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CLEAN-UP AND ACTIVATION BY MISCH METAL AND THE RARE EARTH METALS

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FIG. 1.

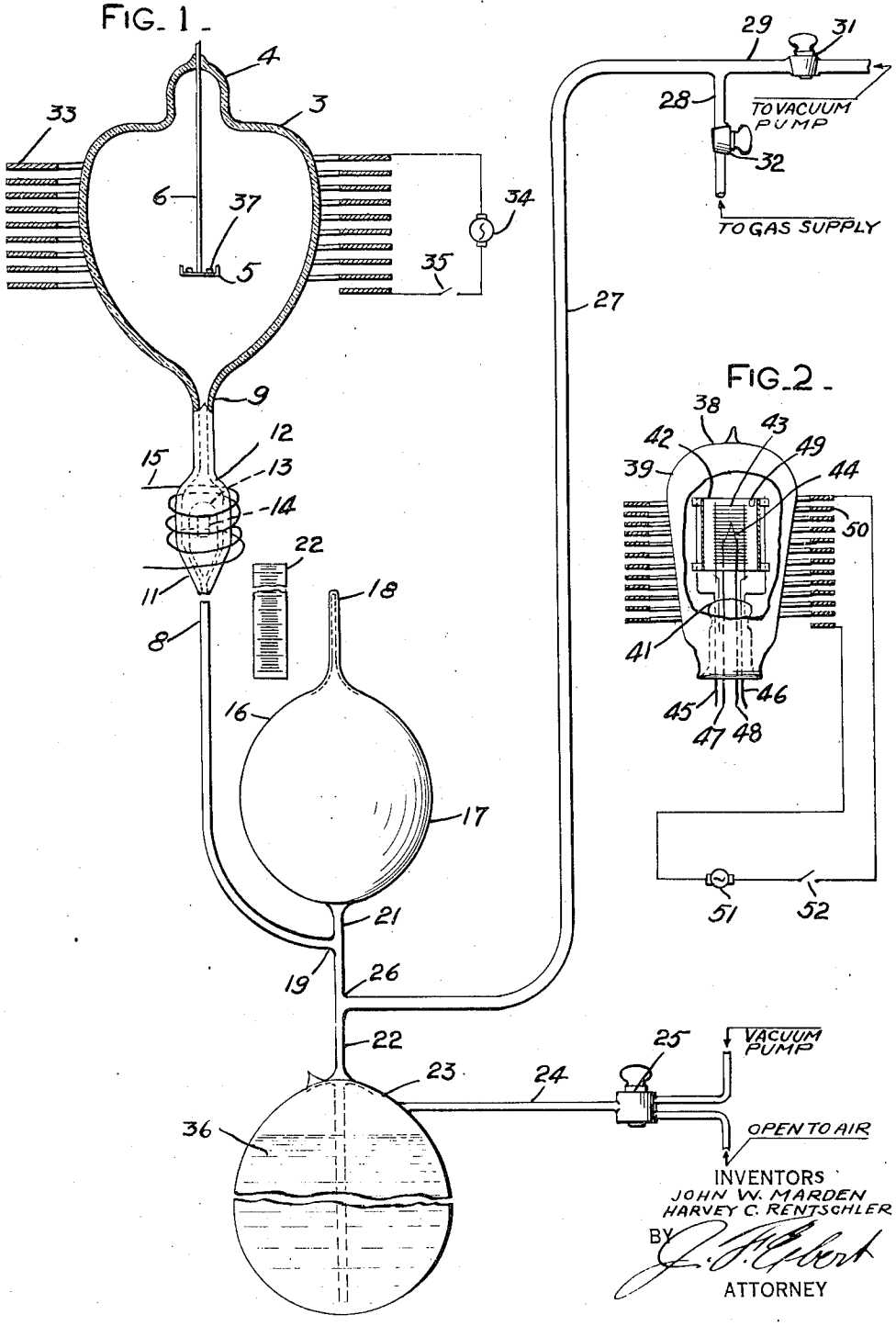


FIG. 2.

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UNITED STATES PATENT OFFICE.

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CLEAN-UP AND ACTIVATION BY MISCH METAL AND THE RARE-EARTH METALS.

