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PROCESS OF STORING AND HANDLING ACETYLENE SOLUTIONS

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This application is a continuation-in-part application of our application Serial No. 271,076, now abandoned, which describes the storage or transportation of liquid acetylene which is dissolved at a temperature below —80° C. in a solvent or a mixture of solvents for acetylene. The solvents or mixture of solvents being present in an amount of at least about 22 percent calculated upon the weight of the acetylene.

The present invention relates to the safe handling, storing or transporting of liquid acetylene and comprises storing and handling acetylene at temperatures below its boiling point and dissolved in at least one solvent for acetylene with the solvent being present in an amount of at least about 22 percent calculated upon the weight of the acetylene solution. Certain solutions of acetylene in mixtures of solvents are new. They are an object of the present invention.

It is an object of this invention to store acetylene in a safe manner.

It is another object of this invention to provide a method of transporting acetylene over far distances in a safe manner.

It is a further object of this invention to provide a method of transporting highly concentrated solutions of acetylene in a safe manner.

We have found that acetylene can safely be handled, stored and transported in the liquid state in the form of solutions which are obtained by introducing gaseous acetylene into a mixture of solvents capable of readily dissolving the acetylene being cooled to a temperature below about —80° C. and which are kept below the temperature at which the acetylene escapes from the solution. This temperature is dependent on the pressure under which the acetylene solutions are kept and is for instance —76° C. at atmospheric pressure.

Since acetylene, and particularly liquid or solid acetylene, belongs to the class of violently explosive compounds, it cannot be stored as other hydrocarbons under pressure in steel bottles unless these steel bottles contain a filling material and the acetylene is compressed into a solvent such as acetone. Such acetylene, designated as "dissolved acetylene gas," possesses the disadvantage that only a relatively small quantity may be stored in a bottle and that a large and expensive stock of bottles must therefore be maintained. Considerable expense occurs through frequent required repairs to the steel bottles and the valves. Many attempts have already been made to convert the acetylene into the solid form and to store it in that form, but this has been impossible in practice in view of the explosive property of the product. According to another suggestion, the liquid acetylene should be stored in a fully enclosed pressure reservoir cooled by means of solid carbon dioxide and acetone. This process is not satisfactory for industrial purposes because it is too dangerous.

The mixtures of solvents used according to the present invention are liquid at temperatures of about —80° C. and below, e.g. at about —115° C. The solvents themselves and the components of the mixtures have a boiling point above 0° C. and preferably above 20° C. The use of such solvents has the advantage over the use of solvents boiling below 0° C. and above —80° C. in that it is possible to recover gaseous acetylene from the acetylene solution which is substantially free from solvent.

In admixture with acetylene, for instance by introducing gaseous acetylene, the mixtures of solvents yield solutions of acetylene which are still liquid at temperatures of about —80° C. and below, e.g. at about —115° C., and in many cases at far lower temperatures than those mentioned in the present patent application. However, it is to be noted that the vapor pressure of acetylene above the solutions according to our invention is, at —80° C. which is the boiling point of pure acetylene, less than 1 atmosphere. Consequently, the acetylene solution may even be stored up to —76° C. when applying atmospheric pressure, or at still higher temperatures when applying slightly superatmospheric pressure.

According to the present invention, it is now possible to transport or to store large quantities of acetylene for prolonged periods of time. For economical reasons, the amount of the solvent used must be as small as possible. For the same reason, it is advisable to apply temperatures as low as possible. The lower the temperature of the acetylene solution, the longer such solutions may be stored in vessels of the same kind in view of the larger heat capacity of a cooler solution compared with a warmer acetylene solution. However, it has been found that acetylene crystals may separate if acetylene solutions are cooled to very low temperatures. The presence of acetylene crystals greatly increases the danger of explosion.

It is necessary in the process according to the present invention that the solvents are present at least in a quantity of about 22 percent calculated upon the weight of the acetylene solution. As has been found, solutions containing less than 22 percent of solvents are highly explosive in contrast to solutions containing 22 percent or more of a mixture of solvents. Preferably, the solvent represents about 25 to 50 percent by weight of the acetylene solution and the optimum amount of solvent is about 25 to 33 percent. The acetylene is preferably present in an amount of at least about 50 percent, and preferably about 67 to 75 percent, especially 67 percent or more.

