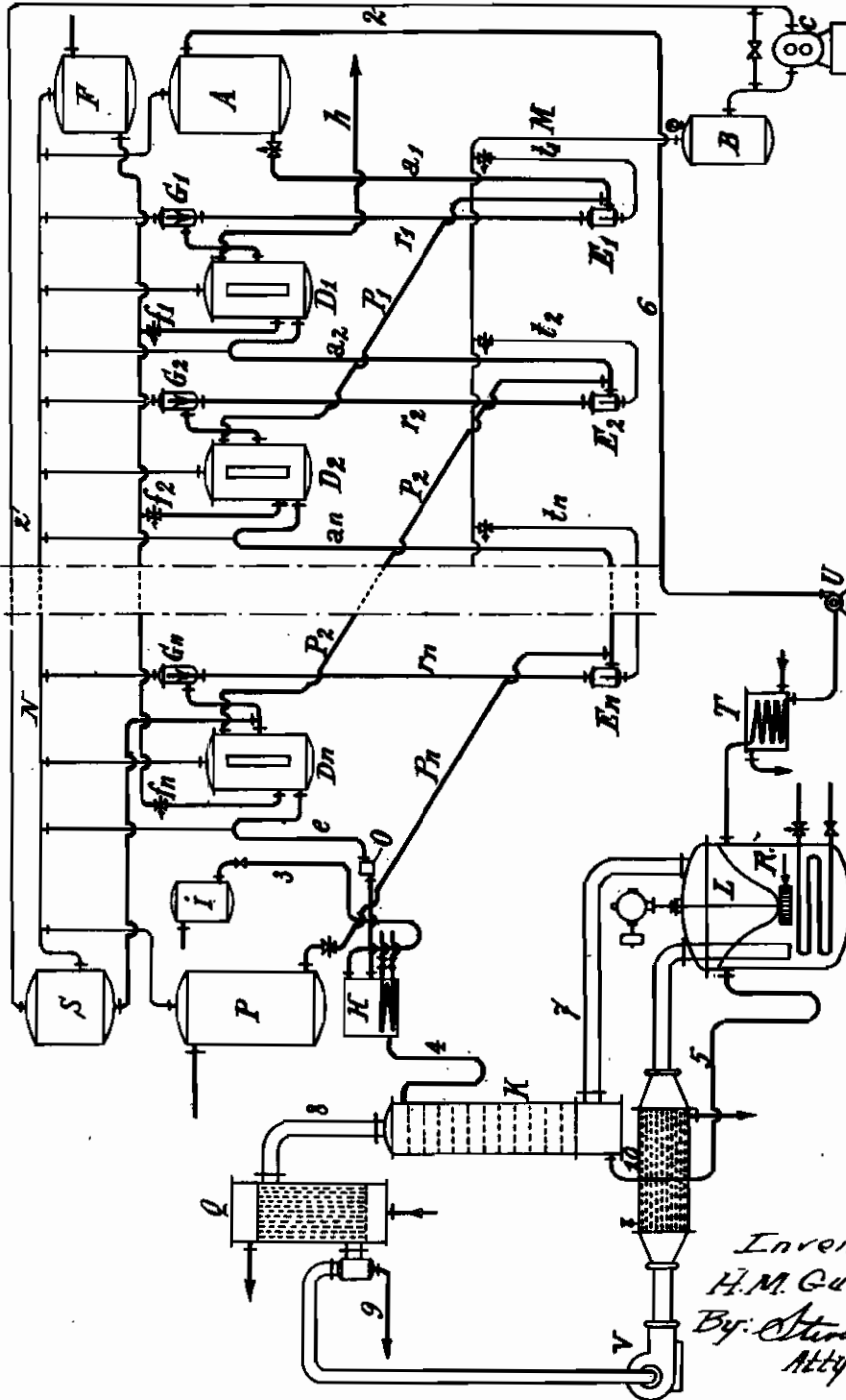


PUBLISHED
APRIL 20, 1943.
BY A. P. C.

H. M. GUINOT
HYDRATION OF OLEFINS
Filed Jan. 8, 1941

Serial No.
373,691



Inventor:-
H. M. Guinot
By: *Stevens & Rowe*
Attys.

