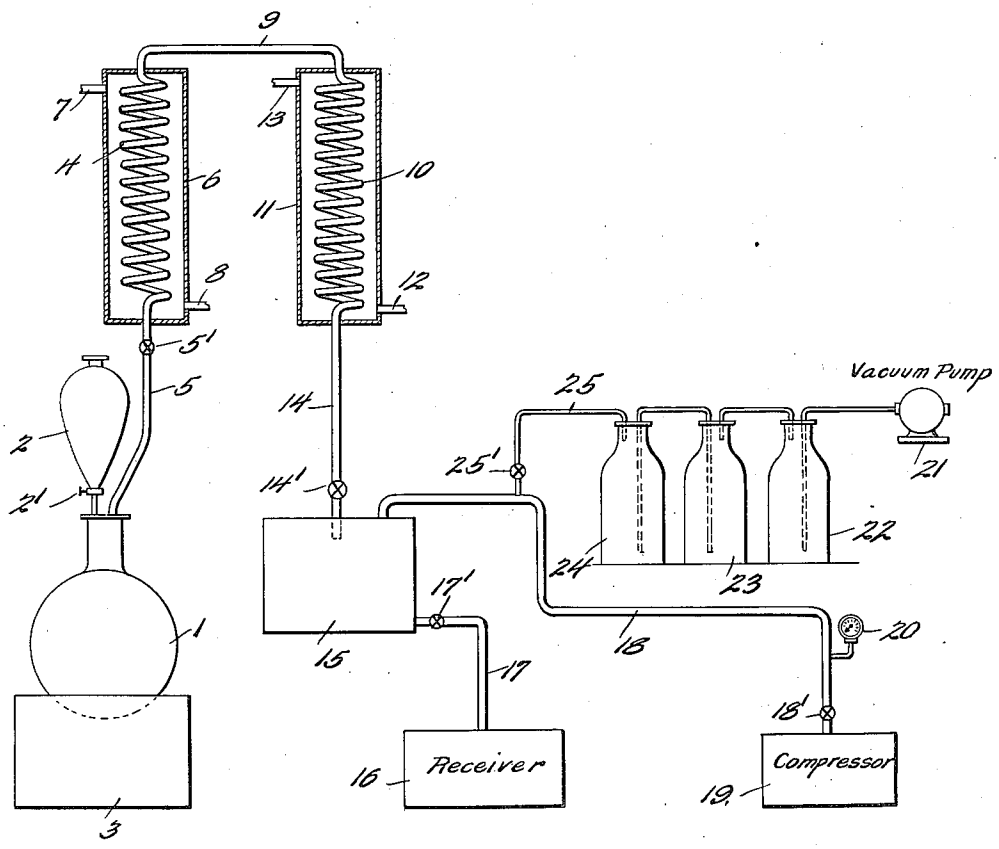
Oct. 17, 1939. L. M. CHRISTENSEN 2,176,208

METHOD OF PRODUCING DENATURANTS OF ALCOHOL

Filed May 13, 1937



Inventor

Leo M. Christensen,

By Seward Davis

Attorney

Patented Oct. 17, 1939

2,176,208

UNITED STATES PATENT OFFICE

2,176,208

METHOD OF PRODUCING DENATURANTS OF ALCOHOL

Leo M. Christensen, Atchison, Kans., assignor to The Chemical Foundation, Incorporated, New York, N. Y., a corporation of Delaware

Application May 13, 1937, Serial No. 142,340

7 Claims. (Cl. 202—77)

This invention relates to the production of denaturing compounds for employment with industrial alcohol, more particularly to an improved method of, and apparatus for, the production of isonitriles.

The denatured alcohol employed in the industries is, as is known, ethyl alcohol which is rendered unfit for beverage purposes and external application by the addition of a denaturant. When properly denatured, such alcohol is tax-free. Typical substances which have been employed in the past for denaturation are; methanol, benzine, "Aldehol", ether, acetone, and the like, that is, substances with markedly disagreeable odors and flavors, and poisonous properties.