Though acetylene solutions of extremely low temperatures may be prepared or used in our process, these will be applied only exceptionally since the cost increases as the temperature of the solvent is lowered when preparing the acetylene solution. The dissolved liquid acetylene, cooled to temperatures of about —115° C., can be transported or stored for many days in a well insulated vessel without undergoing a loss of acetylene and solvent worth mentioning. This means a considerable saving in comparison with the hitherto known processes. The transport of the dissolved acetylene is thus made bearable from an economical point of view, and this the more so, since simple, well insulated reservoirs having relatively thin walls may be used. Neither during the manufacture of the dissolved liquid acetylene is an application of pressure necessary, nor is a pressure produced in an amount worth mentioning during the storing at a temperature of about —80° C. or below. If it is intended to store the dissolved liquid acetylene for a prolonged period, it is recommended to apply refrigeration by means of a corresponding cooling agent. If vessels having thick walls are applied, it is also possible, of course, to dissolve and to store the acetylene with application of pressure at a temperature below the boiling

point of the acetylene under said pressure. The application of pressure is, however, not necessary and generally pressures above 1 atmosphere (gauge) are avoided. Generally, the acetylene gas in the gas phase above the solution is diluted with such an amount of an indifferent gas, such as nitrogen, that the partial pressure of this gas is the difference between the vapor pressure of the acetylene above the acetylene solution at any desired temperature and the desired pressure under which the solution is kept, e.g. atmospheric pressure. The application of a slightly elevated pressure up to 1 atmosphere (gauge) does not increase the explosivity of the acetylene. It is also possible to maintain the solutions of liquid acetylene even under slightly reduced pressure but above the boiling point of acetylene at these reduced pressures. However, this procedure is not very economical.

In the acetylene solutions according to this invention there may be used as suitable solvents, for example, mixtures of monohydric aliphatic alcohols containing 1–4 carbon atoms, such as methanol, ethanol, propanol and secondary butanol; aliphatic aldehydes containing 2–4 carbon atoms, such as acetaldehyde, propionaldehyde and butyraldehyde; aliphatic ketones containing 3–5 carbon atoms, such as acetone, methyl ethyl ketone and methyl propyl ketone; if desired small amounts of methyl isobutyl ketone may also be added to solvent mixtures; aliphatic esters containing 2–6 carbons atoms, such as methyl formate, methyl acetate, methyl propionate, valeric acid methyl ester, ethyl formate, ethyl acetate, ethyl butyrate, propyl formate, butyl acetate, amyl formate; halogenated hydrocarbons containing 1–4 carbon atoms boiling above 0° C., such as methylene chloride, chloroform, monofluorotrichloromethane, difluoro-dichloro-methane, fluoro-dichloro-methane, vinyl bromide, ethyl chloride, ethylidene chloride, trichloro-ethylene, butyl chloride, secondary butyl chloride, butyl bromide or secondary butyl bromide; saturated or mono-unsaturated aliphatic hydrocarbons boiling between about 0° C. and about 100° C. and, in general, containing 5–7 carbon atoms, such as hexane or pentylene; mixtures of hydrocarbons of the group consisting of low and medium boiling acyclic aliphatic and cycloaliphatic hydrocarbons of the benzene series, i.e., fractions which are boiling between about 0° C. and 100° C., are likewise suitable solvents; aliphatic ethers containing 2–8 carbon atoms, such as diethyl ether; tetrahydrofurane, di-isopropyl ether; aliphatic acetals containing 3–9 carbon atoms, such as formaldehyde dimethyl acetal or acetaldehyde dimethyl acetal, aliphatic nitriles, containing 3–4 carbon atoms, such as propionitrile or butyro-nitrile, or similar compounds which are capable of readily dissolving the acetylene and which are still liquid at temperatures between about −115° C. or −80° C.

