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HALOGENATION PROCESS OF MAKING ACETYLENE AND OTHER PRODUCTS

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2 Sheets-Sheet 1

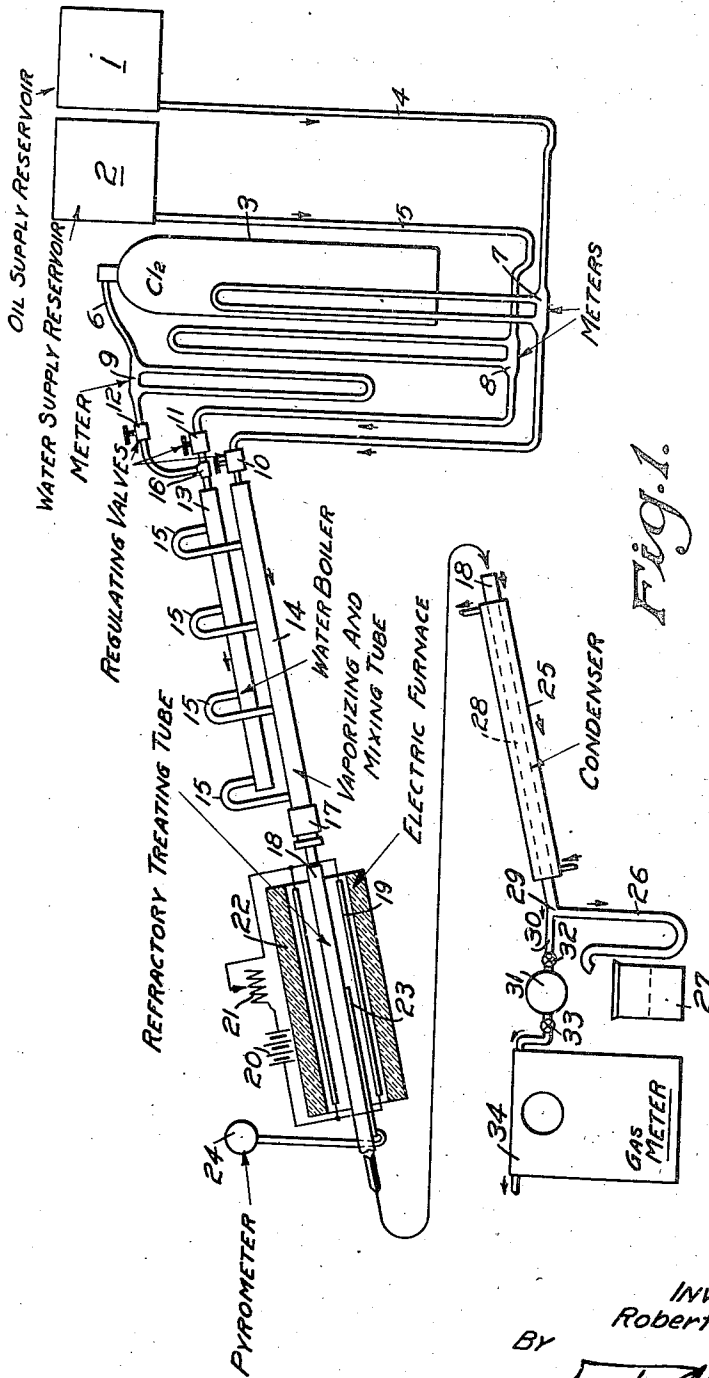


Fig. 1.