The contemplated use of the industrial alcohol largely establishes or determines the particular type of denaturant employed. A substance which is effective for denaturing alcohol for one particular use may be entirely unsuited for denaturing alcohol intended for another use. Thus it is that a large number of formulae, some eighty or more, have been granted in this country for the preparation of denatured alcohol for various industrial uses.

A tremendous potential use for alcohol is as a motor fuel. Blends of alcohol and gasoline have long been employed as a motor fuel in Europe. In this country the potentiality of this type of power fuel is rapidly being recognized and particularly as a method of economically utilizing domestic farm products.

As has been explained in copending application Serial No. 85,181, filed June 13, 1936, the employment of alcohol as a motor fuel presents a special problem in denaturation. A denaturant for power alcohol, in addition to possessing the usual properties of a good denaturant, must also be of such a character that it will have no corrosive action on the metal of the engine and will not tend to form gums from constituents of the hydrocarbon fuel with which it is blended. It furthermore should leave little or no residue upon distillation, as such residues would tend to deposit in the valve seats and thus materially diminish the efficiency of the motor.

As described in the copending application referred to, these desirable characteristics are found in the carbylamines, and particularly in the alkyl carbylamines or alkyl isonitriles. These substances are colorless substances freely soluble in alcohol and ether, and slightly soluble in hydrocarbon oils. They have a characteristic, unbearable, putrid odor and are relatively toxic. The several members of the series have boiling points within the desirable range, that is to say boiling points closely approximating that of ethyl alcohol. These compounds are so pungent that the addition of even minor amounts of them to ethyl alcohol most effectively denatures it.

The extreme potency of these substances, while a marked advantage in use, does, however, render the problem of production exceedingly difficult. The isonitriles, in pure or highly concentrated form, have such a disgusting odor that it is substantially impossible to induce workers to operate with them. In the concentrated form, furthermore, they are highly toxic. Finally, as would be expectable in view of their characteristics, they are extremely difficult to ship and the restrictions imposed on shipment render the shipping cost substantially prohibitive.

It has been found that these highly efficacious denaturants may be made readily available for denaturation of power alcohol and the enumerated objections to the production of these compounds eliminated by a novel method of manufacturing the product. The broad concept of the present invention comprehends the idea of initially producing a solution of isonitrile in a solvent such as alcohol. This is in sharp contradistinction to prior methods in which the substantially pure isonitrile was first produced by known methods and was then dissolved in alcohol. Operating under the present invention, the isonitrile is formed, so to speak, in situ in a special vehicle and any desired degree of dilution. By thus dissolving or extracting the isonitrile, or isonitrile mixture, from the moment of formation, the disadvantages of production above mentioned are largely eliminated. The dilution of the product in situ thus enables the recovery of a solution which, while eminently effective for the denaturation of alcohol, does not present the objectionable characteristics of the pure or highly concentrated isonitrile; that is to say, in the product produced by the present method, the objectionable features are mitigated to such an extent as to permit commercial production of the product.

It is particularly to be observed that when operating under the present invention the mitigating vehicle, so to speak, which is employed performs a number of functions in the method. In the first place the alcohol is employed as a reactant, functioning directly to effect the reaction. In the second place the alcohol serves as a solvent-diluent for the isonitrile, reducing its obnoxious odor and toxicity to the extent that the product may be handled and shipped without undue difficulty. Finally, the mitigating vehicle utilized constitutes the ultimate material which is to be employed, namely a power alcohol.

The invention, therefore, may be considered to relate to the production of a denaturant in power alcohol in which the denaturant is produced in situ in the alcohol, thus at the one time forming a denaturant and intimately blending it with the material with which it is to be ultimately employed. This, again, is in sharp contradistinction

to prior methods of denaturation in which the denaturant was separately prepared and then shipped to some blending plant to be there admixed with the alcohol. Under the present method the denaturant is formed directly in the alcohol with which it is to be employed. The invention, therefore, may be equally well defined as a method of producing a denatured alcohol concentrate which may be directly blended with additional quantities of alcohol, or may be shipped to a distant blending plant.