Some specific mixtures of solvents which solidify at very low temperatures are set forth below. Consequently, solutions of acetylene in these mixtures of solvents may be transported over very long distances since the heat capacity of these solutions is very high. These specific solutions are obtained by introducing gaseous acetylene into a mixture of about 40 to about 98 parts by weight of acetaldehyde and 60 to 2 percent of diethyl ether and/or formic acid methyl ester. Other suitable mixtures of solvents may be obtained by adding to these mixtures of acetaldehyde and diethyl ether and/or formic acid methyl ester 6–50 parts by weight of acetone, the percentage figures being calculated upon the mixture of acetaldehyde and diethyl ether and/or formic acid methyl ester. Other suitable mixtures may be obtained by adding to the mixture of acetaldehyde and diethyl ether and/or formic acid methyl ester 1–20 parts by weight of propionitrile. The same amount of propionitrile may be added to mixtures of acetaldehyde and diethyl ether and/or formic acid methyl ester to which acetone is added. However, the total amount of acetone and propionitrile shall be in the range from 7–50 percent calculated upon the mixture of acetaldehyde and diethyl ether and/or formic acid methyl ester.

It is desirable to keep as low as possible the temperature at which a solidification of the acetylene dissolved in the mixtures of solvents occurs since the solidified solution or a solution containing acetylene crystals can no longer be handled with complete safety. Already with some solvents, for instance, with acetaldehyde, it is possible to obtain solutions of high strength which solidify only at a temperature considerably below −80° C. If, however, mixtures of solvents are used, the solidification point is, in general, pressed down to a lower degree. The quantitative proportion of the various solvents in these mixtures may vary within wide limits. It is particularly suitable to use the various constituents in such quantities that eutectic mixtures are formed.

The quantitative proportions in which the solvents or the mixtures of solvents, on the one hand, and the acetylene on the other hand, may be used may vary to a large extent. The quantity of the mixtures of solvents may even be superior to that of the acetylene, though the use of such solutions is not very economical.

Since the acetylene from the solution may be directly used for filling bottles of dissolved acetylene gas, it is advisable, during the manufacture of the acetylene solution, to use a well purified acetylene, in order to avoid a purification at a later date.

The solutions of acetylene in mixtures of solvents being cooled to −80° C. or below do not detonate with the detonators usually applied in explosive tests. Furthermore, the said mixtures were subjected to tests which consisted in severely heating the solution contained in a nearly sealed metal tube. The metal tube of a length of about 40 cm. and containing 1 liter of the solution was heated in a slightly inclined position with 6 strong Teclu burners. The acetylene with the solvent was permitted to escape through an aperture of a diameter of 1.55 mm. at one extremity of the tube and burnt off merely with a strong flame, whereas meta-dinitrobenzene detonated when tested in the same manner. It must be emphasized that meta-dinitrobenzene is not regarded as an explosive for purposes of transport.

The industrial progress attained by the process of the present invention is thus proved.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto, the parts being by weight.

Example 1

60–70 parts of gaseous, well purified and dried acetylene are gradually introduced at a temperature of −100° C. into a mixture of 3 parts each of methanol, ethanol and propanol and 11 parts of acetone, the temperature of −100° C. being constantly maintained during this introduction. This liquid mixture can be handled with safety. It does not detonate under the influence of a detonator normally applied in explosion tests. Moreover, this solution burns very quietly when it is ignited in an open porcelain dish.

Example 2

60 parts of gaseous acetylene are introduced at a temperature of −100° C. into a mixture of 4 parts of acetic acid ethyl ester, 1 part of acetone and 15 parts of acetaldehyde. A liquid mixture is obtained which even at −107° C. does not contain any acetylene crystals. The mixture can be handled with safety.

Example 3

A mixture of 11 parts of acetone, 9 parts of formic acid methyl ester and 60 parts of acetylene, which is prepared in the same manner as described in Examples 1 and 2, is still a thin liquid at −95° C. and shows the

same properties as the mixture of the aforementioned examples.

Example 4

By replacing the quantity of formic acid methyl ester of Example 3 by 9 parts of methylene chloride, a solution is obtained which is still a thin liquid at —95° C. It can likewise be safely handled.

Example 5

9 parts of acetone, 5 parts of di-ethyl ether and 6 parts of acetic acid ethyl ester are cooled to —100° C., 60 parts of acetylene are introduced into the mixture thus formed and condensed therein. A solution is obtained which even at —94° C. is free from acetylene crystals. The properties of this mixture resemble those of the mixture described in the above examples.

Example 6

7 parts of tetrahydro-furane, 7 parts of acetone and 6 parts of acetaldehyde are mixed, 58 parts of acetylene are added in the manner described in the preceding examples. The mixture is free from crystals at —94° C. and, according to the detonation test, it may be safely handled.

