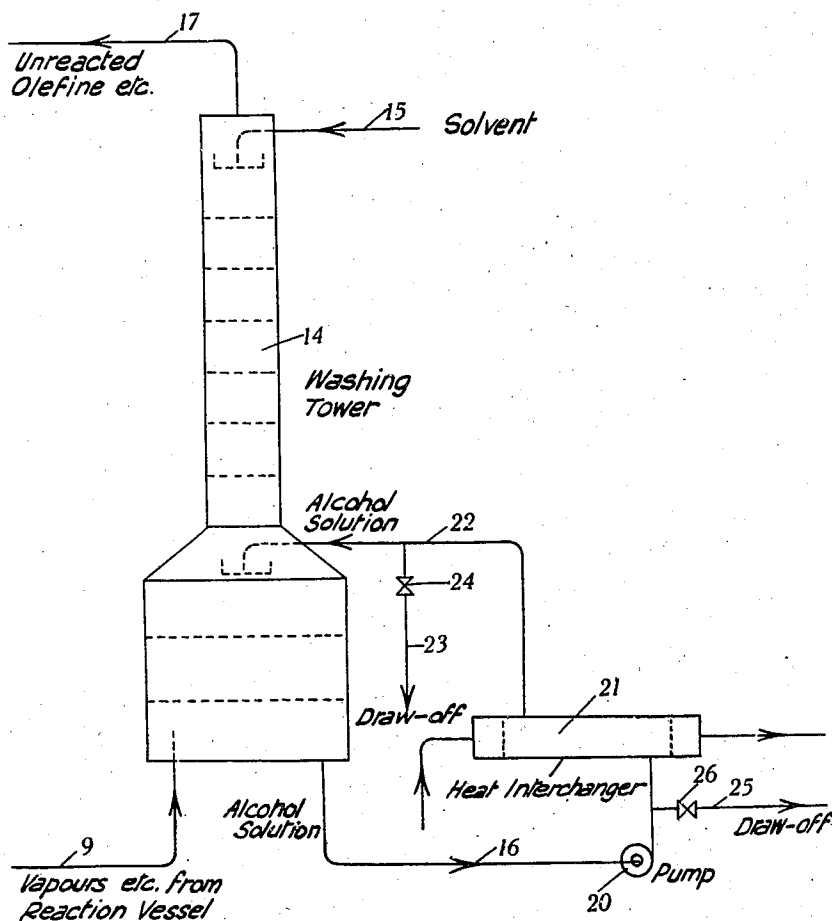
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RECOVERY OF ALCOHOLS FROM OLEFINE HYDRATION PRODUCTS

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RECOVERY OF ALCOHOLS FROM OLEFIN
HYDRATION PRODUCTSHenri Martin Guinot, Niort, France; vested in the
Allen Property CustodianApplication August 15, 1939, Serial No. 290,317
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1 Claim. (Cl. 260—643)

This invention relates to the recovery of alcohols from olefin hydration products.

It is known that olefins such as ethylene, propylene and the butylenes can be hydrated to give alcohols in the presence of certain hydration catalysts, such as sulphuric acid. Various authors have shown that, under certain conditions of acidity and temperature, it was possible to eliminate the alcohol from the reaction vessel by entraining or by distillation.

In a recent patent specification of application Serial No. 240,593 the applicants have emphasized the necessity of not allowing the hydrating bath to increase considerably in alcohol content in order to avoid secondary reactions which lead finally to loss of yield and which are indicated by destruction of the hydrating reagent, in other words, it is necessary to eliminate the alcohol from the reaction bath as soon as it is formed. The applicants had found that this was an essential condition for the satisfactory operation of the process.

It has previously been proposed to pass a mixture of olefin and water vapour under pressure into an acid catalyst at a suitable concentration, and to cool the resulting gases to separate therefrom, by condensation, the entrained alcohol, before returning them to the hydrating bath.

Now it has been found that in carrying out this previously proposed process the rapid elimination of alcohol from the hydrating bath takes place under unfavourable conditions, since gases charged with water and alcohol give up this latter with difficulty. In particular, when it is sought, as in the process previously proposed, to separate the alcohol contained in the gases by simple cooling, it is observed that only quite a small portion of the alcohol entrained in the body of circulating gases, condenses, so that the residual gases returned to the hydrating bath cause the major proportion of the alcohol which it was desired to eliminate, to accumulate in this bath. There results from this not only a very reduced speed of production, but also the usual disadvantages arising from an excessive proportion of alcohol in the hydrating bath, that is to say, the production of polymers, damage to the bath and diminution of yield.

The following example shows the importance of the discovery set forth above.