Application filed December 8, 1923. Serial No. 679,489.

This invention relates to vacuum devices and more particularly to the clean-up of residual gases and the activation of incandescible filaments therein.

An object of our invention is the provision of a clean-up agent for residual gases and vapors within vacuum devices capable of materially shortening the period normally required for exhausting said devices.

Another object of our invention is the provision of a substance capable of functioning not only as a clean-up agent for residual gases and vapors within vacuum devices, but also adapted for the purpose of activating incandescible elements of such devices.

Another object of our invention is the utilization of one or more of the metals of the cerium group of rare earths, or a mixture or alloy thereof, which we have discovered may be employed for reducing the normal period required in exhausting vacuum devices and for improving the vacuum of such devices.

A further object of our invention is the activation of filamentary material in an electron device by means of misch metal, or a metal of the cerium group of rare earth metals therein, whereby an immediate increase in electron-emissivity is effected without the necessity of the usual seasoning.

A still further object of our invention is the utilization of misch metal or a metal, mixture, or alloy of metals of the cerium group of rare earth metals, for the purification of argon or other rare gas, by combining with and removing deleterious impurities when heated or vaporized therein.

A more specific object of our invention is the use of misch metal as a clean-up agent of residual gases and for the activation of incandescible filaments in vacuum devices for purification purposes.

Other objects and advantages of the invention will become apparent upon reading the following description.

Various materials have been employed in evacuated devices for removing the last appreciable traces of certain gases and vapors for improving the vacuum therein. Materials which have been previously used comprise metals such as magnesium, aluminum, zinc, etc., and combinations thereof.

In the copending application of H. C. Rentschler, Serial No. 582,261, filed August 16, 1922, vacuum devices and method of exhausting the same and assigned to the Westinghouse Lamp Company, is described and claimed a method of cleaning up residual gases in electron tubes by vaporizing aluminum or aluminum and magnesium or the like therein. The said application sets forth how the use of such clean-up agents obviates the necessity of producing a very high vacuum in the device by mechanical means, such as a vacuum pump, and therefore makes it possible to merely exhaust the device to a moderate degree and then produce the required high vacuum by vaporizing or activating the particular clean-up agent used.

Clean-up agents, such as heretofore mentioned, have been used with varying degrees of success, but are merely suitable for effective clean-up purposes of certain gases or vapors, which have a deleterious effect on the active material of the filament, and have no beneficial effect as regards the activation of a filament or the like in an electron device, for the purpose of increasing its electron-emissivity. When thoriated filamentary material, for example, is used as the electron-emitting element in an electron device, it is usually heat treated in the presence of carbon or carbon-yielding material, for the purpose of rendering it susceptible of being activated by a further heat treatment, when in place in the electron device, with which it is to be used. That is, after the carbonized filament has been placed in the device, for example, a radio tube, it is necessary to heat it for a considerable length of time to cause a development of free thorium therein. Such a procedure is designated as the seasoning of the filament. The seasoning schedule is an additional operation and necessarily complicates the manufacture and increases the cost of such devices.

According to our invention, the necessity of the seasoning schedule is obviated, residual gases are efficiently cleaned up and activation of thoriated filamentary tungsten and the like effected by the use of a material such as cerium or one of the metals of the cerium group of rare earth metals, a mixture or alloy thereof. A relatively cheap, commercial alloy suitable for the purpose is misch metal, which is a mixture of the cerium group of rare earth metals comprising mainly cerium and secondly, lantha-

num. The effect obtained when using misch metal, compared with other materials such as magnesium, aluminum, potassium, sodium and calcium, has been demonstrated by experiment and it is found that misch metal gives a quicker and very much better clean-up in a vessel or evacuated device than any of the aforementioned materials.

It has also been found that when misch metal is vaporized in an electron device, for example, for accomplishing the clean-up of residual gases and vapors, a portion thereof is deposited on the electron-emitting filament and serves to increase its electron-emissivity. Such a filament, activated by misch metal, or cerium, which is the principal constituent thereof, may then be employed for the desired purpose.