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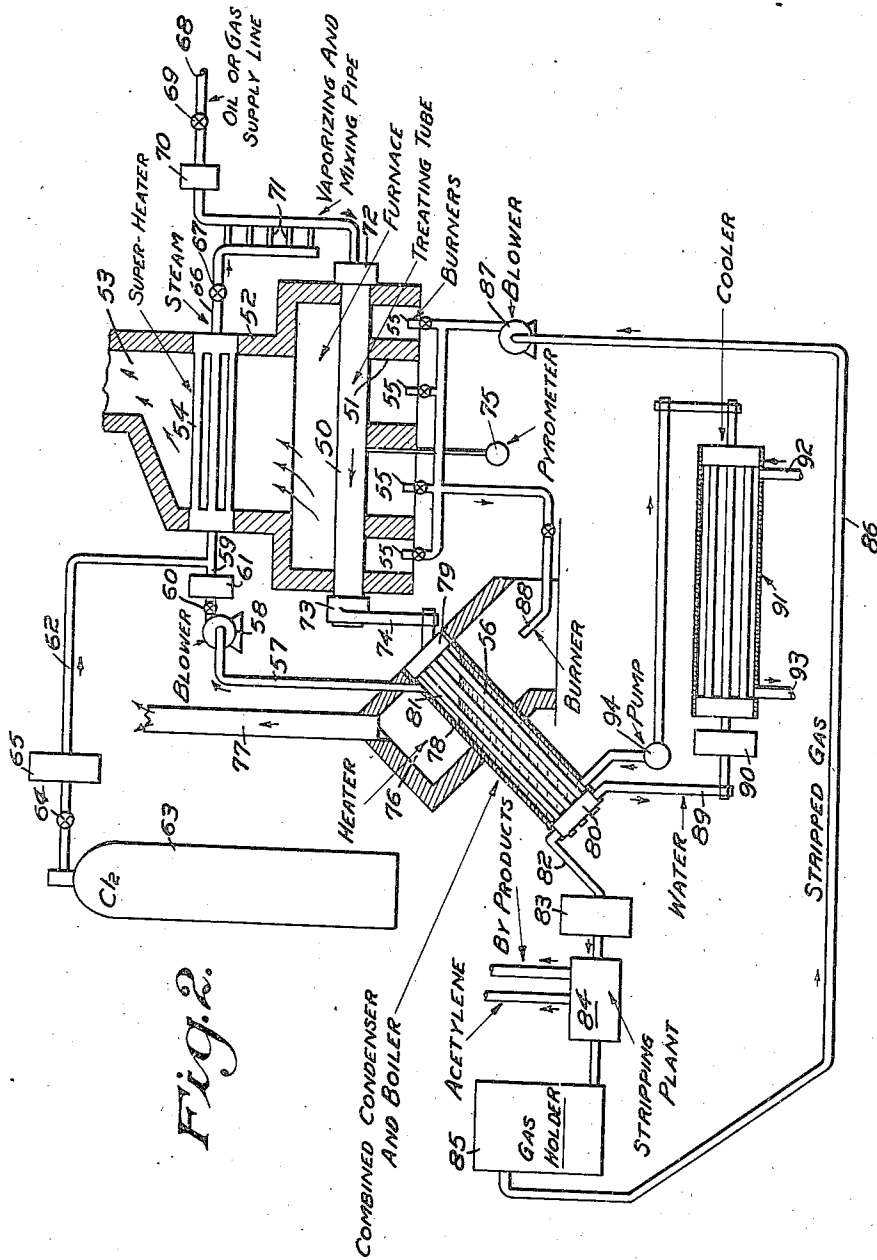
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2 Sheets-Sheet 2



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## UNITED STATES PATENT OFFICE

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## HALOGENATION PROCESS OF MAKING ACETYLENE AND OTHER PRODUCTS

Application filed March 27, 1929. Serial No. 350,197.

In four previous applications I have described how acetylene gas is formed at high temperatures when hydrocarbons of widely different characteristics are passed through highly heated refractory tubes and then cooled as quickly as possible thereafter.

These applications are:

- Serial No. 281,406, filed May 29, 1928,
- Serial No. 302,359, filed Aug. 27, 1928,
- Serial No. 309,547, filed Oct. 1, 1928,
- Serial No. 309,749, filed Oct. 2, 1928.

This application, while constituting a different and improved invention over the applications cited, is a continuation in part of each of them.

In several of the above applications there was described the use of various inert diluents for the vaporized hydrocarbons which were passed through the heated tube. By the use of such diluents, the partial pressure of the hydrocarbons has been decreased during the time of reaction so that an effect approximating the use of a partial vacuum has been obtained. The diluents had, however, so far as known, no purely chemical function.

In the present process, lower temperatures may be used, and an active diluent, chlorine, bromine, or sulfur vapor, not only decreases the partial pressures of the hydrocarbons to be reacted, but actively assists the reaction chemically by removing hydrogen from them as a hydride such as HCl gas. In a modification of my new process, not only chlorine is used as a diluent, but steam may be used in addition and it has been established that the full beneficial effect of both is so obtained.

