June 7, 1949. H. BELLER ET AL 2,472,084

CARBURETOR PROCESS FOR ACETYLENE REACTIONS

Filed Oct. 10, 1945

4 Sheets-Sheet 1

Fig. 1

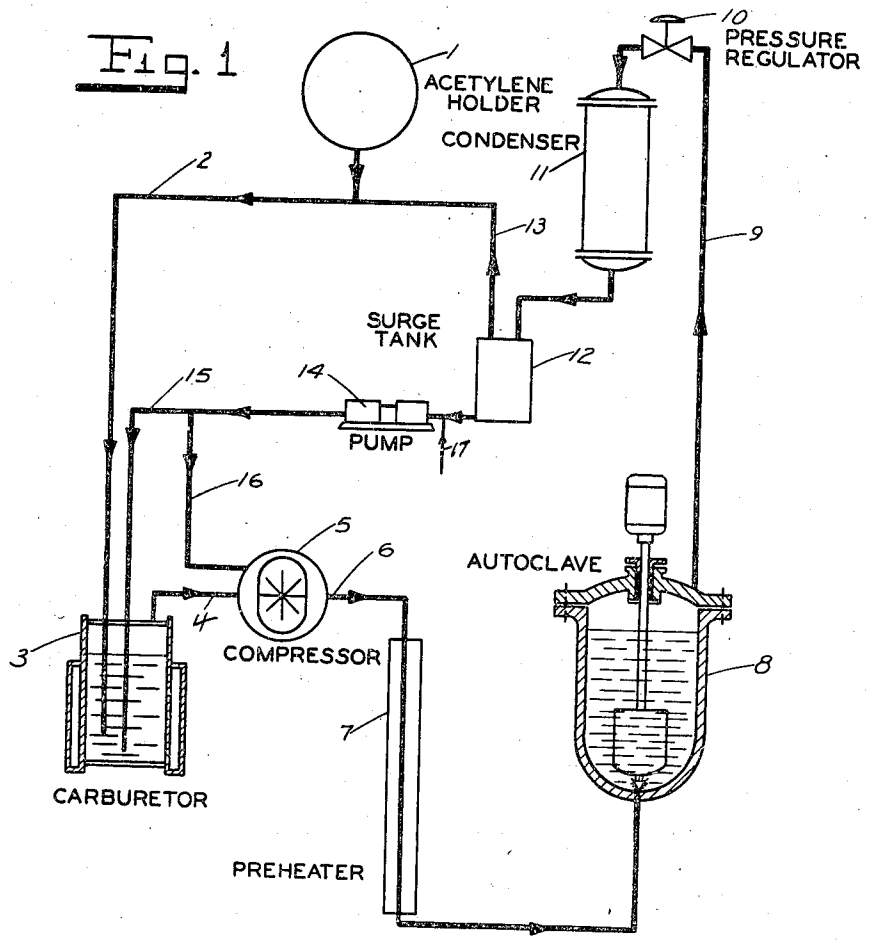
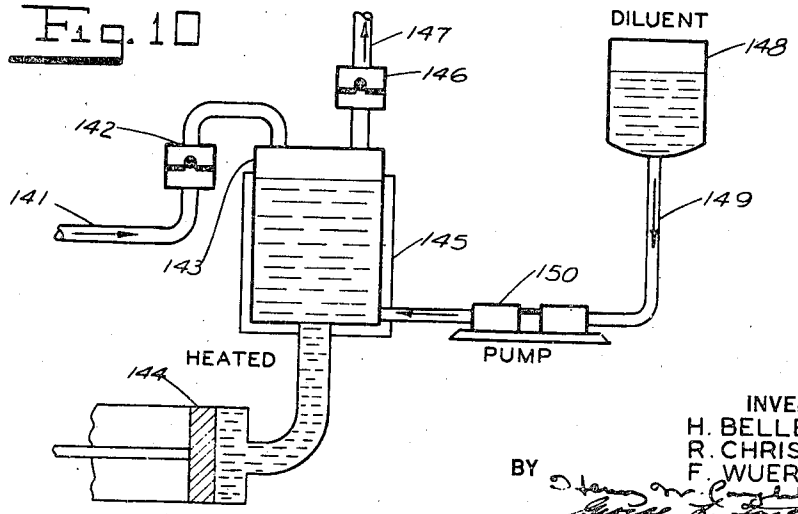


Fig. 10



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CARBURETOR PROCESS FOR ACETYLENE REACTIONS

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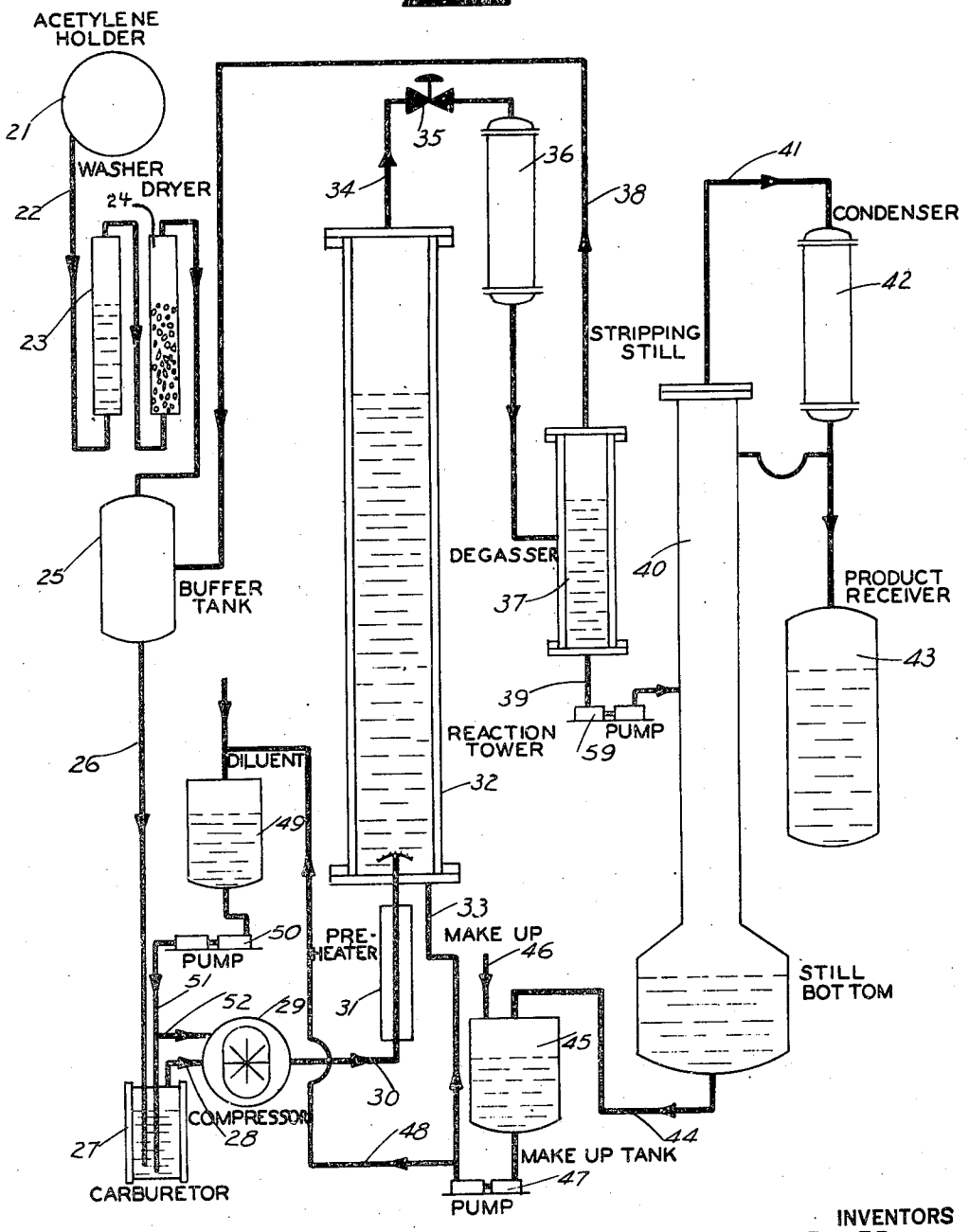
Fig. 2



