

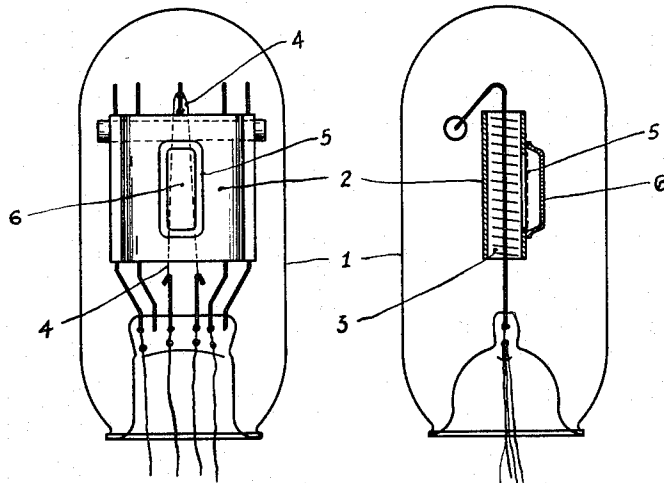
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METHOD OF INTRODUCING ACTIVE METAL INTO ELECTRIC DISCHARGE DEVICES

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METHOD OF INTRODUCING ACTIVE METAL
INTO ELECTRIC DISCHARGE DEVICES

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This invention relates to a process of introduc-
ing a chemically active metal into a vacuum tube.
Such chemically active metals among which the
alkaline earth and alkali metals play an im-
portant part are inserted into vacuum tubes for
different purposes, for example, for forming an
electron active coating on an incandescent cath-
ode or for taking up residual gases or gaseous
impurities.

On account of their other great affinity for
oxygen these metals cannot be exposed to open
air and for this reason various methods have
been adapted for introducing the metals into
a vacuum tube without running the risk of their
combining with oxygen from the air.

One method consists in introducing into the
tube a compound of the active metal which upon
heating will free the metal and which is not
itself subject to be attacked by oxygen. In this
method use is made essentially of active metal
azides which decompose upon heating and thus
set free the active metal with the development
of nitrogen. Very satisfactory results have been
obtained by this method.

In order to avoid the necessity of removing the
nitrogen developed it has been suggested that
an alkaline earth oxide, for example, barium
oxide, be admixed with aluminium and that this
mixture be so treated as by heating it outside
the discharge tube in which the barium is to be
inserted, that the barium oxide is reduced by
the aluminium. The mixture is heated to such
a temperature that the reduction ensues with the
formation of barium metal and aluminium oxide
but the barium formed does not volatilize or vol-
atilizes only partially. In this case the remain-
ing reaction-products are left in the form of a
mixture of aluminium oxide and barium. This
mixture is introduced into the discharge tube
and after the exhaustion of the tube the mixture
is heated to such a temperature that the barium
is expelled.

Since aluminum readily alloys with alkaline
earth metals a considerable part of the barium
developed during the treatment outside the dis-
charge tube will alloy with the aluminum. The
aluminum-barium alloy thus formed and then
introduced into the discharge tube is decomposed
only at a higher temperature than that at which
barium is liberated from a mixture of barium
oxide and aluminum oxide so that an important
advantage of the method described is lost. By
reason of the higher heating required there is
also the risk that the heating may be carried so
high that although aluminum has a higher tem-

perature of volatilization than barium part of
the aluminum volatilizes and deposits also on
those parts of the discharge tube where barium
is to be precipitated. This may be very detri-
mental, for example, when the barium is de-
posited on a cathode, for if in this case the barium
is admixed with a little aluminum, the presence
of the latter metal may cause a considerable re-
duction of the electron emission of the cathode.

According to the invention these difficulties are
obviated by introducing the active metal into the
vacuum tube after admixture with an insulating
compound of an alkaline earth metal, such as
calcium compound. This mixture can be pre-
pared by admixing a compound of the active
metal to be inserted with calcium and heating
this mixture in a vacuum or in a neutral atmos-
phere to such a temperature that the compound
of the active metal is reduced and a mixture of
the active metal to be inserted and a calcium
compound is formed, as calcium does not alloy
to any serious extent with this active metal or
at least forms alloys which readily decompose
so that the mixture after its introduction into
the vacuum tube need be heated to but a compara-
tively low temperature for causing the active
metal to volatilize. Moreover it is possible by
gently heating this mixture to expel the active
metal slowly from the mixture, other substances
in the mixture being thus prevented from vola-
tilizing simultaneously. If nevertheless a little
calcium does volatilize and deposit, for example,
on a cathode it has practically no injurious effect
as the electron emission of the cathode is not
lowered. Preferably, the active metal to be in-
serted will be admixed with calcium oxide and
for this purpose a mixture of barium oxide and
calcium will be initially used and by heat con-
verted at least partially into barium and calcium
oxide.