Our invention will be better understood by referring to the accompanying drawing, in which,

Fig. 1 shows, in side elevation, partly diagrammatically, an apparatus first experimentally used for testing the effect of misch metal or similar material, as compared with other materials previously used for clean-up purposes; and,

Fig. 2 is a side elevation, shown partly in section and partly diagrammatically, of a radio tube in which misch metal is used according to our invention, together with apparatus for vaporizing the same to accomplish the desired clean-up action therein.

Referring to Fig. 1, a vessel 3 is illustrated provided with a seal 4, from which is supported a disc or pan 5, preferably formed of molybdenum or the like. The means for supporting the pan or disc 5 from the seal 4 is immaterial, but it is shown in the drawing as being connected to the lower end of a rod of tungsten or the like 6, extending through said seal.

The vessel 3 is connected to the tube 8. A valve 11 is also provided, as shown, in said tube so as to shut off the test bulb 3 while a compression chamber is being exhausted. Said valve 11 preferably comprises an enlarged portion 12 in the tube 8, a closure member 13 inside of the enlarged portion 12 and adapted to allow mercury to flow past in an upward direction, but to normally prevent its passage in a downward direction. The closure member 13 may be provided with an iron core 14, whereby it may be governed by a surrounding solenoid 15 energized from any suitable source of electricity (not shown).

Connected to the lower portion of the tube 8 is a modified MacLeod gauge 16 comprising a compression chamber 17, with a capillary extension 18 therefrom as shown. The compression chamber 17 is connected to the tube 8 at juncture 19 by means of tube 21. The sizes of the various parts are preferably formed, so that the volume of vessel 3 and its connecting tube to the juncture 19, is about equal to that of the volume of the pressure chamber 17, capillary tube 18 and the connecting tube 21, whereby ease in calibration of the device is obtained. That part of the tube 8 adjacent the capillary tube 18 is preferably formed as a capillary tube of the same bore and a scale 22 is preferably provided between and adjacent them both, for the purpose of conveniently reading the difference between the columns of mercury therein, in roder to measure the pressure in the vessel 3.

From the junction 19, a tube 22 extends to a mercury reservoir 23, as shown, connected by a tube 24 and a two-way valve 25, either to a vacuum pump (not shown) or the like or open to the atmosphere. The tube 22 is connected from junction 26, by means of tube 27, to branches 28 and 29, whereby the gauge and the associated apparatus may be either connected to a vacuum pump or the like (not shown) through valve 31, or to a gas supply (not shown) through valve 32.

A coil 33 may be provided of such a construction, that it is adapted to be placed around the vessel 3, as shown, and energized from any suitable source of high frequency current 34, for the purpose of heating the plate 5 in the vessel 3, by means of electromagnetic induction. A switch 35 is provided for connecting and disconnecting the coil 33 with respect to the source of high frequency current 34.

The operation of the apparatus before described for testing the properties of misch metal or other material, as compared with magnesium, aluminum or the like for clean-up purposes, is preferably as follows. The receptacle 23 is partially filled with mercury 36 as shown. A desired amount of metal or other material 37, which is to be tested for clean-up action, is placed on the plate or disc 5, inserted in the vessel 3 and sealed in thoroughly as shown.

The valve 31 to vacuum pump, is opened to evacuate the vessel 3, while the walls thereof are heated in any desired manner to remove moisture therefrom, the valve 13 at the same time being raised by means of solenoid 11, to open the passage in the tube 8 to the vessel 3. While the vessel 3 is being exhausted by having the valve 31 open, the two-way valve 25 may also be turned to connect the vessel 23 to a vacuum pump, to keep the mercury 36 from flowing up into the tube 22 and blocking the connection between the tube 8 and the tube 27.

After the vessel 3 has been exhausted to the highest possible degree obtainable from the vacuum pump used, the two-way valve 25 is turned to close the tube 24. The valve 31 is closed and the valve 32 is opened to admit a small amount of the desired gas to be tried in connection with the clean-up mate-

rial 37. The pressure of the gas admitted is then measured by means of the MacLeod gauge 16. It should be understood that in manipulating this MacLeod gauge to read pressures in the vessel 3, the mercury is caused to rise to the desired level by adjusting the degree of pressure in the vessel 23 by means of the two-way valve 25. The scale 22 is calibrated so that the pressure may be determined by the reading thereon, the calibration of the instrument being facilitated by the fact that the vessel 17 and tubes 18 and 21 to the junction 19 are of about the same volume as that of the vessel 3 and its connecting tube to the junction 19.

