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PURIFICATION OF GASES
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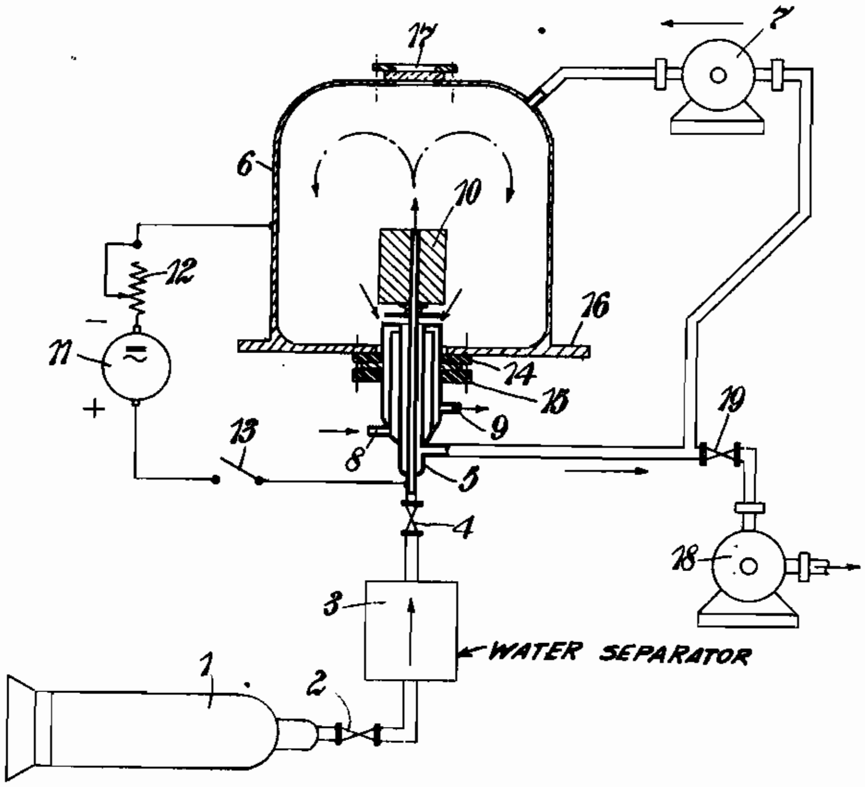