Referring now to the drawings:

Fig. 1 is a side elevational view of a laboratory apparatus suitable for carrying out the process.

Fig. 2 is a side elevational view of an industrial apparatus.

Both views are more or less diagrammatic. It will be understood that the process may be carried out in other apparatus.

In Fig. 1 numeral 1 represents an oil supply reservoir, 2 a water supply reservoir, and 3 a cylinder containing liquid chlorine. These various reservoirs are respectively provided with delivery pipes 4, 5, and 6, in which

there are liquid meters 7, 8 and 9 of the orifice-manometer type. The delivery pipes 4, 5, and 6 are provided with valves 10, 11, and 12 respectively, the valve 12 being a pressure-reducing valve suitable for handling chlorine.

The delivery tube 5 connects with a vaporizing tube 13 which is merely a metal tube which may be heated by an internal or external wrapping of electric resistance wire, not shown. The tube 13 is connected to a combination vaporizing and mixing tube 14 by means of a plurality of ducts 15. A chlorine delivery pipe 16 is arranged to connect into the vaporizing pipe 13 after the valve 11. By such an arrangement no back flow or pressure of chlorine into the meter 8 can occur when the valve 11 is closed.

The tube 14 is adapted to be the place of vaporization of oil delivered to it by the tube 4. Such vaporization is accomplished by the chlorine, or chlorine and steam mixture, flowing through the ducts 15 into the tube 14. A gas-tight coupling 17 joins the tube 14 with a reaction tube 18, made of refractory material such as sillimanite, carborundum, or fused silica. If this tube is of small diameter, say below one-half inch diameter, no filling is necessary, but tubes of larger diameter should contain broken fragments or crystals of one of the three refractory materials mentioned. The tube for laboratory work may be from nine to fifteen inches long. The reaction tube is adapted to be electrically heated by carborundum or other resistor rods 19, which are part of the electric circuit energized by a battery 20 or its equivalent, through a rheostat 21. The tube 18 and resistors 19 are enclosed by a tubular refractory housing 22, adapted to keep the heat in its interior. A thermocouple 23 is placed inside the housing next to the hottest zone of the tube 18, and the temperatures there registered are read from a pyrometer 24.

The tube 18 connects at its exit end with a condenser 25, of the Liebig type, capable of being supplied with cooling water. At the exit end of the condenser there is a V-shaped delivery tube 26, capable of allowing the escape of liquids without passage of gases.

A beaker 27 is shown at the exit end of said tube. A branching of the reaction products delivery tube 28 of the condenser occurs at 29, the gases being delivered through a tube 30 in which there is a gas sampling bulb 31. Suitable valves 32 and 33 are provided on either side of this bulb to assist sampling. The tube 30 then enters a gas meter 34, from whence it may go to a gas-holder, not shown.

When using the above described apparatus, the process is carried out as follows:

The reaction tube 18 is first heated so that its hottest zone will be in excess of 750° F. Temperatures above 1800° F. will not be required in this process, although the reaction will still occur. The vaporizing tube 13 is then heated and the valves 10 and 11 opened, admitting a supply of hydrocarbon and water to the reaction tube. The water is not fed into tube 18 as such, but is converted into steam in the tube 13. Condensing water is turned into condenser 25. Chlorine is then supplied to the tube 13 by opening the valve 12 to a suitable degree. The amounts of chlorine, hydrocarbon, and water supplied may be gauged by the relative height of liquid in the arms of the various manometers, which are part of the meters. The process may be conducted in the absence of steam, as has before been mentioned.