Example 7

By mixing 50 parts of acetylene with 7.5 parts of acetaldehyde-dimethyl-acetal, 7.5 parts of acetaldehyde, 4 parts of acetic acid ethyl ester and 1 part of acetone, a liquid is obtained which solidifies at —99° C.

Example 8

10 parts of acetaldehyde, 5 parts of formaldehyde-dimethyl-acetal, 4 parts of di-ethyl-ether and 1 part of acetone and 50 parts of acetylene yield a liquid mixture which solidifies at —99° C. It can be safely handled.

Example 9

By introducing at a temperature below —80° C., 50 parts of acetylene into a mixture of solvents consisting of 5 parts of acetaldehyde, 5 parts of formaldehyde-dimethyl acetal, 5 parts of acetaldehyde-dimethyl acetal, 4 parts of acetic acid ethyl ester and 1 part of acetone, a liquid is obtained which solidifies at —99° C. and can be safely handled.

Example 10

By introducing at a temperature below —80° C., 67 parts of acetylene into 20 parts of acetaldehyde, a solution is obtained which is still fluid at —102° C.

Example 11

A solution of acetylene in a solvent mixture consisting of 50 parts of acetaldehyde, 25 parts of diethyl ether and 25 parts of acetone which contained 70.1 parts of acetylene and which was obtained by introducing well purified and dried acetylene at a temperature below —80° C. into a mixture of the mentioned solvents is liquid when being cooled down to a temperature of —104° C.

Example 12

An acetylene solution which contains 69.5 percent of acetylene in a solvent mixture consisting of 80 parts of acetaldehyde, 5 parts of diethyl ether and 15 parts of acetone, is liquid when being cooled down to a temperature of —106° C.

Example 13

An acetylene solution which contains 69.8 percent of acetylene in a solvent mixture consisting of 96 parts of acetaldehyde and 4 parts of diethyl ether is liquid when being cooled down to a temperature of —104° C.

Example 14

An acetylene solution which contains 69.6 percent of acetylene in a solvent mixture consisting of 89 parts of acetaldehyde, 9 parts of diethyl ether and 2 parts of formic acid methyl ester is liquid when being cooled down to a temperature of —106° C.

Example 15

An acetylene solution which contains 69.9 percent of acetylene in a solvent mixture consisting of 90 parts of acetaldehyde, 3 parts of acetone, 5 parts of propionitrile, and 2 parts of diethyl ether is liquid when being cooled down to a temperature of —104° C.

Example 16

An acetylene solution which contains 69.5 percent of acetylene in a solvent mixture consisting of 80 parts of acetaldehyde, 4 parts of acetone, 2 parts of propionitrile, 8 parts of diethyl ether and 6 parts of formic acid methyl ester is liquid when being cooled down to a temperature of —104° C.

Example 17

An acetylene solution which contains 69.5 percent of acetylene in a solvent mixture consisting of 90 parts of acetaldehyde, 5 parts of propionitrile, 2 parts of diethyl ether and 3 parts of formic acid methyl ester is liquid when being cooled down to a temperature of —104° C.

Example 18

An acetylene solution which contains 69.4 percent of acetylene in a solvent mixture consisting of 75 parts of acetaldehyde, 15 parts of propionitrile and 10 parts of formic acid methyl ester is liquid when being cooled down to a temperature of —104° C.

We claim:

1. The process of storing and handling acetylene solutions with a high concentration of at least 50% acetylene at low temperatures at substantially normal pressure for prolonged periods of time without danger of explosion which comprises dissolving, storing and handling acetylene at temperatures below about —80 C. and under a pressure of at most 1 atmosphere (gauge pressure) in a solvent mixture for acetylene boiling above 0° C. and being selected from the group consisting of aliphatic monohydric alcohols containing 1–4 carbon atoms, aliphatic aldehydes containing 2–4 carbon atoms, aliphatic ketones containing 3–5 carbon atoms, aliphatic esters containing 2–6 carbon atoms, halogenated hydrocarbons containing 1–4 carbon atoms, mono-unsaturated aliphatic hydrocarbons boiling between about 0° C. and about 100° C., aliphatic ethers containing 2–8 carbon atoms, aliphatic acetals containing 3–9 carbon atoms, aliphatic nitriles containing 3–4 carbon atoms, said solvent being present in an amount ranging from about 22% to about 50%, calculated upon the weight of the acetylene solution, and the solution being maintained above the solidification point.