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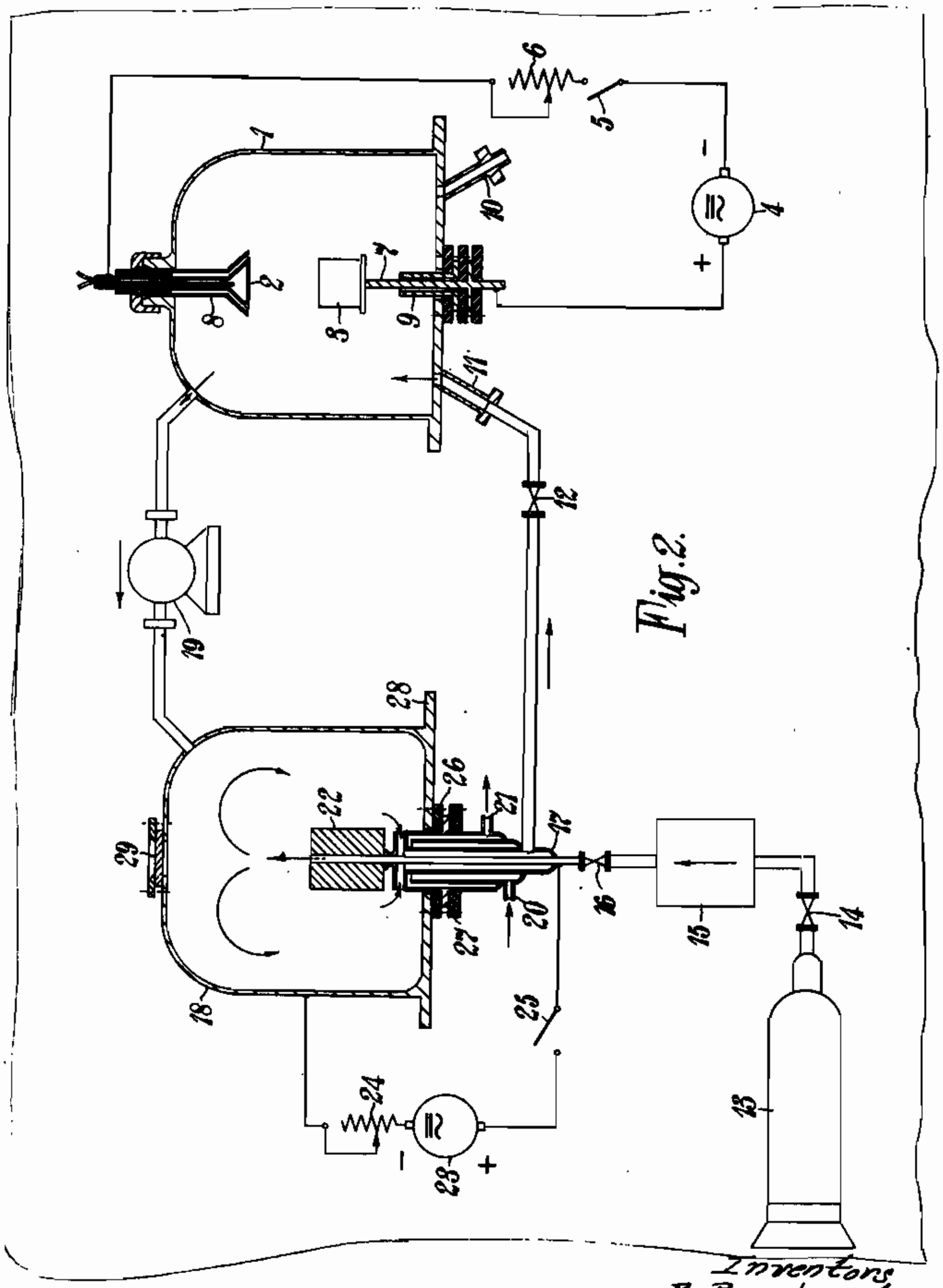

Fig. 2.