Consonant with the fundamental principle of the present invention, that is the practical and safe production of denatured alcoholic concentrates containing isonitriles, a further feature of the method is its effectuation in a closed system. In these circumstances, therefore, the isonitrile is formed in a closed or sealed system and the isonitrile, as formed, is dissolved or extracted in any desirably large quantity of a solvent vehicle to produce a denatured alcohol concentrate which may be readily handled, shipped and mediately or immediately blended with additional quantities of alcohol and/or gasoline.

In carrying out the process, the desired isonitrile, or mixture of isonitriles, is produced by utilizing a modified carbylamine reaction, that is to say, by reacting primary amines with chloroform to produce the corresponding alkyl cyanide according to the following equation:

$$R.NH_2+CHCl_3 \rightarrow R.N=C$$

wherein R represents an alkyl group.

The reaction is effected in the presence of alcohol. It has been found that this reaction may be carried out by utilizing cheap technical sodium hydroxide rather than the more expensive potassium hydroxide, as has been done in the past. In one form of the invention, therefore, a suitable primary amine (or mixture of amines) is caused to react with chloroform in the presence of at least a stoicheometrical amount of sodium hydroxide and in the presence of a marked excess of ethyl alcohol. The reaction is carried out in a closed system and preferably with gradual additions of the chloroform to the primary amine-caustic mixture.

After the reaction has run to completion, the alcoholic mixture is distilled, preferably under reduced pressure, and the distillate, comprising the isonitrile dissolved in alcohol, is collected in a closed receiver in which, if desired, it may be absorbed in additional quantities of alcohol. The liquid product in the closed receiver may then be transferred through a closed pipe system to a storage vessel, preferably by pneumatic pressure. In these circumstances, as will be appreciated, the isonitrile is taken up or extracted, as formed, in a solvent-diluent vehicle and co-distilled and transported with such vehicle. As will be understood, the degree of dilution of the isonitrile may be controlled and varied to any degree desired. The denaturant concentrate thus produced may be piped directly to a blending plant to be dissolved in additional quantities of alcohol and/or gasoline in the proportions desired for the ultimate use or, if desired, the concentrate may be packed in suitable sealed containers for shipment.

In order to enable a more ready comprehension of the invention, a simplified apparatus in which the process may be effected is shown diagrammatically in the single figure of the accompanying drawing.

By way of preliminary explanation, it is to be understood that it is well known that primary alkylamines may be reacted with chloroform, in the presence of alcoholic potash, to produce the corresponding alkyl-isocyanide. In fact this reaction, known as the carbylamine reaction, is the one generally used in analytical work to distinguish the primary from the secondary and tertiary amines.

In this typical carbylamine reaction but a small amount of alcohol is necessary to institute and complete the reaction. Thus when substantially stoichiometrical amounts of the reagent are employed, for example 22.5 grams of monoamylamine, 31 grams of chloroform, and 44 grams of potassium hydroxide, less than 8 grams of ethyl alcohol are required to effect the reaction. In the past, as indicated, the carbylamine reaction was utilized for analytical work and, as a relatively pure or concentrated isocyanide was desired, an excess of alcohol was not employed and was not desirable. This reaction is to be carefully distinguished from that contemplated under the present process in which a marked excess of alcohol is definitely established for the purpose of insuring a positive and novel result.

In one phase of the invention, therefore, a primary amine is reacted with chloroform and technical sodium hydroxide in the presence of a marked excess of ethyl alcohol. In operating the novel process for the denaturation of alcohol by producing the denaturant in situ in the alcohol, the reagents are admitted in any desired sequence to the still or reactor 1. This element is provided with means, such as the dropping funnel 2, having a control valve 2', for admitting chloroform in regulated amounts. With the still 1 also is associated a heater 3 for the purpose of heating the reaction product to distillation temperatures. In a preferred procedure, chosen quantities of the primary amine, caustic and alcohol, are first admitted to the reactor 1, the reactor is then sealed and the chloroform is admitted slowly and in regulated amounts from the vessel 2.

