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PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in or relating to Glass to Metal Seals

We, THE GENERAL ELECTRIC COMPANY LIMITED, of Magnet House, Kingsway, London, W.C.2, a British Company, and MAURICE MANNERS and JOHN HENRY PARTRIDGE, both of Research Laboratories of The General Electric Company Limited, Wembley, Middlesex, both British Subjects, do hereby declare the nature of this invention to be as follows:—

This invention relates to processes for making glass to metal seals and more particularly, but not exclusively, to seals between normal borosilicate glasses and metals such as tungsten, kovar and molybdenum. The invention relates particularly to glass to metal seals for use in glass envelopes or glass parts of envelopes other than the envelopes of thermionic valves.

It has been found that seals between tungtsen and normal borosilicate glasses fail under tropical conditions where high ambient temperature and humidity exist and examination has shown that, in such seals, the tungsten oxide layer between the tungsten and the glass contains sodium tungstate formed by reaction between the tungsten oxide and the glass. The sodium tungstate appears to be soluble in hot water and its solubility would appear to explain why normal seals leak or fail under tropical conditions.

It has previously been proposed to make what are termed "oxide free seals" by wrapping a layer of alkali free borosilicate glass onto tungsten rod at very high temperature, greater than 2000° C. in an oxy-coal gas flame. However, the temperature at which the wrapping takes place is so high that a considerable amount of the tungsten rod is oxidised away and this results in substantial thinning of the rod. Moreover, the process is such that only rods of fairly large diameter can be successfully treated in this way, thinner rods of a diameter less than about 2 mm. being so much reduced in diameter due to oxidation that the rods are useless.

One object of the present invention is the provision of a process for making oxide free seals which is applicable to any size of tungsten wire or rod and which does not result in any thinning of the wire or rod.

According to the present invention, a process for making an oxide free seal between a metal surface and glass comprises the step of applying a thin coating of non-reducible glass to the metal surface by an enamelling process, the enamel being fired onto the metal surface in a reducing atmosphere. The glass applied by enamelling may be an alkali free glass.

According to one aspect of the present invention, a process for making glass to metal seals, more particularly seals between normal borosilicate glasses and metals such as tungsten and molybdenum, includes the step of applying a thin coating of borosilicate glass to a metal surface by an enamelling process, the enamel being fired onto the metal surface in a reducing atmosphere. Preferably the said glass is an alkali free glass.

The enamel may be fired on in a furnace in an atmosphere of dry hydrogen at a temperature of about 1400° C.

According to another aspect of the invention, a process for making seals between normal borosilicate glasses and metals, such as tungsten and molybdenum, comprises the steps of applying to a metal surface an enamel slip of an alkali free borosilicate glass and firing the enamel slip and the metal surface in a reducing atmosphere.

After enamelling, the enamelled metal surface can be sealed to a normal borosilicate glass.

Thus, to seal a tungsten wire into a normal borosilicate glass part or envelope, a thin coating of glass of the order of 0.05 mms. is applied to the wire by an enamelling technique, using an alkali free borosilicate glass and firing in a furnace in an atmosphere of dry hydrogen at a temperature of about 1400° C. only part of the length of the wire will need to be enamelled, the length of the enamelled part depending on the diameter of the wire and the type of seal in which it is to be used.

After enamelling, the enamelled part of the wire is provided, in known manner

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with a sheathing of normal borosilicate glass and care should be taken that there is no direct seal between the said glass and the tungsten wire; the borosilicate glass sheathing should not overlap the ends of the enamelled layer of glass. After sheathing, the wire may be used in the normal manner for making seals, for example, it may be sealed alone or with other similar wires into a borosilicate glass pinch.

As will be appreciated, the enamelling technique can be applied to wires or rods of any diameter and there is no danger of the wire or rod being oxidised away because the firing at high temperature is done in a reducing atmosphere and the later sheathing is done at a much lower temperature, about 700° to 800° C. The enamel slip can be applied by dipping, spraying or painting accurately to the necessary length of wire or rod and, if dipped or sprayed, suitable masking would be used to limit the extent of the enamelling.