2. The process of storing and handling acetylene solutions with a high concentration of at least 50% acetylene at low temperatures at substantially normal pressure for prolonged periods of time without danger of explosion which comprises dissolving, storing and handling acetylene at temperatures below about —80° C. and under a pressure of at most 1 atmosphere (gauge pressure) in a solvent mixture for acetylene boiling above 0° C. and being selected from the group consisting of aliphatic monohydric alcohols containing 1–4 carbon atoms, aliphatic aldehydes containing 2–4 carbon atoms, aliphatic ketones containing 3–5 carbon atoms, aliphatic esters containing 2–6 carbon atoms, halogenated hydrocarbons containing 1–4 carbon atoms, mono-unsaturated aliphatic hydrocarbons boiling between about 0° C. and about 100° C., aliphatic ethers containing 2–8 carbon atoms, aliphatic acetals containing 3–9 carbon atoms, aliphatic nitriles containing 3–4 carbon atoms, said solvent being present in an amount ranging from about 25% to about 50%, calculated upon the weight of the

acetylene solution, and the solution being maintained above the solidification point.

3. The process of storing and handling acetylene solutions with a high concentration of at least 50% acetylene at low temperatures at substantially normal pressure for prolonged periods of time without danger of explosion which comprises dissolving, storing and handling acetylene at temperatures below about —80° C. and under substantially atmospheric pressure in a solvent mixture for acetylene boiling above 0° C. and being selected from the group consisting of aliphatic monohydric alcohols containing 1–4 carbon atoms, aliphatic aldehydes containing 2–4 carbon atoms, aliphatic ketones containing 3–5 carbon atoms, aliphatic esters containing 2–6 carbon atoms, halogenated hydrocarbons containing 1–4 carbon atoms, mono-unsaturated aliphatic hydrocarbons boiling between about 0° C. and about 100° C., aliphatic ethers containing 2–8 carbon atoms, aliphatic acetals containing 3–9 carbon atoms, aliphatic nitriles containing 3–4 carbon atoms, said solvent being present in an amount ranging from about 22% to about 50%, calculated upon the weight of the acetylene solution, and the solution being maintained above the solidification point.

4. The process of storing and handling acetylene solutions with a high concentration of at least 50% acetylene at low temperatures at substantially normal pressure for prolonged periods of time without danger of explosion which comprises dissolving, storing and handling acetylene at temperatures below about —80° C. and under a pressure of at most 1 atmosphere (gauge pressure) in a mixture of 40% to 98% of acetaldehyde and 60 to 2% of a solvent mixture for acetylene selected from the group consisting of diethylether, formic acid-methyl-ester, the solvent mixture being present in an amount ranging from about 22% to about 50% calculated upon the weight of the acetylene solution and the solution being maintained above the solidification point.

5. The process of storing and handling acetylene solutions with a high concentration of at least 50% acetylene at low temperatures at substantially normal pressure for prolonged periods of time without danger of explosion which comprises dissolving, storing and handling acetylene at temperatures below about —80° C. and under a pressure of at most 1 atmosphere (gauge pressure) in a mixture of solvents for acetylene obtained by adding a solvent selected from the group consisting of acetone, propionitrile and mixtures thereof to a mixture of 40% to 98% of acetaldehyde and 60% to 2% of a solvent selected from the group consisting of diethylether, formic acid methyl ester and mixtures thereof, the amount of propionitrile being in the range of 1% to 20%, the amount of acetone being in the range of 6% to 50% and the amount of the mixture of propionitrile and acetone being in the range from 7% to 50%, the percentage figures of acetone and propionitrile and of mixtures thereof being calculated on the amount of the mixture of acetaldehyde and a solvent selected from the group consisting of diethylether, formic acid methyl ester and mixtures thereof, said solvent mixtures being present in an amount ranging from about 22% to about 50% calculated upon the weight of the acetylene solution, and the solution being maintained above the solidification point.

6. A process of claim 1 in which the solvent is present in an amount ranging from about 25% to about 33% calculated upon the weight of the acetylene solution.

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