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Fig. 3

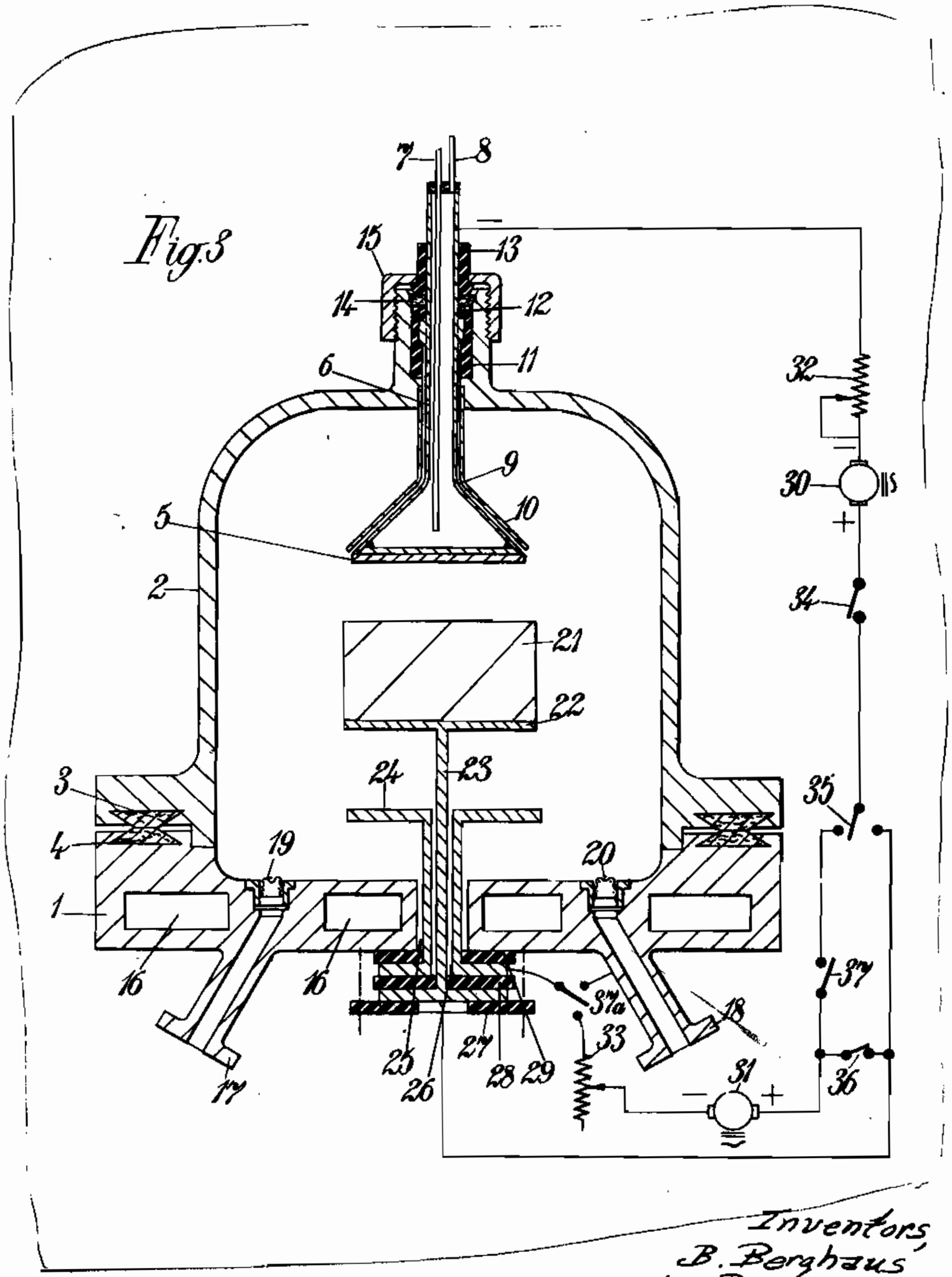

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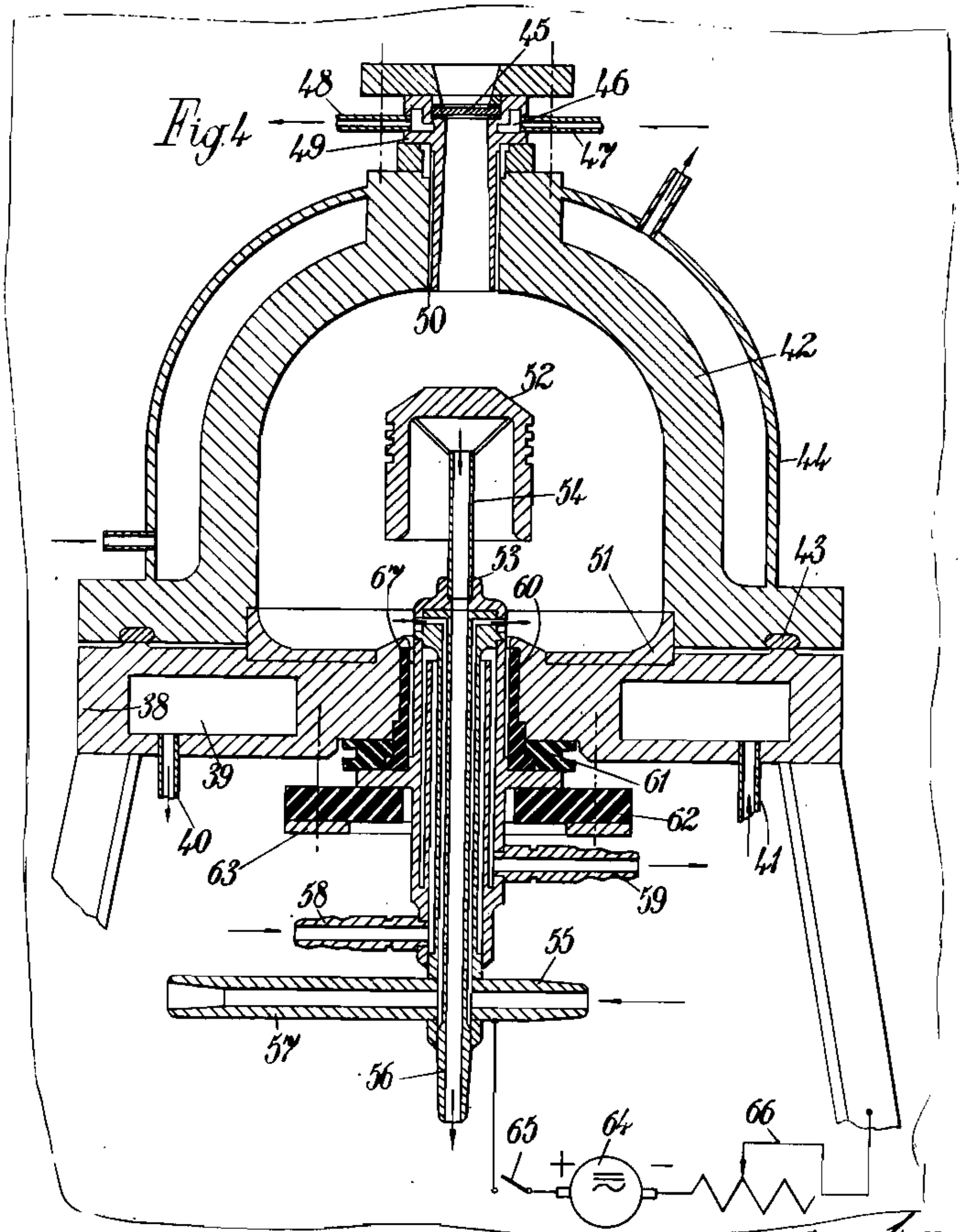
Fig. 4