The volume of chlorine to be used in relation to volumes of gasified hydrocarbon under the same conditions of temperature and pressure may range from two to seven times the volume of such hydrocarbon. For gas oil vapor, one of my hydrocarbon raw materials, the ratio should be about one gas oil vapor to six chlorine gas. In so diluting my hydrocarbon raw material, I aim to supply at least enough chlorine to react with all of the hydrogen present in the hydrocarbon in excess of the amount of hydrogen required to convert substantially all of the carbon in said hydrocarbon to acetylene. In doing so I am aware that I am contributing another useful effect; namely, that of lowering the partial pressure of the hydrocarbon. Reactions of the type here described are favored by lowered pressures, so the lowering of the partial pressure by the addition of a diluent actually assists the progress of the reaction. While chlorine is capable of acting as a diluent as well as a hydrogen remover, the steam is only a diluent and cheapening agent in rendering unnecessary the use of a large proportion of chlorine, where and when chlorine is expensive. While chlorine, on account of expense, should not be added in unlimited quantities, a slight excess does no harm to the reaction. An excess of steam likewise is harmless. Any volume of diluent over about eight volumes of diluent to one of hydrocarbon vapor may be considered an excess and in the case of straight chlorine, anything over six volumes.

The hydrocarbons which may be converted by my process into gases rich in acetylene and containing other products, are not limited to any one series. Paraffines, olefines, and aromatics may be so converted. Among the suitable raw materials are:

1. Paraffins.
  - a. Pure methane.
  - b. Pure ethane.
  - c. Casinghead gas vapor.
  - d. Natural gas consisting of 85% CH<sub>4</sub> and 15% higher hydrocarbons.
  - e. Gas oil containing from 30% to 35% naphthenes, 10% to 12% aromatics, and the remainder paraffins.
  - f. Crude petroleum, kerosene, gasoline, or any other liquid fraction.
  - g. Natural gas carburetted with casinghead gasoline or any other fraction of crude petroleum.
2. Olefines.
  - a. Ethylene.
  - b. Higher olefines.
3. Naphthenes.
  - a. Those in gas oil.
4. Aromatic hydrocarbons.
  - a. Benzol.
  - b. Toluol.

While it has been found that acetylene can be formed from methane, according to my process, it should be stated that yields are low in comparison to those obtained from ethane or higher members. I therefore prefer, in using natural gas as raw material, to use gas as high in higher members of the paraffin and olefine series as possible.

My process yields, besides acetylene, other gases and oils in admixture with it. The reaction product is a mixture of gases carrying yellowish or yellowish-gray fog particles, which are tars and oils in suspension. These may be, and are preferably separated from the gas before any other treatment, except cooling, is given it. Any ordinary form of gas filter or scrubber or the Cottrell precipitator may be used for this purpose. Oil or kerosene may be used for scrubbing. Some of the oils which have been collected in course of my experiments were much lighter in body than those which were the initial materials. Even where gas is used as the starting material in place of oil, light oils are obtained. Any or all of said oils and hydrocarbon condensates may be collected and added to the original raw material for another heat treatment to form acetylene. Scrubbing with acetone, or other well known means of separating acetylene, may be used to recover this main product.

The residual gas is a fuel gas of high calorific value. In the preferred form of my process, I burn this stripped gas under the reaction tube, thus making the process very

economical of oil or other hydrocarbon used as raw material in forming acetylene.

Among the other products beside acetylene which may be formed under various conditions are the following:

- HCl, Hydrochloric acid
- CH<sub>3</sub>Cl, Methyl chloride
- CH<sub>2</sub>Cl<sub>2</sub>, Methylene dichloride
- CHCl<sub>3</sub>, Chloroform
- 10 CCl<sub>4</sub>, Carbon tetrachloride.
- C<sub>2</sub>H<sub>5</sub>Cl, Ethyl chloride
- C<sub>2</sub>H<sub>4</sub>Cl<sub>2</sub>, { Ethylene dichloride
- { Ethylidene chloride
- 15 C<sub>2</sub>HCl<sub>3</sub>, Trichlorethylene
- C<sub>2</sub>H<sub>2</sub>Cl<sub>4</sub>, Tetrachlorethane

and other mono- and poly-chlorinated paraffins, both saturated and unsaturated. An important by-product resulting in some phases of operation is lampblack.

Since many of these products, as well as acetylene, decompose if they are held for any considerable length of time at the temperatures at which they are formed, I do not allow the reacting or reacted products to linger in the hot zone of the reaction tube any longer than necessary to form the desired products. The period during which the reacting gases may remain within the hottest zone of the refractory tube ranges from 2/1000 second to 5 seconds. Another condition of successful operation is that copper and iron be absent from the reaction tube since they decompose acetylene at high temperatures.

