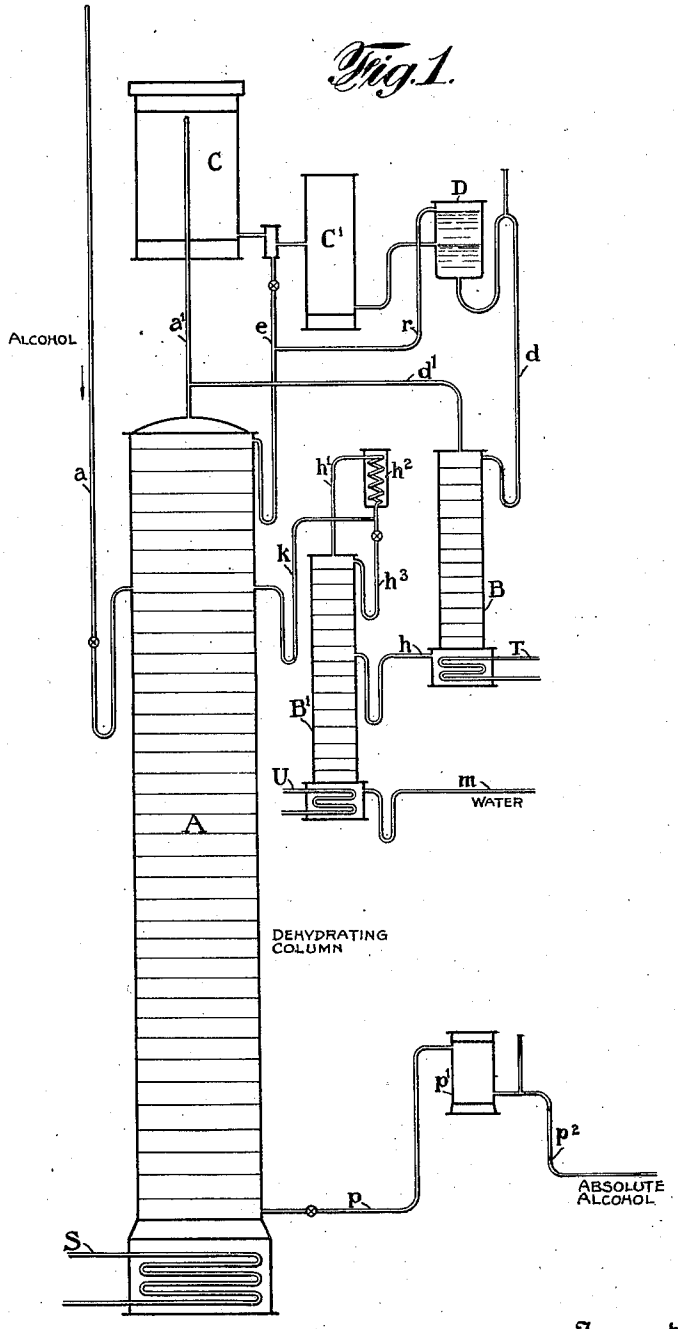
June 17, 1930. E. RICARD 1,763,722

PROCESS FOR THE DEHYDRATION OF IMPURE ETHYL ALCOHOL

Filed Nov. 20, 1925 4 Sheets-Sheet 1

Fig. 1.