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ALIEN PROPERTY CUSTODIAN

PURIFICATION OF GASES

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The invention relates to an apparatus for the purification of gases, more particularly noble gases, by the removal of undesirable admixtures, such as for instance oxygen, nitrogen, hydrogen or hydrocarbons. The invention consists in this that an easily vaporisable metal, such as zinc, magnesium, lithium, calcium, beryllium, lead etc., in the form of a solid body mounted in an electrically insulated manner, connected up as an anode, or permanently or temporarily as a cathode, is heated up by the heating action of the gas discharge in a gas discharge chamber, the wall of which may permanently or temporarily constitute the cathode to such a temperature that a metal vapour partial pressure of at least 10^{-4} mm Hg, preferably 10^{-2} to 1 mm Hg is produced. The metal body to be vaporised is preferably mounted in the middle of the gas discharge chamber.

The speed of vaporisation of the metal may be regulated by the vacuum which is produced, or by the electric power which is applied.

The metal to be vaporised preferably consists of magnesium or a magnesium alloy, such as elektron. The gas purification may be carried out at a vacuum of 30 to 0.001 mm, preferably 3 to 0.1 mm Hg. The gas discharge chamber may also be made of magnesium or a magnesium alloy and is preferably cooled. The gas supply and discharge is preferably effected by the insulated, screened and cooled current lead-in. The purification of the gas by the vaporised metal is effected at voltages between 150 and 5,000 volts. The discharge current or the discharge power is dependent upon the dimensions of the apparatus to be operated and the amount of gas passing through.

Experiments have shown that a purification of noble gases may be quickly effected, if, for instance, magnesium is vaporised in the purification chamber. The impurities which easily react chemically with the magnesium which is present in its vapour form are deposited on the cooled wall of the discharge chamber. Even at a temperature of 340° C and a pressure of 0.1 mm Hg of the filling gas the magnesium develops an amount of vapour of 1 milligram per cm^2 surface and hour of the body to be vaporised. With the amount of specified vaporisation one can combine an amount of oxygen of 0.36 cm^3 at 760 mm Hg. The amount of gas to be passed through the apparatus depends on the amount of the magnesium vapour which is developed. For instance, at a temperature of 500° C, 4 gramms of magnesium would be converted into vapour per cm^2 of surface of the magnesium body and hour. With this amount one can combine an amount of oxygen of 1.5 litres at 760 mm Hg or the corresponding equivalent of nitrogen. It will be seen that with a magnesium body having a suitably large surface one can obtain economical purification of noble gases. The extremely quick purification action by the metal vapour is apparently due to the ionisation of the metal vapour in the gas discharge chamber. The purification, which could be ascertained by the reduction in pressure, took place almost instantaneously, always when the spectrum of the metal vapour became visible.

The installation is suitable for the obtention of spectrum pure argon from technical argon and as accessory apparatus for the purification of noble gases for cathode disintegration purposes in a flow or circulating installation.

