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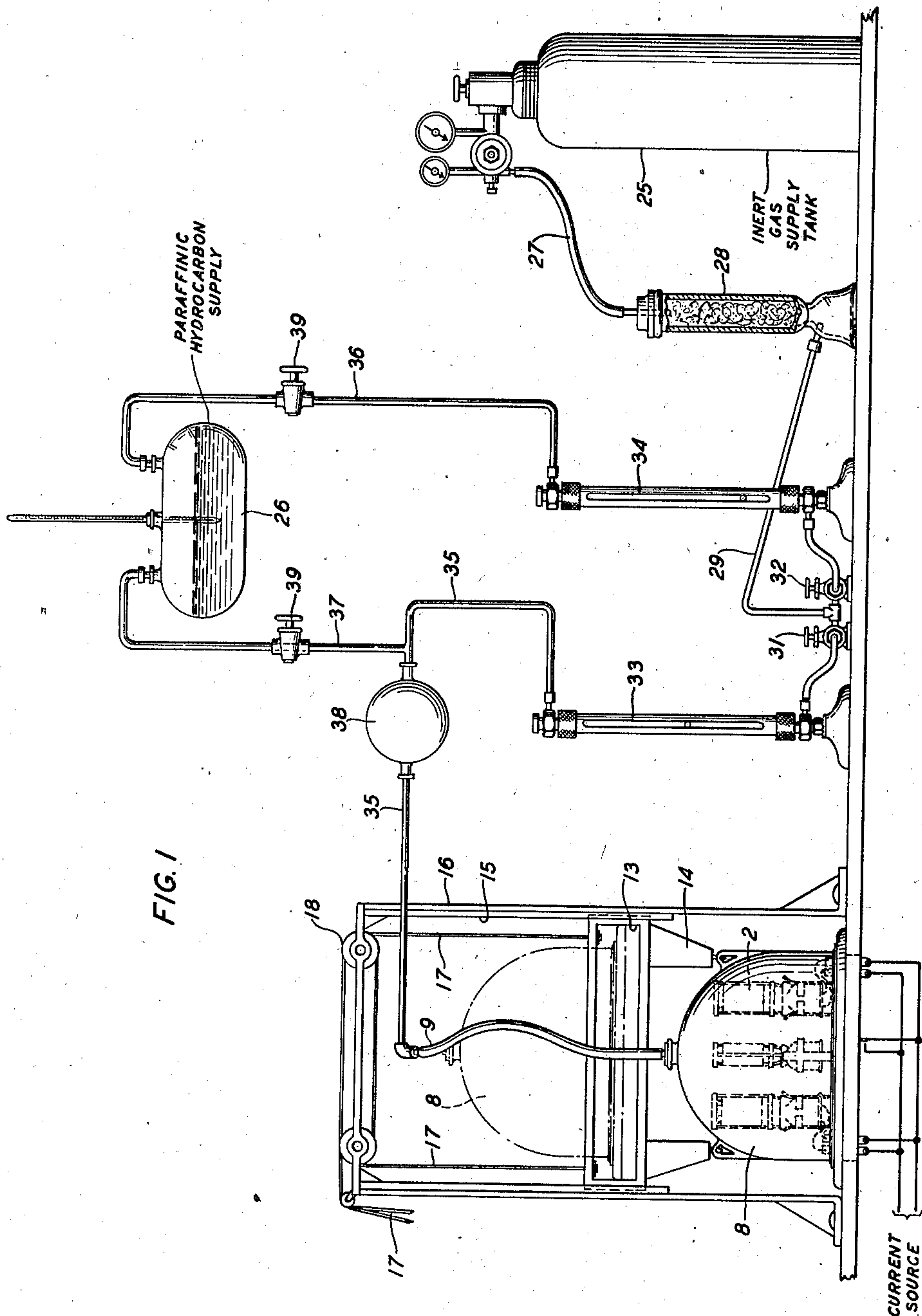
E. A. THURBER ET AL