ALIEN PROPERTY CUSTODIAN

HYDRATION OF OLEFINES

Henri Martin Guinot, Nlort, France; vested in the
Alien Property Custodian

No Drawing. Application filed January 8, 1941

In the industrial practice, available olefines are mostly accompanied with an important proportion of corresponding saturated hydrocarbons the separation of which for the purpose of isolating the pure olefine presents certain difficulties due to the close similtude of boiling points.

It is therefore advantageous to be able to treat directly such mixtures, in gaseous phase or in liquid phase, in order to hydrate olefines contained therein without having preliminarily to separate different components thereof.

It has already been proposed to treat directly such mixtures, particularly propane-propylene fractions obtained by rectification of cracking products of crude petroleum oils, by means of hydrating solutions, such as concentrated sulphuric solution, in order to absorb olefines comprised therein. The solutions obtained are then diluted in order to bring about the hydrolysis of alcoyl sulphuric acids transitorily formed. The liberated alcohols are finally isolated by suitable means, for example by distillation or extraction by means of solvents.

However, the processes heretofore propounded present many disadvantages, the principal ones residing in the impossibility of bringing about a complete exhaustion in olefine of the mixture of hydrocarbons by the hydrating solution, owing to an inadequate treatment, and in the necessity of putting in highly concentrated sulphuric solutions the recovery of which is costly and involves decreases in the yield of alcohols, the latter being partially destroyed in the course of regeneration.

The present invention, while from different points of view improving technical means heretofore set forth, permits of eliminating aforesaid inconveniences and of obtaining excellent results.

The process, object of this invention, substantially consists first in liquefying the mixture of hydrocarbons and then in bringing about in an absolutely methodical manner the exhaustion within a battery of absorption. Such battery comprises a certain number of decantation elements interconnected by means of vertical pipings which permit of causing both the mixture of hydrocarbons to be hydrated and the hydrating solution to circulate in a counter-current; such circulation is ensured by means of blowing in an inert gas preliminarily compressed. At the ends of the battery there are gathered, on one part, a liquid constituted by saturated hydrocarbons, practically free from olefine and employable for any suitable purpose, and, on the other part, a hydrating solution, saturated with olefine and

containing alcohol caused to appear therein by dilution and heating.

The intimate contact between the mixture of hydrocarbons and the hydrating solution is ensured in the very course of the upflow by the inert gas; this permits of doing away with various means for intense mechanical stirring which have been employed in the most of prior processes and theretofore considered as absolutely necessary. It was then impossible to foresee that the short contact between the two liquids in a piping system designed for their upflow would have been sufficient for obtaining a rapid action of the hydrating liquid upon the diluted olefine.

The hydrating solution, hydrolysed at the outlet end of the battery for causing the alcohol to appear, is completely exhausted in this compound within a still of any suitable type scavenged from its bottom to its top by a current of hot inert gas. In this manner, the regeneration of the acid by concentration in the hot way is carried out in the absence of any trace of alcohol, whereby inevitable destructions inherent to prior processes are avoided. Thus, the formation of coal products is prevented and the initial effectiveness of hydrating bath is almost infinitely maintained.

In order to show how the invention may readily be carried into practical effect, the same will now be described with reference to the accompanying drawing which diagrammatically illustrates one embodiment thereof and is not to be construed in a limiting sense.

This drawing, in one sole Figure, schematically shows an olefine hydrating plant according to the present invention.

The absorption portion of this plant comprises a series of decantation elements $D_1, D_2 \dots D_n$, the number of which varies according to the nature of the mixture to be treated, the rate of concentration of hydrated acid and operative conditions selected. These decanters are interconnected by means of suitable pipings which will be described further below. Respectively adjoined to each decanter is a gas exhaust head $G_1, G_2 \dots G_n$. The whole battery operates under a pressure made sufficient to maintain the mixture of hydrocarbons in liquid state at a temperature under consideration.

