Aug. 28, 1951 A. M. BOUNDS 2,566,115

ALLOY FOR CATHODE ELEMENT

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Fig.1

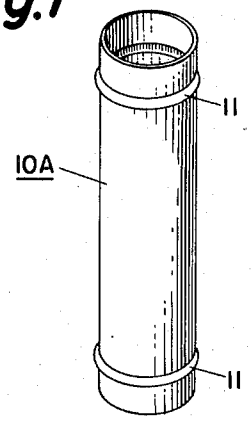


Fig.2

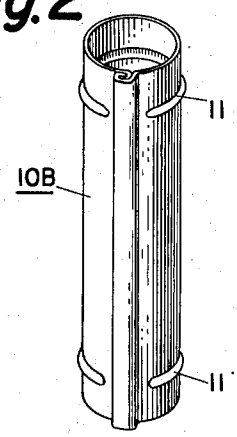


Fig.3

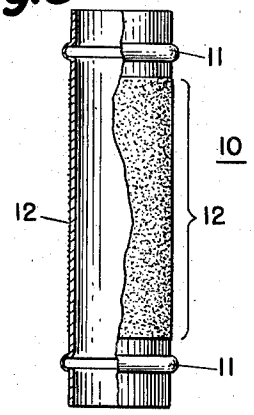


Fig.4

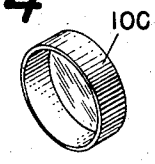


Fig.5

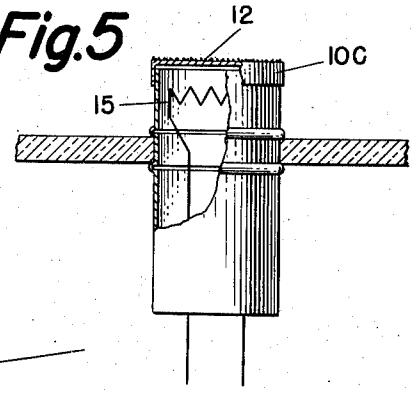


Fig.10

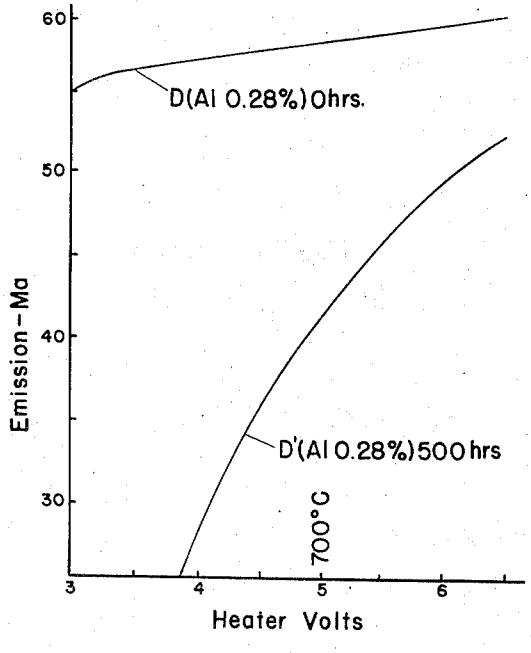
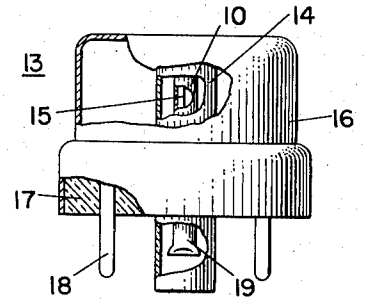