Inventor
Eloi Ricard

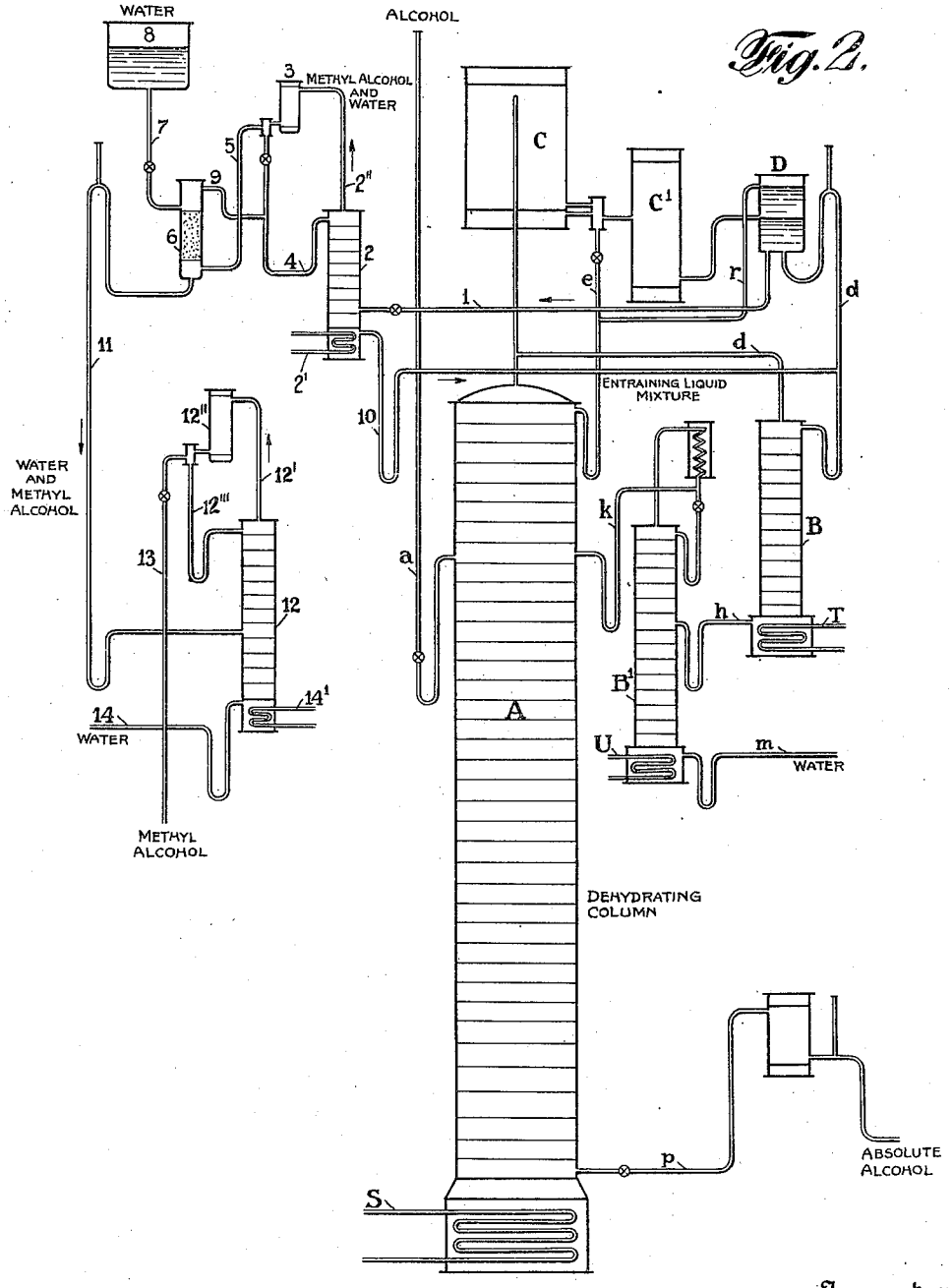
By his Attorneys
Pindle, Wright, Neal & Beau

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PROCESS FOR THE DEHYDRATION OF IMPURE ETHYL ALCOHOL

Filed Nov. 20, 1925 4 Sheets-Sheet 2

Fig. 2.