It is often desirable that the mixture to be in-
troduced into the tube should contain such a
quantity of calcium oxide and sometimes also of
another insulating substance refractory enough
to stand the heating so that the mixture is elec-
trically insulating. Thus the advantage is ob-
tained that if particles of the mixture shaped,
for example, into the form of a pellet should
become loose, these particles cannot establish
conductive connections between live parts. The
insulating substance may consist only of calcium
oxide but the mixture may contain in addition
other insulating substances preferably refrac-
tory oxides such as magnesium oxide or zirco-
nium oxide if initially for the preparation of the

mixture a plentiful supply of barium oxide is used so that this can be reduced only partially by the calcium, the mixture introduced into the tube will also contain barium oxide which is substantially an insulator when cold.

The mixture of the calcium compound and the active metal to be introduced into the vacuum tube may have added to it a binder and may be kept in a vacuum or under an air-excluding liquid. It is possible to expose the mixture for a short time to open air without the active metal being attacked to any serious extent by the oxygen of the air.

In order that the invention may be clearly understood and readily carried into effect one embodiment thereof will now be described more fully by way of example with reference to the accompanying drawing, in which Figs. 1 and 2 show an electric discharge tube the cathode of which is superficially coated with barium.

The discharge tube shown in the drawing has a glass envelope 1 and is adapted to receive or to amplify electric oscillations. The tube contains an anode 2, a grid 3 and an electron emitting cathode 4. The tube is constructed in the usual manner, hence its construction need not be set out more fully. The anode has an aperture 5 in front of which is arranged externally to the anode a capsule 6 fixed to the anode and if necessary closed by a gauze. Prior to the mounting of the electrodes in the envelope this capsule is filled with a mixture of barium and calcium oxide and after the exhaustion of the envelope by a pump the capsule is heated by suitable means for example, by a high frequency magnetic field to a temperature at which barium is set free in the form of vapour. The barium is deposited on the cathode and forms there, sometimes after oxidation, a layer of high electron emitting power. The barium vapour is expelled at a comparatively low temperature. The calcium oxide prevents an excessively rapid formation of vapour and has itself such a low vapour pressure that it does not produce any harmful vapours in the tube.

For the purpose of preparing the mixture to be introduced into the tube, a small quantity of barium oxide and metallic calcium may be

brought together in a glass vessel which is subsequently exhausted by a pump. After that the communication between the vessel and the vacuum pump is broken and the mixture present in the vessel is brought to a temperature of about 800° C. and the barium oxide is reduced by the calcium, at least partially with the formation of metallic barium. The temperature to which the mixture is heated is kept so low that a large portion of the barium developed during the reduction remains so that a mixture is formed which contains barium and calcium oxide. This mixture can be kept in the vessel used in preparing it or in a receptacle under an air-excluding liquid. When the mixture is being introduced into the discharge tube it can be exposed to air for some time, as the calcium oxide forms a satisfactory cover so that at the most only a little barium at the surface will be attacked by air. If it is desired that barium oxide should not be initially used, use may be made of other salts of barium for example of barium fluoride, and this compound may be reduced by means of calcium. In this case the mixture to be introduced into the tube contains barium and calcium fluoride.

It is not necessary that the mixture containing the active metal should be introduced into the discharge tube itself as it may be introduced into a separate chamber communicating with the tube. In this case, the vapour of the active metal developed in this chamber can flow from this chamber into the discharge tube.

I claim:

1. A clean up agent for use in electric discharge devices consisting of an electrically insulating mixture of barium, calcium oxide, and barium oxide.

2. An electron discharge tube comprising a plurality of electrodes including a plate, a capsule carried by the plate, and a mixture, introduced into said capsule in the form of a pellet, of barium, calcium oxide and a barium compound in such proportions that said mixture is substantially electrically insulating.

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