2,400,893

PROCESS OF CARBIDING

Filed April 24, 1944

2 Sheets-Sheet 1



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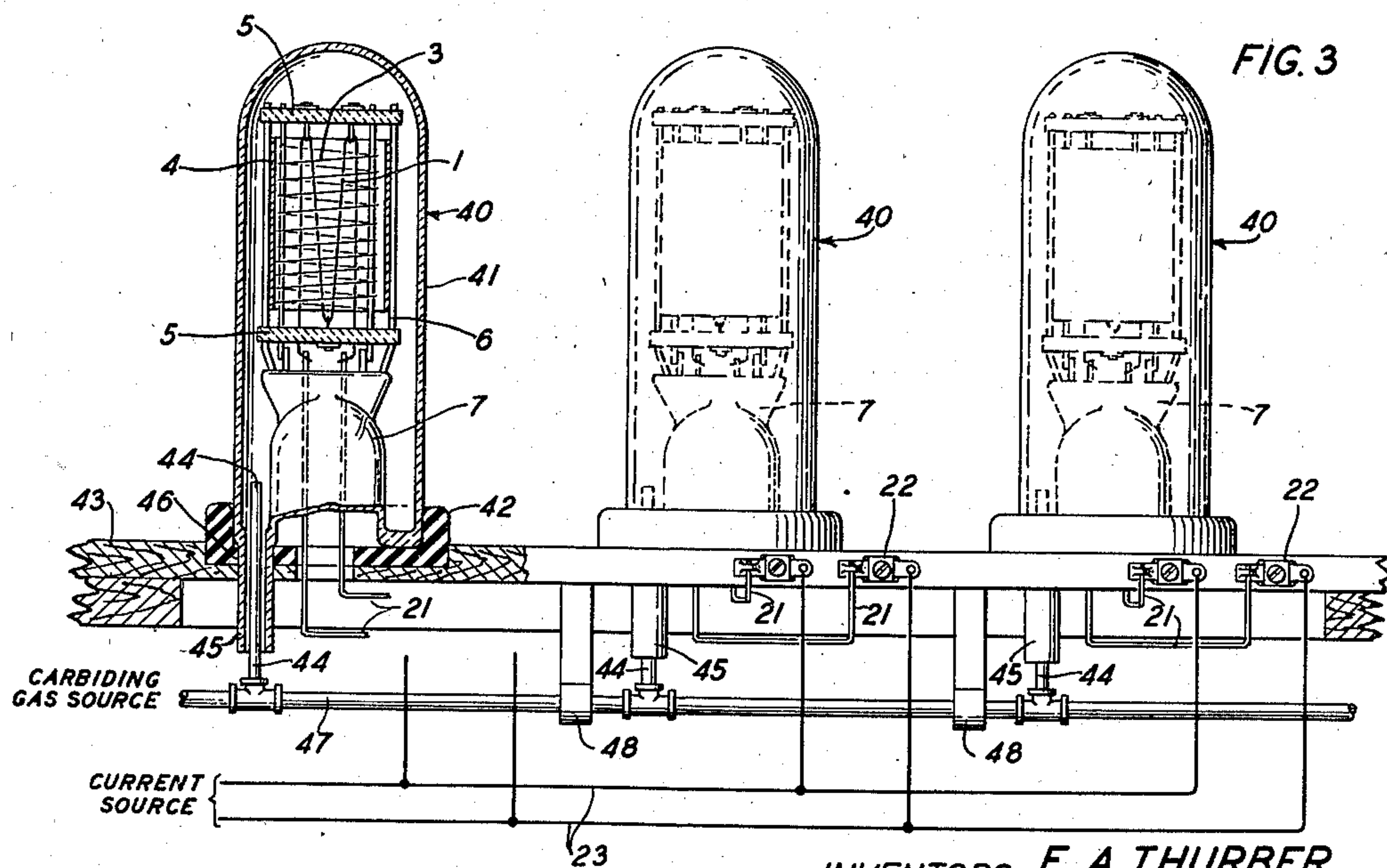
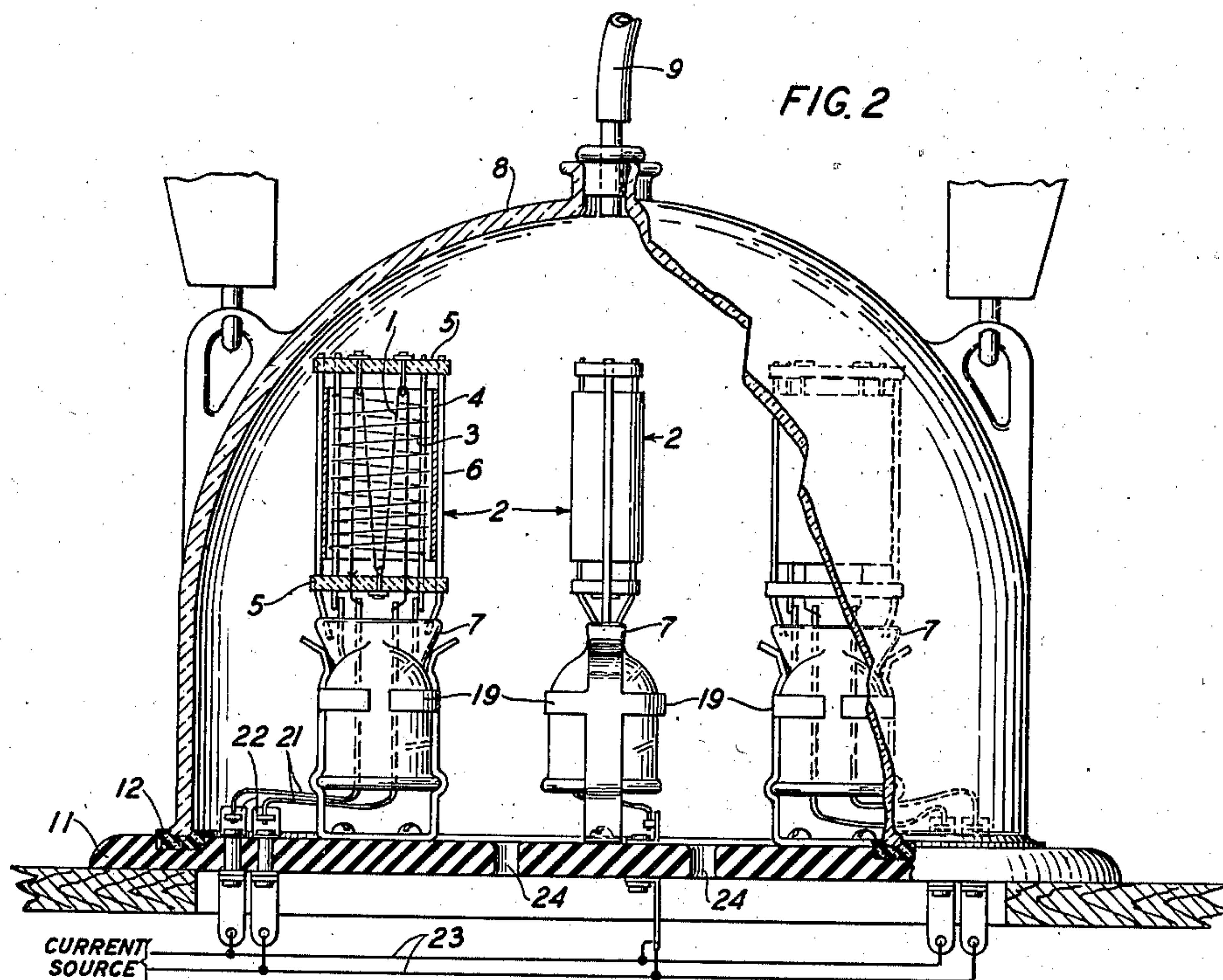
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UNITED STATES PATENT OFFICE