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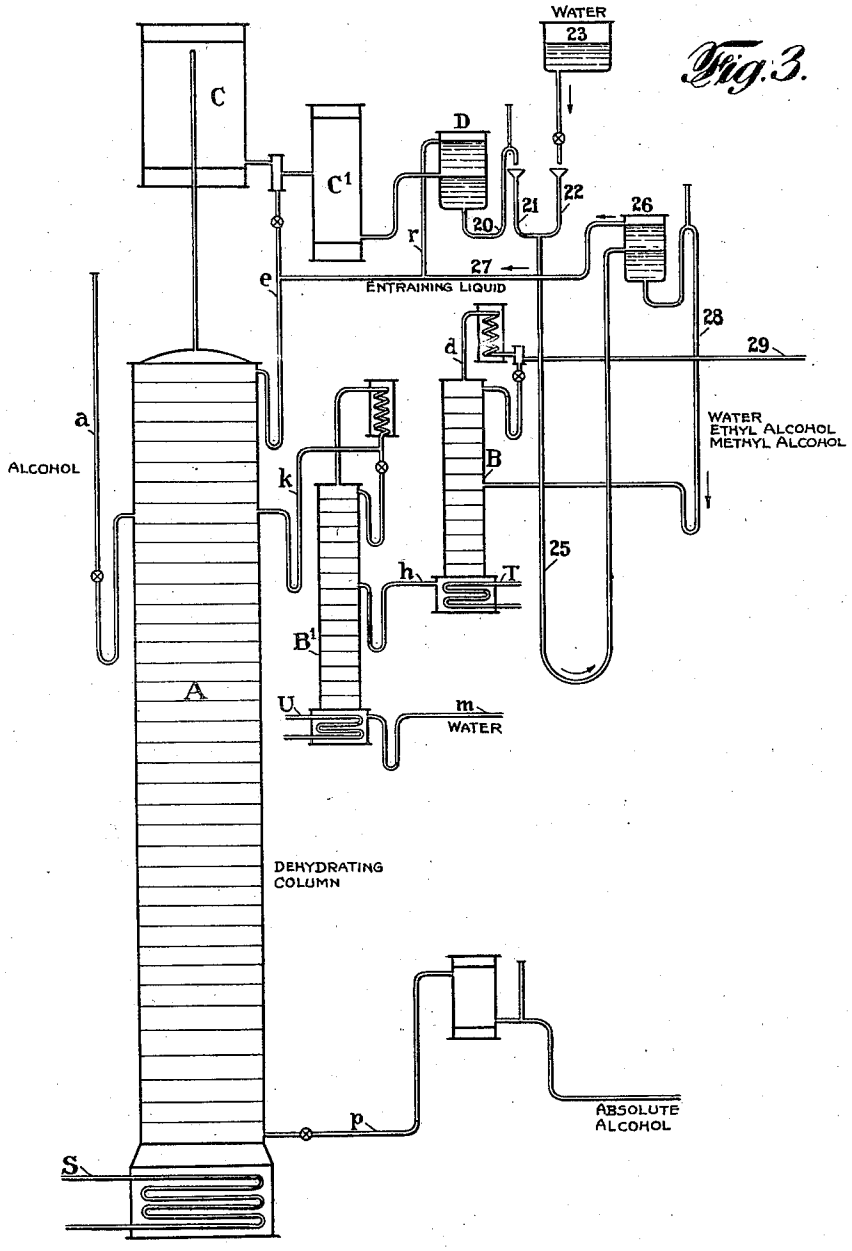
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PROCESS FOR THE DEHYDRATION OF IMPURE ETHYL ALCOHOL

Filed Nov. 20, 1925 4 Sheets-Sheet 3

Fig. 3.