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CARBURETOR PROCESS FOR ACETYLENE REACTIONS

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Fig. 3

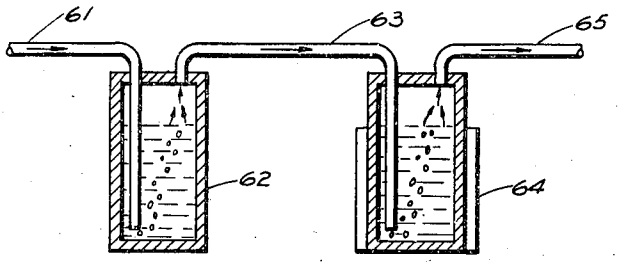


Fig. 4

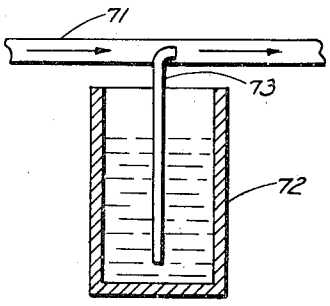


Fig. 5

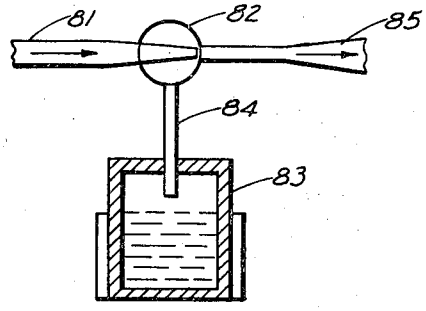


Fig. 6

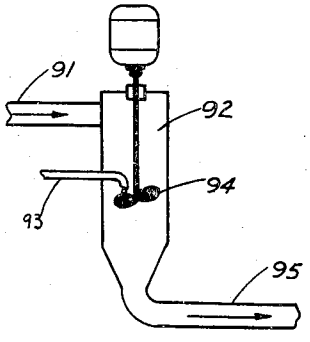
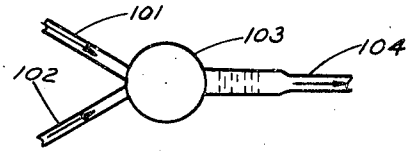


Fig. 7



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CARBURETOR PROCESS FOR ACETYLENE REACTIONS

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Fig. 8

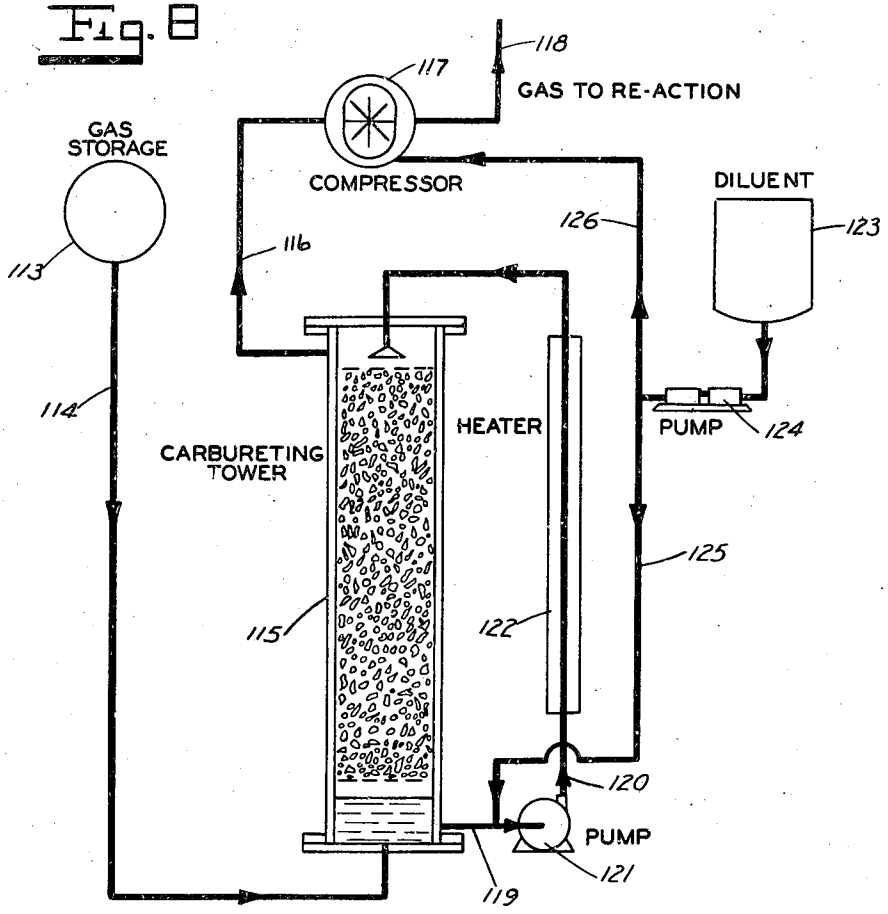
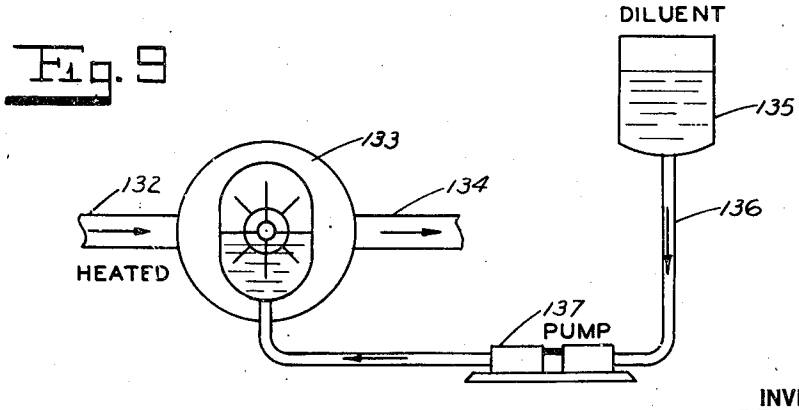


Fig. 9



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Patented June 7, 1949 2,472,084

UNITED STATES PATENT OFFICE

2,472,084

CARBURETOR PROCESS FOR ACETYLENE REACTIONS

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Application October 10, 1945, Serial No. 621,620

12 Claims. (Cl. 260—614)

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The present invention relates to the handling of acetylene and is particularly concerned with an improved method of handling acetylene at elevated temperatures and/or pressures, in order to eliminate the explosive hazards characteristic of acetylene under such conditions. In its more specific embodiments, the present invention is particularly concerned with improvements in reactions involving the use of acetylene under elevated temperatures or pressures.

From the standpoints of economics and prospective availability, acetylene remains one of the most attractive raw materials in the entire organic chemical field. Although many valuable reactions involving acetylene are known, the commercial exploitation thereof has been greatly retarded by the fear of violent explosions. As is well known to those experienced in this art, acetylene, under elevated pressures and particularly at elevated temperatures, is inherently unstable. In general, a pressure of about 15 pounds per square inch is considered the maximum pressure at which acetylene may be handled with relative safety and, at all higher pressures or at elevated temperatures or under a combination of both conditions, great care has to be exercised and expensive and complicated mechanical installations have to be provided in order to minimize the danger of explosion. However, even with the most elaborate safety precautions, explosions may occur simply because acetylene, under elevated pressures and temperatures, is inherently unstable.

The instability of acetylene at elevated pressures and temperatures has seriously limited its use and complicated its handling and use. Thus, acetylene is commercially transported only in special commercial shipping containers, cylinders filled with acetone and an inert filler body. When attempts have been made to employ acetylene in chemical reactions requiring the use of elevated temperatures or pressures, the installations required in chemical plants employing such process have been extremely expensive, due to the precautions which must be taken in order to minimize the danger of explosion. Thus, it has been common practice to dilute the acetylene with an inert gas, such as nitrogren, hydrogen, carbon monoxide or mixtures thereof. However, the amount of diluent gas required to render the mixture non-explosive under normal operating conditions, is high, generally 50% or higher, so that the investment due to the larger sized compressors, pipes, storage vessels and the like, which are required, is substantially increased, even for

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merely handling the acetylene with safety. The effects of the use of inert gases in order to produce a diluted acetylene which is non-explosive, are even more pronounced in many chemical process steps to which the acetylene is subjected. Thus, the use of a diluent gas substantially increases the over-all pressure which must be employed in processing steps, thus further increasing the capital cost. At the same time, the presence of a diluent frequently results in a lowered rate of reaction and has other undesirable process effects. The explosive limits of acetylene-nitrogen mixtures, for example, which have been employed most commonly heretofore, demand that, above 100° C. and 100 pounds per square inch pressure, where the vast majority of acetylene reactions must be run to proceed at a practical rate, the acetylene be diluted with at least 55% nitrogen to remain within the non-explosive range. It is obvious that when one adds together the partial pressure due to the inert gas, the partial pressure due to the starting materials and the partial pressure due to the reaction products, the grand total makes the partial pressure exhibited by acetylene appear low. The relatively low concentration of acetylene in such mixtures therefore adversely affects the reaction rate and diminishes it to such an extent that many processes involving the use of acetylene have been rendered economically unsound. It is, therefore, obvious that nitrogen and other diluent gases can be employed to introduce a safety feature into a process involving the use of acetylene at an elevated pressure or temperature only at the expense of a high over-all operating pressure and a relatively low partial pressure of acetylene with a consequent lowering of the reaction rate.

Briefly stated, the present invention comprises a process for rendering acetylene non-explosive in order that it may be safely handled or employed in chemical reactions by saturating the acetylene with the vapors of a normally liquid, suitable diluent. We have discovered that when acetylene is diluted with a normally liquid diluent having a relatively high vapor pressure, substantially smaller amounts of such diluent may be employed to produce a non-explosive mixture, as compared with inert diluent gases. The saturated acetylene may be safely handled and particularly outstanding advantages are obtained in process steps to which the saturated acetylene is employed. Thus, we have found that the over-all pressure required is frequently substantially reduced, while at the same time, the reaction rate is substantially increased. Additional advantages

are provided by savings in the size of necessary compressors and compressing work, particularly in processes requiring recirculating of the gas.