2,400,893

PROCESS OF CARBIDING

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17 Claims. (Cl. 148—13.1)

This invention relates to the application of carbon to metallic surfaces, and more particularly to a process for carbiding the surfaces of thoriated tungsten electrodes of the type employed in electron discharge devices.

It has been known that in an electron discharge device of the type comprising a heated electron emissive tungsten cathode, the electron emission properties of the cathode are greatly improved if a small amount of thorium, usually in the form of an oxide, is incorporated in the tungsten. It is the usual practice, moreover, to carbide the surface of such a thoriated tungsten cathode; this has been found to result in important advantages, such as making possible activation of the cathode to a higher and more stable electron emission level, operation of the cathode at lower temperatures, and substantially increasing useful cathode life.

In carbiding a thoriated tungsten cathode, it has been the usual practice to perform the carbiding operation by glowing the cathode in a carbonaceous gas, usually acetylene, or benzene diluted with hydrogen, maintained at a low pressure substantially below atmospheric pressure, whereby the glowing cathode decomposes the hydrocarbon gas which comes into contact with it and effects a chemical combination between the resulting carbon and the tungsten of the cathode to form a crust or coating of carbide on the surface of the cathode. Apparently to produce the advantages indicated above it is necessary that the carbide produced be substantially, if not entirely, ditungsten carbide W_2C .

Because of the complications induced by the necessity of maintaining a low pressure of carbiding gas and because of other difficulties arising in such low pressure process, it is desirable to employ a carbiding process in which the carbiding gas is maintained at atmospheric pressure.

Prior attempts to carbide thoriated tungsten cathodes by a process in which the carbiding gas was maintained at atmospheric pressure, however, have not been as successful as desired. In general, difficulties have arisen due to deposition of improper amounts of carbon; usually excessive amounts of carbon are deposited with the formation of soot on the cathode or adjacent parts, or with the formation on the cathode of high carbon tungsten carbides such as WC which are harmful to electron emission properties. Moreover, the carbide coatings which have been formed have been non-uniform in thickness and in chemical compositions. Usually it has been necessary to subject the carbide cathode to an after-treat-

ment, consisting of glowing the cathode in a non-carbonaceous gas such as hydrogen, to correct at least in part these deficiencies of the carbon-containing coatings. Such treatment not only adds to the difficulty and cost of the process, but also results in the production of carbided cathodes of impaired electron emission properties.

In prior processes, moreover, it has been found and has heretofore been believed necessary to carbide the cathodes by flashing them periodically, since attempts to carbide by a process wherein the cathode was glowed continuously resulted in deposits of soot on the cathode and adjacent parts, non-uniform carbiding, and other difficulties. Periodic flashing, however, has also resulted in non-uniform heating and non-uniform formation of carbide, and requires expensive electrical equipment.