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PROCESS FOR THE DEHYDRATION OF IMPURE ETHYL ALCOHOL

Filed Nov. 20, 1925 4 Sheets-Sheet 4

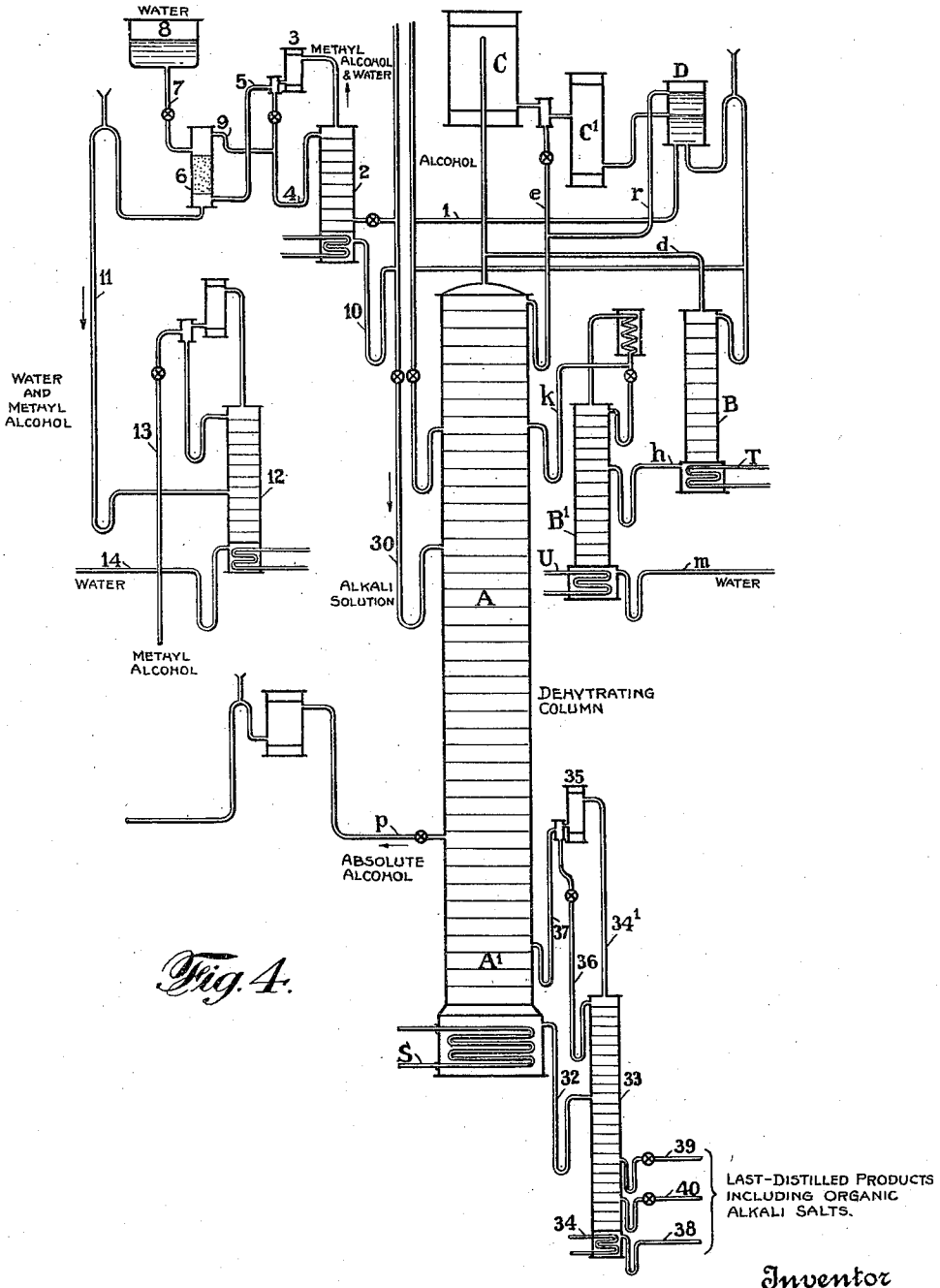


Fig. 4.

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Patented June 17, 1930 1,763,722

UNITED STATES PATENT OFFICE

ELOI RICARD, OF MELLE, FRANCE, ASSIGNOR, BY MESNE ASSIGNMENTS, TO U. S. INDUSTRIAL ALCOHOL CO., OF NEW YORK, N. Y., A CORPORATION OF WEST VIRGINIA

PROCESS FOR THE DEHYDRATION OF IMPURE ETHYL ALCOHOL

Application filed November 20, 1925, Serial No. 70,319½, and in Belgium November 20, 1924.

My invention relates particularly to a process for the dehydration of ethyl alcohol containing impurities.

The object of my invention is to provide a process by means of which the alcohol containing impurities may be dehydrated so as to obtain absolute alcohol in an advantageous manner and without unnecessary preliminary rectifications of the alcohol. The process for the dehydration of ethyl alcohol which is based upon azeotropic action as ordinarily employed, cannot be used when the alcohol to be treated contains certain natural or added impurities which are of such nature as to gradually accumulate in the main distilling apparatus. Such impurities are prejudicial to the dehydration, and will even stop the operation altogether.

To obviate that difficulty, recourse may be had to a preliminary rectifying operation, of an expensive nature, whereby the impurities may be eliminated, but in the case of impurities which are difficult to eliminate, such as methyl alcohol, it becomes impossible to obtain the desired results. The present invention provides a process in which any preliminary rectification is obviated and in which the impure commercial alcohols may be dehydrated directly.