Fig.6



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ALLOY FOR CATHODE ELEMENT

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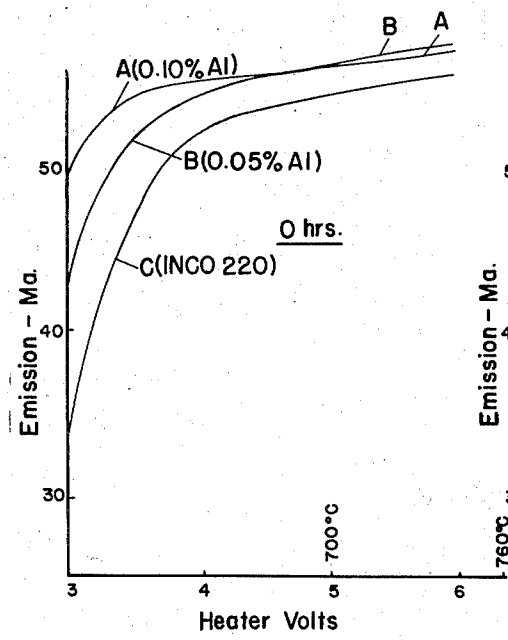


Fig.7

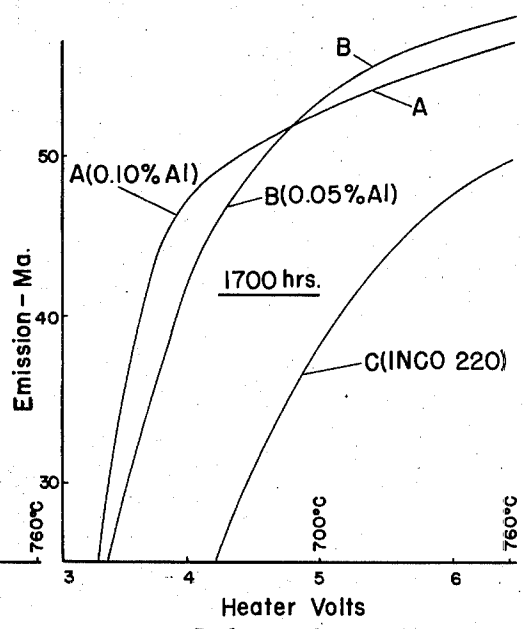


Fig.8

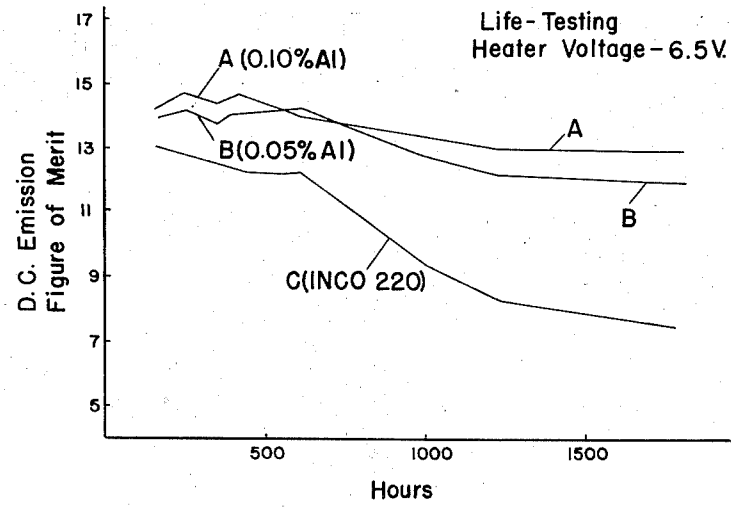


Fig.9

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Patented Aug. 28, 1951

2,566,115

UNITED STATES PATENT OFFICE

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ALLOY FOR CATHODE ELEMENT

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Application July 21, 1950, Serial No. 175,138

4 Claims. (Cl. 75—170)

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This invention relates to cathodes of the indirectly-heated type used in electronic tubes.

In general, such cathodes each consist of a nickel element, generally in the form of a sleeve or cup, having thereon a thin coating or layer which preliminarily is of alkaline earth carbonates. After assembly of the coated cathode and other electrodes within the envelope of an electronic tube, the cathode coating is activated by temporarily heating it substantially above normal operating temperature. In subsequent use of the tube, its cathode is heated to lower temperature, the effective life of the tube terminating when the electron emission from the cathode becomes definitely subnormal.

