Standard Oil Company 4/12
(Indiana)

INFORMATION DIVISION TRANSLATION T46-70

API-TOM Reel 68, Frames 408, 410, 412 and 414 - June 26, 1943

Plan for a Process to Dealcoholize Hydrocarbon-Alcohol Mixtures

In the synthetic production of hydrocarbons there are formed often mixtures of hydrocarbons with a certain content of alcohols, which causes trouble in the technical utilization of the hydrocarbon. Therefore, one is cautioned to take out most completely as possible the alcohol that is contained in the hydrocarbon. So far, one uses predominantly acids or acid-reacting salt solutions like sulfuric acid, phosphoric acid, and zinc chloride solution. Good results have been obtained with these agents generally. But a disadvantage is connected with their use. The dealcoholization of hydrocarbon is connected with a large fixed consumption of expensive reagents. Also, their use requires in the large scale technique acid resistant apparatus materials. This causes a further difficulty for the technical operation. Also, in these processes the alcohol cannot be recovered because they are altered by the reagents.

It is now known that the dealcoholization of hydrocarbons can be successful with avoiding the mentioned disadvantages. It has to be carried out with the aid of solutions of surface active materials, in place of the mentioned acid reagent, at normal temperatures or with increased temperatures up to about 100°C. Primarily aqueous or aqueous-alcoholic solutions of fatty acid or sulfonic acid salts have proven themselves as suitable. The concentration of these solutions is kept between 5 and 25%, preferably around 10% referred to the saponified acids. It is advised to maintain a pH of 7.0-9.5 in the solutions that are caused for alcohol elimination. It is practical to measure the amount of soap solution that is to be used for dealcoholization in the following manner: the acid molecules should be equal to or more than the amount of alcohol molecules that are to be taken out. Particular advantages are caused by the possibility to carry out the process according to the invention in simple manner by allowing a throughput of circulation of the solution of the surface-active materials. The returning occurs in this case after taking out of the alcohol with solvents that are not water-soluble.

The invented process presents a considerable progress over the methods that were used till now for the dealcoholization of hydrocarbons. Any amount of alcohol-containing hydrocarbons can be freed of its alcohol content with a certain amount of solution of surface-active material through regeneration and therefore unlimited repeated utilization. Because of the operation of the solution in a pH range of 7.0-9.5 there exists the possibility to use simple apparatus constructive materials because the solutions that are used do not act corroding on the container parts with which they come in contact.

The operation of the process is explained through the following examples:

Operation Example 1

1000 cc of a synthetic hydrocarbon oil with density $d_{20}=0.799$, in the boiling range 180-290°C, and a OH number of 40 was stirred for two hours at room temperature (about 20°C) with 2000 cc of a soap solution of the density 0.984, containing 10 wt.% of fatty acid with a saponification number of 260, a pH value of 9.1, as well as an ethyl alcohol content of 10 wt.%. After stopping the stirrer, one obtained two layers that were separated. The upper oil layer consisted of 910 cc neutral oil with the following characterisation numbers:

$d_{20}=0.766$, OH number equals 1

From the lower aqueous layer, 245 g fatty acid was obtained by acidifying with a density $d_{20}=0.871$, saponification No. 199, OH number 126.

The alcohols that were present in the charge oil were absorbed by the soap solution to about 97.5% (Trans.?)

Operation Example 2

500 cc of the same oil as in Example 1 stirred with 1000 cc of a solution of 200 g. 45% sulfonate for two hours at room temperature. One obtained an emulsion which separated into two layers upon addition of about 150 cc ethyl alcohol. The upper layer resulted in 450 cc of density$_{20}$=0.766, OH number = 1 after 3 times washing with 10% ethyl alcohol and subsequent water washing. Thus the alcohols are taken out with the use of solutions of sulfonic acids salts with the same action as has been reached with the use of fatty acids salts.

Operation Example 3

50 cc Diesel oil, of an OH number of 20 and a density of $d_{20}=0.769$, were emulsified for an hour with 150 cc of soap solution which was circulated in the emulsifier E-1, and was separated in the separation vessel T-1. The upper layer of this oil goes into the emulsifer E-2 where it is again emulsified with 150 cc soap solution. Afterwards the separation of soap solution and hydrocarbon takes place in the separation vessel T-2. The soap solution that runs off from T-2 is put into the emulsifier E-1 while the soap solution that runs off from T-1 is conducted into the extractors P-1 and P-2 consecutively. The alcohols that have accumulated in the soap solution and the neutral oil dissolved in it are washed out from the soap solution in the extractors by means of water-insoluble solvent, for instance naphtha or benzol. The soap solution that runs off P-2 is put into the ~~emulsifier E-2. The Diesel oil that has been treated has a density of 0.766.~~ The alcohol removal occurs up to 97%.

Patent Claims

1. A process for dealcoholization of hydrocarbon-alcohol mixtures and such. The mixture is extracted with solutions of surface active materials particularly of fatty acids or sulfonic acid salts at normal temperatures or increased temperature up to about 100°C.

2. Process according to claim 1 in which for dealcoholization one uses aqueous or aqueous-alcoholic solution.

3. Process according to claim 1 and 2 in which the amount of soap solution that is used for dealcoholization is measured in such a manner that the use amounts of acid moles is equal to or more than the amount of alcohol moles that have to be removed.

4. Process according to claim 1 to 3 in which the solution of surface active materials is conducted in circulation after extraction with a solvent that is not soluble in water.

Attachments on Original

Frames 416 and 417 - Dealcoholization XIII
Frame 418 - Fractionation of the Naphtha Wash from Dealcoholization.
Frame 419 - Continuous Separation of Higher Alcohols and Hydrocarbons
Frames 420-425 - Dealcoholization of Cracked Oil Alcohols
Frame 426 - Degree of Activity with 22% Crude Alcohols

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