After the pressure has been measured, the valve 25 is manipulated until the mercury rises to lift the closure member 13, open the valve 12 and flow on to the position 9, thereby forcing all the gas in the tube 8 into the vessel 3. The plate 5 is then heated by electromagnetic induction by energization of the coil 33 from the high-frequency source 34. This results in the vaporization of the material 37. The vessel 3 is then allowed to cool the valve 11 opened by energizing or moving the solenoid and the pressure therein measured in a similar manner to that in which the pressure previously present was measured.

The comparative results obtained by using the aforegoing apparatus under a given set of conditions for testing out magnesium, aluminum, potassium, sodium, calcium and misch metal with the gases hydrogen, nitrogen and carbon dioxide and also with no gas introduced into the vessel and also no clean-up agent, the disc 5 being merely heated to show the gas evolved therefrom, are indicated in the following table:—

Metal used	Pressure of gas started with				Pressure resulting in microns
	Air	H_2	N_2	CO_2	
None [1]					250.
Mg					200.
Mg		170			400–500.
Mg			160		110.
Mg				115	Too high to measure with the gauge.
Al					100.
Al		140			142.
K					15.
Na					15.
Ca					25.
Misch metal					Less than 2.
Misch metal		125			Less than 1.
Misch metal			145		Less than 1.
Misch metal				155	Less than 2.

[1] Gas from molybdenum disk and glass (no clean up agent).

It will be appreciated from an inspection of the table that misch metal is vastly superior to the other metals tried as clean-up materials. It must be remembered that the data given holds only for the exact conditions of the experiment, but these are comparative and show the relative merits of each metal tried. In view of these experiments, it is our belief that misch metal or the constituents thereof, are probably superior to practically any other clean-up agent to be used in this way. Misch metal is comparatively cheap, as it is a by-product of the thorium industry. It is now on the market for the use in pyrotechnics, gas lighters, etc.

At the present time, we believe that the principal gases to be cleaned up are hydrogen, resulting from water vapor from the glass, carbon dioxide, carbon monoxide and nitrogen from the metal plates. These gases are easily cleaned up by misch metal, while magnesium and aluminum fail to clean up the hydrogen under similar conditions. An additional advantage of misch metal is that when it is volatilized, it condenses on the walls of the bulb with a clean metal surface, which may combine with the hydrogen, dissolve it or in some other manner, remove this gas. Misch metal may not only be used free, but is also suitable in the form of a compound, for example, as a carbide or other compound yielding the metal upon the dissociation thereof.

The life of a radio tube is considered to be dependent on the gas clean-up. The misch metal gives a better clean-up and therefore a longer life of activation. Misch metal is especially suitable to use in connection with the present activated filaments.

Fig. 2 illustrates one embodiment of our invention using misch metal, cerium or other cerium group rare earth metal or alloy thereof as clean-up material and for the purpose of giving immediate activation of an electron-emitting filament in a radio tube or for only one of such purposes, as desired. The radio tube or electron device 38 shown in Fig. 2, preferably comprises a bulb 39 with a stem 41 sealed therein. Supported on the stem 41 is an electrode or plate 42, another electrode or grid 43 and a cathode, in the form of an electron-emitting filament 44. The stem, together with the aforementioned suitably-supported electrodes form the mount of the electron device 38.

Lead-in wire 45 extends from the plate 42 and lead-in wire 46 connects with the grid 43. The filament 44 is provided with leading-in wires 47 and 48 for the purpose of connecting the same to a suitable source of electricity, for maintaining it at an electron-emitting temperature.

Misch metal or cerium, which is the principal ingredient thereof, or other cerium group rare earth metal, is preferably applied by being welded, pasted or otherwise suitably fastened to the interior surface of the plate 42, as shown at 49. After sealing such a mount, as heretofore described into the bulb, evacuating to the desired degree and tipping off in the usual manner, a coil 50, suitably connected to a high frequency generator 51

or other suitable source of high frequency current, through a switch 52, may be applied therearound as shown in the drawing.