In operating on an industrial scale, large volumes of HCl gas will be produced. Chlorine may be recovered from such combination by any appropriate process of oxidation of the hydrogen, as for instance by the well known Deacon process. The recovered chlorine may be used over and over again in the process.

Fig. 2 of the drawings illustrates a plant in which my process may be carried out on an industrial scale. In this view, which is a diagrammatic side elevation partly in section, 50 represents a reaction tube supported by refractory brick piers 51. Surrounding the tube 50 is a furnace 52, across the flue 53 of which a super-heater 54 is provided. The furnace is fired by a battery of gas burners 55. Steam is obtainable from a condenser 56 through a pipe 57 by means of a blower 58. The steam is passed through a pipe 59 in which there is a valve 60 and a meter 61.

Joining the pipe 59 is a chlorine delivery pipe 62, which conveys chlorine from a cylinder or gas-holder 63. In the pipe 62 there is a valve 64, which may be a pressure reducing valve, and a corrosion-proof meter 65.

The pipe 59 connects into the superheater 54 and emerges as a pipe 66 on the other side of the flue 53. In the pipe 66 there is a valve 67. The pipe 68 is an oil or gas supply pipe

having a valve 69 and a meter 70. The pipes 66 and 68 are joined by a number of smaller connecting pipes 71, the function of which is to supply superheated steam and chlorine to the pipe 68 to vaporize the oil therein or to dilute the hydrocarbon vapor therein with steam, chlorine, or both. The pipe 68 is connected with the reaction tube 50 through a gas-tight gland 72.

The reaction tube 50 is provided at its opposite end with a somewhat similar gland 73 having a vertical downcomer 74 through which the hot reacted gases may be delivered to the interior of the condenser 56. A pyrometer 75 is provided to indicate the heat at the hottest point of the reaction tube 50. About the upper portion of the condenser 56, which is inclined at an angle approximating 45°, is provided a furnace 76 provided with a flue or stack 77.

The condenser 56 consists of a shell 78 of cylindrical form, sealed at either end by a pair of headers 79 and 80. Such headers are connected by a plurality of steel tubes 81. Water is maintained in the shell, the level thereof being within the furnace 76. The pipe 57 connects with the vapor space inside the shell, thereby insuring the delivery of fairly dry steam. At the lower end of the condenser a pipe 82 taps the header 80 for the delivery of gaseous reaction products first to a preliminary purification plant 83 where the gases may be subjected to washing for the purpose of removing HCl, Cl<sub>2</sub>, solid matter, and such chlorinated hydrocarbons and oils as may have been left in the vapor state.

The pipe 82 conveys the residual gases to an acetylene and by-products stripping plant 84 where the gases may be scrubbed with acetone, acetaldehyde, or other acetylene solvent. Certain by-products may also be soluble in acetylene solvents. The pipe 82 continues to a gas-holder 85, provided to store combustible gases from the stripping plant 84, which gases no longer bear any acetylene. Such gases have a high heating power and may be used to maintain the heat under the reaction tube 50. For this purpose a pipe 86 and a blower 87 are provided, by means of which these gases may be conveyed to the burners 55 under the tube 50, and also to a burner 88 under the condenser. Suitable air mixing devices (not shown) are provided.

From the header 80 in the condenser 56 another pipe 89 is arranged to drain off condensed liquid products, including condensed steam, and deliver them to a stripping plant 90 where they may be treated to remove HCl, Cl<sub>2</sub>, chlorinated hydrocarbons, solid matter, etc. The pipe 89 then continues to a cooler 91, similar in structure to the condenser 56, where the purified and neutral water from the stripping plant 90 may be cooled by means of cooling water supplied through an inlet 92 and ejected through an outlet 93. The pipe 89

then continues to a pump 94 adapted to inject the water into the condenser 56 through a continuation of the pipe 89.

It is to be understood that corrosion-proof construction is used in the above described plant wherever necessary.