We term our process of saturating acetylene with a normally liquid diluent having a relatively high vapor pressure as a "carburizing" or "carbureting" process and the non-explosive mixtures, more fully described hereinafter, of acetylene and such normally liquid diluents having relatively high vapor pressures will hereinafter be referred to as "carburized" or "carbureted" acetylene. As employed in the present specification, the terms "carburize," "carburete" and the like are used in the broad sense of enriching a gas with the vapors of a volatile normally liquid compound, and are not used in the restricted sense of enriching a gas by the addition thereto of an agent of a higher carbon to hydrogen ratio than the lean gas itself. Such a restricted meaning for the term is obviously inapplicable in the present instance, since, in general, the diluents available for use in the present invention have a lower carbon to hydrogen ratio than acetylene.

The diluent which is employed to carburize the acetylene may be an inert diluent or frequently may advantageously be a compound with which the acetylene is to be reacted or a product of the reaction. Thus, in the event the acetylene is to be employed in a chemical reaction in which one of the reactants is a normally liquid compound having a relatively high vapor pressure, as is frequently the case, such reactant may advantageously be employed as the diluent for the acetylene in the manner more duly hereinafter described. Again, in many cases, some product of the reaction may be a normally liquid compound which is suitable for use as a diluent and may be so used advantageously. However, if desired, many of the advantages of the present invention may be obtained, even in such cases, by employing an inert diluent and, in instances where the compounds to be reacted with acetylene, or the products of the reaction, have too low a vapor pressure to be satisfactory for use as diluents, a normally liquid organic compound, which is inert under the conditions of the reaction, may be used as a diluent.

The particular compound which may most advantageously be employed as the diluent will depend, especially if the acetylene is to be employed in a chemical reaction, on the particular reaction in which it is to be employed and also on the conditions, especially the temperature and pressure, under which the acetylene is to be handled or used. Suitable compounds for use as inert diluents under a relatively wide range of conditions are the lower boiling liquid hydrocarbons, ethers or esters, for example, aliphatic or cycloaliphatic hydrocarbons, such as, hexane, heptane, octane, cyclohexane or others, and isomers or mixtures thereof; also may aromatic or naphthenic hydrocarbons, such as benzene or toluene, may be employed. In addition, certain heterocyclic compounds, such as furfural, pyridine and the like, are suitable for use. Among the esters and ethers suitable for use as diluents are numerous products obtainable from reacting acetylene with alcohols or acids, such as n-butyl vinyl ether, vinyl acetate and others, in addition to such saturated ethers and esters as di-ethyl ether, ethyl acetate and the like. It should be understood that a compound which may serve as an inert diluent under the conditions of one process may be a reactant in or cause an undesirable secondary reaction under the conditions of another process. Those skilled in the art can readily select suitable diluents, either an inert diluent, a reactant or a product of the reaction, for use in any specific process.

In order to simplify the description of the present invention, it will first be described, with particular reference to its use, in reactions involving the use of acetylene. In order to facilitate the present description, there is appended hereto several sheets of drawings in which the several figures are diagrammatic representations of apparatus suitable for use in practicing the process of the present invention.

In the drawings:

Fig. 1 is a schematic representation of one form of apparatus suitable for use in practicing this invention.

Fig. 2 is a flow chart illustrating another form of apparatus suitable for use in practicing this invention.

Figs. 3 to 8, inclusive, are schematic illustrations of several specific forms of "carbureting" devices suitable for use in practicing this invention, while

Figs. 9 and 10 are schematic illustrations of two types of compressors which also are adapted to function as "carbureting" devices for use in practicing this invention.

When it is desired to employ the batch process for acetylene reactions, as is generally the case when the product formed has too high a boiling point to be distilled continuously from the reaction vessel under the conditions of temperature and pressure at which the reaction is carried out, a type of apparatus illustrated in Fig. 1 may be employed to good advantage. As there illustrated, acetylene at a low pressure, atmospheric or at most a few pounds superatmospheric pressure, is led from a suitable source, illustrated in the drawings as gas holder 1, through line 2 to carburetor 3, wherein it is saturated with a suitable diluent, the carburetor 3 being maintained at such a temperature as to cause the desired degree of saturation of the acetylene stream with the diluent vapor. The saturated acetylene is then passed through line 4 to compressor 5, illustrated as a heated liquid seal centrifugal compressor, where it is brought to the desired pressure, and thence through line 6 and preheater 7, if a further increase in temperature to the reaction temperature is necessary, and thence is introduced into the pressure autoclave 8 which is maintained at the correct temperature and pressure for the particular reaction in question to take place.

By this method, the diluent in the carburetor 3 is gradually transferred to the autoclave 8. If the diluent has a vapor pressure greater than the pressure at which the reaction is being run, it may be continuously released through line 9 by means of release valve 10, along with any unreacted acetylene, into condenser 11, wherein the diluent is condensed and thence flows to surge storage tank 12, the acetylene being withdrawn through line 13 and returned to line 2. The recovered diluent is removed from surge tank 12 by make-up pump 14 and returned to carburetor 3 through line 15. A portion of the diluent may be supplied through line 16 to heated compressor 5 to serve as a liquid seal and carbureting agent, as will be more fully described hereinafter.

As stated above, the batch process is most advantageously applicable to acetylene reactions in which a relatively high boiling product, i. e.,

one which is not vaporized at the temperature and pressure existing in the reactor, is produced. Consequently, in such process, the diluent employed is either a reactant or an inert diluent. However, it will be apparent to those skilled in the art that a process may be applied to acetylene reactions in which a relatively low boiling product is produced. In the event that the product is lower boiling than the compound reacted with acetylene, a portion of the product present as a vapor in the autoclave 8 may be removed, along with acetylene, through draw-off line 9, being condensed in condenser 11 and separated from the acetylene in surge tank 12 and returned to carburetor 3 through line 15 by pump 14, and thus serve as a diluent for the acetylene. In the event that a reactant is employed as a diluent, all or a portion of the reactant may be introduced into the process as a diluent through line 17 to pump 14 and thence through line 15 to carburetor 3. Various other modifications will be apparent to those skilled in the art and certain such modifications are more particularly described hereinafter and in the specific examples.

In Fig. 2, there is illustrated diagrammatically, an apparatus suitable for acetylene reactions which may be conducted in a continuous manner. As illustrated in the drawings, acetylene from a low pressure source, such as acetylene holder 21, is introduced into the process through line 22, being passed, if desired, through scrubber 23 and dryer 24 to buffer tank 25. From low pressure buffer tank 25, the acetylene is withdrawn through line 26 to carburetor 27, wherein it is saturated to the desired degree with the vapor of a suitable liquid diluent, the temperature of the carburetor being so adjusted as to give the desired degree of saturation of the acetylene, at the pressure used, with the particular diluent being employed. The saturated acetylene flows then through line 28 to compressor 29, where it is raised to the desired pressure, and is then introduced into reactor 32 through line 30, first passing through preheater 31, if further heating is required in order to maintain the desired reaction temperature. Other reactants may be introduced into reactor 32 through line 33. The reactor 32 may be of any desired design and the reaction products are continuously removed therefrom through line 34 and may be passed to any necessary separating means. As illustrated in the drawings, only such of the reaction products as are vapors under the conditions maintained in reactor 32 are removed through line 34 and, after passing pressure release valve 35 therein, flow through condenser 36 to degasser 37. Any unreacted acetylene is withdrawn from separator 37 to line 38 and returned therethrough to buffer tank 25 for recirculation. The reaction products are continuously withdrawn from the bottom of gas separator 37 through line 39 and introduced by pump 59 into still 40, wherein the desired reaction product is separated from any unreacted liquid reactant or diluent.

Assuming that the desired reaction product is lower boiling than the reactant and that a reactant is being employed as the carbureting agent, the vaporized product is withdrawn from the still 40 as an overhead vapor fraction through line 41 and flows through condenser 42, where it is condensed, and thence to product receiving tank 43. The unreacted starting material is returned from still bottom 40 through line 44 to make-up tank 45. Any necessary additional reactants may be introduced into make-up tank 45 through line 46 and are again introduced into reactor 32 through line 33 by make-up pump 47, a portion of the reactant also being returned through line 48 to surge tank 49. Diluent is withdrawn as needed from tank 49 by pump 50 and introduced through line 51 to carburetor 27, a portion of the diluent being introduced through line 52 to compressor 29, if needed, to serve as a liquid seal and carbureting agent therein.

It will be apparent that the specific method employed for separation of the reaction products withdrawn from degasser 37 forms, per se, no part of the present invention and the particular details thereof may readily be determined by those skilled in the art for effecting the desired separation. In particular, it will be noted that slight modifications of the method of and apparatus for separating the reaction products may be necessitated by the state in which the reaction products are obtained. Thus, depending on the relative boiling points of the various components thereof, the specific method of separating the reaction products may have to be modified somewhat from that just described.