In the metallisation of articles by cathode disintegration the impurities in the filling gas, such as oxygen, nitrogen and the like, as well as the air flowing through owing to the apparatus not being gastight, have a disturbing effect, causing the articles to be metallised to be oxidised, for instance on the surface, which, in addition to causing very bad adhesion of the coated layer, may even render the latter questionable in the case of coating by means of base metals.

This applies also as regards the gases released by the body to be coated at the high temperature.

The invention also relates to a method of metallisation by cathode disintegration the characteristic feature of which is, that the filling gas of the cathode disintegration chamber is supplied through a gas discharge purification apparatus, in which solid metals, such as for instance magnesium or magnesium alloys which are capable of combining oxygen or other undesirable constituents, such as nitrogen and the like, are vaporised by a gas discharge. Further, the filling gas may be circulated in the cathode disintegration and gas discharge purification apparatus.

The metal to be vaporised may be subjected to the gas discharge, preferably glow discharge, in an electrically insulated manner, as anode, or permanently or temporarily connected up as cathode. The pressure of the filling gas at which the gas discharge takes place may be between 30 and 0.001 mm Hg, preferably 3 to 0.1 mm Hg. The voltage applied to the path of discharge may be 150 to 5,000 volts, preferably 200 to 1,000 volts. The gas supply and discharge is preferably effected through the insulated, screened and cooled current lead-in.

The purification of technical noble gases in a circulating system is already known, but it requires a long time before the noble gas is obtained spectrum pure. In the case of vacuum installations which have to be extremely airtight as, for instance, for physical purposes, such a purification by means of a Gehlhoff cell is quite sufficient.

Experiments have shown that, in the case of purification of technical noble gases for disintegration purposes, not only the binding of the existing impurities in the filling gas is important but also the binding of the gases which flow continually owing to the practical apparatus, for instance of metal, not being airtight, as well as of the gases which are freed when the articles to be coated are heated up. The release of gases by metallic articles is especially considerable at 300 to 500° C. In the case of the known purification process these gases are removed far too slowly during the disintegration, so that the disadvantages above referred to are not avoided. According to the invention, owing to any temperature being imparted to the metal to be vaporised it is possible to convert such an amount of metal vapour that the impurities are bound immediately.

For instance, magnesium was vaporised in a purification chamber in order to obtain spectrum pure argon during the coating of iron with aluminium. It was possible in that case, according to the temperature at which the magnesium was desired to be vaporised, to maintain the pressure of the filling gas which was circulated constant, while, when the voltage was removed from the purification plant, there followed immediately a reduction in pressure. In this way the gases which were freed from the iron body to be coated between 300 and 400° C., as well as the air let in owing to the apparatus not being airtight, could be continually removed without the requirements stipulated with respect to the vacuum-tight joint of the apparatus being too strict. By increasing the speed of vaporisation, that is to say, the temperature on the solid magnesium body, it was even possible to consume the noble gas and thus obtain a continuous reduction in pressure during the coating. The temperature of the magnesium body was between 300 and 500° C. The coatings, without a purification plant and when use was made of a gas filling of spectrum pure argon from ampullas of 1 litre capacity as obtainable in the trade, consisted of loose grey powder on the iron bodies. Moreover, the disintegration of the cathode material took place very slowly, the disintegration figure being only 20 mgr. per kilowatt hour. The coating could be easily removed by wiping it off. The chemical investigation showed a mixture of magnesium oxide and magnesium.

By using the purification plant according to the invention by means of magnesium vapour at a partial pressure of about 10^{-4} up to 1 mm. Hg., it was possible to provide reliable crystalline aluminium layers of great adhesion strength. The disintegration amounted to 500 mg. per kilowatt hour. Chemical analysis of the layer showed pure aluminium. The vaporisation of the magnesium body was effected whilst the same was mounted in an electrically insulated manner in the gas discharge chamber. The wall of the gas discharge chamber was connected up as a cathode and supplied the electronic emission required for the heating up of the magnesium body. The same effect could be obtained by connecting the magnesium body as the anode of the gas discharge. The purification could be effected also in a reliable manner by using an alternating current voltage between the wall of the gas discharge chamber connected up as one electrode and the magnesium body to be vaporised connected up as the other electrode. The heat conduction of the magnesium body to be vaporised was kept very low by a suitable support and the wall of the discharge chamber was cooled by means of water.

