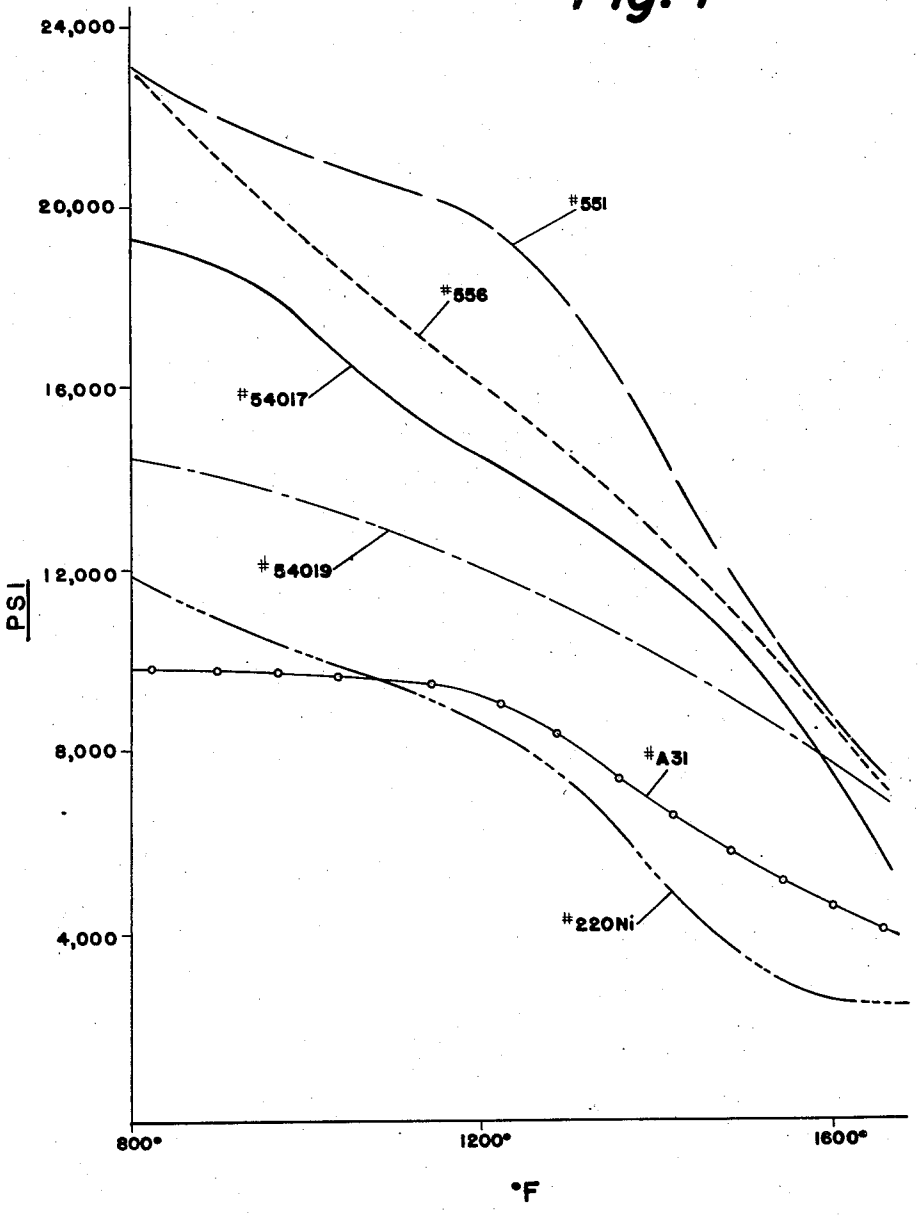
TUNGSTEN-ZIRCONIUM-NICKEL CATHODES

Filed March 7, 1957 4 Sheets-Sheet 1

Fig. 1



TUNGSTEN-ZIRCONIUM-NICKEL CATHODES

Filed March 7, 1957 4 Sheets-Sheet 2

Fig. 2A