The plant may be altered at will by chemical engineers to adapt it to operate on varying materials or with only chlorine as the diluent, or to emphasize the recovery of particular by-products, without departing from the spirit of the invention. It lies within the capabilities of skilled persons to do this if they are in possession of the major facts of my invention here communicated. In general operation it functions as follows:

Gas is supplied from an outside source to the burners 55 and 88 and the reaction tube 50 and the condenser 56 are heated, the former to a temperature within the reaction range already discussed, and the latter just sufficiently to generate steam. Hydrocarbon is then supplied by opening the valve 69. The blower 58 is operated and the chlorine valve 64 opened a suitable distance. Mixed steam and chlorine then pass through the superheater 54, the valve 67 being open, and gasify and mix with the hydrocarbon in the pipe 68. The reaction mixture so formed is fed at a suitable rate into the heated reaction tube 50, the reacted products making exit through the downcomer 74 into the tubes of the condenser 56, where they are cooled as rapidly as possible, the lower end of that condenser being maintained as cool as commercially feasible. Condensation takes place in the lower portion of the tubes 81 with some deposition of lampblack and condensation of liquid hydrochloric acid solution. The liquid condensate, carrying the lampblack in suspension, flows down the pipe 89 into the stripping plant 90 where the lampblack and HCl are separated and the latter oxidized, if desired, to Cl<sub>2</sub>. The chlorine may here be compressed into cylinders. The recovered water (or fresh water) is cooled, if necessary, in the cooler 91 and then returned to the condenser 56.

The gaseous products of the reaction pass through the pipe 82 into the lampblack and HCl separating, and optionally HCl oxidizing plant 83, into the acetylene scrubbing plant 84 where the gases are scrubbed with acetone or equivalent. The resulting solution of acetylene with or without by-products in solution, may be here filled into cylinders or otherwise worked upon. The by-products may be here separated in any known suitable manner. The reaction gases may alternatively be treated with a selective solvent to extract by-products, then be scrubbed with an acetylene solvent.

The residual stripped gases resulting from such operation are stored in the gas-holder 85 until they are needed to keep the reaction

tube 50 hot. Then they are conveyed through the pipe 86 by the blower 87 to the burners, as has been described.

In case it is not desired to use both chlorine and steam, the chlorine only may be used by cutting out the operation of the burner 88 and the blower 58.

To sum up the salient points of my preferred operation, I list certain characteristics of my process. These are:

1. The use of hydrocarbons of many kinds, but when paraffins are used, those preferably above methane in the series.

2. The exposure for an interval from 2/1000 second to five seconds of the reaction gases in a refractory tube to a temperature of over 750° F., preferably about 1800° F., followed by as rapid cooling of the reacted gases as possible.

3. The use of chlorine, bromine, sulfur vapor, or other gas as a dehydrogenating diluent in substantial proportion, with or without the addition of steam.

In a modification of my process, if a large excess of chlorine is used over the proportions above specified, and up to the ratio at which there is enough chlorine to convert all the hydrogen of the hydrocarbon to hydrochloric acid, the reaction will proceed as a combustion without the agency of external heat. There is some formation of acetylene and copious liberation of lampblack. Steam may or may not be used in conjunction, though if too much steam is used, external heat will be necessary. The right to file additional applications covering this modification of my process is reserved.

The apparatus to be used in carrying out combustion with chlorine according to the above described process, while affording a field for invention for improvements, is nevertheless capable of being devised in its simpler and fundamental forms by skilled chemical engineers without the necessity of making inventions in order to carry out the process.

In a like manner, that modification of my process in which sulfur vapor is used as the dehydrogenating agent can also be carried out by skilled persons familiar with the foregoing matter.

I claim as my invention:

1. A process of producing a mixed gas containing acetylene which comprises: forming a vaporous mixture of hydrocarbon material (selected from the group consisting of paraffins, olefines (naphthenes, benzene, and toluene hydrocarbons) and an active diluent (selected from the group consisting of chlorine, bromine, and sulphur); heating said mixture to a temperature preferably considerably in excess of 750° F. and for a period of less than five seconds; and thereafter rapidly cooling said mixture to a temperature at which acetylene is stable.

2. A process of producing a mixed gas containing acetylene which comprises: forming a vaporous mixture of hydrocarbon material (selected from the group consisting of paraffins, olefines, naphthenes, benzene, and toluene hydrocarbons) and a halogen; heating said mixture to a temperature preferably considerably in excess of 750° F. and for a period of less than five seconds; and thereafter rapidly cooling said mixture to a temperature at which acetylene is stable.

