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J. A. STEFFENS
DEHYDRATING ALCOHOL

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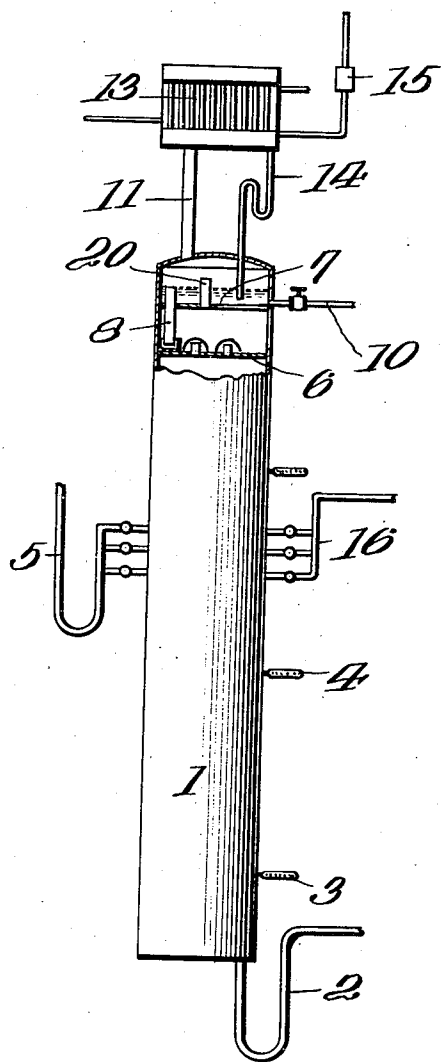


FIG. 1.

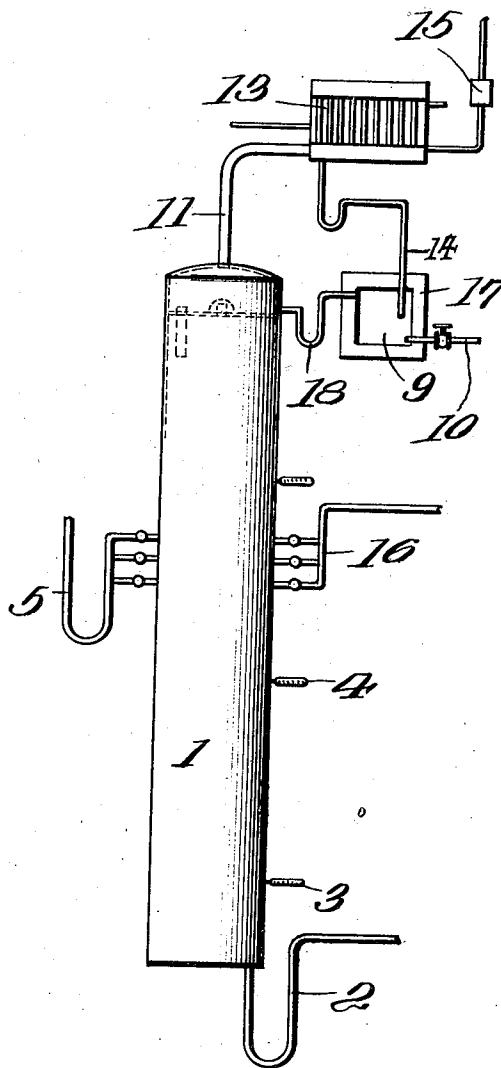


FIG. 2.

Inventor
John A. Steffens.

By K. P. McElroy
Attorney

UNITED STATES PATENT OFFICE.

JOHN A. STEFFENS, OF BROOKLYN, NEW YORK.

DEHYDRATING ALCOHOL.