The present invention provides a process of carbiding thoriated tungsten cathodes in the form of thoriated tungsten filaments or other suitable structures which is free of the above-mentioned and other difficulties of the prior processes. According to the process of the present invention, a thoriated tungsten cathode is glowed in a carbiding gas maintained at atmospheric pressure and consisting of inert gas mixed with specific proportions of one or more of certain saturated paraffinic hydrocarbon vapors. The temperature range in which the cathode is glowed, and the nature of the hydrocarbon vapor and its relation to the inert gas are quite critical. The process of the present invention, being carried out at atmospheric pressures, avoids the difficulties inherent in the prior low pressure processes. The process of the present invention provides on a thoriated tungsten cathode a superior carbide coating which is of highly uniform and desirable thickness, highly uniform chemical composition, and which consists almost wholly of a tungsten carbide which provides the highest electron emission, which tungsten carbide is W_2C . No after-treatment of the cathode to correct the deficiencies of the carbide coating is required.

A more detailed description of the process of the invention and a fuller explanation of the above and other advantages of the process of the invention, will be apparent from the following description in connection with the accompanying drawings, in which:

Fig. 1 is a semidiagrammatic illustration of an apparatus for carrying out the process of the invention by carbiding thoriated tungsten filaments which are assembled with grids and plates

into "mounts" adapted to be sealed into the envelopes of electron discharge devices;

Fig. 2 represents to a larger scale a portion of the apparatus of Fig. 1, showing more particularly the mounts and the enclosure in which the filaments are glowd in the carbiding gas; and

Fig. 3 is an illustration to the same scale as Fig. 2 of a portion of another apparatus for carrying out the process of the invention by carbiding thiorated tungsten filaments after they are built into the envelopes of electron discharge devices.

According to the process of the present invention a thiorated tungsten cathode, advantageously in the form of a thiorated tungsten filament, is glowd by being heated electrically or by other suitable means, to a temperature lying between 2350°K . and about 2550°K . in a carbiding gas, maintained substantially at atmospheric pressure, consisting of inert gas such as nitrogen argon, helium or the like containing from about 1 per cent to about 5 per cent, by weight of the inert gas, of a paraffinic hydrocarbon vapor consisting of one or more of the paraffinic hydrocarbons having from five to ten carbon atoms. The cathode being carbided may be glowd continuously or may be flashed periodically until a carbide coating of the desired thickness is formed on the cathode; in general, it is advantageous to glow the cathode until the final thickness of the carbide coating is of the order of ten per cent of the total thickness of the carbided cathode.

The proportion of carbon to hydrogen in the hydrocarbon is highly important since it determines whether the hydrocarbon will be cracked at a rate such that all, or substantially all, of the carbon resulting from the cracking can react with the metal to form a carbide of the desired kind, or whether the hydrocarbon will be cracked at such a rapid rate that the resulting carbon reacts to form a substantial amount of an undesired carbide such as WC or deposits as soot. The paraffinic hydrocarbons having from five to ten carbon atoms which are employed in the process of the present invention have a proportion of carbon to hydrogen such that, when the hydrocarbon is mixed with the inert gas in the required proportions indicated above, the hydrocarbon cracks at a rate such that a coating of the desired tungsten carbide is formed without difficulty. These hydrocarbons, moreover, although liquids at room temperatures have volatility characteristics such that at room temperatures their vapors may be readily mixed with the inert gas and carried into contact with the glowing cathode. Examples of particularly suitable hydrocarbons of this type are n-hexane, n-heptane and n-octane. Of these hydrocarbons, n-hexane appears to be the most advantageous because of its ready availability, its volatility characteristics which permit it to be easily mixed with the inert gas at room temperatures, and the desirable nature of the resulting carbide coating produced on the cathode.

The proportion of the paraffinic hydrocarbon mixed with the inert gas to form the carbiding gas is also important, since it controls the amount of carbon which will result from cracking of the hydrocarbon. When one or more paraffinic hydrocarbons having from five to ten carbon atoms is mixed with the inert gas in the proportion contemplated by the invention of from about 1 to about 5 per cent by weight of the inert gas, the carbon which results from the cracking of the

hydrocarbon is of an amount proper to form the desired carbide; the carbon is not insufficient to provide a complete, uniform coating of carbide, and is not excessive so that soot is deposited or an undesired carbide is formed.

The paraffinic hydrocarbons employed in the process of the invention are also advantageous since they are non-toxic, in contrast to certain hydrocarbons heretofore employed, such as benzene, which necessitated precautions because of their toxicity.

The employment of an inert gas such as nitrogen, helium, argon or the like, in admixture with the hydrocarbon is advantageous for numerous reasons. It renders the resulting carbiding gas mixture non-inflammable and non-explosive. It appears, moreover, that the carbiding reaction proceeds more slowly when such an inert gas is employed in admixture with the hydrocarbon, than when hydrogen is employed in admixtures with a hydrocarbon as was the usual practice heretofore; the slower rate of the carbiding reaction is advantageous since it makes the carbide reaction more readily controllable to produce the desired degree of carbiding. The slower reaction rate, moreover, makes possible the use of a higher carbiding temperature than ordinarily can be employed, so that the formation of undesired carbides such as WC is suppressed.