The principal objects of the present invention are to shorten the activation period of the cathode to attain higher electron emission at the same or lower operating temperature than required for present cathodes, to insure permanent bonding of the coating to the cathode sleeve or equivalent, to maintain extremely high leakage resistance between electrodes of the tube, and to insure negligible electrical resistance of the interface between the cathode coating and its supporting sleeve or equivalent cathode element. It is also an object of the invention to attain the aforesaid electrical characteristics of the cathode without introduction of metal-working difficulties in production of the metallic cathode elements.

The invention further resides in indirectly-heated cathodes having the features of novelty and utility hereinafter described.

For a more detailed understanding of the invention and for illustration of cathodes embodying it, reference is made to the accompanying drawings in which:

Figs. 1 and 2 respectively illustrate tubular cathodes of specifically different types;

Fig. 3 illustrates the cathodes of Figs. 1 and 2 after application of a coating thereto;

Fig. 4 is a perspective view of a disk type of indirectly-heated cathode;

Fig. 5 is an elevational view, partly in section, of a sub-assembly including the cathode of Fig. 4;

Fig. 6 is an elevational view with parts broken away of an electronic tube including the cathode of Fig. 3; and

Figs. 7 to 10 are curves referred to in comparison of cathodes embodying the invention with prior standard cathodes.

In the manufacture of seamless cathode elements, a length of metal tubing is drawn to size by one or more drawing operations and cut to

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proper length; cathode elements with a butt-welded seam may be made by first rolling strip stock to tubular form, welding the seam edges, and then drawing the welded tubing to proper size for the cathode. The cathode 10A shown in Fig. 1 is exemplary of a cathode made by either of these methods. In either case, prior to severance of the individual cathode sleeves from the parent tubular stock, they may be further worked to form integral supporting beads 11, as by mechanism disclosed in U. S. Letters Patent 2,248,720: alternatively, the beads 11 may be formed on individual sleeves after severance from the parent stock.

In the manufacture of lock-seam cathodes 10B, Fig. 2, cathode blanks are cut from flat strip stock, shaped over a small mandrel and the edges of the blank formed into a lock seam. During the formation of the seamed cathode sleeves, they may also be shaped to form integral supporting beads 11. Apparatus for making lock-seam cathodes, with or without beading, is disclosed in U. S. Letters Patent 2,116,971. Various forms of such cathode sleeves and their mounting in an electronic tube are disclosed in U. S. Letters Patent 2,116,788.

Cathodes 10C, Fig. 4, for use in electron guns and in so-called "planer-electrode" type of electronic tubes are punched or stamped from flat strip stock and concurrently with or after such punching are shaped to cup or cap form having a very small radius of curvature between the flat circular face and the rim.

After completion upon them of the metal-working operations and just before their assembly in electronic tubes, the cathode elements, whether of tubular, disk or other non-filamentary shape, are coated, Figs. 3 and 5, with a thin layer 12 of activatible material, usually carbonates of alkaline earth metals—preferably barium and strontium. The volume of the coating 12 is small compared to the volume of the cathode sleeve or disk. This is in contrast to the situation existent with directly-heated cathodes of the coated filament type in which the volume of the coating is comparable to or greater than that of the cathode filament and gives rise to emission and life problems not encountered with coated filaments and not solved by the practices and techniques of that art.

The individual cathode elements after coating are assembled with other tube electrodes in tube envelopes and before the envelopes are sealed off from the vacuum pump which exhausts them from air and other gases, the cathodes are acti-

vated by heating them to a temperature above their subsequent temperature of operation. The application of the coating 12 and its activation are usually performed by the tube manufacturer rather than the manufacture of the cathode sleeves, disks or the like. During the activation period, the carbonates of coating 12 are decomposed into oxides and then reducing constituents of the sleeve alloy react with the coating oxides to liberate barium, strontium and possibly calcium in the typical example given. The liberated ions of the earth metals convert the coating 12 to a semi-conductor and some of them migrate to the outer surface of the coating to form a monomolecular layer of low work function.