The thin coating of alkali free borosilicate glass between the tungsten wire or rod and the normal borosilicate glass is sufficient to prevent failure of the seals under tropical conditions and compositions of alkali free glasses suitable for the enamelling process are:—

	1	2	3	4	5	6
SiO_2:—	85	72	82.5	60	60	60
B_2O_3:—	9	4	12.5	—	—	2.5
Al_2O_3:—	5	16	5.0	30	28	18
CaO:—	.5	4	—	8	5	10
BaO:—	.5	4	—	—	3	—
MgO:—	—	—	—	2	2	9.5
ThO_2:—	—	—	—	—	2	—

It will be understood that an alkali free borosilicate is one which is entirely free from alkali or contains only traces thereof, that is to say, less than 0.2% which is not an intentional addition to the glass composition but may be present due to unavoidable impurities in the glass making ingredients.

Dated the 16th day of July, 1945.

For the Applicants:
F. S. PEACHEY,
Chartered Patent Agent.

COMPLETE SPECIFICATION

Improvements in or relating to Glass to Metal Seals

We, THE GENERAL ELECTRIC COMPANY LIMITED, of Magnet House, Kingsway, London, W.C.2, a British Company, and MAURICE MANNERS and JOHN HENRY PARTRIDGE, both of Research Laboratories of The General Electric Company Limited, Wembley, Middlesex, both British Subjects, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to processes for making glass to metal seals in the manufacture of electric lamps and similar devices other than thermionic valves and more particularly, but not exclusively, to processes for making seals between normal borosilicate glasses and metals such as tungsten, kovar and molybdenum.

It has been found that seals between tungsten and normal borosilicate glasses fail under tropical conditions where high ambient temperature and humidity exist and examination has shown that, in such seals, the tungsten oxide layer between the tungsten and the glass contains sodium tungstate formed by reaction between the tungsten oxide and the glass. The sodium tungstate appears to be soluble in hot water and its solubility would appear to explain why such seals leak or fail under tropical conditions.

It has previously been proposed to make what are termed "oxide free seals" by wrapping a layer of alkali free borosilicate glass onto tungsten rod at very high temperature, greater than 2000° C., in an oxy-coal gas flame. However, the temperature at which the wrapping takes place is so high that a considerable amount of the tungsten rod is oxidised away and this results in substantial thinning of the rod. Moreover, the process is such that only rods of fairly large diameter can be successfully treated in this way, thinner rods of a diameter less than about 2 mm. being so much reduced in diameter due to oxidation that the rods may be quite useless.

One object of the present invention is the provision of a process for making oxide-free seals which is applicable to any size of tungsten wire or rod and which does not result in any excessive thinning of the wire or rod as does the known process referred to above.

According to the present invention, a process for making an oxide free seal between a metal surface and glass in the manufacture of electric lamps and similar devices other than thermionic valves, comprises the step of applying a thin coating of glass to the metal surface by an enamelling process, the enamel being fired onto the metal surface in a non-oxidising atmosphere. The glass applied by enamelling may be a non-reducible alkali

free glass and the atmosphere may be a reducing atmosphere. By an enamelling process is meant a process in which an enamel slip is applied to the metal surface and fired.

According to one aspect of the present invention, a process for making glass to metal seals in the manufacture of electric lamps and similar devices other than thermionic valves, more particularly seals between normal borosilicate glasses and metals such as tungsten and molybdenum, comprises the step of applying a thin coating of borosilicate glass to a metal surface by an enamelling process, the enamel being fired onto the metal surface in a non-oxidising atmosphere. Preferably the said glass is a non-reducible alkali free glass and the atmosphere a reducing atmosphere.

The enamel may be fired on in a furnace in an atmosphere of dry hydrogen at a temperature of about 1400° C.

After enamelling, the enamelled metal surface can be sealed to a normal borosilicate glass.

Thus, to seal a tungsten wire into a normal borosilicate glass part or envelope, a thin coating of glass of the order of 0.05 mms. is applied to the wire by an enamelling technique, using an alkali free borosilicate glass and firing in a furnace in an atmosphere of dry hydrogen at a temperature of about 1400° C. Only part of the length of the wire will need to be enamelled, the length of the enamelled part depending on the diameter of the wire and the type of seal in which it is to be used.