Moreover, each of the inert gases employed in the process of the invention has a low accommodation coefficient, much lower than that of the hydrogen usually employed; this minimizes heat losses from the incandescent cathode and prevents variations in the temperature along the length of the cathode as well as fluctuations in cathode temperature due to irregular heat losses to the carbiding gas because of convection currents. This results in the production of a highly uniform carbide coating throughout the length of the cathode. Because the inert gas has such a slight cooling effect on the incandescent cathode, the employment of such gas results in reduced consumption of power required for heating the cathodes.

Of the inert gases, nitrogen appears to be the most advantageous because of its low cost, ready availability, and the particularly beneficial results it produces in the carbiding reaction, particularly in slowing the rate of the reaction and because of its exceptionally low accommodation coefficient in minimizing heat losses from and temperature irregularities in the hot cathode due to convection currents.

Both the hydrocarbon and the inlet gas should be substantially pure, and in particular should be free of oxygen or water vapor which can cause difficulties in the process.

The carbiding gas consisting of the paraffinic hydrocarbon and inert gas of the character indicated above being non-inflammable, non-explosive, and non-toxic, reduces the danger to employees, and makes possible the employment of less expensive carbiding apparatus because it is not necessary to prevent the escape of the carbiding gas into the air.

The temperature to which the surface of the cathode is heated during the carbiding operation is also critical. If the temperature is too high the hydrocarbon will be cracked too rapidly and soot will deposit upon the cathode and adjacent elements; if the temperature is too low the hydrocarbon may not decompose at all, or if it does decompose the carbide crust formed will be substantially if not entirely of the undesired carbide

WC which has poor electron emission characteristics. The most advantageous temperature to be employed is between about 2350° K. and about 2550° K.; exceptionally good results are obtained when the temperature is between about 2400° K. and about 2500° K. The temperature of the surface of the cathode may be determined by a pyrometer or from the cathode resistance characteristics. Apparently, as carbiding proceeds the surface temperature of the cathode decreases somewhat; the temperature indicated above is the initial temperature of the cathode surface. If the cathode is heated electrically, satisfactory results are obtained if the voltage of the heating current applied to the cathode is maintained constant throughout the carbiding operation, although if desired the voltage may be increased somewhat as carbiding proceeds. If the cathode is heated during carbiding by being flashed periodically, the maximum temperature of the cathode surface should lie within the range indicated above. Since, however, the average temperature of a cathode which is flashed periodically is below the maximum optimum temperature, the carbide coating which is obtained may not be as advantageous as that which is obtained by continuous glowing.

The time of heating in general is not as critical as are other factors in the process. The time of heating to a certain extent depends upon the cross-sectional size of the cathode being carbided, and the desired thickness of the carbide layer. If the cathode is heated by the passage of an electric current therethrough, the time of heating can be readily controlled by the change in the electrical resistance of the cathode as it becomes carbided; of course, the time of heating for all cathodes of a type may be set after experimental determination. For thoriated tungsten filaments of the ordinary sized employed in electron discharge devices, the filament may be glowed continuously in the carbiding gas for from 20 to 30 seconds, or may be flashed periodically for about one-second long intervals from twenty to fifty times to produce a satisfactory carbide layer.

The cathodes may be carbided according to the invention in various manners. However, in general, it is most advantageous to carbide the cathode after it is built into its supporting means; this avoids damage due to handling of the cathode in its carbided condition, since carbiding usually causes embrittlement. For this advantage the cathode may be carbided after it has been built into a "mount" or the internal structure of an electron discharge tube comprising the glass base member, the cathode, the anode, the grid, if any, and the supporting members for these electrodes; or the cathode may be carbided after it has been built into the envelope of an electron discharge tube.

In order that the invention may be more fully understood it will be discussed in more detail in connection with the two forms of apparatus illustrated in the accompanying drawings for carrying out the process of the invention.

In the apparatus illustrated in Figs. 1 and 2, the cathode to be carbided takes the form of a thoriated tungsten filament 1 built into a mount 2. As is shown in detail in Fig. 2, mount 2 comprises filament 1 which is to be carbided, grid 3, and plate 4, all fixed by insulators 5 and supporting members 6 to glass press 7 adapted to be sealed into an electron discharge tube en-

velope. A plurality of such mounts 2 are mounted in an enclosure taking the form in the illustrated apparatus of a glass bell jar 8 to the interior of which the carbiding gas is supplied through tube 9. The bell jar 8 makes an air-tight contact with the base member 11 by resting on a sponge rubber sealing ring 12 mounted in a groove in said base member 11. As is shown in Fig. 1, the glass bell jar 8 is adapted to be raised to the position indicated by broken lines and lowered to the position shown in full lines to permit the placing and removal of the mounts 2. The bell jar 8 is fixed to slidable supporting member 13 by means of brackets 14. Said member 13 is slidably mounted in tracks 15 carried by vertical members 16 and is adapted to be raised and lowered together with the bell jar 8 by means of cables 17 and pulleys 18 actuated by suitable means, not shown.