Upon closing the switch 52, high frequency current in the coil 49 will induce corresponding current in the plate. These induced currents heat the plate and other conducting parts of the device, until the plate becomes sufficiently heated to cause vaporization of the misch metal 49 applied thereon. It is obvious that other means for vaporizing the misch metal may be used, if desired. When the misch metal is vaporized, not only is the clean-up action quickly affected on the residual gases in the bulb, by chemical action thereon, but a certain proportion of the metal is deposited on the filament 44, resulting in an immediate activation or increase in the electron-emissivity thereof. If said filament is of the usual type of thoriated filament adapted to be activated by the usual seasoning process, said seasoning process may be omitted in the present instance if the experiment is properly done, as sufficient electron-emissivity will be immediately obtained.

Radio tubes as before described and illustrated in Fig. 2, have been made having misch metal welded onto a molybdenum plate. These tubes all showed excellent clean-up without any large amount of blackening of the glass bulb with the misch metal and thus not only had a good clean-up, but a better appearance. The misch metal may be sawed up and welded to plate, but it might be preferable to pour it into thin sheets, when it can then be broken up into small pieces of the desired sizes. Such pieces are then suitable for welding to the plate.

It is possible to prepare cerium and lanthanum separately in metallic condition, and very good results can be secured by such metals, as well as by misch metal which contains such materials alloyed together. If pure cerium and lanthanum are used, these metals may be rolled into sheets, as the pure metals are more malleable than misch metal, which sheets may then be cut up and used as aluminum and magnesium are now used.

Incandescent electric lamps may be made having discs or cylinders of molybdenum, tungsten or other high melting metal, with misch metal or the like welded thereto in the base or neck or some other part of the lamp. It is then not necessary to evacuate such lamps to a high degree as is now done, thereby saving on the use of very expensive pumps. X-ray tubes, power radio tubes, high voltage rectifiers of the Kenetron type, for example, may also be quickly evacuated and have their incandescible filaments activated, according to our invention as well as other similar devices.

It has been found by trial, that the exhaust period for a high voltage Kenetron, for example, may be reduced, by using misch metal according to our invention, to less than one quarter the time, formerly required under normal conditions. From this it is apparent, that the time required for exhausting evacuated devices of all types, including those above mentioned, may be materially reduced by employing rare earth metal of the cerium group or a commercial allow thereof, such as misch metal, for example, to clean-up residual gases therein upon vaporization thereof, according to our invention.

As misch metal and the like, quickly cleans up residual gases in evacuated devices to such a high degree, a relatively large margin of safety is provided, so that relatively inexpensive vacuum pumps may be utilized for the evacuation of such devices. If during the evacuation of incandescent electric lamps, for example, mechanical or other difficulties are experienced resulting in "gassy" lamps, and misch metal or the like is used for clean-up purposes therein, a satisfactory vacuum may be secured, which would not be possible with the use of other clean-up agents under like circumstances.

Misch metal or constituents thereof, may be prepared in the lamp by the salt reactions, such as $NaLaF_4$ or $2LaF_3.3NaF$ plus magnesium and aluminum, thereby obtaining a similar effect, as magnesium and aluminum will displace such metals from such compounds. Such a method is described in Patent #1,437,984 to John W. Marden, granted December 5, 1922, preparation of rare metals and assigned to the Westinghouse Lamp Company.

According to Schiotz Zeit fur Elecktro Chem. 27, 521, (1921), cerium and lanthanum can be electrolytically deposited as an alloy with iron. The method is similar to that for depositing thorium-iron alloys, described and claimed in the copending application of Marden, Conley and Thomas, Serial No. 578,813, filed July 31, 1922, electrolytic deposition of thorium and assigned to the Westinghouse Lamp Company. In this way these metals can be introduced for the desired purposes as electroplating on the filament or plate.

Instead of applying rare earth or misch metal to the plate in an electron device or lamp, an auxiliary filament may be introduced containing the material or the metal may be applied to the incandescible filament therein in any desired manner. A binder solution, for example, may be used to apply the metal in powdered form to the filament. If an auxiliary filament is used, it should be of such size as to burn out after the gas clean up. Molybdenum or tungsten wire may be dipped in the melted metal which may be kept in such a condition under fused salt. This will result in the application of

such metal thereto in a manner similar to that in which iron is galvanized by zinc, thereby serving as an additional means for the introduction thereof. Rare earth metal may also be used in the form of an alloy, for example, with magnesium, aluminum and the like.