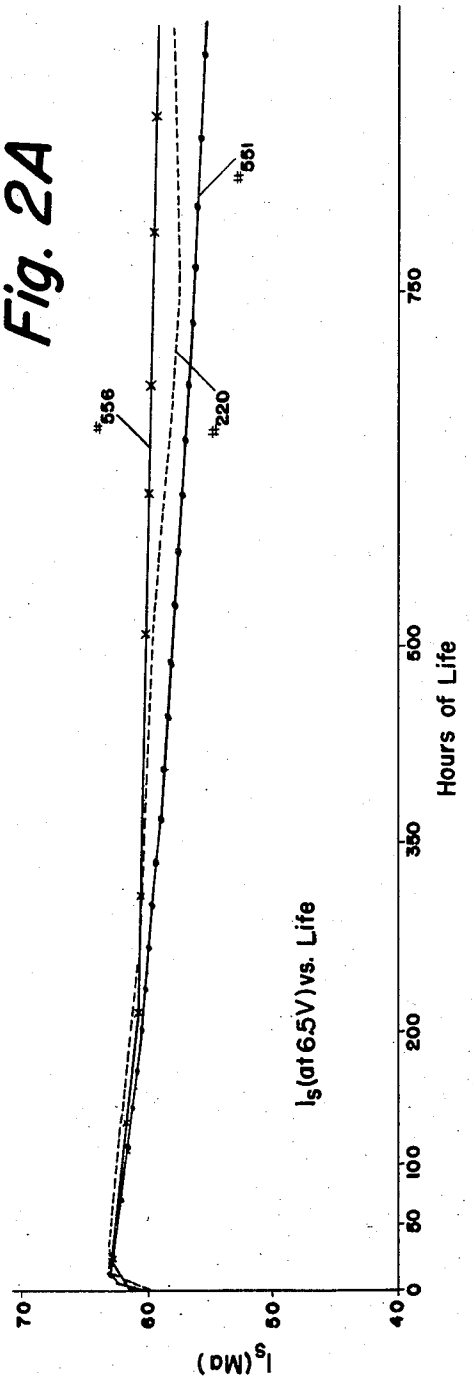



Fig. 2B

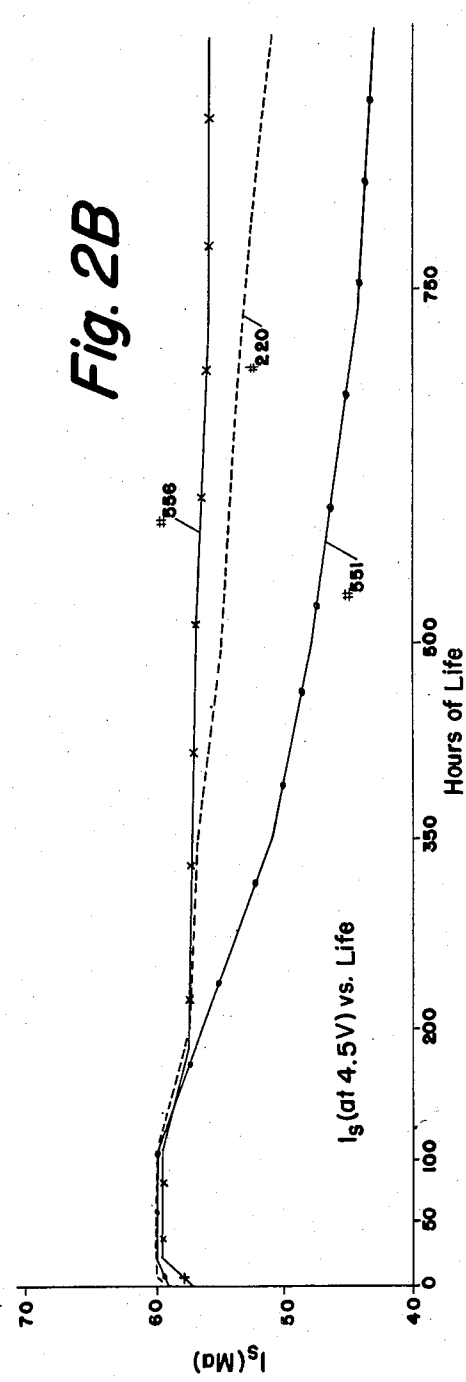


Fig. 3A

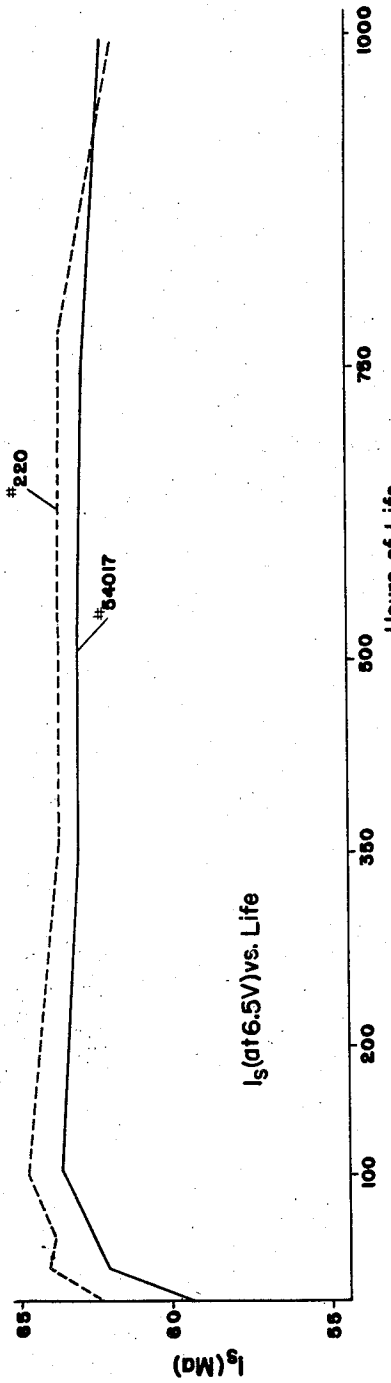

#220
#54017
Hours of Life
$I_S$(at 6.5V) vs. Life
$I_S$(MΩ)
65
60
55
100
200
350
500
750
1000