The particular tube 13, Fig. 6, is a diode in which a tubular anode 14 surrounds a coated cathode sleeve 10 which in turn surrounds an electrical heater element 15. The tube envelope 16 in the particular form of tube shown is a metallic shell suitably hermetically sealed to the tubular stem 19 of glass or metal which supports the tube electrodes and through which the envelope is exhausted of air. After exhaustion of air from the envelope 16, the stem or pinch tube 19 is sealed closed permanently to retain the vacuum. The terminal pins 18 which extend through base insert 17 provide external connections to the tube electrodes and heater. Further description of the construction and manufacture of tube 13, per se known, is unnecessary for understanding of the present invention.

In use of the diode 13, current is supplied to its heater 15 to heat the coated cathode 10 to temperature for which electrons are emitted by the activated coating 12 so to provide a path for flow of electrons from cathode 10 to anode 14 in a circuit including an external voltage source connected to the cathode and anode terminals of the tube. In triodes, pentodes, hexodes and other multi-grid tubes, additional electrodes form part of the electrode assembly and are connected to corresponding pins 18 for application of signal or operating voltages.

Prior to the present invention, the general practice has been to make the cathode sleeve or equivalent of a nickel alloy including magnesium or silicon, or both, for reducing the oxides produced during activation of the coating 12. This action continues but at lower rate during subsequent operating life of the tube for which the cathode is operated at lower temperature. In accordance with the present invention, a longer effective life, a shortened activation period, higher emission, unimpaired insulation between electrodes, permanent bonding of the sleeve and coating, and substantially perfect electrical conduction between the cathode sleeve, or cup, and its coating are all obtained by using a nickel alloy including aluminum, within a narrow range of very low percentages, in addition to, or in replacement of the usual magnesium or silicon constituents. The optimum percentage of aluminum for attainment of all of the objects is about 0.10% and within limits of from about 0.01% to about 0.20% which should not be exceeded. This range and the limits for other constituents, if present in the predominantly nickel alloy, are later herein set forth in tabular form.

As to rate of activation, which is of great economic import in mass production of electronic tubes, it has been found that the nickel-aluminum cathodes pass through optimum activation in substantially less time than required for optimum activation of prior cathodes:

Specifically, indirectly-heated cathodes similar to mine except lacking the aluminum component reach maximum emission about 25 hours or more later.

From comparative checks against indirectly-heated cathodes of prior standard composition (curve C of Figs. 7 and 8), it has been determined that nickel-aluminum cathodes having approximately 0.10% aluminum (curve A of Figs. 7 and 8) and 0.05% aluminum (curve B of Figs. 7 and 8) have superior emission immediately following activation (Fig. 7) and throughout a very long life thereafter (Fig. 8). The inclusion of as little as 0.03% aluminum in the basic sleeve alloy provides a high initial emission substantially equal to that obtainable in prior aluminum-free nickel alloys by inclusion of magnesium or silicon but only for such percentages thereof that shortened cathode life and other adverse effects result. Cathode sleeves of nickel alloy with predominantly magnesium-reducing agents (0.15% Mg) and no aluminum have undesirably short emission life probably because of rapid migration of the magnesium constituent from the cathode sleeve due to its high vapor pressure and mobility. The aluminum component of my new cathodes longer remains in the nickel sleeve and is a powerful reducing agent for the barium oxide of the coating: it is more powerful than silicon. Furthermore, as appears from these curves (curves A, B, of Figs. 7–8), the emission of the nickel-aluminum cathodes is substantially higher at lower heater voltages than the emission of prior standard cathodes (curve C, Figs. 7–8), which means that battery-operated electronic apparatus equipped with tubes using the new cathodes has a substantially extended operating life, a matter of material importance particularly in certain types of mobile equipment. Continued high emission at low heater voltage is also of advantage because the equipment will continue to function normally over a substantial range of variation of supply-voltage without need for use of regulating equipment.