The impurities considered in my said process may be of widely varying character, but in general they are usually characterized by the following properties: They are more volatile than alcohol and they are generally soluble in water or unable to form either with water or with alcohol, taken separately, binary mixtures having a minimum boiling point. Among the products possessing these qualities may be mentioned acetic aldehyde, sulphuric ether, acetone, ethyl formate, methyl alcohol, and the like, which are given by way of example.

Further objects of my invention will appear from the detailed description of the same hereinafter.

While my invention may be carried out in many different ways, for the purpose of illustration I shall describe only certain ways of carrying out the same hereinafter, and have shown only certain types of apparatus for use in connection therewith in the accompanying drawings, in which—

Figure 1 is a diagrammatic representation of an apparatus used in carrying out the dehydration process, as set forth in my application for Letters Patent, Serial No. 688,050, filed January 23, 1924, Patent #1,704,213, granted March 5, 1929, and which is utilized in carrying out my invention;

Figure 2 is a diagrammatic representation of an apparatus which may be used in carrying out my invention showing thereon equipment which is especially adapted for accomplishing the purposes above referred to as one embodiment thereof;

Figure 3 is a diagrammatic representation of another form of apparatus which may be used in carrying out my invention; and

Figure 4 is a diagrammatic representation of an apparatus similar to that shown in Figure 2, but with a further addition to the same, as hereinafter described.

In describing my said process, I will briefly mention with reference to Figure 1, the process for the dehydration of purified alcohol according to the practice as set forth in application Serial No. 688,050 aforesaid.

The alcohol of ordinary strength is fed by a pipe *a* into a distilling column A provided with a steam heating coil S. The resulting vapors evolved through a pipe *a'* are condensed in a condenser C. A part of the hot liquid returns to the column A through a pipe *e*. Another part is cooled in a cooling apparatus C' and is discharged into a separating chamber D in which it separates into two layers. Each layer contains the three substances, water, ethyl alcohol and an entraining liquid such as benzol, for example, which may be fed in by pipe *a* with the alcohol. One layer, for instance the top layer, contains the major part of the entraining liquid which is returned to the column A through a conduit *r*. The second layer, herein the bottom layer, is treated in a small distilling apparatus B and B'.

The apparatus B is comprised of a column provided with a steam coil T and serves to remove the whole of the entraining liquid from the liquid layer, which is supplied

thereto through a pipe d. The entraining liquid is drawn off from the column B as a vapor mingled with a small amount of a vapor of the other two constituents of the layer and, thus, returned to the pipe a' by the pipe d'. The other two constituents, comprising alcohol and water, are drawn off from the column B into the column B' through a pipe h. The column B' is heated by a steam coil U and serves to remove, in the form of a vapor, alcohol of a high strength through the pipe h to a condenser h^2, which delivers the condensate partly to the top of the column B' by a valved pipe h^3, but mainly by a pipe k to the dehydrating column A. The water is discharged from the column B' by an outlet pipe m. The absolute alcohol is discharged from the dehydrating column A by means of a valved outlet pipe p, which is connected to a cooler p' having a vented outlet pipe p^2. In the case where an apparatus of this type is fed with an alcohol containing 5%, for example, of methyl alcohol, it would be found that methyl alcohol has no exit from the apparatus as it does not descend to the bottom of the column to be drawn off through the pipe p with the absolute alcohol, nor does it pass out with the water issuing from the bottom of the column B, but it is found that it collects at the top of the column A and will be prejudicial to obtaining the proper usual ternary constant boiling mixture. Accordingly, the decantation in the separating chamber will be hindered and will finally be prevented, thus, preventing the dehydration from continuing.

Accordingly, in carrying out my invention, an outlet for methyl alcohol, when present, is provided for.