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This invention relates to dehydrating alcohol; and it comprises a method of dehydrating alcohol (and like liquids) with the aid of water-immiscible volatile liquids, such as benzol, wherein the alcohol to be dried is delivered to a column still containing benzol and dry alcohol is drawn off at the base of such still, and all vapors arising from the distilling operation are condensed to form a 2-layer condensate at the temperature of the head of the column, one such layer containing a greater amount of water than the other, and there is returned to the still head all of the layer relatively poor in water and about two-thirds of the layer rich in water, return being while at such temperature, the remaining third of the latter layer being withdrawn for appropriate treatment elsewhere, conditions being so adjusted that the amount of water in the withdrawn liquid balances that entering the system with the alcohol to be dried; and it also comprises an assemblage of apparatus elements adapted for use in the performance of the described method; such assemblage comprising a column still with appropriate heating means, means for introducing alcohol as vapor or liquid at a midpoint, means for withdrawing dry alcohol at the base, means for totally condensing vapors leaving the head of the still, means for gravitally separating the condensate into two liquid layers at the temperature of the still head, and means for withdrawing a portion of the heavier liquid while refluxing the residue of said liquid and all of the lighter liquid into said still head; all as more fully hereinafter set forth and as claimed.

As is well known, ethyl alcohol (grain alcohol) containing water cannot be brought to a strength beyond about 95 per cent by simple distillation in ordinary stills whatever the efficiency of the distilling means. It is easily possible to produce alcohol of about 95 per cent by many types of column still; but beyond this, the operator cannot go by simple distillation in commercial operation. An alcohol of about 95 per cent strength has a lower boiling point than either stronger or weaker alcohol; and spirit of this strength therefore goes to the head of the still and thence to the condenser.

There is however a considerable commercial demand for "absolute" alcohol; or alcohol stronger than 95 per cent. In particu-

lar it is desired for making composite motor fuels; blended fuels of which alcohol is one component and kerosene or some other petroleum oil is another. Apart from the undesirability of water in the fuel, 95 per cent alcohol does not blend well with most petroleum oils and in general where it is used, it is necessary to have a third body present as a blending agent, benzol, ether, etc., in greater or less quantity. Where the alcohol is dry, this blending agent may be dispensed with, thereby cheapening and simplifying the manufacture of the fuel. With an alcohol which is more or less moist, the drier the alcohol, the less blending agent need be used.

The commercial demand for absolute alcohol is in part met by modifications of the ordinary laboratory methods in which alcohol is distilled to 95 per cent and then dried by hygroscopic chemicals; lime, calcium chlorid, potassium carbonate, sodium, calcium carbid, etc. In part, it is met by modifications of the so-called "Young's method", wherein water is distilled out of strong alcohol by the addition of a third volatile body, generally benzol. With a mixture containing alcohol, water and benzol, on distillation a mixture of vapors poor in alcohol is formed and goes to the head of the column, while anhydrous alcohol can be drawn off at the base. It is to this latter type of process that the present invention pertains.

In this manner of drying alcohol, not all the alcohol supplied to the still is drawn off at the base; some inevitably distills over with the benzol and water. The vapors coming from the head of the still, on condensation and standing, separate into two superimposed "liquid phases" or strata: an upper or overlying stratum of benzol containing a little water and a little alcohol, and an underlying layer of water and alcohol containing some benzol kept in solution by the alcohol. The upper layer, is, or may be, returned to the still to serve anew. It is customary to dilute the lower aqueous layer to separate the dissolved benzol and then re-rectify the diluted liquid to obtain 95 per cent alcohol which can re-enter the operation. Obviously, the greater the proportion which the dry alcohol obtained at the base of the still bears to the alcohol which goes over with the vapors of water and ben-

zol and which must be reconcentrated, the greater the economy of the operation. By the most approved methods now in use, it is difficult however in practical operation to obtain more than 70 to 80 per cent of the alcohol directly as dry alcohol; 30 to 20 per cent going over with the benzol and water and requiring redistillation and reconcentration.

10 The yields stated are below those theoretically possible and there is room for much improvement in the practical operation of the process. It is the object of the present invention to provide such an improvement.