Fig. 3B

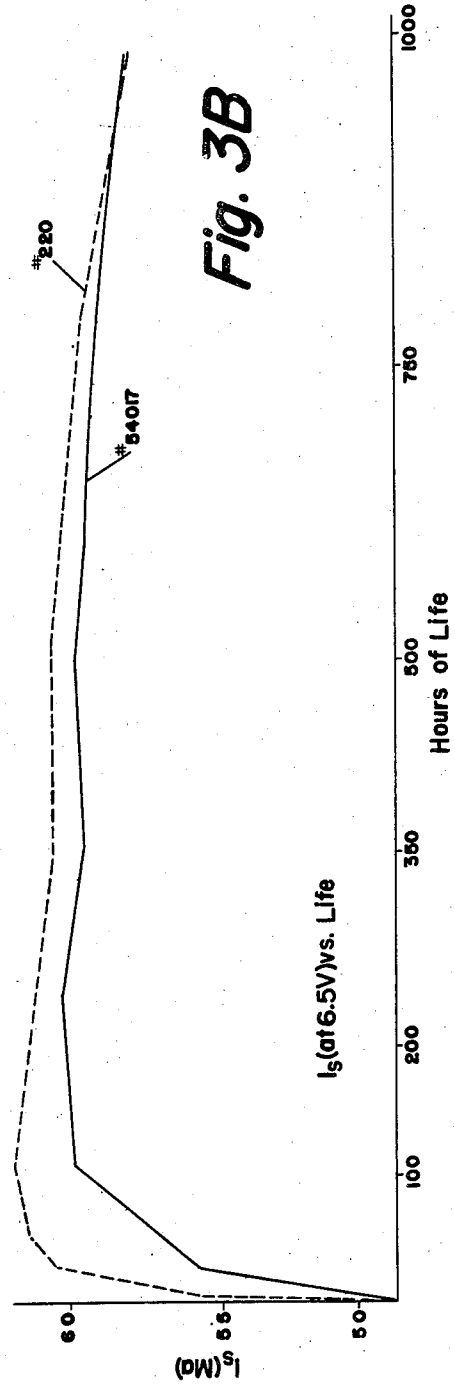
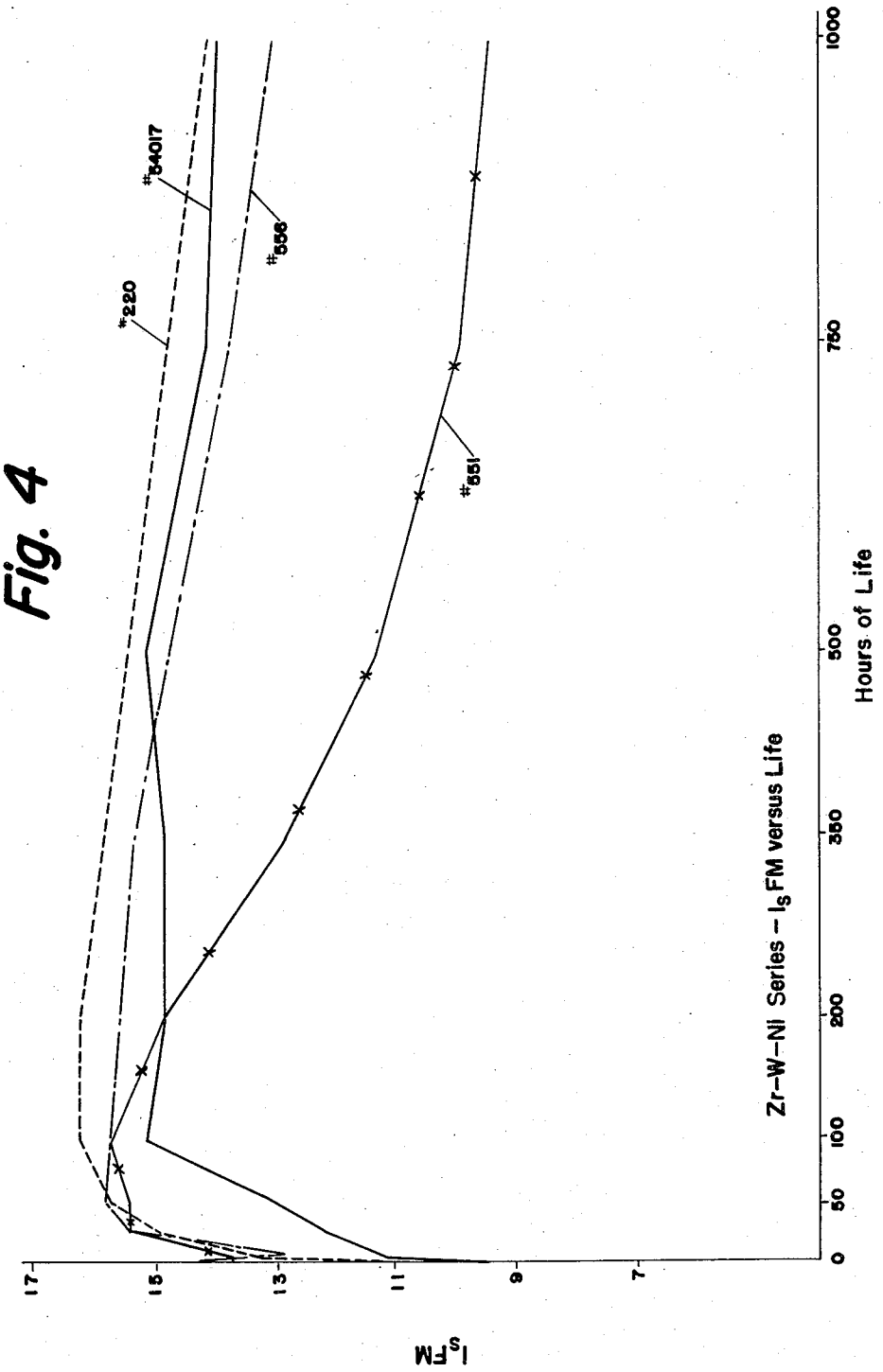