I have, thus, provided for this purpose an apparatus as shown in Figure 2. This apparatus is constructed and operates in the same manner as the apparatus shown in Figure 1 so far as the parts disclosed in Figure 1 are found in Figure 2. In addition thereto I have provided, however, an apparatus for carrying out the purpose above referred to. For this purpose I have provided a valved pipe 1 for drawing off from the separating chamber D a part of the decanted layer, in this instance the lower layer, in which the methyl alcohol is found in the greatest quantity. This is conveyed by the pipe 1 to a distilling column 2 provided with a steam heating coil 2'. The mixture therein is distilled so as to form a binary azeotropic mixture which collects at the top of the column 2 and is driven off through a pipe 2'' to a condenser 3. A part of the condensate flows back through a pipe 4 to the top of the column 2 and a part is discharged through a conduit 5 into a scrubber 6 of any desired type. Water from the tank 8 is delivered through a valved pipe 7 to the scrubber 6. Water dissolves the methyl alcohol, thus producing a plurality of layers therein with the methyl alcohol mainly in the lower layer. The upper layer containing the remaining quantity of the entraining liquid, flows away from the top of the separating chamber, thence to the pipe 4 and thence to the top of the column 2. The liquid at the lower part of the column 2 is very poor in methyl alcohol and is returned through a conduit 10 to the pipe d and thence to the distilling column B. The lower layer in the scrubber 6 is carried off by a vented pipe 11 to a distilling column 12 in which the two liquids, comprising methyl alcohol and water, are separated. The methyl alcohol is evolved from the top of the column in the form of a vapor and conveyed by a pipe 12' to a condenser 12'', part of the liquid condensed being returned by a pipe 12''' to the column 12, and the remainder being carried off by a valved outlet 13. The water from the column 12 is carried away by an outlet pipe 14. For heating the column 12 there is, as shown in the drawings, a steam heating coil 14'. By carrying out the process in this manner I have obtained a continuous abstraction of the methyl alcohol, thus avoiding the accumulation of the methyl alcohol in the top of the distilling apparatus so that, as a consequence, the distilling process may be carried on continuously without any interruption.

Instead, if desired, I may carry out the operation in a somewhat simpler manner. In the case of not dealing with an impurity, which will tend to form a binary azeotropic mixture with the entraining liquid, the impurity in the alcohol can be made to separate directly out in the pure state at the top of the distilling apparatus. In this instance, accordingly, I am able to eliminate the scrubber 6 and the distilling column 12. In carrying out this form of my invention I utilize an apparatus such as shown in Figure 3. The apparatus shown in this figure comprises the parts which are shown in Figure 1 but in addition thereto has certain features added to the same as hereinafter described. The lower layer from the separating chamber D containing the water, ethyl alcohol, entraining liquid, and a large percentage of impurity, is discharged through a conduit 20 into a pipe 21 arranged to receive water from a tank 23 through a pipe 22. The pipes 21 and 22 are arranged to intermingle the said lower layer and the water, especially with the aid of a pipe 25 connected thereto, which leads to a separating chamber 26 where the liquid forms into a plurality of layers. The entraining liquid accumulates in the upper layer and is returned by a pipe 27 to the pipe e, where it is returned to the dehydrating column A.

The bottom layer, which contains the water, ethyl alcohol and methyl alcohol, is discharged through a conduit 28 to the distilling column B. The vapors accumulating in the top of the column B are comprised mostly of the impurity or the methyl alcohol, which is condensed and discharged through a conduit 29. From the lower part of the distilling column B there is conveyed to the column B′ a mixture of water and methyl alcohol, which is distilled therein as hereinabove referred to.

In the case where, instead of one impurity the mixture contains a certain number of impurities, the operation, in treating the same in the apparatus shown in Figures 2 and 3, would be carried out in the same manner except that the mixture of impurities to be eliminated would be discharged through the conduit 13 in Figure 2, or the conduit 29 in Figure 3.

In the case where the simultaneous dehydration and purification of alcohol is to be carried out containing impurities of a widely varying character such as ethers, acids and tail products in general, I can resort to a different procedure as hereinafter described. My process is, thus, applicable to the treatment of raw commercial alcohol or to alcohols to be again treated after having been used as solvents in certain branches of manufacture.

In carrying out my process containing the impurities last mentioned, I may proceed as follows, for example: I neutralize the acids and saponify the saponifiable ethers by the continuous measured addition of an alkali such as caustic soda, caustic potash, etc. at the top of the distilling apparatus and at a point below the region in which the first distilled impurities, if any, are being eliminated, the operation being performed in this manner in order to obviate the rectifying of the first distilled impurities, because this would give rise to an odor difficult to eliminate. The organic salts or esters thus formed are soluble in alcohol and in the tail products and, accordingly, reach the lower part of the distilling column whence they are discharged. In case the product treated contains acids but not ethers, I may, if desired, neutralize the acids by the continuous measured addition of an alkali. If the products are not neutralized they will act in the same manner as the tail products and discharge therewith as above indicated.