It should be understood that in place of a simple carburetor of the type diagrammatically illustrated in the accompanying flow charts, Figs. 1 and 2, any suitable type of carburetor may be employed. Thus, a series of simple carburetors, as illustrated in Fig. 3, may be employed. As there illustrated, the acetylene gas flowing through line 61 is bubbled through a pool of diluent in receiver 62 and is partially saturated therewith. It then flows through line 63, through a second pool of diluent in receiver 64 which may be maintained at a higher temperature by suitable heating means, illustrated in the drawings as a steam jacket, and is further saturated with the diluent and leaves through exit pipe 65. Obviously, any number of such carburetors in series may be employed.

In Fig. 4, there is illustrated an aspirator-type of carburetor in which acetylene, passing through line 71, is carbureted by a diluent from container 72, through Pitot tube 73. In Fig. 5, there is illustrated a carburetor based on the Venturi principle. Acetylene enters through pipe 81 into chamber 82, where it is mixed with vapors of carburizing agent coming from heated container 83 through tube 84. The carbureted gas leaves through exit pipe 85. In Fig. 6, there is illustrated a mechanical type carburetor in which acetylene enters the mixing chamber 92 through pipe 91. The liquid carburizing agent is introduced into the chamber through pipe 93 onto a mechanically driven distributor plate 94. The carbureted gas leaves the chamber through exit pipe 95. In Fig. 7, there is illustrated a baffle type carburetor in which acetylene enters the mixing chamber 103 through pipe 101. The vapors of the carburizing agent are led into the mixing chamber through pipe 102, and the carbureted acetylene leaves through exit pipe 104. In large commercial installations, the carburization of acetylene may be performed with advantage in towers, as illustrated in Fig. 8. Acetylene from storage tank 113 is drawn through line 114 to carbureting tower 115, where it passes upward over filler bodies and out through exit pipe 116 to compressor 117, where it is raised to the desired pressure and the compressed carbureted gas is removed through line 118. The carbureting agent is circulated over the filler bodies by means of lines 119 and 120 by pump 121 and is

heated to the desired temperature in heater 122. Carbureting medium is withdrawn from storage tank 123 by pump 124, as needed, and introduced through line 125 to the suction side of pump 121, a portion of the carbureting agent being sent through line 126 to compressor 117 to serve as a liquid seal and carbureting agent therein.

In order to avoid any explosion hazards during the compression of the acetylene gas from atmospheric or lower pressure to the pressure at which the reaction takes place, it is advisable to add the diluent vapor before the acetylene enters the compression stage or, if desired, the acetylene may be carburized at some intermediate stage of its compression. Thus, by using slow acting compressors, it is possible to compress acetylene safely to higher pressures, provided the temperature of the solvent saturated gas is increased sufficiently before compression so that no condensation of the vapors can occur in the compressor. An additional safety feature may be provided in this case by maintaining the temperature of the compressor above the dew point of the diluent vapor at the given pressure. The carbureted acetylene may also be compressed by using blowers, liquid piston pumps or other suitable apparatus which permit the compression of moist gases.

It is also possible, by employing a blower-type compressor with a liquid seal (Nash Hytor type), to cause the sealing medium to act as the carburizing agent, by the simple means of keeping the blower at a suitable temperature to ensure proper saturation of the acetylene passing therethrough.

Equipment which is satisfactory for the simultaneous carburization and compression of acetylene is schematically shown in Figures 9 and 10. In Fig. 9, there is illustrated a carbureting centrifugal compressor, the acetylene entering through line 132 into the heated compressor 133, where it is carburized and compressed, and leaves through exit pipe 134. The carburizing agent, which acts as a liquid seal in the compressor, is replenished from storage tank 135 through lines 136 by means of make-up pump 137.

In the carbureting piston compressor, illustrated in Fig. 10, acetylene enters through inlet pipe 141 over suction valve 142 into the compression chamber 143, filled with the liquid carburizing agent. The liquid in chamber 143 is moved by mechanical piston 144 and acts as a liquid piston. Suitable means, such as jacket 145, are provided for heating the carburized liquid in order to effect the desired degree of saturation of acetylene. The compressed carburized acetylene leaves the chamber 145 over discharge valve 146 and exit pipe 147. The carburizing agent is replenished from storage tank 148 through lines 149 by make-up pump 150.

It should be noted that in practicing the process of the present invention, it is desirable that the acetylene be diluted, at all times, while it is under pressure or at an elevated temperature. Thus, referring back to Fig. 1, it will be noted that if all the acetylene does not react in autoclave 8 and a portion thereof is withdrawn for recirculation through line 9, the diluent employed should be such that, in the vapor space in autoclave 8, a sufficient amount of diluent will be vaporized to dilute the acetylene collecting therein and withdrawn through line 9. After the acetylene passes pressure release valve 10 and the pressure is reduced sufficiently to remove the danger of explosion, the diluent may be separated from the acetylene, as illustrated in the drawings. Likewise, in the type of apparatus illustrated in Fig. 2, any vapor space in the reactor 32 should be filled with a diluted mixture of unreacted acetylene, if any, and diluent, and only after the pressure on the acetylene has been reduced on passing pressure release valve 35 should the acetylene be separated from the diluent, as illustrated in the drawings. The necessity of this precaution should be borne in mind in selecting a diluent for use in any particular process, in order that in any vapor space in the apparatus in which acetylene, under pressure, may collect, it will be diluted and thus rendered non-explosive. It will be apparent that at times, one diluent, for instance a reactant, may be employed as a diluent for acetylene prior to its entering the reaction zone, and another diluent, for instance a reaction product, may function as a diluent for the acetylene while it is still under pressure and after it leaves the reaction zone.

The degree to which the acetylene should be diluted with a diluent of the type specified will of necessity vary with the pressure at which the acetylene is to be used and, at a given pressure, the extent of dilution which is necessary varies with the particular diluent being employed. For example, with methanol vapor as a diluent, the explosion limits are shown in the following data:

Methanol—acetylene explosion limits

Lbs./sq. in. Abs.	Per Cent Acetylene
40	78
60	72.5
80	69
100	66
120	64

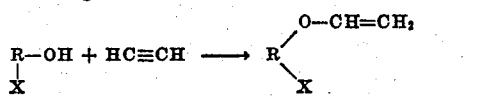
Those skilled in the art can readily determine experimentally the degree of dilution which is required at any particular pressure and with any specific diluent. Likewise, the temperature at which the carburetor should be held in order to secure the desired degree of dilution can readily be determined by simple experimentation by those skilled in the art. For example, the limits of explosibility may easily be determined by enclosing acetylene gas together with a predetermined amount of diluent vapor in a pressure vessel, heating the vessel up to the test temperature, and initiating a possible explosion by means of an electrically heated wire, provided inside the pressure vessel.

In order to more fully illustrate the practice of the present invention, examples of its use are given in several different fields. It should be understood that these examples are merely for the purpose of illustration and that the invention is not limited thereto. It will be understood that the pressures referred to in these specific examples and elsewhere in this specification are gauge pressures (superatmospheric), unless they are otherwise specifically defined.

Example 1

The process of the present invention may advantageously be employed for the production of vinyl ethers, for instance, by the process described in United States Patent No. 1,959,927 to Reppe, in accordance with which acetylene is caused to

react on hydroxy compounds in an alkaline medium. The general formula for such reaction is:



in which X represents either H,COOH, —COO metal, —NY_2, —$(OR)_n$—OY, groups Y being —H, —R or —ROH, and R being an alkyl, aryl or aralkyl radical.

In the production of methyl vinyl ether by employing the principles of the present invention, a type of apparatus illustrated in Fig. 2 may be employed. The vinylation tower **32** is charged approximately ¾ full with a suitable heat transfer means, (for instance, di-n-butyl acetal, B. P. 186° C., or a white hydrocarbon oil, B. P. 340–345° C.), in which is dispersed approximately ¼ part-by-weight of potassium hydroxide in a finely flocculent state. The entire system is kept anhydrous as well as oxygen-free to prevent the formation of undesirable by-products. Acetylene from the holder **21** is passed through the scrubber **23** to remove impurities, and thence through drier **24** to remove water, and into buffer tank **25** where it is held at a pressure of, for instance, 5 pounds per square inch. The acetylene then is passed into carburetor **27**, containing liquid methanol at a temperature of 64° C. The acetylene becomes saturated with methanol and thence passes to compressor **29** where it is brought to a pressure of 45 pounds per square inch. The compressed acetylene then flows through the preheater **31**, held at 145° C., and finally into the vinylation tower **32** which is held under a pressure of 45 pounds per square inch and a temperature of 145° C. The temperature of the carburetor is adjusted so that the molar ratio of methanol:acetylene entering the tower is 3:1. One mole of methanol is consumed in the formation of methyl vinyl ether per mole of acetylene in vinylation tower **32** according to the following equation:

$$CH_3OH + HC{\equiv}OH \rightarrow H_2C{=}CH{-}O{-}CH_3$$

To ensure that there is always an excess of diluent present, methanol is supplied continuously to the carburetor by means of pressure pump **47** from the make-up kettle **45**. Methyl vinyl ether, methanol and unreacted acetylene are continuously withdrawn from the top of the vinylation tower and, on passing over pressure release valve **35**, set at 45 pounds per square inch, the pressure thereon is reduced to 5 pounds per square inch. The methyl vinyl ether and methanol are condensed in condenser **36** and the acetylene separated therefrom in degasser **37**. Acetylene is returned to the buffer tank **25** via the return line **38**. The methyl vinyl ether and methanol are continuously withdrawn from the bottom of degasser **37** and pumped into the continuous stripping column **40**. Methanol is collected in the still bottom and is ultimately returned to make-up tank **45** through line **44**. The methyl vinyl ether is passed from the top of the stripping column **40** through line **41** to condenser **42** and is finally collected in product receiver **43**. The methyl vinyl ether is obtained in 96–98% yields as a clear colorless liquid boiling at 10° C. at atmospheric pressure.