Each of the plurality of mounts 2 disposed in the interior of the bell jar is carried by a spring clip 19 fixed to the base member 11, and the leads 21 from each filament 1 are connected to clips 22 mounted on base member 11 which is formed of suitable insulating material. Clips 22 are connected to a suitable source of electrical current (not shown) through leads 23. Openings 24 in the base 11 permit the discharge of carbiding gas from the interior of the bell jar 8.

While the carbiding gas may be supplied to the interior of the bell jar by any suitable means, that shown in Fig. 1 has been found convenient.

In the gas supply apparatus of Fig. 1 nitrogen, which in this case is the inert gas, is supplied from a tank 25 while n-hexane, which in this case is the paraffinic hydrocarbon, is supplied from container 26. Nitrogen from tank 25, which should be in the purified state and free from oxygen, passes at a pressure slightly above atmospheric pressure through tube 27 to drying tower 28 containing magnesium perchlorate or other suitable drying substance capable of removing water vapor, after which the gas passes through tube 29 to the valves 31 and 32. Part of the nitrogen passes through valve 31 through meter 33 while the other part passes through valve 32 through meter 34. The meters 33 and 34 are of a commercially available type which indicate the volume of the gas passing therethrough per unit of time; by adjustment of valves 31 and 32, and observation of the meters 33 and 34, the two streams of nitrogen may be properly proportioned. The larger volume of nitrogen passes through meter 33 and tube 35; the smaller volume passes through meter 34 and tube 36 through the container 26 containing n-hexane. Since this hydrocarbon is quite volatile although liquid at normal room temperatures, need not be maintained at a fixed elevated temperature in container 26 while the nitrogen passes there-through; the nitrogen passing through the container 26 becomes substantially saturated with n-hexane vapor. When other paraffinic hydrocarbons are employed, it may be desirable to maintain the temperature above or below room temperature to obtain the desired vapor pressure. The saturated nitrogen leaves container 26 through tube 37 which joins the main stream of nitrogen in tube 35. A mixing chamber 38 is shown in tube 35 to provide for a thorough mixing of the paraffinic hydrocarbon gas and the nitrogen. The resulting carbiding gas containing the paraffinic hydrocarbon gas in the desired proportion relative to the inert gas passes from tube 35 through tube 9 into the bell jar 8.

The proportion of hydrocarbon relative to the nitrogen in the inert gas passing into the bell jar 8 may, as is apparent, be controlled by the relative volumes of the two streams of nitrogen passing through tubes 35 and 36, which in turn are adjusted by means of valves 31 and 32 and meters 33 and 34. When the apparatus is not in use, the container 26 may be cut off from the rest of the system by valves 39 to prevent air from leaking into container 26.

In operation of the apparatus shown in Figs. 1 and 2 the bell jar 8 is raised, mounts 2 are fixed in spring clips 19 and leads 21 of the filaments 1 of mounts 2 are connected to clips 22, and the bell jar 8 is then lowered into contact with the rubber ring 12 with which it makes an air-tight seal. Nitrogen gas alone, or a carbiding gas consisting of nitrogen and n-hexane in the proper proportions, is then passed into the jar 8 to displace all of the air therein. Thereafter, each filament is glowed either continuously or periodically at the desired temperature. The current and voltage necessary to obtain this temperature of the filament, of course, had been previously determined by pyrometer tests or from the filament characteristics. During the operation, the hydrocarbon gas in contact with the glowing filaments is decomposed and a coating of carbide is formed thereon. The excess carbiding gas supplied to the interior of the bell jar 8 passes out through openings 24. After completion of the carbiding the glowing is discontinued, the flow of gas is halted, the bell jar 8 is lifted and the mounts 1 removed and built into the electron discharge tubes.

Fig. 3 illustrates another form of apparatus for carrying out a modified process embodying the invention. In this process, the filaments are carbided after they have been built into an electron discharge tube. More specifically, in the illustrated apparatus the filaments of a plurality of electron discharge tubes 40 are simultaneously carbided. Each of these tubes comprises an envelope 41 containing a filament 1, grid 3, and plate 4, carried by insulators 5 and supports 6, from a glass press 7 sealed to the envelope 41. Each of the tubes 40 is removably but firmly mounted in a cup member 42 formed of resilient material such as rubber fixed to the base member 43. A gas supply tube 44 projects into the envelope 41 through tubulation 45 of the electron discharge tube 40 which extends through opening 46 in the base member 43 and cup member 42. The outside diameter of tube 44 is smaller than the opening through the tubulation space through which the excess carbiding gas discharges. Said tube 44 for each electron discharge tube is connected to a pipe 47 which communicates with a suitable source of carbiding gas such as that illustrated in Fig. 1. Mounting members 48 firmly position tubes 44 and supply pipe 47. The filament leads 21 for the electron discharge tube are connected to clips 22 fixed to the edge of the base member 43 which is formed of suitable non-conducting material. Said clips are connected to a suitable source of current, not shown, by leads 23.