I eliminate the tail products, the boiling point of which is higher than that of alcohol, and which consists usually of the higher alcohols, acetal, aldol, croton-aldehyde, the furfurolic bases, amines, aldehydes of the fatty series, the heavy ethers which are not saponified, the volatile fatty acids, and the like, by causing the same to descend during the dehydrating process, below the point of discharge of the ethyl alcohol, with which the said products descend in the column, as I add a certain number of plates upon which the said products will be accumulated. The said products may be removed in the form of a liquid or vapor by means of a discharge valve, and they are then rectified in an auxiliary distilling column where they are freed from ethyl alcohol. All of the above-mentioned last-distilled products are insoluble, or but slightly soluble, in water, and, thus, will afford mixtures which have a constant boiling point, and which can be distilled below 100° C. In fact, the presence of a small amount of water, which lowers the boiling point in the rectifying process, makes the separation of said products very difficult, but in the absence of water their boiling point remains unchanged, but this boiling point, thus, will readily permit their fractional distillation. For example, isoamyl alcohol will distill at 95° C. when in the presence of a small quantity of water, and at 131° C. when it is anhydrous. In the first instance its boiling point differs from that of alcohol by only 16.5°, while in the second instance it differs by 53° C.

The following example, referring to the apparatus shown in Figure 4, will exemplify the process as carried out in the form of my invention just described. The apparatus shown in Figure 4 has all of the features as shown in Figure 2 but in addition thereto I have provided an equipment for introducing the alkali and taking care of the constituents present in the treated alcohol which boil at a higher point than the absolute alcohol which is drawn off by the pipe *p* in the manner above described. Therefore, in said apparatus it will be understood that the apparatus above described in detail will eliminate the acetic aldehyde, acetone and any methyl alcohol in the product. Any ethyl acetate, which often forms the chief impurity of alcohol, has a tendency to form in the middle part of the column A. Through a pipe 30, connected to the column A, I introduce a concentrated solution of caustic soda which may be either an aqueous or alcoholic solution, which, accordingly, spreads out upon the plates in the column. During the heating of the column A the acids in the alcohol are neutralized and the ethers are saponified. The organic sodium salts resulting therefrom are soluble in alcohol and descend to the bottom of the column A, where they are evacuated with the last-distilled products, a number of plates A′ being added for this purpose. These last-distilled products, in crude state, pass out through a pipe 32 which conveys them to a distilling column 33 steam-heated by means of a coil 34. The vapors from the column 33 escape by a pipe 34′ to a condenser 35, a part of the conden-

sate being returned by a valved pipe 36 to the column 33, and the remainder being conveyed to the plates A′ through a pipe 37. The last-distilled products in concentrated state, in which are dissolved the organic alkaline salts, are extracted as a mixture from the lower end of the column 33 by means of a pipe 38, or they may be removed individually at different heights, according to their boiling points, through valved pipes 39, 40, etc.

While I have described my invention above in detail I wish it to be understood that many changes may be made therein without departing from the spirit of the same.

I claim:

1. The process which comprises dehydrating aqueous ethyl alcohol containing low boiling impurities compared with the ethyl alcohol by distilling off an azeotropic mixture of a minimum boiling point with the aid of benzol as an entraining liquid, condensing the vapors of the azeotropic mixture, allowing the condensate to separate into liquid layers, decanting the layer containing the principal part of the low boiling impurities and treating the same so as to remove said impurities.

2. The process which comprises dehydrating aqueous ethyl alcohol containing low boiling impurities compared with the ethyl alcohol by distilling off an azeotropic mixture of a minimum boiling point with the aid of benzol as an entraining liquid, condensing the vapors of the azeotropic mixture, allowing the condensate to separate into liquid layers, decanting the layer containing the principal part of the low boiling impurities and treating the same so as to remove said impurities by distillation.

3. The process which comprises dehydrating aqueous ethyl alcohol containing low boiling impurities compared with the ethyl alcohol by distilling off an azeotropic mixture of a minimum boiling point with the aid of benzol as an entraining liquid, condensing the vayors of the azeotropic mixture, allowing the condensate to separate into liquid layers, decanting the layer containing the principal part of the low boiling impurities and treating the same so as to remove said impurities by distillation and washing.