As is known, the reaction described proceeds spontaneously and vigorously with considerable evolution of vapors. To insure complete reaction the still is connected with a reflux condenser 4, through the vapor line 5, controlled by valve 5'. The reflux condenser may be of any suitable type. It is illustrated as a simple liquid cooled worm of conventional type. The worm may be positioned within any suitable container 6, through which a cooling medium flows by way of the inlet and outlet lines 7 and 8 respectively.

The reflux condenser is connected, by the overhead line 9, to the distillation condenser 10. This, similarly, may be of any desired type and of a size sufficient to satisfy the requirements of the particular installation. Condenser 9 preferably is set within a container 11 and is positively cooled by a cooling medium admitted through inlet 12 and discharged through outlet 13.

The distillation condenser 9 is connected by the condenser line 14, controlled by valve 14', to the sealed container 15. The container 15, in turn, is connected to a receiver or storage vessel 16 through the line 17, controlled by valve 17'. The line 16, it is to be observed, is connected to a low point of the container 15; that is to say, below the liquid level of the condensate collecting in container 15. In these circumstances the full hydrostatic head of liquid in the container, in addition to any positive pressure imposed on the liquid surface, is utilized for discharging the contents.

As indicated hereinbefore, a salient feature of

the present invention is to eliminate handling of the product and to prevent the escape of noxious fumes or vapors. This is done not only by effecting the reaction in a closed or sealed system, but also by effecting the transfer of the product in a sealed circuit, in which circuit the isonitrile, or isonitrile mixture, is absorbed in an absorbent vehicle.

For the purpose of transferring the alcohol-isonitrile concentrate from the container 15 to the receiver 16, positive air pressure is utilized. As shown, the upper portion of the condensate container 15 is connected through the line 18, controlled by valve 18', to the compressor 19. Interposed in the line 18 is a gauge 20 for indicating the pressure or vacuum obtaining during the operation. With this type of construction, the compressor may be operated to impose any desired degree of pneumatic pressure on the condensate in container 15 and thus readily force such condensate through a closed pipe line to storage.

As will be appreciated, the present treatment is carried out in two steps or stages. In the first stage the reagents react according to the following equation:

$$R.NH_2+CHCl_3+3NaOH \rightarrow R.N:C+3NaOH+3H_2O$$

As the reagents interact, the vapors evolved are condensed in condenser 6 and reflux condensate flows back into the still. The desired reaction product, that is the alkyl isonitrile in solution in alcohol, is then recovered by distillation.

To avoid any decomposition of the isonitrile the distillation is preferably carried out at a reduced pressure, and the distillation is so controlled as to produce a substantially homogeneous distillate comprised essentially of isonitrile dissolved in alcohol.

The distillation under reduced pressure may be accomplished, as will be appreciated by those skilled in the art, by utilizing any suitable type of apparatus. That shown in the drawing is merely illustrative of any system which is effective to establish a reduced pressure in the still and to enable a low temperature distillation. As shown, a source of suction or vacuum, such as a vacuum pump 21, is connected through a suitable trap system, such as traps 22, 23 and 24, to the distillation apparatus. In the particular apparatus chosen for illustration the vacuum line 25, having the control valve 25', communicates with the line 18 and thence with the container 15. Manifestly, however, such connection may be made at any other suitable point in the system.

Similarly, in lieu of the vacuum pump 21, any other apparatus which is effective to establish a reduced pressure in the distillation system may be used. Thus, in lieu of the vacuum pump, an eductor unit may be utilized. For example, a high velocity stream of alcohol may be forced through an eductor or inspirator, the suction inlet of which is connected to line 14, and the discharge from which empties into container 15. In the operation of this type of structure the high velocity stream of alcohol passing through the eductor induces or establishes a reduced pressure in line 14, condensers 10 and 6 and still 1. This high velocity stream also functions to condense and absorb the evolved vapors of isonitrile and alcohol.