The invention also relates to an apparatus for carrying out the method hereinbefore described, its characteristic feature being that a gas discharge purification apparatus is used, which consists of a gas discharge chamber with the metal to be vaporised mounted in the center in one circuit with the cathode disintegration chamber.

The invention also relates to a method for the metallisation of articles by cathode disintegration the characteristic feature of which is, that, in order to remove the impurities of the filling gas in addition to the cathode used for the metallisation, there is connected up a second cathode of a material which will bind the impurities of the filling gas, such as oxygen, nitrogen etc. In order to remove the impurities of the filling gas a cathode of magnesium or magnesium alloy is also connected up in the path of the discharge. The purifying cathode may be operated by its own circuit the intensity of the discharge of which can be varied. The purifying cathode may, however, also be constituted by parts of the wall of the cathode disintegration chamber. A very efficient arrangement is to use very large surfaces as purifying cathode, such as, for instance, the whole of the inner surface of the cathode disintegration chamber. The latter may, in this case, be made of magnesium or its alloys and be subjected as a purifying cathode to a discharge by means of its own electric circuit. Magnesium and its alloys bind oxygen, nitrogen, as well as hydrocarbon and other impurities, which flow through the apparatus owing to its joints not being airtight, or are at present in the filling gas which is used or are liberated by the bodies to be coated while they are being heated. Owing to the impurities being bound by the purifying cathode the latter is hindered in its disintegration and, therefore, does not contribute to the coating of the article to be coated. When using a single cathode it is an advantage to place the same direct in the proximity of the gas inlet or at the sealing points of the apparatus. It has been found especially effective to connect the purifying cathode with the gas inlet. The inlet of the gas through the purifying cathode had to be covered with a grid or filter of very fine mesh, in order to prevent discharges in the supply pipe. The gas enters direct into the discharge, whereby the impurities are held on to the magnesium cathode. By using these arrangements for the continuous removal of the impurities during disintegration while using, for instance, noble gases, it is possible to obtain pure firmly adhering coatings of close texture by disintegration. It has been found especially advantageous to effect a purification while coating metal articles which have been heated by the discharge, for instance to 200 to 1,000° C and which, therefore, more especially in the case of light metals, form chemical compounds with the impurities of the filling gas on their outer zone, which chemical compounds ensure the adhesion of the disintegrated metal which is coated on at the same time. The introduction of the purifying electrode has, moreover, the advantage that, owing to the unavoidable leakages of an apparatus as used in practice, the incoming undesirable gases, such as oxygen and nitrogen, are continually bound, so that it was possible with one single gas filling to effect a coating, even over long periods of time, without any change in pressure, that is to say, while the gas was in a stationary state. With a purifying electrode having its own circuit the speed of consumption can be so regulated that the air which leaks in is continually bound. Also when the articles are heated by the gas discharge the gas liberated can be removed from the filling gas continually by the regulation of the power applied to the purifying electrode. If the purifying electrode is operated together with the disintegration electrode, its surface is made so large that, with the disintegration power required on the discharge path, in addition to the impurities being continually bound, also noble gas is bound. In the case of a cathode disintegration apparatus, as used in practice for engine pistons, it was, for instance, easily possible to bind continually in addition to the impurities also small amounts of noble gas. The capacity of the apparatus was about 6 litres at atmospheric pressure; during a period of operation of 4 hours and with a vacuum of 0.1 mm Hg 1 cm^3 of argon at 760 mm Hg was continually supplied through a diffusion valve. In addition to the energy for the operation of the pumps with forced passage or circulation through special purification plant one economises, in the case of this process, in the expensive noble gases, since one is able to carry out the operation at constant pressure with small amounts and for many hours.

The accompanying drawings illustrate diagrammatically and by way of example four different modes of carrying the invention into effect.

Figure 1 is a section through a gas discharge purifying plant;

Figure 2 is a section through a cathode disintegration plant with gas discharge purifying apparatus through which the filling gas circulates;

Figure 3 is a section through a chamber for the metallisation of articles by cathode disintegration which is provided with a separate purifying device for the filling gas or gas remainder present in the disintegration chamber; and

Figure 4 is a section through a cathode disintegration chamber in which the wall of the vessel constitutes the cathode and a portion of the wall of the vessel is constructed as a gas purifying electrode.