After enamelling, the enamelled part of the wire is provided, in known manner, with a sheathing of normal borosilicate glass and care should be taken that there is no direct seal between the said glass and the tungsten wire; the borosilicate glass sheathing should not overlap the ends of the enamelled layer of glass. After sheathing, the wire may be used in the normal manner for making seals, for example, it may be sealed alone or with other similar wires into a borosilicate glass pinch.

As will be appreciated, the enamelling technique can be applied to wires or rods of any diameter and there is no danger of the wire or rod being oxidised away because the firing at high temperature is done in a reducing atmosphere and the later sheathing is done at a much lower temperature, about 700° to 800° C. The enamel slip can be applied by dipping, spraying or painting accurately to the necessary length of wire or rod and, if dipped or sprayed, suitable masking would be used to limit the extent of the enamelling.

The thin coating of alkali free borosilicate glass between the tungsten wire or rod and the normal borosilicate glass is sufficient to prevent failure of the seals under tropical conditions and compositions of alkali free glasses suitable for the enamelling process are:—

	1	2	3	4	5	6
SiO_2:—	85	72	82.5	60	60	60
B_2O_3:—	9	4	12.5	—	—	2.5
Al_2O_3:—	5	16	5.0	30	28	18
CaO:—	.5	4	—	8	5	10
BaO:—	.5	4	—	—	3	—
MgO:—	—	—	—	2	2	9.5
ThO_2:—	—	—	—	—	2	—

It will be understood that an alkali free borosilicate is one which is entirely free from alkali or contains only traces thereof, that is to say, less than 0.2% which is not an intentional addition to the glass composition but may be present due to unavoidable impurities in the glass making ingredients.

Instead of using an atmosphere of hydrogen in the enamelling of a wire, an atmosphere of nitrogen may be used and an oxide free seal on copper may be obtained by using a lead glass enamel and firing in an atmosphere of nitrogen.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. In the manufacture of electric lamps and similar devices other than thermionic valves, a process for making an oxide free seal between a metal surface and glass comprising the step of applying a thin coating of glass to the metal surface by an enamelling process, the enamel being fired onto the metal surface in a non-oxidising atmosphere.

2. In the manufacture of electric lamps and similar devices other than thermionic valves, a process for making seals between normal borosilicate glasses and metals such as tungsten and molybdenum, comprising the step of applying a thin coating of borosilicate glass to a metal surface by an enamelling process, the enamel being fired onto the metal surface in a non-oxidising atmosphere.

3. A process as claimed in Claim 1 or Claim 2, wherein the glass applied by enamelling is a non-reducible alkali free glass and the atmosphere is a reducing atmosphere.

4. A process as claimed in Claim 1, 2 or 3, wherein the atmosphere is an atmosphere of dry hydrogen.

5. A process as claimed in Claim 2, wherein the enamel fired onto the metal surface in an atmosphere of dry hydro-

free glass and the atmosphere may be a reducing atmosphere. By an enamelling process is meant a process in which an enamel slip is applied to the metal surface and fired.

According to one aspect of the present invention, a process for making glass to metal seals in the manufacture of electric lamps and similar devices other than thermionic valves, more particularly seals between normal borosilicate glasses and metals such as tungsten and molybdenum, comprises the step of applying a thin coating of borosilicate glass to a metal surface by an enamelling process, the enamel being fired onto the metal surface in a non-oxidising atmosphere. Preferably the said glass is a non-reducible alkali free glass and the atmosphere a reducing atmosphere.

The enamel may be fired on in a furnace in an atmosphere of dry hydrogen at a temperature of about 1400° C.

After enamelling, the enamelled metal surface can be sealed to a normal borosilicate glass.