Any other type of apparatus functioning in an equivalent manner may be employed. The precise operations carried out under the present method will have been appreciated from the foregoing description. Thus for the preparation, for example, of a denaturant concentrate of alcohol and amyl isonitrile, the following operation may be carried out. A charge comprising approximately 1000 grams of technical sodium hydroxide (76%), 542 grams of mixed monoamylamine and 920 grams of ethyl alcohol is admitted to the still. It is to be observed that the quantity of alcohol here employed is approximately five times the theoretical amount actually required. The still 1 is then closed, valve 5' is opened and chloroform is added slowly from the funnel 2. The flow of chloroform is preferably controlled so as to maintain the reaction mass in a state of gentle ebullition. After the addition of all of the chloroform, the reaction mixture is allowed to reflux for a period of thirty minutes more or less, that is until the reaction has ceased. During this period the evolved vapors are condensed in reflux 6 and the condensate drained back to the still. The temperature and velocity of the cooling medium for the condenser are controlled so as to secure efficient condensation, in the manner known to those skilled in the art.

After the reaction has ceased and all condensate is drained from condenser 6 to the still, conditions are adjusted to insure distillation. For this purpose valves 25' and 14' are opened (valve 18' being closed) and the pump 21 is operated to establish a reduced pressure in the distillation system 1—6—10—15. The reaction mixture is then heated, by heater 3, to distillation temperatures and the mixture distilled to dryness.

In these circumstances a mixture of alcohol, isonitrile and water vapor is evolved and condensed in condenser 10. The total condensate flows through line 14 to container 15. After the completion of the distillation cycle the vacuum pump is stopped and the vacuum in the system released, as for example through valve 2'.

The condensate in tank 15 is then forced to receiver 16 where, if desired, it may be absorbed in or blended with additional quantities of alcohol. To effect this transfer valves 14' and 25' are closed and valves 17' and 18' are opened. The compressor 19 is operated and the pneumatic pressure thus developed is utilized to force the denaturant concentrate through line 17 to receiver 16, or to any other unit of the plant. When the condensate in tank 15 has been discharged, the valve 18' is closed and the pressure in the tank 15 is relieved through line 17 or any suitably positioned blowoff valve.

In practise it is preferred to cleanse the still prior to each reaction cycle. For this purpose the still may be flushed with a suitable cleansing medium, such for example as dilute sulphuric acid. The acid may then be removed and the still flushed with water or other suitable fluid so as to thoroughly cleanse it prior to the next cycle.

Operating under the conditions described above, and with the quantities of materials indicated, approximately 4 lbs. of isonitrile-alcohol concentrate is produced. The concentrate contains approximately 35% of impure isonitrile. As noted hereinbefore, the quantity of isonitrile in the concentrate may readily be varied by utilizing a greater excess of alcohol. Furthermore, as described, the concentration of the isonitrile may be further diminished by absorbing the distillate in additional quantities of alcohol in receiver 16.

It is particularly to be observed that, when operating under the principles of the present

method, the final product recovered from the closed system is a solution of the isonitrile in the alcohol with which it is to be used. The process may be carried out so as to control the concentration of the isonitrile at all times and at all stages of the process. This advantage, coupled with the fact that the entire reaction and blending is carried out in a closed or sealed system, eliminates the personal hazards and acute discomfort which heretofore attended the production of similar products.

The present method presents other potential advantages. For example, this method is ideally suited to the production of special blends of denaturants of the type described in copending application Serial No. 122,478, filed Jan. 26, 1937. A denaturant concentrate of an isonitrile, or mixture of isonitriles, with methanol, acetone, and the like, may readily be produced in this system. For this purpose methanol may be admitted to the still 1 at the termination of the reaction period, and may be co-distilled with the ethyl alcohol and isonitrile to produce an intimately blended concentrate. Again, if desired, the methanol or other denaturant may be admitted to the stream of the alcohol-isonitrile condensed in transit to the receiver 16. Yet again the supplemental denaturant may be primarily admixed with the vapors passing through line 9 or condenser 10 to be intimately blended with these vapors while at the same time functioning as a condensing agent. In short, the additional denaturant may be intimately blended with the main concentrate at any suitable stage in the system and in either the vapor or liquid phase.