3. A process of producing a mixed gas containing acetylene which comprises: forming a vaporous mixture of hydrocarbon material (selected from the group consisting of paraffins, olefines, naphthenes, benzene, and toluene hydrocarbons) and sulphur; heating said mixture to a temperature preferably considerably in excess of 750° F. and for a period of less than five seconds; and thereafter rapidly cooling said mixture to a temperature at which acetylene is stable.

4. A process of producing a mixed gas containing acetylene which comprises: forming a vaporous mixture of hydrocarbon material (selected from the group consisting of paraffins, olefines, naphthenes, benzene, and toluene hydrocarbons) and an active diluent (selected from the group consisting of chlorine, bromine, and sulphur); adding to said mixture an inactive diluent; heating said mixture to a temperature preferably considerably in excess of 750° F. and for a period of less than five seconds; and thereafter rapidly cooling said mixture to a temperature at which acetylene is stable.

5. A process of producing a mixed gas containing acetylene which comprises: forming a vaporous mixture of hydrocarbon material (selected from the group consisting of paraffins, olefines, naphthenes, benzene, and toluene hydrocarbons) and a halogen; adding to said mixture an inactive diluent; heating said mixture to a temperature preferably considerably in excess of 750° F. and for a period of less than five seconds; and thereafter rapidly cooling said mixture to a temperature at which acetylene is stable.

6. A process of producing a mixed gas containing acetylene which comprises: forming a vaporous mixture of hydrocarbon material (selected from the group consisting of paraffins, olefines, naphthenes, benzene, and toluene hydrocarbons) and sulphur; adding to said mixture an inactive diluent; heating said mixture to a temperature preferably considerably in excess of 750° F. and for a period of less than five seconds; and thereafter rapidly cooling said mixture to a temperature at which acetylene is stable.

7. A process of producing a mixed gas containing acetylene which comprises: forming a vaporous mixture of hydrocarbon material (selected from the group consisting of paraffins, olefines, naphthenes, benzene, and toluene hydrocarbons) and an active diluent (selected from the group consisting of chlorine, bromine, and sulphur); heating said mixture to a temperature of about 1800° F. and for a period of less than five seconds; and thereafter rapidly cooling said mixture to a temperature at which acetylene is stable.

8. A process of producing a mixed gas containing acetylene which comprises: forming a vaporous mixture of hydrocarbon material (selected from the group consisting of paraffins, olefines, naphthenes, benzene, and toluene hydrocarbons) and a halogen; heating said mixture to a temperature of about 1800° F. and for a period of less than five seconds; and thereafter rapidly cooling said mixture to a temperature at which acetylene is stable.

9. A process of producing a mixed gas containing acetylene which comprises: forming a vaporous mixture of hydrocarbon material (selected from the group consisting of paraffins, olefines, naphthenes, benzene, and toluene hydrocarbons) and sulphur; heating said mixture to a temperature of about 1800° F. and for a period of less than five seconds; and thereafter rapidly cooling said mixture to a temperature at which acetylene is stable.

10. A process of producing a mixed gas containing acetylene which comprises: forming a vaporous mixture of gas oil and an active diluent (selected from the group consisting of chlorine, bromine, and sulphur); heating said mixture to a temperature preferably considerably in excess of 750° F. and for a period of less than five seconds; and thereafter rapidly cooling said mixture to a temperature at which acetylene is stable.

11. A process of producing a mixed gas containing acetylene which comprises: forming a vaporous mixture of gas oil and a halogen; heating said mixture to a temperature preferably considerably in excess of 750° F. and for a period of less than five seconds; and thereafter rapidly cooling said mixture to a temperature at which acetylene is stable.

12. A process of producing a mixed gas containing acetylene which comprises: forming a vaporous mixture of gas oil and sulphur; heating said mixture to a temperature preferably considerably in excess of 750° F. and for a period of less than five seconds; and thereafter rapidly cooling said mixture to a temperature at which acetylene is stable.

In testimony whereof, I have hereunto set my hand at Los Angeles, California, this 6th day of March, 1929.

ROBERT G. WULFF.