15 The difficulty lies in the relatively complex nature of the operation and the nice regulation of conditions necessary to ensure that neither benzol (which has about the same boiling point as alcohol) nor water passes out with the dried alcohol at the base of the still. The difficulties of operation are accentuated in methods of operation where the layer rich in benzol is fed directly back to the still as it separates from the cold condensate. Under these conditions, with any slight change in the composition or proportion of the alcohol feed, either benzol or water tends to creep downward in the column and reach the absolute-alcohol discharge.

In the stated methods of the prior art, the column still and its condenser are used in the ordinary way; the vapors reaching the top of the column or the still head being withdrawn through a suitable vapor outlet and sent to a condenser. This condenser is intended to, and usually does, deliver a relatively cold condensate; a condensate at a temperature considerably less than that of the still head. This condensate on standing in suitable settling tanks or devices, separates into two liquid layers or phases which are individually treated. The upper, or lighter layer, which contains most of the benzol, together with some water and some alcohol is often directly returned to the still.

In the present invention, I employ a column still, but I use it in a different way and in lieu of forming and stratifying a condensate in a cold state as two distinct layers, I condense the vapors coming from the still head by a device in the nature of a reflux condenser, thereby producing a 2-layer condensate and, while at still head temperature, reflux directly back to the still the portion of the condensate containing but little water, together with a major fraction of the portion containing more water. While both layers contain all three components, water, alcohol and benzol, for the sake of convenience, the layer containing the major portion of water is hereafter called the aqueous layer, and the other the non-aqueous layer. In effect, however, I perform a gravital separation of the two immiscible liquids or

liquid phases at still head temperature. There are several important and advantageous results in so doing.

Gravital separation depends on a difference in specific gravity; and this difference is greater at still head temperature than at lower temperatures. Hot separation gives a heavy liquid material richer in water and poorer in benzol and alcohol, and, therefore, relatively heavier while, conversely, the light liquid is richer in benzol and alcohol and, therefore, relatively lighter. Since the object of the process is the elimination of water, this production of a heavy layer richer in water is in itself desirable while there is the further advantage of the stated increased difference in specific gravity. This gives a quicker and easier separation; and I find that in practice by operating on a condensate at still head temperature, it is not necessary to wait for the production of two well stratified and distinct layers; that I can operate on the condensate as fast as it is delivered.

In any distillation of this type, in normal operation there is a certain necessary fixed relationship between the three component bodies, alcohol, benzol and water, in the composition of the vapors in the still head; water vapor being as necessary as the other vapors. The condensate yielded, as a whole, has of course the same fixed composition. And I find that in practice, I can best preserve the normality of vapor conditions in the still head by returning to it all the lighter portion of the condensate given by the reflux and about two-thirds of the heavier portion. The 1:2 ratio given is of course approximate; in practice I aim to withdraw such a proportion of the heavier liquid as will contain water in amount corresponding to that entering the system with the alcohol to be dried. In so doing there is a minimum of interference with normal vapor conditions in the still head.

Because of the quick and clean separation which is practicable at still head temperature I find that I can deliver the whole body of condensate into and somewhat below the surface of a body of liquid in or near the still head and overflowing into it. In so doing the light liquid, rich in benzol, rises through the body and overflows with it, while the heavier liquid separates at the bottom. Such portion of this latter as is to be withdrawn can be tapped off cleanly at or near the bottom.

In practical embodiments of my invention, I use a column still delivering vapors to a reflux condenser having liquid, as well as vapor, communication with the head of the still. In the liquid communication line, however, I interpose a liquid collecting device which may be simply the top plate in

the still—suitably modified of course to adapt it to its new functions. This collecting device I maintain at the temperature of the still head; this maintenance taking place automatically where the collecting device is the modified top plate. If the collecting device is outside the still proper, as mechanical convenience sometimes indicates, care is taken to shield it against loss of heat; as by lagging with magnesia, silica, etc.