If vinyl methyl ether is prepared in the same equipment but employing nitrogen as the diluent for the acetylene in place of carburizing the same, a pressure of 250 pounds per square inch is required. In the following table is given a comparison between the process using nitrogen as a diluent and the process of the present invention in which methanol is used as a diluent, on parallel runs in the same equipment, covering a period of 40 hours.

Operating Conditions	"Nitrogen Process"	"Carburetor Process"
System Pressure pounds per square inch	250	45
Temp. of Reaction Tower °C.	145	145
Acetylene Concentration per cent	65	99
Nitrogen Concentration do	35	0
Catalyst Concentration ($KOCH_3$) per cent	25	25
Time of run hours	40	40
Yield Methyl Vinyl Ether pounds	780	1,212
Yield per hour do	19.5	30.3
Yield based on Methanol per cent	80	96

Example 2

As described in above-mentioned United States Patent No. 1,959,927, ethyl vinyl ether may be prepared at 150° C. under a pressure of 15 to 30 atmospheres (225–450 pounds per square inch) using nitrogen and acetylene in the proportions of 1:2.

The process of the present invention may be applied to the production of ethyl vinyl ether, advantageously in an apparatus similar to that described in Fig. 2. The vinylation tower **32** is charged until it is substantially ¾ full with a suitable heat transfer medium (dibutyl acetal, B. P. 186° C., or white hydrocarbon oil, B. P. 340–345° C.) in which is dispersed approximately ¼ part-by-weight of potassium hydroxide in a finely divided flocculent state. The entire system is kept anhydrous and oxygen-free to prevent the formation of undesirable by-products. Acetylene is passed from holder **21** through scrubber **23** and dryer **24** to buffer tank **25**, as described in Example 1. From tank **25**, the acetylene, at a pressure of 4 pounds per square inch, flows into carburetor **27** containing liquid ethanol at a temperature of 75° C. The acetylene becomes saturated with ethanol in the carburetor and is then compressed by compressor **29** to 45 pounds per square inch, and then flows into preheater **31**, held at 145° C., and thence into vinylation tower **32**, held at a temperature of 145° C. and under a pressure of 45 pounds per square inch. Ethanol is supplied continuously to the bottom of the tower by means of pressure pump **47** from make-up tank **45**. In tower **32**, the acetylene reacts with ethanol to form ethyl vinyl ether in accordance with the following equation:

$$C_2H_5OH + HC{\equiv}CH \rightarrow H_2C{=}CH{-}O{-}C_2H_5$$

Ethyl vinyl ether, ethanol and unreacted acetylene are continuously withdrawn from the top of tower **32** through line **34** and, on passing through pressure release valve **35**, the pressure thereon is reduced to approximately 4 pounds per square inch. Ethyl vinyl ether and ethanol are condensed in condenser **36**, the acetylene separated therefrom in degasser **37** and returned to buffer tank **25** through line **38**. The ethanol and ethyl vinyl ether are withdrawn from degasser **37** to line **39** and introduced into still **40**, wherein they are separated, the ethyl vinyl ether being withdrawn as an overhead vapor fraction and collected in product receiver **43**, while the ethanol collects in the bottom of the still and is withdrawn therefrom through line **44** to make-up tank **45**, and thence is returned by pump **47** to

reaction tower 32 and partly through line 48 to carburetor 27.

The ethyl vinyl ether is obtained in 94–98% yield as a clear colorless liquid boiling at 36° C.

In the same apparatus, except that the carburetion of the acetylene with ethanol was omitted and instead the acetylene was diluted with nitrogen, an over-all pressure of 250 pounds per square inch was used. A comparison of the conditions and results for continuous 8 hour runs in the same apparatus, using nitrogen and ethanol as diluents for the acetylene, is given in the following table:

Operating Conditions	"Nitrogen Process"	"Carburetor Process"
System Pressure pounds per square inch	250	45
Temp. of Vinylation °C	150	145
Acetylene Concentration In Gas to Reactor per cent	67	99
Nitrogen Concentration In Gas to Reactor per cent	33	0
Catalyst Concentration do	25	25
Time of Run hours	8	8
Yield Ethyl Vinyl Ether pounds	168	272
Yield per hour pounds per hour	21.0	34
Yield based on Ethanol per cent	88	97

Example 3

In the production of n-butyl vinyl ether in accordance with the principles of the present invention, an apparatus of the type illustrated in Fig. 2 may be employed. The vinylation tower 32 is charged approximately ¾ full with n-butanol in which is dissolved slightly less than ¼ part of potassium butylate, the ratio by weight of butanol to potassium butylate being 240:62.3. The entire system is kept anhydrous and oxygen-free. Acetylene from holder 21 is passed through water-scrubber 23, dryer 24 and buffer tank 25, held at a pressure of 4 pounds per square inch, and introduced into carburetor 27, containing liquid n-butanol at a temperature of 102° C. The acetylene becomes saturated with n-butanol and is then compressed by compressor 29 to 45 pounds per square inch, and thence passes into preheater 31, held at 145° C., and thence finally into the bottom of vinylation tower 32.

The vinylation tower is held at a temperature of 150° C. and under a pressure of 45 pounds per square inch. n-Butanol is supplied continuously to the bottom of the tower through line 33 by means of pressure pump 47 from make-up tank 45. In the reaction column 32, the acetylene reacts with the n-butanol to form n-butyl vinyl ether in accordance with the following equation:

$$C_4H_9OH + HC{\equiv}CH \rightarrow H_2C{=}CH{-}O{-}C_4H_9$$

There is continuously withdrawn from reactor 32 through line 34 a mixture of n-butyl alcohol, n-butyl vinyl ether and unreacted acetylene, the pressure thereon being reduced on passing pressure release valve 35 to approximately 4 pounds per square inch. The separation and recovery of the n-butyl vinyl ether and recirculation of acetylene and butanol is the same as that described under Examples 1 and 2 for methyl vinyl ether and ethyl vinyl ether respectively. The vinyl n-butyl ether is obtained in 96–98% yields as a clear colorless liquid, boiling at 93–94° C.

Under substantially the same conditions of operation as those mentioned above, the vinyl ethers of other lower aliphatic alcohols, such as n-propyl, isopropyl, iso- and secondary butyl alcohol may readily be produced.

Example 4

The specific process described above in which there is continuously removed from the reactor a mixture of reactants and product in vapor phase, cannot readily be applied to the production of vinyl ethers of alcohols containing more than 4 carbon atoms, due to the fact that the vapor pressures of the resulting vinyl ethers are too low to distill out of the reaction tower under the operating conditions. However, the process of the present invention may readily be applied to the production of the vinyl ethers of higher alcohols by slight modification of the process and may advantageously be carried out in apparatus of the type illustrated in Fig. 1. Thus, octadecyl vinyl ether may readily be prepared from acetylene and octadecyl alcohol.

The autoclave 8 is charged with 340 parts of octadecanol, 14 parts of potassium hydroxide and 40 parts of cyclohexane. The entire system is purged free of oxygen by nitrogen and the nitrogen is then removed by evacuation. The temperature of the autoclave is brought to 160° C., the major portion of the cyclohexane being vaporized and transferred during this time via line 9, release valve 10, condenser 11, surge tank 12 and pump 14 to carburetor 3. The carburetor 3 is filled with cyclohexane and brought to 79° C. Acetylene from holder 1, at a pressure of 4 pounds per square inch, is passed through the carburetor 3, where it becomes saturated with cyclohexane and the saturated gas is passed into the compressor 5, where it is brought to a pressure of 45 pounds per square inch. Thence it is passed through preheater 7, maintained at 145° C., and finally enters the autoclave where it reacts with the octadecanol to form octadecyl vinyl ether in accordance with the following equation:

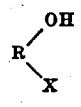
$$C_{18}H_{37}OH + HC{\equiv}CH \rightarrow H_2C{=}CH{-}O{-}C_{18}H_{37}$$

A total of 33 parts of acetylene is absorbed over a period of 2 hours. During the reaction, the cyclohexane in the carburetor is gradually transferred into the autoclave and is continuously withdrawn therefrom, along with unreacted acetylene, through line 9 and on passing pressure release valve 10, the pressure thereon is reduced to 4 pounds per square inch. The cyclohexane is condensed in condenser 11 and the condensate separated from acetylene in surge tank 12, the acetylene being returned through line 13 to the line 2, while cyclohexane is removed from surge tank 12 by pump 14 and returned to carburetor 3. The condensing of the cyclohexane, and the returning of the condensate into the carburetor by means of pump 14 may be avoided by mixing the saturated cycle gas, after pressure release with make-up acetylene in a suitable buffer tank, and feeding the mixture into the carburetor and compressor. On completion of the reaction in the autoclave to the desired extent, the reaction mixture therefrom may be distilled under vacuum and vinyl octadecyl ether, boiling at 190° C. at 10 mm., is obtained in a yield of 98%.