In operation of the apparatus of Fig. 3, each of the plurality of electron discharge tubes 40 is mounted in its corresponding supporting cup 42 in such a manner that the gas supply tube 44 projects into the envelope 41. The filament leads 21 of each electron discharge tube are connected to their corresponding clips 22. The carbiding gas is then passed into the interior of the envel-

ope in each of said electron discharge tubes until the air therein is completely displaced after which the filaments of the tube are heated either continuously or periodically, by means of the current passing therethrough, to the desired temperature. The carbiding gas which passes into the interior of each envelope 41 through the corresponding tube 44 and which contacts the glowing filament decomposes to form a carbide layer on the filament, while the excess carbiding gas passes out through tubulation 45 the opening of which is larger than tube 44. After the filaments have been glowed for a predetermined time sufficient to form the desired carbide coating thereon the electrical current is cut off, and the flow of gas is halted. The electron discharge tubes are then removed for further operations.

In both types of apparatus discussed above the carbiding gas is maintained substantially at atmospheric pressure.

In general it is more advantageous to employ a higher proportion of hydrocarbon in the carbiding gas when cathodes are carbided after they are built into the envelopes of electron discharge tubes as shown in Fig. 3, since some of the carbon supplied by the carbiding gas may be consumed by the moisture and oxygen liberated from said envelopes as they become heated from the glowing filament. In general it is advantageous to employ a carbiding gas containing a proportion of the paraffinic hydrocarbon corresponding to about 3 to 5 per cent of the weight of the inert gas for such a carbiding operation; it is satisfactory to employ a carbiding gas containing the paraffinic hydrocarbon in an amount corresponding to about 1 to 3 per cent of the weight of the inert gas for carbiding filaments in mounts in a large enclosure containing a plurality of such mounts.

As a specific example of the process of the invention, a thoriated tungsten filament about 0.0115 inch in diameter, forming part of a mount, was electrically heated to a substantially constant temperature of about 2450° K. for about twenty-five seconds in a carbiding gas maintained at atmospheric pressure and consisting of purified nitrogen mixed with about 2 per cent by weight of the nitrogen of n-hexane; carbiding apparatus similar to that shown in Figs. 1 and 2 was employed. The resulting filament had a carbide coating of highly uniform composition and had excellent electron emission characteristics when built into an electron discharge tube.

As another example, a similar thoriated tungsten filament was carbided on similar apparatus by being flashed for one-second long intervals, for thirty times, to a maximum temperature of about 2500° K. in a carbiding gas at atmospheric pressure consisting of purified nitrogen mixed with about 1 per cent by weight of the nitrogen of n-hexane. The resulting filament had a carbide coating of highly uniform composition, and had excellent electron emission characteristics and long life when built into an electron discharge tube.

As another example, in apparatus similar to that of Fig. 3, a gas supply tube was inserted through the tubulation into the envelope of a partly constructed electron discharge tube having built into the envelope a thoriated tungsten filament of about 0.008 inch in diameter. A carbiding gas, consisting of purified nitrogen mixed with about 3 per cent by weight of the nitrogen of n-hexane, was passed by mean of the tube into the envelope, and the filament was electrically

heated to a substantially constant temperature of about 2400° K. in the gas at atmospheric pressure for about thirty-five seconds. After completion of the electron discharge device, the resulting carbided thoriated tungsten filament displayed excellent electron emission properties and an exceptionally long life.

As another example, the above process was repeated, except that the filament was flashed for second long intervals for forty times in the presence of the gas to carbide the filament. After completion of the electron discharge device, the resulting carbide filament displayed excellent electron emission properties and long life.

The present invention provides a process which, among other advantages thereof, produces on thoriated tungsten cathodes superior carbide coatings of a high degree of uniformity; which is simple and requires no accurate control and yet produces highly uniform results; which operates at atmospheric pressures and thus avoids the complexities of low pressure processes; which produces little or no soot on the cathode or adjacent parts; which makes possible successful carbiding with either continuous or periodic glowing of the cathode; which requires no expensive or complicated equipment; which provides a substantial saving in power required for heating the cathodes; and which employs a carbiding gas which is non-inflammable, non-explosive, and non-toxic.

Various modifications may be made in the processes and illustrative apparatus discussed above without departure from the spirit of the invention. The specific examples described above are given as illustrations of advantageous conditions but are not intended to limit the invention.

It is intended that the patent shall cover, by suitable expression in the appended claims, whatever features of novelty reside in the invention.