The reflux condenser condenses all the vapors leaving the head of the still and delivers them to the collecting device. This condensate comprises benzol, alcohol and water and it tends to separate into two immiscible portions of liquid; this separation however, being at still head temperature, say, about 65° C. The proportions and composition of the two liquids at this temperature are, as stated, different from the proportions and compositions secured in settling at lower temperatures or at the ordinary temperature. The collector I provide with means for withdrawing a certain amount of the heavy liquid settling out of the mixture of liquids flowing back from the reflux. The rest of the condensed liquids are allowed to overflow back into the still by appropriate connections. Withdrawals are so controlled that about one-third of the more aqueous and heavier liquid coming from the reflux is withdrawn, while two-thirds go back into the still system. In operating in the way described, the withdrawal of about one-third of the total watery condensate will make the withdrawal of water from the system balance the input of water with the alcohol to be dried. This input of wet alcohol may be as vapor or as liquid; the particular way of feeding the alcohol into the still forming no part of the present invention. Put in another way, for every three parts by volume of watery liquid condensing in the reflux in a time unit, about one part by volume is withdrawn in a more or less continuous manner, and the residue of the refluxed condensate is returned to the still. The withdrawal may be controlled either in the manner stated: by balancing water output against water input, or, and more simply, by watching a thermometer somewhat below the collecting device stated. As long as the temperature in this thermometer stays constant, the amount of liquid withdrawn is correct. The particular temperature registered by this thermometer will vary somewhat, according to its location in the column. At lower points the temperature will be greater than at higher points. Generally the temperature to be established in this thermometer is somewhere between 72° and 74° C. Other indicating means, such as the usual continuous testers, may be employed.

Absolute alcohol is drawn off from the

base of the still in the usual manner. It may be absolute, that is dry, or substantially so, or it may be of any controlled proportion of moisture between the 94-95 per cent alcohol entering the still and absolute alcohol.

The withdrawn third of the total aqueous liquid delivered by the reflux condenser to the collecting device is sent to another column still. Here it is distilled in the usual manner; that is, water is withdrawn at the base of the still and a concentrated alcoholic liquid is delivered by the usual type of condensers. All the water in the alcohol supplied to the primary still passes off as such at the base of this secondary still. A condensate may be obtained containing all the alcohol and benzol; and if distillation be so conducted as to deliver a condensate containing about 10 per cent benzol to 90 per cent of alcohol and water, the whole condensate may be then returned to the primary still as it is, without disturbance in the operation of such primary still.

The withdrawn watery liquid, and particularly with some rather impure alcohols, generally contains some aldehyde; and it is a useful expedient in operating the second column to use a little permanganate in admixture with the liquid to be distilled, thereby oxidizing the aldehyde.

It is found that in the practice of the present method some 90 per cent of the alcohol delivered to the primary or drying column is recovered at its base as dry alcohol, leaving only 10 per cent to be strengthened in the secondary column.

In the accompanying illustration, I have shown, more or less diagrammatically, certain assemblages of apparatus elements embodying my invention and capable of use in the performance of the described process. In this showing

Figure 1 is a central vertical section, certain parts being shown in elevation, and

Figure 2 is a similar view of a modification having the collecting device outside the column.

In both showings, element 1 represents diagrammatically a vertical column of copper or other suitable metal provided with the usual shelves or plates (only one being shown). At the base, the columns are provided with an ordinary trapped outlet 2, for withdrawing dry alcohol and sending it to a suitable cooler. The temperature of the base is indicated by a thermometer 3, which in the case of dry ethyl alcohol, should indicate a temperature of about 78.3° C. Materially above the base, but below the point of alcohol input, is the control thermometer 4 previously referred to. With the type of column shown, its readings are generally somewhere between 72° and 74° C. As stated, other indicating devices may be used; but a