Argon and other inert rare gases may be purified by heating and vaporizing therein misch metal or one or a mixture or alloy of the cerium group of rare earth metals. By using such metal or metals instead of calcium, at present used for such purpose, the purification is obtainable quicker and more efficiently.

The term "rare earth metal" is used, for convenience, in this application, to mean one or a plurality of the rare earth metals of the cerium group, or a mixture or alloy thereof.

The rare earth metals of the cerium group include, according to the accepted classification, cerium, lanthanum, praseodymium, neodymium and samarium.

Although we have described what is now considered a preferred manner of utilizing our invention, it is to be understood that the same is merely illustrative, and that we are not limited to using rare earth or misch metal in radio tubes or even electron devices, as the same are suitable for general clean-up purposes. Other modifications may occur to those skilled in the art, within the spirit and scope of the appended claims.

What is claimed is:

1. The method of cleaning up residual gases and vapors in a gas tight enclosure, comprising heating misch metal therein to effect a reaction of the misch metal with said residual gases.

2. The method of cleaning up residual gases and vapors in a gas tight enclosure, comprising vaporizing a rare earth metal of the cerium group therein to effect a reaction of the rare earth metal with said residual gases.

3. The method of activating an electron-emitting element and creating a high vacuum in a gas tight enclosure which comprises vaporizing a rare earth metal of the cerium group therein.

4. The method of cleaning up residual gases in an evacuated gas tight enclosure, containing a metallic plate, comprising affixing a quantity of misch metal to said plate and heating the plate to vaporize the misch metal to effect a reaction thereof with the residual gases in said enclosure.

5. The method of removing common gases from a gas tight enclosure containing one or more electrodes, comprising applying to one of said electrodes a rare earth metal of the cerium group and heating said electrode electrically to vaporize the rare earth metal to effect a reaction thereof with said gases.

6. The method of removing common gases from a gas tight enclosure comprising vaporizing a metal of the cerium group of rare earth metals therein, to effect a reaction between said metal and said gases.

7. A clean-up material for common gases contained within a gas tight enclosure, consisting of misch metal.

8. A vacuum device comprising an exhausted gas tight enclosure containing an electrical conductive support having a quantity of rare earth metal of the cerium group attached thereto, said metal being adapted to be vaporized for reaction with residual gas within the enclosure.

9. A vacuum electric device comprising a sealed exhausted envelope having an electrode therein and a quantity of misch metal affixed to said electrode and adapted to be vaporized for the purpose of improving the vacuum within said envelope.

10. An electron discharge device comprising a sealed exhausted envelope containing an electron-emitting cathode, an anode and a quantity of misch metal attached to said anode adapted to be vaporized to improve the emission of said cathode and clean-up residual gas in the envelope.

11. The combination of a gas tight enclosure, cooperating electrodes therein, one of which is adapted to be heated to an electron emission temperature and a quantity of misch metal in said enclosure in a state whereby it is rendered capable of combining with the common gases in said enclosure.

12. An evacuated container having therein a rare earth metal of the cerium group and a metallic member to which said rare earth metal is attached, said metallic member being adapted to be heated to a sufficiently high temperature to vaporize said rare earth metal and being composed of a metal resistant to attack by said rare earth metal during such vaporization.

13. An evacuated container having therein a quantity of misch metal and a metallic member to which said misch metal is attached, said metallic member being adapted to be heated to a sufficiently high temperature to vaporize said misch metal and being composed of a metal with which said misch metal does not deleteriously react during such vaporization.

14. An electrode for an evacuated electric discharge device having a quantity of rare earth metal of the cerium group attached thereto, said electrode being composed of a material which is resistant to attack by said rare earth metal when the electrode is heated to vaporize such metal.

In testimony whereof, we have hereunto subscribed our names this 6th day of December, 1923.

JOHN WESLEY MARDEN.
HARVEY CLAYTON RENTSCHLER.