Moreover, as indicated by test curves A and B of Fig. 9, the figure of merit of the nickel-aluminum cathodes after 1700 hours of operation in a diode (equivalent to over double that time in the operating life of a tube with a control grid) is still high for satisfactory operation, whereas the figure of merit of the prior standard type of nickel cathode (curve C of Fig. 9) falls off sharply after about 750 hours of operation. The "figure of merit" method of evaluating the life quality of a cathode is based upon the location of the knee of the emission curve. This method is discussed in "Physical Review," vol. 78, No. 3, May 1, 1950. The life superiority of nickel-aluminum cathode sleeves (curves A and B) is clearly shown in Fig. 9. The break in curve C at about 750 hours indicates the end of useful life of the "check" cathodes lacking aluminum: this break or sharp downward trend indicates that poisons, such as oxygen, liberated in operation of the tube have overcome the reactivating power of the magnesium and/or silicon components of the cathode alloy. Curves A and B indicate that the re-activating power of the aluminum component of my cathode sleeves is not only initially high but remains high for a greatly extended period of time. As in Figs. 7 and 8, the curve C of Fig. 9 is a characteristic of a standard alloy (INCO 220) in widest present use for indirectly-heated cathodes.

Other significant advantages in use of aluminum instead of magnesium in indirectly-heated cathode sleeves, cups or the like, are that the output current of the tube is free of an objectionably high noise component, even after long use, and that the inter-electrode leakage resistance remains extremely high. As above stated, magnesium has high vapor pressure and rate of mobility. Consequently, the magnesium sublimes rapidly and forms current-leakage paths on insulators or insulation between the tube electrodes. Other prior activating agents are far slower than magnesium to sublime but are far less active. In my cathodes, the aluminum provides at least the major activating power and no evidence that it sublimes in objectionable or even noticeable amount has been discovered.

Furthermore, it has been determined by measurements made after operation of over 500 hours, that the electrical interface resistance between the coating and nickel-aluminum sleeve was essentially zero, whereas prior art cathodes used for check purposes exhibited definite interfacial resistance increasing with age. Furthermore, there was no evidence in the nickel-aluminum cathodes of any disintegration or growth of the interfacial bond between the sleeve and coating: presumably migration from the bond to the coating is substantially balanced by migration from the sleeve to the bond. The bond neither disappears in time nor does it grow with resultant fracturing of the thin overlying coating 12. When the sleeve alloy contains as much as 0.5% aluminum, the interfacial layer becomes so thick the coating 12 separates from the sleeve presumably because the temperature coefficient of the aluminates in the coating is substantially different from that of the sleeve. When the aluminum content of the sleeve alloy is not greater than about 0.20%, the interfacial layer never attains a thickness great enough to result in peeling off of the coating 12.

The low interfacial resistance of my aluminum-nickel cathodes is of particular significance for high emission pulsed operation of electronic tubes as occurs in certain radar, television and industrial applications. Peak electron currents drawn from a cathode under pulsed conditions may be as high as 50 to 100 amperes per square centimeter (cm.^{2}) of surface of coating 12 in contrast to the 0.1 to 0.2 ampere per cm.^{2} under usual steady emission conditions. Thus, in pulsed operation there are excessive I^2R losses if there is appreciable ohmic resistance in the cathode. Such resistance exists and increases with time when silicon, titanium, chromium and the like are used as activating agents in the sleeve alloy: these components form in the sleeve-coating interface triple compounds (Ba_2SiO_4, $BaTiO_4$, etc.) of high electrical resistance and of thickness which increases with life of the tube with consequent reduction of pulse emission values. Magnesium and carbon are less objectionable from this standpoint, but have other disadvantages, some of which are elsewhere herein discussed.

With aluminum as the activating agent in the cathode alloy, the interface compound is a complex aluminate which apparently does not take the free barium into combination. Apparently, the barium remains interspaced in the interface layer as it does in the bulk coating and thus provides for good electrical conduction. In any event, with aluminum in the sleeve alloy, the interface is of low electrical resistance as evidenced by high pulse emission initially and throughout the life of the tube. When, however, the percentage of aluminum is higher than 0.3%, the interface bond between the sleeve and coating becomes weak and of electrical resistance unsuited for pulsed operation: such higher percentage also shortens the tube line for reasons later mentioned in discussion of Fig. 10.