Referring to Figure 1, the gas which may for instance have to be freed of oxygen and nitrogen is contained in the bottle 1 and passes through a valve 2 into the water separator 3 from which it goes past the regulating valve 4 and the hollow and coolable lead-in conductor 5 into the gas discharge chamber 6, in which the gas is freed of oxygen, nitrogen or like undesirable constituents by vaporised magnesium or magnesium alloys, such as elektron. By means of a pump 7 the purified gas can be circulated through the purifying apparatus. The purified gas is supplied to the storage container or consuming apparatus through the valve 19 and the vacuum pump 18. The vacuum pump 18 enables a pressure of about 30 to 0.001 mm, preferably 3 to 0.1 mm Hg, to be obtained in the purifying chamber. A cooling medium may be supplied through the pipe connection 8 to the current lead-in 5 and be discharged through the pipe connection 9. The wall of the gas discharge chamber 6 and the electrode 16 consist of magnesium or magnesium alloys, such as elektron. The source of continuous or alternating current voltage 11 having preferably a voltage of 200 to 1,000 volts is connected, on the one hand, over an adjustable resistance 12 to the gas discharge chamber and, on the other hand, over a switch 13 to the current lead-in 5 and the metal 10 to be vaporized. 14 is an insulating ring and 15 an insulating and clamping ring which is clamped on by means of screws not shown. 16 is the bottom plate and 17 an inspection window. The operation of the purifying device is such that the magnesium, preferably vaporised at pressures of 3 to 0.1 mm Hg, binds the oxygen and similar impurities.

The wall of the purifying apparatus may be cooled. It is, however, an advantage to heat it by the gas discharge, to such a temperature that the magnesium which is vaporised thereon is vaporised again. At temperatures of over 300° C the time for the purification of, for instance argon, having the same admixtures, is substantially shorter as compared with the cooled electrodes. Over 400° C commences a very intensive vaporisation of the magnesium, so that not only are the impurities quickly removed but a spectrum pure argon is also bound by the magnesium vapour which is condensing.

Referring to the construction shown in Figure 2, 1 is the cathode disintegration chamber with the cathode 2 to be disintegrated and the article 3 to be metallised, 4 being the source of continuous or alternating current which is connected, on the one hand, through a switch 5 and an adjustable resistance 6 to the coolable screened and insulated cathode 2 and, on the other hand, with the screened and insulated anode 7. The screening of the cathode is effected by the metal screen 8 which is arranged at a short distance from the cathode. The screening of the anode is effected by the metal covering 9 which is arranged at a short distance from the anode. A vacuum pump is connected to the pipe connection 10, by means of which a vacuum of about 10 to 0.001 mm, preferably 5 to 0.1 mm Hg, is maintained in the cathode disintegration chamber. The purified filling gas, for instance argon or hydrogen, is introduced through the regulating valve 12 and pipe connection 11. The filling gas which is contained in the bottle 13 comes through a valve 14 into the water separator 15, from which it flows through the valve 16 and a hollow and coolable current lead-in 17 into the gas discharge purifier 18, in which it is liberated of oxygen, nitrogen and similar undesirable constituents by disintegrated and/or vaporised magnesium or magnesium alloys, such as elektron. By means of the pump 19 the purified gas can be circulated through the cathode disintegration apparatus 2 and the gas discharge purifier 19. A cooling medium may be supplied to the current lead-in through the pipe connection 20 and be discharged through the pipe connection 21. The wall of the gas discharge purifier 18 and the electrode 22 consist of magnesium or magnesium alloys, such as elektron. The source of continuous or alternating current voltage 23 having a voltage of preferably 200 to 1,000 volts is connected, on the one hand, through an adjustable resistance 24 to the wall of the purifier and, on the other hand, through the switch 25 to the current lead-in 17 and the counter-electrode 22. 26 is an insulating ring and 27 an insulating and clamping ring which is clamped on by means of screws, not shown. 28 is the bottom plate and 29 an inspection window. The operation of the purifying device is such that the magnesium disintegrated, preferably at pressures of 10 to 0.001 mm Hg, binds the oxygen and similar impurities. The electrode 22, as well as the wall of the purifying apparatus may be cooled. It is, however, an advantage to heat them by the gas discharge to such a temperature that magnesium is appreciably vaporised. At temperatures of over 300° C the purification of, for instance, argon having the same impurities can be effected during a much shorter period of time as compared with cooled electrodes. Beyond 400° C there begins a much more intensive vaporisation of the magnesium so that, not only are the impurities quickly removed but a spectrum pure argon is also bound by the condensing magnesium vapour.