What is claimed is:

1. The process of carbiding a thoriated tungsten element comprising heating the thoriated tungsten element to a temperature between about 2350° K. and about 2550° K. in a carbiding gas maintained at substantially atmospheric pressure and consisting of inert gas and mixed therewith paraffinic hydrocarbon vapor in which the paraffinic hydrocarbon has from five to ten carbon atoms which vapor, constitutes from about 1 to about 5 per cent of the weight of the inert gas.
2. The process of carbiding a thoriated tungsten element comprising heating the thoriated tungsten element to a temperature between about 2350° K. and about 2550° K. in a carbiding gas maintained at substantially atmospheric pressure and consisting of inert gas and mixed therewith paraffinic hydrocarbon vapor in which the paraffinic hydrocarbon is chosen from the group consisting of n-hexane, n-heptane and n-octane which vapor constitutes from about 1 to about 5 per cent of the weight of the inert gas.
3. The process of carbiding of claim 1 in which said hydrocarbon is n-hexane.
4. The process of carbiding of claim 1 in which said hydrocarbon is n-heptane.
5. The process of carbiding of claim 1 in which said hydrocarbon is n-octane.
6. The process of carbiding of claim 1 in which said inert gas is nitrogen and said hydrocarbon is n-hexane.
7. The process of carbiding a thoriated tungsten element comprising glowing the thoriated tungsten element to a temperature between about

2350° K. and about 2550° K. continuously for a short period in a carbiding gas maintained at substantially atmospheric pressure and consisting of inert gas and mixed therewith paraffinic hydrocarbon vapor in which the paraffinic hydrocarbon has from five to ten carbon atoms which vapor constitutes from about 1 to about 5 per cent of the weight of the inert gas, substantially all of the carbiding of the thoriated tungsten element being accomplished while it is thus continuously glowed.

8. The process of carbiding of claim 7 in which said inert gas is nitrogen and said hydrocarbon is n-hexane.

9. The process of carbiding a thoriated tungsten element comprising non-continuously glowing the thoriated tungsten element to a maximum temperature between about 2350° K. and about 2550° K. in a carbiding gas maintained at substantially atmospheric pressure and consisting of inert gas and mixed therewith paraffinic hydrocarbon vapor in which the paraffinic hydrocarbon has from five to ten carbon atoms which vapor constitutes from about 1 to about 5 per cent of the weight of the inert gas.

10. The process of carbiding of claim 9 in which said inert gas is nitrogen and said hydrocarbon gas is n-hexane.

11. The process of carbiding a thoriated tungsten element comprising heating the thoriated tungsten element to a temperature between about 2400° K. and about 2500° K. while it is in an enclosure filled with a carbiding gas at substantially atmospheric pressure and consisting of inert gas and mixed therewith paraffinic hydrocarbon vapor in which the paraffinic hydrocarbon has from five to ten carbon atoms which vapor constitutes from about 1 to about 5 per cent of the weight of the inert gas.

12. The process of simultaneously carbiding a plurality of thoriated tungsten cathodes comprising placing in an enclosure a plurality of mounts comprising thoriated tungsten cathodes, filling said enclosure with a carbiding gas at substantially atmospheric pressure and consisting of inert gas and mixed therewith paraffinic hydrocarbon vapor in which the paraffinic hydrocarbon has from five to ten carbon atoms which vapor constitutes from about 1 to about 5 per cent of the weight of the inert gas, and heating each of said cathodes to a temperature between about 2350° K. and about 2550° K. in the presence of said carbiding gas until a layer of carbide is formed on the surface of said cathode.

13. The process of carbiding a thoriated tungsten cathode built into an electron discharge device, comprising inserting a tube into the envelope of said electron discharge device, filling the envelope of said electron discharge device from said tube with a carbiding gas at substantially atmospheric pressure and consisting of inert gas and mixed therewith paraffinic hydrocarbon vapor in which the paraffinic hydrocarbon has from five to ten carbon atoms which vapor constitutes from about 1 to about 5 per cent of the weight of the inert gas, and heating said cathode to a temperature between about 2350° K. and about 2550° K. in the presence of said carbiding gas until a layer of carbide is formed on the surface of said cathode.

14. The process of carbiding a thoriated tungsten element comprising heating the thoriated tungsten element to a substantially constant temperature between about 2350° K. and about

2550° K. in a carbiding gas maintained at substantially atmospheric pressure and consisting of inert gas and mixed therewith paraffinic hydrocarbon vapor in which the paraffinic hydrocarbon has from five to ten carbon atoms which vapor constitutes from about 1 to about 5 per cent of the weight of the inert gas, substantially all of the carbiding of the thoriated tungsten element being accomplished while it is thus heated at a substantially constant temperature. 10

15. The process of carbiding of claim 14, in which said inert gas is nitrogen and said hydrocarbon is n-hexane.

16. The process of carbiding a thoriated tungsten element comprising non-continuously heat- 15

ing the thoriated tungsten element to a temperature between about 2350° K. and about 2550° K. in a carbiding gas maintained at substantially atmospheric pressure and consisting of inert gas and mixed therewith paraffinic hydrocarbon vapor in which the paraffinic hydrocarbon has from five to ten carbon atoms which vapor constitutes from about 1 to about 5 per cent of the weight of the inert gas.

17. The process of carbiding of claim 16, in which said inert gas is nitrogen, and said hydrocarbon is n-hexane.

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