If 1000 m.³/hour of propylene are made to circulate through a hydrating bath formed by a ton of sulphuric acid of 60% strength and raised to a temperature of 100°, isopropyl alcohol is formed which is entrained, as soon as it is pro-

duced, by the unabsorbed gases. It is observed that in cooling the gases to 30° C. for example, in a water-cooled condenser, 130 litres per hour of an aqueous solution containing 9% of isopropanol can be separated: but the gases which return to the circuit are saturated with the vapour emitted by these 9% alcoholic solutions, the said vapours being about 60% isopropanol, so that if the gases leaving the condenser are submitted to a very intense cooling (down to about -15° C. for example) another 90 litres per hour of 50% isopropanol solution are condensed, i. e., 45 kg. of pure isopropanol.

Thus in the previous process, for 56.7 kg. of isopropanol obtained, 45 kg. or 80% of the whole return to the hydrating bath, whereas only 11.5 kg. are retained by the water cooled condenser.

It will therefore be understood that the simple condensation at ordinary temperature specified in the previous process is absolutely insufficient, and that it is necessary to take very efficacious supplementary measures if it is desired to avoid the inconveniences mentioned above.

As previously indicated, intense cooling of the gases is a possible way of removing the alcohol from the body of gases after leaving the hydrating bath, but it would be quite difficult to carry out economically in industrial practice the cooling to -15° C. of a considerable body of gas charged with condensable vapours and having a high latent heat.

Now it has been discovered that the alcohol may be separated from the body of gases with which, in a vapour state, it is mixed, in a manner which is both economical and effective by the use of a solvent which has a selective solvent capacity for alcohol as compared with olefins.

According, therefore, to the present invention, there is provided a process of hydrating olefins by passing a stream of olefin-containing gas through a hydrating bath, in which the alcohol entrained in the gases leaving the bath is separated therefrom by means of a solvent having a selective solvent capacity for alcohols as compared with olefins.

The following are examples of solvents which can be used: pure water, organic substances such as cresols and their homologues, the higher alcohols like cyclohexanol, glycol, glycerine, alone or mixed, salt solutions such as solutions of calcium chloride.

The accompanying drawing illustrates diagrammatically a suitable arrangement of apparatus for carrying out the present invention, and

wherein the figure shows an arrangement for removing the alcohol for the circulating olefin-containing gases.

According to this invention, after hydration, instead of making a preliminary separation by condensation precede the washing, the condenser may be eliminated and a tower 14 arranged in such a manner that it operates alone as an injection condenser, in this case it serves at the same time for cooling the gases, for condensing the vapours and for extracting the alcohol. However, the quantity of washing water which it is normally necessary to use to obtain an alcoholic solution of sufficiently high concentration at the base of the tower will be too small to absorb the excess of calories brought over by the gases and vapours. It is therefore advantageous to utilise for this purpose the alcoholic solution itself in accordance with the arrangement described below and illustrated.

At the top of the washing tower 14, there is introduced by the pipe 15 a convenient quantity of solvent (water for example) which circulates in counter-current in relation to the gases and vapours coming from the reaction vessel (not shown) and which enter the tower at 9. The alcoholic solution which flows away at the base of the tower through the tube 16 is taken by a pump 20, cooled in a heat interchanger 21 and returned to the tower at 22. This alcoholic solution thus circulates in a closed circuit in the lower zone of the washing tower where it ensures the cooling of the gases. A part of this solution is withdrawn at the desired speed at any point of the circuit, for example by the pipe 23 provided with a stop-cock 24, or, preferably, before cooling by the pipe 25 provided with a stop-cock 26, whereas the gases exhausted of alcohol leave at the top of the washing tower by the pipe 17 in order to be returned to the hydrating circuit.

The two following non-limitative examples will make the operation of this process of alcohol elimination, more clearly understood.

Example 1

1000 m.³ per hour of ethylene are circulated in a bath formed of 72% sulphuric acid heated to 130° and there is thus formed 11 kg. per hour of ethyl alcohol.

By making the gases leaving the reaction vessel pass into a tower supplied with water and operating like an injection condenser the 11 kg. of alcohol are withdrawn in the form of a 5° Gay Lussac solution where as if operation had been by simple cooling of the gases to 30° C. there would only have been separated 4.8 kg. of alcohol.

Example 2

1000 m.³ per hour of propylene are circulated in a bath formed by a ton of 60% sulphuric acid heated to 100°, from whence they emerge charged with 54 kg. of isopropanol. These gases are washed with 500 kg. per hour of butyl cresol in the washing tower 14, from the base of which there is withdrawn a 10% solution of isopropanol which is separated from the butyl cresol by distillation.

What I claim is:

In a process for the hydration of olefins which consists essentially in passing a stream of olefin-containing gases through an acid hydrating bath, the steps of passing the mixture of vapours and gases leaving the bath through a tower in which it passes in counter-current to a solvent selected from the group consisting of water, cresols and their homologues, higher alcohols and mixtures thereof, withdrawing the solution of alcohol in the solvent used at the base of said tower, cooling said solution in a heat interchanger, returning said cooled solution to a point in the tower intermediate the mixture and solvent inlets to assist in the condensation and dissolving of the alcohol and withdrawing a proportion of the solution from the tower through the circuit in which the heat interchanger is located.

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