simple thermometer suffices. As shown, alcohol to be dried is introduced into the still through inlet 5, shown as communicating with the still at a midpoint. In Figure 1, above the top plate 6 of a regular conventionally shown liner system is collecting device formed by plate 7 through which pass vapor conduit 20 and overflow pipe 8. The latter extends above this plate a sufficient distance to give a pool or body of liquid thereon. Valved outlet pipe 10 communicates with the bottom of this body. Above this point, the still head is shown as provided with vapor outlet 11 leading to reflux condenser 12. As shown, this condenser has a water jacket surrounding vertical tubes 13; the side and end walls being removed to show the tubes. Trapped liquid return pipe 14 delivers the entire condensate of the reflux condenser into the stated collecting device somewhat below the level of the body of liquid therein. A vent pipe, cooled at 15 is provided to take care of any permanent gases or uncondensable vapor.

Where the liquid withdrawn at 10 is sent to a second or recovery column (not shown) to remove the water and recover the alcohol and benzol in concentrated form, the condensate there produced may be returned to the column 1 either through the alcohol inlet means 5 previously mentioned, or through a special inlet system 16.

The apparatus of Figure 2 is exactly the same as that of Figure 1, with the exception that the collecting device 9, in lieu of being located within the head of the column, is located outside and is surrounded by heat insulating lagging 17. Overflow communication with the head of the still is through trapped pipe 18.

The present invention may be used in dehydrating other hygroscopic liquids, such as the propyl and butyl alcohols, the glycols, etc. Instead of using benzol, other volatile liquids, insoluble, or substantially insoluble, in water, such as gasoline, petroleum ether, etc., may be employed.

What I claim is:—

1. In the dehydration of alcohol containing water in a column still with the aid of benzol, the process which comprises so operating such column as to produce a mixture of the vapors of alcohol, water, and benzol at its head having such a composition that two liquid layers would be formed upon condensing said mixture, condensing substantially the entire body of vapors from the head to form a condensate at substantially still head temperature, separating and withdrawing from the condensate a minor fraction of the layer of liquid occurring therein which contains a greater per cent of water than the other layer therein, and returning the rest of the condensate to the still.

2. In the dehydration of alcohol containing water in a column still with the aid of benzol, the process which comprises so operating such column still as to produce a mixture of the vapors of alcohol, water, and benzol at its head having such a composition that two liquid layers would be formed upon condensing said mixture, condensing substantially the entire body of vapors from the head to form a condensate at substantially still head temperature, said condensate containing a layer rich in water but including a small amount of alcohol and benzol, and a second layer immiscible with the layer rich in water, returning to the still the said second layer and a major fraction of the layer rich in water, introducing fresh alcohol containing water to the still, and withdrawing from the system the remaining minor fraction of the layer rich in water, the amount of the minor fraction so withdrawn being that which will carry water in an amount equal to the water entering the still with the alcohol containing water to be dehydrated.

3. In the dehydration of alcohol containing water in a column still with the aid of benzol, the process which comprises so operating such column still as to produce a mixture of the vapors of alcohol, water, and benzol at its head having such a composition that two liquid layers would be formed upon condensing said mixture, condensing substantially the entire body of vapors from the head to form a condensate at substantially still head temperature, separating and withdrawing from the condensate about one-third of the layer rich in water, and returning to the still the other layer and the remaining two thirds of the layer rich in water.

4. In the dehydration of alcohol containing water in a column still with the aid of benzol, the process which comprises so operating such column still as to produce a mixture of the vapors of alcohol, water, and benzol at its head having such a composition that two liquid layers would be formed upon condensing said mixture, condensing substantially the entire body of vapors from the head to form a condensate at substantially still head temperature, separating and withdrawing about one-third of the layer rich in water and returning to the still the other layer and the remaining two thirds of the layer rich in water, redistilling the withdrawn third so as to obtain water and a distillate containing benzol and alcohol in concentrated form, returning said distillate to the stated still, and discharging the residual water.

In testimony whereof, I have hereunto affixed my signature.

JOHN A. STEFFENS.