Thus, to seal a tungsten wire into a normal borosilicate glass part or envelope, a thin coating of glass of the order of 0.05 mms. is applied to the wire by an enamelling technique, using an alkali free borosilicate glass and firing in a furnace in an atmosphere of dry hydrogen at a temperature of about 1400° C. Only part of the length of the wire will need to be enamelled, the length of the enamelled part depending on the diameter of the wire and the type of seal in which it is to be used.

After enamelling, the enamelled part of the wire is provided, in known manner, with a sheathing of normal borosilicate glass and care should be taken that there is no direct seal between the said glass and the tungsten wire; the borosilicate glass sheathing should not overlap the ends of the enamelled layer of glass. After sheathing, the wire may be used in the normal manner for making seals, for example, it may be sealed alone or with other similar wires into a borosilicate glass pinch.

As will be appreciated, the enamelling technique can be applied to wires or rods of any diameter and there is no danger of the wire or rod being oxidised away because the firing at high temperature is done in a reducing atmosphere and the later sheathing is done at a much lower temperature, about 700° to 800° C. The enamel slip can be applied by dipping, spraying or painting accurately to the necessary length of wire or rod and, if dipped or sprayed, suitable masking would be used to limit the extent of the enamelling.

The thin coating of alkali free borosilicate glass between the tungsten wire or rod and the normal borosilicate glass is sufficient to prevent failure of the seals under tropical conditions and compositions of alkali free glasses suitable for the enamelling process are:—

	1	2	3	4	5	6
SiO_2:—	85	72	82.5	60	60	60
B_2O_3:—	9	4	12.5	—	—	2.5
Al_2O_3:—	5	16	5.0	30	28	18
CaO:—	.5	4	—	8	5	10
BaO:—	.5	4	—	—	3	—
MgO:—	—	—	—	2	2	9.5
ThO_2:—	—	—	—	—	2	—

It will be understood that an alkali free borosilicate is one which is entirely free from alkali or contains only traces thereof, that is to say, less than 0.2% which is not an intentional addition to the glass composition but may be present due to unavoidable impurities in the glass making ingredients.

Instead of using an atmosphere of hydrogen in the enamelling of a wire, an atmosphere of nitrogen may be used and an oxide free seal on copper may be obtained by using a lead glass enamel and firing in an atmosphere of nitrogen.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. In the manufacture of electric lamps and similar devices other than thermionic valves, a process for making an oxide free seal between a metal surface and glass comprising the step of applying a thin coating of glass to the metal surface by an enamelling process, the enamel being fired onto the metal surface in a non-oxidising atmosphere.

2. In the manufacture of electric lamps and similar devices other than thermionic valves, a process for making seals between normal borosilicate glasses and metals such as tungsten and molybdenum, comprising the step of applying a thin coating of borosilicate glass to a metal surface by an enamelling process, the enamel being fired onto the metal surface in a non-oxidising atmosphere.

3. A process as claimed in Claim 1 or Claim 2, wherein the glass applied by enamelling is a non-reducible alkali free glass and the atmosphere is a reducing atmosphere.

4. A process as claimed in Claim 1, 2 or 3, wherein the atmosphere is an atmosphere of dry hydrogen.

5. A process as claimed in Claim 2, wherein the enamel fired onto the metal surface in an atmosphere of dry hydro-

gen at a temperature of about 1400° C.

6. In the manufacture of electric lamps and similar devices other than thermionic valves, a process for sealing a tungsten wire or rod into a normal borosilicate glass comprising the steps of coating a portion of the length of the wire or rod with an enamel slip of a non-reducible alkali free borosilicate glass, firing the wire or rod and the slip in a reducing atmosphere, and sheathing the enamelled part of the wire or rod with a normal borosilicate glass.

7. A process as claimed in Claim 6, wherein the enamel slip is applied to the wire or rod by dipping, painting or spraying.

8. An electric lamp or similar device other than a thermionic valve having a glass to metal seal produced by a process according to any one of the preceding claims.

9. A process for sealing a tungsten wire into a normal borosilicate glass part or envelope of an electric lamp or similar device other than a thermionic valve substantially as hereinbefore described.

Dated the 24th day of May, 1946.

For the Applicants:
F. S. PEACHEY,
Chartered Patent Agent.

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