In a similar process using nitrogen as a diluent for the acetylene in a ratio of 1:1 by volume, a pressure of 150–225 pounds per square inch and a temperature of 150° C. is required to obtain a satisfactory rate of reaction.

In addition to the production of the specific vinyl ethers described in the foregoing examples, 1–4 inclusive, it will be understood that the process of the present invention is broadly applicable to the field of preparation of vinyl ethers

and those skilled in the art can readily adapt the principles of this invention to the production of any specific vinyl ether. Thus, the process of the present invention may be considered to be broadly applicable to the reaction of acetylene with hydroxy compounds corresponding to the formula:



in which X represents —H, —COOH, —COO metal, —NY_2, —$(OR)_nOH$ or —$(OR)_n$—OR groups, R being an aliphatic, hydroaromatic, or aromatic, preferably hydrocarbon radical, or an aralkyl radical, Y being —H, —R or —ROH and n being naught or any integral number.

The organic hydroxy compounds may be chosen from mono- and polyhydric aliphatic and cyclic alcohols, from phenols, naphthols, hydroxy-carboxylic acids, or metals thereof, respectively, and partially etherified polyhydric alcohols, partially esterified polyhydric alcohols reacting like mixtures of alcohols and acids owing to a saponification by the alkali present.

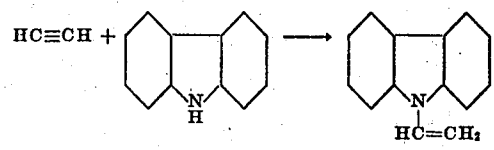
Specific compounds of these types are, for example, alcohols, such as methanol, ethanol, n- and iso-propanol, butanols, hexanols, octanol, decanol, dodecanol, tetra- and octadecanols, docosanol and montanol; glycols such as ethylene-, propylene-, 1.3-butylene-, diethylene-, triethylene-, and tetraethylene glycols; polyhydroxy compounds such as glycerol, pentaerythritol and their alkyl and aryl ethers; hydroxy-carboxylic acids, or their salts, respectively, such as alkali metal glycolates; amino alcohols, as for example mono-, di- or tri-alkylol amines, such as mono-, di-, or tri-ethanol or propanol amines or mono-alkyl mono- or di-ethanol amines such as N-methyl, or N-cyclohexyl, -N-di-ethanol amines, and hydroxy compounds containing aromatic nuclei, such as phenol, and alkyl-substituted phenols, cresol, benzyl alcohol and α- and β-naphthols. As specific phenols may be mentioned para-tertiary-butyl phenol, or para-isooctyl phenol.

Another process to which the present invention may conveniently be applied is the production of N-vinyl compounds by the reaction of acetylene with compounds containing the pyrrole ring, as for example, naphthocarbazole and indole; with secondary N-diaryl-amines which are free from hydroxyl groups, diphenyl-amine, phenyl-para-tolyl amine, α-α'-dinaphthylamine, phenyl-α-naphthylamine, p-tolyl-α-naphthylamine and N-phenyl-2-amino-anthracene. The application of the process of the present invention in this field is illustrated by the following specific Examples 5 and 6. From a consideration thereof, those skilled in the art may readily determine the specific details necessary for applying the invention to the production of other compounds in this field.

Example 5

For the production of N-vinyl carbazole from acetylene and carbazole, the type of apparatus shown in Fig. 1 may be used conveniently. The autoclave 8 may be charged with a solution or suspension of carbazole in a suitable solvent, for instance a cyclohexane solution of carbazole in which the ratio of cyclohexane to carbazole is approximately 2:1 by weight. The necessary catalyst may also be incorporated in the solution charged to the autoclave and the entire system purged free of oxygen by means of nitrogen and the nitrogen then removed by evacuation.

The carburetor 3 is filled with cyclohexane and brought to a temperature of 79° C. and the autoclave is brought to 165° C. Acetylene from holder 1, at a pressure of 4 pounds per square inch, is passed through the carburetor 3, where it becomes saturated with cyclohexane, and then is compressed to a pressure of 170 pounds per square inch. Thence it passes through preheater 7, maintained at 145° C., and finally into the autoclave 8, where it reacts with the carbazole present therein to form vinyl carbazole in accordance with the following equation:



During the reaction, unreacted acetylene is drawn off through line 9, together with vaporized cyclohexane, and on passing pressure release valve 10, set at 170 pounds per square inch, the pressure is reduced to 4 pounds per square inch. The cyclohexane is condensed in condenser 11 and the condensate separated from the acetylene in surge tank 12. The acetylene is returned through line 13 to line 2, while the cyclohexane is returned by pump 14 to carburetor 3. When the theoretical amount of acetylene has been employed (in approximately 2 hours), the reaction mixture is allowed to cool. After cooling, the reaction mixture may be filtered to remove insoluble catalysts and the filtrate subjected to fractional distillation. After removal of the cyclohexane by distillation, the vinyl carbazole may be distilled under vacuum. The yield obtained is 95–99% of the theoretical yield.

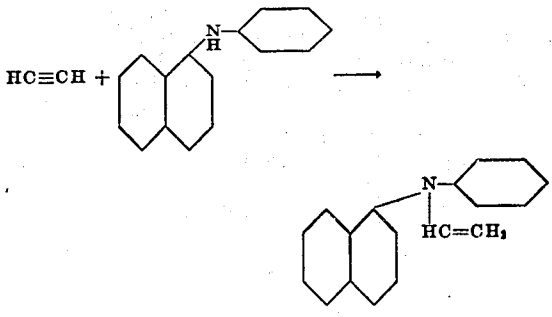
In comparison with the above process in which the diluent employed for the reaction is employed to carburize the acetylene, when a 60/40 acetylene-nitrogen mixture is employed in an otherwise identical process, the reaction requires somewhat higher pressures, a longer time, approximately 14 hours, and the yield is lower, amounting to only 90%.

Example 6

Another N-vinyl compound which may readily be produced in accordance with the present invention is N-vinyl phenyl alpha-naphthylamine, an apparatus of the type illustrated in Fig. 1 being suitable for this purpose.

The autoclave 8 is charged with 30 parts of phenyl alpha-naphthylamine, 30 parts of pyridine and 1 part of potassium hydroxide. The entire system is purged free of oxygen by means of nitrogen and the nitrogen is then recovered by evacuation. The carburetor 3 was filled with pyridine and brought to a temperature of 114° C., and the autoclave was brought to 160° C. Acetylene from the holder 1, at a pressure of 4 pounds per square inch, is passed through the carburetor 3, where it becomes saturated with pyridine at 130° C., and is compressed to 120 pounds per square inch. It is then passed through preheater 7, maintained at 145° C., and finally to the autoclave 8 where it reacts with phenyl alpha-naphthylamine to form N-vinyl

phenyl alpha-naphthylamine in accordance with the following equation:



During the reaction, unreacted acetylene diluted with pyridine vapors is continuously withdrawn through line 9 and on passing pressure release valve 10, set at 120 pounds per square inch, the pressure is reduced to 4 pounds per square inch. The pyridine is condensed in condenser 11 and the pyridine and acetylene separated in surge tank 12. The acetylene is returned through line 13 to line 2, while the pyridine is returned by pump 14 to carburetor 3. After the theoretical amount of acetylene is absorbed, the reaction mixture is cooled, filtered and distilled under reduced pressure. N-vinyl phenyl α-naphthylamine is obtained in 90–95% yield; boiling point 168–170° C. under 1 mm. pressure.

In comparison with the above process, in a similar process for producing N-vinyl phenyl alpha-naphthylamine described in United States Patent No. 2,087,079 in which a mixture of acetylene and nitrogen in proportions of 2:1 is employed in place of acetylene carburized with pyridine, temperatures of 180–190° C. and pressures of 225–375 pounds per square inch are required.

Another broad field to which the process of the present invention is broadly applicable is the production of vinyl esters by the action of acetylene on carboxylic acids of all types, i. e., the vinyl esters of aliphatic, saturated and unsaturated, mono- and poly-carboxylic acids; of cyclic, that is aromatic, cycloaliphatic and heterocyclic, mono- and polycarboxylic acids and of mixed aliphatic-aromatic and mixed aliphatic, cycloaliphatic, mono- and polycarboxylic acids, the carboxylic groups of which mixed acids may be fixed to the aliphatic as well as the cyclic residue.