While, for the purpose of explaining the invention, the conversion of a particular alkylamine (amylamine) has been described, it will be understood that this is merely illustrative and that other isonitriles may be produced in the same manner and in the same apparatus; it is equally apparent that a mixture of such isonitriles may be simultaneously produced.

It is further to be observed that the present system may be utilized, whenever it is desired, for the production of relatively pure isonitriles. In these circumstances a type of reaction described may be carried out in which the amount of alcohol is reduced to substantially that theoretically required. After reaction the isonitrile may be distilled and recovered in receiver 15. The condensate may be allowed to settle in tank 15, or may be transferred to receiver 16, so as to permit stratification and separation of the aqueous from the isonitrile layer. The separated isonitrile may then be removed and passed to suitable storage or otherwise disposed of.

It is to be noted that in this type of operation the major advantages of the utilization of a closed system are retained; that is to say, by utilizing the principles of the present invention, relatively pure isonitriles may be produced without the disadvantages of the older methods. The relatively pure isonitrile, while still maintained in a closed circuit, may be dissolved in alcohol or other solvent for utilization as a denaturant.

While preferred modifications of the invention have been described, it is to be understood that these are given to illustrate the underlying principles and as indicating the great flexibility of the process and the wide permissive range of products obtainable. The invention is not intended to be limited to the particular methods or products described, except as such limitations are clearly imposed by the appended claims.

I claim:

1. A method of denaturing ethyl alcohol which comprises, producing an alkyl isonitrile in a closed system and in contact with a portion of the alcohol to be denatured, then blending the resulting alcohol-isonitrile concentrate with the remaining ethyl alcohol to be denatured.

2. A method of producing denatured ethyl alcohol which comprises, producing an alkyl isonitrile from the corresponding alkyl amine in a closed system and in the presence of a marked excess of alcohol, co-distilling and co-condensing the isonitrile and alcohol in a closed system, and forcing the resulting concentrate through a closed circuit to the receiver and blending additional ethyl alcohol, to be denatured, with the concentrate in said closed circuit.

3. A method of producing denatured ethyl alcohol which comprises, producing an alkyl isonitrile from the corresponding alkyl amine in a closed system and in the presence of a marked excess of alcohol; co-distilling and co-condensing the distillable and condensable reaction products in a closed system and forcing the resulting concentrate through a closed circuit to a receiver, and blending the concentrate with additional ethyl alcohol in such receiver.

4. A method of producing denatured ethyl alcohol which comprises, producing the desired alkyl isonitrile from the corresponding alkyl amine in a closed system and in the presence of a marked excess of alcohol, co-distilling the formed isonitrile and alcohol under a vacuum, co-condensing the vapors of isonitrile and alcohol in a closed condenser and forcing the condensate, under pneumatic pressure, through a closed circuit to a receiver, and blending the concentrate with additional ethyl alcohol to be denatured.

5. A method of producing denatured power alcohol, which comprises, reacting a primary alkyl amine with chloroform, caustic soda, and an excess of ethyl alcohol to produce the corresponding alkyl isonitrile; distilling the reaction products, and recovering the alkyl isonitriles in solution in the quantity of alcohol employed in the reaction, and blending such concentrate with additional ethyl alcohol to be denatured.

6. A method of producing denatured power alcohol, which comprises reacting a primary alkyl amine with chloroform and caustic soda, in a closed system and in the presence of a marked excess of ethyl alcohol; co-distilling and co-condensing the volatile reaction products together with the excess of ethyl alcohol in a closed distilling and condensing system, and blending additional ethyl alcohol to be denatured with the said condensed reaction products in the system.

7. A method of producing denatured ethyl alcohol to produce a power alcohol fuel which comprises, reacting a primary amine with chloroform and with caustic soda, in the presence of the ethyl alcohol which is to be denatured, co-distilling and co-condensing the volatile and condensable reaction products together with such excess alcohol, and blending the condensate thus produced with additional quantities of alcohol to be employed as a fuel.

LEO M. CHRISTENSEN.