4. The process whch comprises dehydrating aqueous ethyl alcohol containing low boiling impurities compared with the ethyl alcohol by distilling off an azeotropic mixture of a minimum boiling point with the aid of benzol as an entraining liquid, condensing the vapors of the azeotropic mixture, allowing the condensate to separate into liquid layers, decanting the layer containing the principal part of the low boiling impurities and treating the same so as to remove said impurities by distillation, washing, separation into liquid layers and distillation of the layer containing the principal part of the low boiling impurities.

5. The process which comprises dehydrating aqueous ethyl alcohol containing high boiling impurities compared with the ethyl alcohol by distilling off an azeotropic mixture of a minimum boiling point with the aid of benzol as an entraining liquid while adding an alkali to the alcohol being dehydrated so as to form high boiling products by chemically combining with said impurities; and separating the absolute alcohol from the high boiling products of the dehydration, by drawing off said products in the same distilling operation.

6. The process which comprises dehydrating aqueous ethyl alcohol containing high boiling impurities compared with the ethyl alcohol by distilling off an azeotropic mixture of a minimum boiling point with the aid of benzol as an entraining liquid while adding an alkali to the alcohol being dehydrated, and separating the absolute alcohol from the high boiling products of the dehydration by subjecting the same to distillation by drawing off said products in the same distilling operation.

7. The process which comprises dehydrating aqueous ethyl alcohol containing high boiling impurities compared with the ethyl alcohol by distilling off an azeotropic mixture of a minimum boiling point with the aid of benzol as an entraining liquid while adding an alkali to the alcohol being dehydrated, and separating the absolute alcohol from the high boiling products of the dehydration by subjecting the same to distillation in the same distilling operation and separately drawing off the high boiling products and the alcohol.

8. The process which comprises dehydrating aqueous ethyl alcohol containing low boiling and high boiling impurities compared with the ethyl alcohol by distilling off an azeotropic mixture of a minimum boiling point with the aid of benzol as an entraining liquid, condensing the vapors of the azeotropic mixture, allowing the condensate to separate into liquid layers, decanting the layer containing the principal part of the low boiling impurities, treating the same so as to remove said impurities while adding an alkali to the alcohol being dehydrated, and separating the absolute alcohol from the high boiling products of the dehydration by drawing off said products in the same distilling operation.

9. The process which comprises dehydrating aqueous ethyl alcohol containing low boiling and high boiling impurities compared with the ethyl alcohol by distilling off an azeotropic mixture of a minimum boiling point with the aid of benzol as an

entraining liquid, condensing the vapors of the azeotropic mixture, allowing the condensate to separate into liquid layers, decanting the layer containing the principal part of the low boiling impurities, treating the same so as to remove said impurities while adding an alkali to the alcohol being dehydrated, and separating the absolute alcohol from the high boiling products of the dehydration by subjecting the same to distillation by drawing off said products in the same distilling operation.

10. The process which comprises dehydrating aqueous ethyl alcohol containing low boiling and high boiling impurities compared with the ethyl alcohol by distilling off an azeotropic mixture of a minimum boiling point with the aid of benzol as an entraining liquid, condensing the vapors of the azeotropic mixture, allowing the condensate to separate into liquid layers, decanting the layer containing the principal part of the low boiling impurities, treating the same so as to remove said impurities while adding an alkali to the alcohol being dehydrated, and separating the absolute alcohol from the high boiling products of the dehydration by subjecting the same to distillation in the same distilling operation and separately drawing off the high boiling products and the alcohol.

11. The process which comprises dehydrating aqueous ethyl alcohol containing low boiling and high boiling impurities compared with the ethyl alcohol by forming an azeotropic mixture of a minimum boiling point with the aid of benzol as an entraining liquid, condensing the vapors of the azeotropic mixture, allowing the condensate to separate into liquid layers, decanting the layer containing the principal part of the low boiling impurities, and treating the same so as to remove said impurities while returning the entraining liquid recovered from said layer to the alcohol being dehydrated.

In testimony whereof I have signed this specification.

ELOI RICARD.