A compressor C permits of bringing to the necessary pressure the inert gas serving to effect the upflow. This gas is stored in a tank B from which it is supplied to emulsion vessels $E_1, E_2 \dots E_n$ by means of a pipe M and pipes $t_1, t_2 \dots t_n$ provided with suitable valves.

A collecting conduit N permits of recovering the

gas which has served for the upflow in the different elements, and of directing the same back to the compressor C through the medium of a separator S and pipe 2.

The liquid mixture of hydrocarbons to be treated and contained in a tank P is introduced through a pipe P_n into one end of the battery, while the hydrating solution, for example an aqueous solution of sulphuric acid supplied from a tank A, is introduced into the other end thereof through a pipe a₁.

The hydrating solution is encountered in the emulsion vessel E₁ by the mixture of hydrocarbons which, being already almost exhausted in olefine and constituting the upper layer in the decanter D₂, arrives at this vessel E₁ through the pipe P₁. Under the action of the inert gas blown in through the pipe t₁ both liquids, under the form of an emulsion, are forced to flow up into the head G₁, wherefrom after separation of the gas the mixture flows into the decanter D₁ and is therein divided into two layers. The upper layer constituted by saturated hydrocarbons practically free from olefine flows out of the system through a conduit h. The lower layer of D₁, constituted by sulphuric acid already comprising a certain proportion of alcoyl sulphuric acid, flows through the pipe a₂ into the emulsion vessel E₂ in which it is encountered by the upper layer of decanter D_n arriving thereat through the pipe P₂. From the vessel E₂ both liquids are caused by the inert gas to flow up into the head G₂ to be thereafter separated in the decanter D₂, and so on from element to element.

In the emulsion vessel E_n the hydrating solution, already charged almost at maximum with alcoyl sulphuric acid, is encountered by a fresh mixture of hydrocarbons outflowing from the tank P. After flowing up into G_n and decanting in D_n the hydrating solution is finally drawn out of the battery through the pipe e.

The chemical phenomena produced in the battery are pretty complex owing to the fact that two reactions take place therein simultaneously but at different velocities, viz :

(a) At first, at the contact with olefine a certain proportion of sulphuric acid of the hydrating solution gets fixed under the form of alcoyl sulphuric acid. This results in a decrease of the free acidity of the bath and, consequently, in a reduction of the titration of the latter, the quantity of water having remained without variation.

(b) Simultaneously there is observed partial hydrolysis of alcoyl sulphuric acid, reaction which not only liberated sulphuric acid, but also produced consumption of water and, consequently, tends to increase the titration of hydrating solution.

Velocities of these two parallel reactions depend upon a certain number of factors and, in particular, upon the temperature of the hydrating bath, its degree of concentration and content in alcoyl sulphuric acid. One therefore ascertains, from one element to the other in the battery, a variation of the free acidity and of the titration defined by the ratio:

$$\frac{\text{free SO}_4\text{H}^2}{\text{SO}_4\text{H}^2 \text{ plus water}}$$

In order to insure the constancy of this ratio, which is necessary for obtaining good results, it is expedient to provide on each element of the battery a water supply adjustable at will; such

water comes from a tank F and is supplied by pipes f₁, f₂ . . . f_n.

At any rate, the hydrating solution charged with olefine flowing out of the battery through the pipe e is slackened in its pressure to the ordinary pressure at O and then submitted in a tank H to a heat and a dilution by water inflowing from a tank I through a pipe 3, for the purpose of hydrolysing as completely as possible alcoyl sulphuric acid comprised therein and liberating alcohol therefrom.

The hydrating solution charged with alcohol is then introduced through a pipe 4 to the upper portion of a still K of baffle plate type or checker pile type travelled from its bottom to its top by a hot inert gas current. The hydrating solution, which falls down from baffle to baffle towards the bottom of such still, gets rid of alcohol and of a portion of water contained therein, whereafter it flows out through a pipe 5 into a boiler L. The latter is provided with heating means and a stirring device R and a strong current of inert gas is blown thereinto by means of a fan V.