The cathode disintegration chamber according to Figure 3 comprises a bottom part 1 and a removable upper part 2 which are connected together in an airtight manner by means of the packings 3 and 4. The cathode 5 to be disintegrated and which may consist of, for instance, copper or silver, is mounted in the upper part on a hollow coolable current lead-in 6. A cooling medium is supplied through the pipe 7 and discharged through the pipe 8. The coolable current lead-in is screened by means of a screen 10 through the interposition of a narrow screening gap 9. The screening gap is so narrow that no glow discharge can take place therein. 11, 12 and 13 are insulating bodies and 14 is a packing ring, whilst 15 is a screw ring for clamping purposes.

A cooling channel 16 is provided in the bottom plate and a pipe 17 is used for the purpose of supplying a filling gas in a regulated amount. A vacuum pump, which is not shown, is connected to the pipe connection 18, being used to produce a vacuum of, for instance, 30 to 0.001 mm, preferably 5 to 0.1 mm Hg. The pipe connections 17 and 18 are provided with protecting sieves 19 and 28 for the purpose of keeping back electrical discharges which may take place in the cathode disintegration chamber. The article 21 to be metallised rests on a metal plate 22 which is supported by the current lead-in 23. 24 is a purifying electrode connected up as a cathode according to the invention, and consists of, for instance, magnesium or magnesium alloy, being insulated by the narrow screening gaps 25 and 26. 27, 29 and 29 are insulating and packing rings, of which the outer ring 29 is clamped on by screws which are not shown. 30 and 31 are sources of continuous or alternating current voltage for the disintegration and purification, while 32 and 33 are regulating resistances and 34, 35, 36, 37 and 37a are switches which are connected up according to requirements. The article may be connected up in an electrically-insulated manner and the vessel as an anode. The article and the vessels may serve at the same time as anode. However, the wall of the vessel may be connected up as a purifying cathode. The operation of the apparatus is such that the purified cathode 24 removes, for instance, the impurities such as oxygen, from the filling gas which is present in the cathode disintegration chamber.

The cathode disintegration chamber with the purifier according to Figure 4 consists of a coolable bottom plate 38, which is provided with a cooling channel 39 to which a cooling medium is supplied through the pipe connection 40, being discharged through the pipe connection 41. On the bottom plate there is placed the upper part 42, which is connected up as the cathode to be disintegrated, consisting for instance of aluminium, the said upper part being mounted thereon through the intermediary of the seal 43 in a gastight manner and provided with a cooling jacekt 44. 45 is an inspection window, which may be eooled by the cooling channel 46 to which a cooling medium may be supplied through the pipe connection 47 being discharged by the pipe connection 48. The inspection window rests in an annular supporting metal member 49 which is screened and insulated by a narrow screening gap 50 with respect to the wall of the vessel connected up as a cathode. The purifying member 51 is mounted in the bottom plate 38, being connected up as a cathode and forming a part of the wall of the chamber; it preferably consists of magnesium or a magnesium alloy, such as elektron. The article to be metallised, for instance, a piston 52, which may be connected up as an anode or be electrically insulated, is supported on a hollow current lead-in 53 by means of a pipe connection 54, which current lead-in serves at the same time as a supply and discharge for the filling gas. The filling gas is supplied through the pipe connection 55, being discharged through the pipe connection 56 to which the vacuum pump (not shown) is connected.

A pressure gauge (not shown) is connected to the pipe connection 57. The current lead-in is made coolable, the cooling medium being supplied through the pipe connection 58 and discharged through the pipe connection 59. 60, 61, 62 are insulating and packing rings and 53 is a clamping ring which is clamped on by means of screws, not shown. 64 is a source of continuous or alternating current voltage and 85 is a switch and 66 an adjustable resistance.

A narrow screening gap 67 is provided between the insulating member 60 and the current lead-in.

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