All of the beneficial effects of aluminum within the limited range sepcified obtain if the alloy includes a small percentage of magnesium or silicon, or both. Impurities, such as copper, iron, sulphur and titanium should not be present in percentages much higher than specified in the table below. Cobalt, usually present with nickel, does not affect the emission characteristics unless greater than about 1%.

In tabular form, the percentage composition of the sleeve alloy for concurrent attainment of all objects of the invention may be expressed as:

Ni, 98% min.
Co, 1% max. } base alloy
Al, 0.01% min.—0.2% max. (0.1% optimum)
Mn, 0.20% max.
Si, 0.25% max.
Cu, 0.2% max.
Fe, 0.2% max.
S, 0.01% max.
C, 0.2% max.
Mg, 0.15% max.
Ti, 0.05% max.

As above stated, the optimum percentage of aluminum in the cathode stock is about 0.1%: with aluminum present in less than 0.01%, its beneficial effects are insubstantial, whereas percentages of aluminum much above about 0.2% are unsatisfactory in one or more respects. For example, from experimentation with cathode sleeves of nickel alloys having upwards of 0.25% aluminum, it has been found that although they activate rapidly and initially have high emissive (curve D, Fig. 10), their effective life is materially shorter (curve D', Fig. 10) than for cathodes of composition within the proper percentage range of aluminum and is even much less than that of prior indirectly-heated cathodes. Moreover, it was found that a heavy black interface formed between the sleeve and coating and that the coating became a loose cylinder which readily fractured. A similar disintegration of the bond between coating and sleeve has been observed in prior art nickel cathodes, particularly those including titanium, and appears probably responsible for the flaking or peeling of the coating and high electrical resistance of the interface.

In addition, nickel alloys having upwards of 0.25% aluminum are difficult to fabricate into tubing of small diameter and in general during cathode-forming operations of nature discussed in connection with Figs. 1, 2 and 4 there is often edge-cracking and flaking of the metal precluding use of the resulting defective cathode sleeves or cups in electronic tubes. Nickel-aluminum cathode stock within the narrow percentage range of aluminum above specified does not present difficulty in drawing, shaping or other metal-working operations incident to formation of indirectly-heated cathodes therefrom.

In brief summary, for indirectly-heated cathodes, aluminum, within the specified narrow range of very low percentage, is a definitely superior activating constituent of the nickel-alloy because affording high emission level, rapid activation, long life, freedom from sublimed leak-

age deposits and negligible interface resistance: further, it may be combined with other activating constituents to compensate for their shortcomings. Additionally, the inclusion of aluminum in such low percentages does not introduce difficulty or production losses in fabrication of the cathodes by drawing, stamping, punching or other metal-working steps performed on the tubular or strip stock.

What is claimed is:

1. A metallic cathode element of the indirectly-heated type, being of an alloy comprising nickel not less than about 98%, aluminum within the range of from 0.01% to 0.2% and the remainder impurities with not significantly in excess of about 1% cobalt, 0.2% manganese, 0.25% silicon, 0.2% copper, 0.2% iron, 0.01% sulphur, 0.2% carbon, 0.15% magnesium, 0.05% titanium.

2. A cathode element as in claim 1 in which the alloy includes magnesium within the range of from 0.01% to 0.15%.

3. A cathode element as in claim 1 in which the alloy includes silicon within the range of from 0.02% to 0.25%.

4. A cathode element as in claim 1 in which the alloy includes magnesium and silicon within the combined percentage range of 0.03% to 0.40% and within the maximum limits of 0.15% magnesium, 0.25% silicon.

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REFERENCES CITED

The following references are of record in the file of this patent:

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Number	Name	Date
2,223,862	Widell	Dec. 3, 1940
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