Suitable mono-aliphatic carboxylic acids are, for example, formic acid, acetic acid, propionic acid, lauric acid, palmitic acid, margaric acid, stearic acid, and oleic acid; suitable dicarboxylic acids are, for instance, succinic acid, adipic acid, myristic acid and sebacic acid; suitable cyclic acids are, for example, aromatic carboxylic acids such as benzoic acid, o-, m-, and p-toluic acids or abietic acids, and the different isomers of naphthoic acid, cinnamic acid, phenylglycine, and polybasic cyclic acids or their acid esters, such as, phthalic acid and phthalic acid monoalkyl esters, for example, monoethyl, n- or isobutyl esters, cyclic hydroxy-carboxylic acids, as for example, salicyclic acid or hydroxy-naphthoic acid, and heterocyclic acids, such as pyridine and quinoline carboxylic acids, and hydroaromatic carboxylic acids, as for example, hydrophthalic acid. Instead of pure acids, partially esterified acids or resins showing a high acid value, such as colophony, or mixtures of acids may be employed, as for example, the mixtures of acids obtainable by the saponification of natural fats and fatty oils containing esters or fatty acids, or the mixtures of acids obtainable by oxidizing paraffin wax or Montan wax. The specific use of the present invention in the production of vinyl esters is illustrated by the following specific examples, 7–9, inclusive, and from a consideration thereof, those skilled in the art can readily determine the specific details of applying the present invention to the production of other vinyl esters.

Example 7

A process for producing vinyl esters is described in United States Patent No. 2,066,075 to Reppe, in accordance with which vinyl esters are prepared, working in liquid phase, by the action of acetylene on carboxylic acids using zinc or cadmium salts of carboxylic acids as catalysts, using preferred temperatures of 160–190° C. and preferred pressures of 10–20 atmospheres and in which the acetylene is diluted with inert gases, such as nitrogen, hydrogen, or carbon monoxide in order to preclude explosions, may readily be practiced in accordance with the present invention by carburizing the acetylene in place of using an inert diluent gas. When so modified, it can be run at greatly reduced pressures, free from danger of explosion.

Thus, vinyl acetate may readily be produced in accordance with the present invention in an apparatus of the type shown in Fig. 2. The vinylation tower 32 is charged with glacial acetic acid, in which is dissolved approximately 4% by weight of zinc acetate. The entire system is kept anhydrous as well as oxygen-free to prevent the formation of undesirable by-products. The tower 32 is held at a temperature of 170° C. and under a pressure of 45 pounds per square inch.

Acetylene from holder 21 is passed through water-scrubber 23 and dryer 24 in order to remove water-soluble impurities, particularly acetone, and the last traces of moisture, and thence flows to buffer tank 25 where it is held at a pressure of 4 pounds per square inch. The acetylene from buffer tank 25 passes into carburetor 27, containing acetic acid held at 118° C. The acetylene becomes saturated with acetic acid and then is compressed in compressor 29 to 45 pounds per square inch and thence passes into preheater 31, held at a temperature of 145° C., and finally into vinylation tower 32. Glacial acetic acid is continuously supplied to the tower 32 through line 33 by pump 47 from make-up tank 45. In the tower 32, the acetylene reacts with the acetic acid in accordance with the following equation:

$$HC{\equiv}CH + CH_3COOH \rightarrow H_2C{=}CH{-}O{-}CO{-}CH_3$$

The vinyl acetate, along with unreacted acetic acid and acetylene, is continuously withdrawn from the top of tower 32 and on passing through pressure release valve 35, set at 45 pounds per square inch, the pressure is reduced to 4 pounds per square inch. The vinyl acetate and acetic acid are then condensed in condenser 36 and the acetylene separated therefrom in degasser 37 and returned through acetylene return line 38 to buffer tank 25. The vinyl acetate and unreacted acetic acid are continuously withdrawn from degasser 37 and introduced into stripping still 40. The vinyl acetate is taken off overhead at 73–74° C. through line 41, condensed in condenser 42 and collected in product receiver 43. The unreacted acetic acid is returned from the still bottom through line 44 to make-up tank 45.

On subsequent conventional fractionation of the product from receiver 43, vinyl acetate is ob-

tained as a colorless liquid, boiling at 73° C. in 85–95% yield.

Example 8

In the production of vinyl valerate in accordance with the present invention, by applying the principles thereof to the process described in the above-mentioned United States Patent No. 2,066,075, an apparatus of the type disclosed in Fig. 1 may be employed advantageously.

The autoclave 8 is charged with 40 parts-by-weight of valeric acid, 5 parts-by-weight of cyclohexane and 1 part-by-weight of zinc acetate. The entire system is purged free of oxygen by means of nitrogen and the nitrogen is then removed by evacuation. The temperature of the autoclave is then brought to 170° C. During this period, the majority of the cyclohexane is transferred to the carburetor 3 through pressure release valve 10, set at 45 pounds per square inch. The carburetor 3 is filled with cyclohexane and brought to a temperature of 79° C. Acetylene from holder 1, at a pressure of 4 pounds per square inch, is passed through the carburetor 3, where it becomes saturated with cyclohexane at 79° C. and is then compressed by compressor 5 to a pressure of 45 pounds per square inch. Thence it passes through the preheater 7, held at 145° C., and finally enters the autoclave 8 where it reacts with valeric acid to produce vinyl valerate in accordance with the following equation:

$$HC{\equiv}CH + C_4H_9COOH \rightarrow H_2C{=}CH{-}O{-}CO{-}C_4H_9$$

During the reaction, acetylene and cyclohexane are continuously removed from the autoclave through line 9 and on passing pressure release valve 10, the pressure thereon is reduced from 45 pounds per square inch to 4 pounds per square inch. The cyclohexane is condensed in condenser 11 and the acetylene separated therefrom in surge tank 12, the acetylene being returned through line 13 to line 2, while the cyclohexane is returned through pump 14 to carburetor 3.

When acetylene is no longer absorbed in the autoclave, the reaction mixture is allowed to cool and is then filtered to remove zinc valerate. The filtrate may then be subjected to fractional distillation in order to distill off the cyclohexane. Vinyl valerate, boiling at 132–134° C. at atmospheric pressure, is obtained in 93–95% of the theoretical yield.

As compared with the above-described process, the process described in United States Patent No. 2,066,075 for producing vinyl valerate in which the acetylene is diluted with nitrogen in the ratio of 2:1, requires a temperature of 180° C. and a pressure of 20–25 atmospheres (300–375 pounds per square inch).

Example 9

In a like manner, the process of the present invention may be applied to the production of vinyl oleate by combining the teachings of above-mentioned United States Patent No. 2,066,075 therewith. For this process, an apparatus of the type described in Fig. 1 is suitable. The autoclave 8 is charged with 200 pounds of oleic acid, 40 pounds cyclohexane and 14 pounds of zinc acetate. The system is purged with nitrogen and the nitrogen removed by evacuation. The autoclave is then brought to 160° C. During this time, the major part of the cyclohexane returns to the carburetor 3 through pressure release valve 10, set at 45 pounds per square inch, condenser 11, surge tank 12 and pump 14. The carburetor 3 is filled with cyclohexane and brought to a temperature of 79° C. Acetylene from holder 1, at a pressure of 4 pounds per square inch, is passed through carburetor 3 where it becomes saturated with cyclohexane, and is then compressed by compressor 5 to 45 pounds per square inch. It flows thence through preheater 7, maintained at 145° C., and finally into the autoclave 8 where it reacts with the oleic acid present therein to form vinyl oleate in accordance with the following equation:

$$HC{\equiv}CH + C_{17}H_{33}COOH \rightarrow H_2C{=}CH{-}O{-}CO{-}C_{17}H_{33}$$

During this reaction, acetylene and cyclohexane are withdrawn from reactor 8 through line 9 and on passing pressure release valve 10, the pressure thereon is reduced from 45 pounds per square inch to 4 pounds per square inch. The cyclohexane is condensed in condenser 11 and is separated from the acetylene in surge tank 12, the acetylene being returned over line 13 to line 2 while the cyclohexane is returned via pump 14 to carburetor 3.

When the theoretical amount of acetylene has been absorbed, the reaction mixture is allowed to cool. It is then filtered to remove zinc acetate and the filtrate fractionally distilled. After separating off the cyclohexane, vinyl oleate, boiling at 173–175° C. at 2 mm. pressure, is obtained in 90–95% yield.

It should be understood that the foregoing examples are illustrative only and that the present invention is in no way intended to be limited to them. In particular, it should be noted that the conditions of reaction, aside from the essential features of the present invention, caused by the carburetion of acetylene with a normally liquid diluent, may be varied through a relatively wide range. Specifically, it should be noted that the catalysts noted in the specific examples are merely illustrative of preferred catalysts and other agents, known to catalyze the particular reaction under consideration, may be substituted for those specifically disclosed. It should further be noted that other process variables, such as pressure, temperature, time, relative proportions of reactants, etc., may frequently be varied through a relatively wide range. The particular extent of such variation which is permissible is dependent on the specific process with which it is concerned. It will be noted, however, that in general lower over-all pressures may be employed in accordance with the present invention and higher effective concentrations of acetylene will be employed than was possible under prior art processes, except when they were varied in accordance with the present invention.