Under the action of said heating and stirring the gas is saturated with water steam, whereby the sulphuric solution in the boiler is caused to concentrate. Such concentration may be adjusted to the desired extent by acting upon the intensity of heating and upon the discharge of inert gas in fonction of the hydrating solution supply. In this way there is effected a perfect regeneration of the hydrating reagent which after cooling at T is reintroduced into the tank A by means of a pump U and pipe 6.

The inert gas charged with water steam penetrates through a conduit I into the bottom portion of the still K where, as has been seen, it causes the elimination of alcohol contained in the supplied solution. The gases and steam released at the top of the still K are introduced through a conduit 6 into a condenser Q; at the outlet end 8 of the latter there is gathered hydrated alcohol which may be concentrated in an apparatus of known kind (not shown). The non-condensed gases freed from alcohol and water are then retaken up by the intake end of the fan V, eventually reheated at 10 and then blown again into the boiler L, thereby accomplishing a complete closed cycle.

The invention is not limited to the particular embodiment above illustrated and described, for modifications may be effected therein without departing from the scope of the invention. For instance, instead of separating alcohol by mere condensation, a washing tower may be employed to extract therein the alcohol from the entraining gas by means of a suitable solvent, as is indicated in the French patent No 850,938.

Also, the upflow pipes f₁, f₂ . . . f_n of the battery may be encased with a view to regulating the temperature of reaction.

It may also be advantageous to make the upflow pipes of unequal length in different elements throughout the battery with a view to compensating, by conveniently timing the contact, for variations in the reaction velocity from one point to the other of the battery.

Neither will the scope of the invention be departed from by the recovery of heat between certain elements of the plant. In particular, there may be utilised hot water from the tank Q or T, or both, for reheating the gas at 10.

It may also be advantageous to provide in the still K one or more intermediate evaporators to

insure reheating of the hydrating solution in the course of its exhaustion in the said still.

Example

It was proposed to manufacture isopropyl alcohol from a liquid mixture constituted by:

	Per cent
Propane -----	80
Propylene -----	20

The operation was effected in the plant previously described and the operative conditions were as follows:

Hydrating solution: SO^4H^2 at 75% ;
 Number of elements in the battery: 12;
 Temperature in the battery: 40° cent.;
 Pressure: 20 kgs/sq. cent.;
 Nature and pressure of the inert gas for up-flow;
 Nitrogen at 25 kgs/sq. cent.;
 Discharge of liquid propane-propylene mixture introduced into the battery through Pn;
 500 kg/hour;
 Discharge of hydrating solution entering into the battery through a₁:
 850 kgs/ hour;
 Hydrolysis of the hydrating bath leaving the battery:
 Dilution at 50% and heating at 80° cent. for one hour;
 Inert gas employed in the phase of concentration-desalcoholization:
 Hydrogen;
 Regeneration temperature of the acid in L:
 120° cent.;
 The following results were obtained:
 Discharge and purity of propane leaving the battery through h:
 400 kgs of propane containing less than 0.25% propylene;

Discharge of isopropyl alcohol gathered through 9:

139 kgs meant pure;
 Efficiency: 97,5%

Although the above stated example was relevant to the treatment of the propane-propylene mixture, the present invention is in no way limited to the treatment of such mixture and is as well applicable to other homologous products, in particular to butane-butylene mixtures.

According to the present process there may also be treated mixtures comprising saturated and not saturated hydrocarbons having a different number of carbon atoms, such for example as mixtures containing hydrocarbons having 3 and 4 carbon atoms. Different alcohols formed will be simultaneously eliminated by the gaseous current in the still K and there will be gathered at 9 a mixture of corresponding alcohols which will be separated by ordinary means.

Finally the invention is applicable to mixtures rich in olefines and comprising but some percents of saturated hydrocarbons.

As a gas to serve for the operation of the battery, there may be employed hydrogen instead of nitrogen, or else hydrocarbons, saturated or not saturated, under the only condition that they be gaseous and practically without action upon the hydrating solution selected within ranges of temperature and pressure under consideration, for example, methane, ethane, ethylene, etc.

Identically as to the inert gas employed in the phase of regeneration-desalcoholization, but in this case it will be advantageous to make use of a light gas having the best qualities with regards to the calorific exchange, for example hydrogen.

HENRI MARTIN GUINOT.