In addition to the specific acetylene reactions, illustrated by the foregoing examples, the present process of the invention is also applicable to a wide variety of other reactions involving the use of acetylene under high temperatures and pressures. Therefore, it may be applied to such reactions as the production of mono-vinyl acetylene, the production of vinyl chloride, the production of acetaldehyde by the mercury process, and the production of acetylene compounds of the formula RC≡CH. We do not, however, in the present application, specifically claim the use of our invention in these last mentioned processes, the claims of the present application being limited, so far as other acetylene reactions are concerned, to generic features thereof.

While we have disclosed herein certain specific examples of the application of the present in-

vention to the production of vinyl esters and N-vinyl pyrrole compounds; these examples have been given for the purpose of illustrating the scope of our invention, and the specific application of this invention to the production of vinyl esters forms the subject matter of and is claimed in our application Serial No. 621,622, and the specific application of this invention to the production of N-vinyl pyrrole compounds forms the subject matter of and is claimed in our copending application Serial No. 621,621, both filed on even date herewith.

What we claim and desire to protect by Letters Patent is:

1. In a process involving the handling of acetylene wherein acetylene, from a low pressure source thereof maintained at conditions of temperature and pressure at which acetylene is non-explosive, is compressed and passed through a high pressure zone maintained at conditions of temperature and pressure at which the acetylene is normally explosive, the method of eliminating the danger of acetylene explosion which comprises contacting a stream of acetylene from said low pressure source while it is still at a low temperature and pressure outside the explosive range of acetylene with a volatile normally-liquid organic compound which is non-explosive at the conditions maintained in said high pressure zone, said liquid with which the acetylene is contacted being in liquid phase and being maintained at a predetermined temperature such that the acetylene on contact therewith becomes saturated with the vapors of said normally-liquid compound in such an amount as to form a mixture of acetylene and said vapors in such predetermined ratio that such mixture is non-explosive at said normally-explosive conditions of said high pressure zone, compressing the thus-obtained mixture of acetylene and vapors of said normally-liquid compound to the pressure maintained in said high pressure zone and introducing the thus-compressed mixture of acetylene and vapors into said high pressure zone while maintaining said mixture of acetylene and said vapors in said high pressure zone and during the compression step specified at a temperature above that at which said vapors will be condensed, withdrawing a stream of acetylene and said vapors from said high pressure zone and adjusting the pressure and temperature of the thus-withdrawn stream to conditions of temperature and pressure at which acetylene is non-explosive and thereafter separating said acetylene from said normally-liquid compound.

2. In a process involving a chemical reaction between acetylene and an organic compound known to be reactable therewith and wherein acetylene is introduced into a reaction zone wherein a mixture of acetylene and said organic reactant are maintained and in which said reaction is effected at predetermined reaction conditions of pressure and temperature within the explosive range of acetylene, the method of eliminating the danger of acetylene explosion which comprises contacting the acetylene which is introduced into said reaction zone while it is under non-explosive conditions of temperature and pressure with a volatile normally-liquid organic compound which is non-explosive at said reaction conditions, said volatile normally-liquid organic compound with which the acetylene is contacted being in liquid phase and being maintained at such a predetermined temperature that the acetylene becomes saturated with the vapors of said normally-liquid organic compound in such an amount as to form a mixture of acetylene and such vapors in such predetermined ratio that said mixture is non-explosive at said normally-explosive reaction conditions, adjusting the pressure and temperature of the thus-formed mixture to said normally-explosive reaction conditions and introducing the thus-obtained mixture into said reaction zone while maintaining said mixture at a temperature above that at which said vapors will condense, effecting the desired reaction between said acetylene and said organic compound known to be reactable therewith in said reaction zone, and recovering the product of said reaction.

3. In a process involving a chemical reaction between acetylene and an organic compound known to be reactable therewith, wherein acetylene is introduced into a reaction zone, wherein a mixture of acetylene and said organic reactant are maintained and in which said reaction is effected at predetermined reaction conditions of pressure and temperature within the explosive range of acetylene and unreacted acetylene removed from said reaction zone and recycled, the method of eliminating the danger of acetylene explosion which comprises contacting the acetylene which is introduced into said reaction zone while it is under non-explosive conditions of temperature and pressure with a volatile normally-liquid organic compound which is non-explosive at said reaction conditions, said volatile normally-liquid compound with which the acetylene is contacted being in liquid phase and being maintained at such a predetermined temperature that the acetylene becomes saturated with the vapors of said normally-liquid organic compound in such an amount as to form a mixture of acetylene and such vapors in such predetermined ratio that said mixture is non-explosive at said normally-explosive reaction conditions, adjusting the pressure and temperature of the thus-formed mixture to said normally-explosive reaction conditions and introducing the thus-obtained mixture into said reaction zone while maintaining said mixture at a temperature above that at which said vapors will condense, effecting the desired reaction between said acetylene and said organic compound known to be reactable therewith in said reaction zone and recovering the product of said reaction, withdrawing from said reaction zone a stream of unreacted acetylene admixed with said vapors in said predetermined non-explosive proportions, reducing the pressure on the thus-withdrawn stream below the explosive range for acetylene and introducing said withdrawn acetylene, after its pressure has been reduced, into the acetylene being supplied to said reaction zone prior to the contacting step specified.

4. A process as defined in claim 2, wherein the volatile normally-liquid organic compound with which the acetylene is contacted in the contacting step specified is a volatile normally liquid organic compound which is not explosive at the reaction conditions employed and which is inert at said reaction conditions.

5. A process as defined in claim 2, wherein the organic reactant specified with which the acetylene is reacted is a volatile organic liquid, and in which said volatile organic liquid reactant is employed as the volatile normally-liquid organic compound specified with which the acetylene is contacted in the contacting step specified.

6. In a vinylation process wherein acetylene is reacted with an organic hydroxy compound

known to be reactable therewith, and in which acetylene is introduced into a reaction zone wherein a mixture of acetylene and said organic hydroxy compound are maintained and in which said reaction is effected at predetermined reaction conditions of pressure and temperature within the explosive range of acetylene, the method of eliminating the danger of acetylene explosion which comprises contacting the acetylene which is introduced into said reaction zone while it is under non-explosive conditions of temperature and pressure with a volatile normally-liquid organic compound which is non-explosive at said reaction conditions, said volatile normally-liquid organic compound with which the acetylene is contacted being in liquid phase and being maintained at such a predetermined temperature that the acetylene becomes saturated with the vapors of said normally-liquid organic compound in such an amount as to form a mixture of acetylene and such vapors in such predetermined ratio that said mixture is non-explosive at said normally-explosive reaction conditions, adjusting the pressure and temperature of the thus-formed mixture to said normally-explosive reaction conditions, introducing the thus-obtained mixture into said reaction zone while maintaining said mixture at a temperature above that at which said vapors will condense, effecting the vinylation reaction between said acetylene and said organic hydroxy compound known to be reactable therewith in said reaction zone and recovering the vinylated product of said reaction.

7. In a process for producing vinyl ethers, wherein acetylene is reacted with an aliphatic alcohol and in which acetylene is introduced into a reaction zone, wherein a mixture of acetylene and said aliphatic alcohol are maintained and in which said reaction is effected at predetermined reaction conditions of pressure and temperature within the explosive range of acetylene, the method of eliminating the danger of acetylene explosion which comprises contacting the acetylene which is introduced into said reaction zone while it is under non-explosive conditions of temperature and pressure with a volatile normally-liquid organic compound which is non-explosive at said reaction conditions, said volatile normally-liquid organic compound with which the acetylene is contacted being in liquid phase and being maintained at such a predetermined temperature that the acetylene becomes saturated with the vapors of said normally-liquid organic compound in such an amount as to form a mixture of acetylene and such vapors in such predetermined ratio that said mixture is non-explosive at said normally-explosive reaction conditions, adjusting the pressure and temperature of the thus-formed mixture to said normally-explosive reaction conditions and introducing the thus-obtained mixture into said reaction zone while maintaining said mixture at a temperature above that at which said vapors will condense, reacting said acetylene and said aliphatic alcohol in said reaction zone to produce a vinyl ether and recovering the thus-produced vinyl ether.

8. A process as defined in claim 7, wherein the aliphatic alcohol reacted with the acetylene is a lower aliphatic alcohol and wherein said lower aliphatic alcohol is employed as the volatile normally-liquid organic compound with which the acetylene is contacted in the contacting step specified.

9. A process as defined in claim 8, wherein the lower aliphatic alcohol specified is methanol.

10. A process as defined in claim 8, wherein the lower aliphatic alcohol specified is butanol.

11. A process as defined in claim 7, wherein the volatile normally-liquid organic compound specified with which the acetylene is contacted in the contacting step specified is a volatile normally-liquid organic compound which is inert to both the acetylene and the aliphatic alcohol specified at the reaction conditions employed in the reaction zone.

12. A process as defined in claim 11, wherein the aliphatic alcohol specified with which the acetylene is reacted is octadecyl alcohol.

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