#220
#54017
Hours of Life
$I_S$(at 6.5V) vs. Life
$I_S$(MΩ)
60
55
50
100
200
350
500
750
1000

Fig. 4


#34017
#558
#220
#551
Zr-W-Ni Series – $I_S$FM versus Life
Hours of Life
$I_S$FM
0
50
100
200
350
500
750
1000
7
9
11
13
15
17

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2,833,647

# TUNGSTEN-ZIRCONIUM-NICKEL CATHODES

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Application March 7, 1957, Serial No. 644,610

3 Claims. (Cl. 75—170)

This invention relates to cathodes of the indirectly-heated type for electron tubes.

In general, the object of the invention is to provide indirectly-heated cathodes which have substantially enhanced resistance to deformation when subjected to shock or vibration at their elevated operating temperatures and which have good emission and sublimation characteristics substantially equivalent to or better than those of nickel alloy cathodes.

In accordance with the present invention, such objective is obtained by making the cathode sleeves, cups or the like from a nickel alloy which includes, within narrow percentage ranges later herein specified, the additives tungsten and zirconium. Considering all of the many factors involved, the preferred composition contains about 4% tungsten and 0.1% zirconium with the remainder of the alloy being essentially nickel.

In the following description, reference is made to the accompanying drawings in which:

Fig. 1 is a group of graphs exemplary of the yield-strength, at cathode operating temperatures, of various tungsten-zirconium-nickel alloys and of reference cathode alloys; and

Figs. 2A, 2B, 3A, 3B and 4 comprise groups of curves referred to in discussion of the emission characteristics of indirectly-heated cathodes made from a reference nickel alloy and from nickel alloys including the additives tungsten and zirconium.

In general, indirectly-heated cathodes consist of a nickel alloy base element, such as a sleeve or cup, having thereon a thin coating of alkaline earth metals such as barium, strontium or the like. The fabrication of the alloy stock into cathode base elements involves hot and cold working steps, such as forging, rolling, drawing, stamping and the like. After assembly of the coated cathode, including its heater and other electrodes within an envelope to form an electronic tube, the cathode is activated by temporarily heating it substantially above its normal operating temperature. During activation, there are reactions between the base element alloy materials and the coating materials which convert the coating to a combination of complex oxides which emit electrons when heated to cathode-operating temperatures in the neighborhood of 1600° F. In the more usual services, the effective life of the tube is terminated when its cathode emission is definitely subnormal at normal heater current. However, for many uses, including field applications where the available source voltage is low or fluctuating, tubes are considered unfit for use when their cathode emission is substantially affected by low or varying heater current.

The operating life of a tube is also affected by cathode characteristics other than electron emission. For example, the normal life of high-voltage rectifier tubes has often abruptly terminated because of eruptive flaking or peeling of the cathode coating from the cathode sleeve. Also, the operation of amplifier, oscillator and mixer tubes has been adversely affected by formation and continued growth of a high-impedance interface between



the cathode sleeve and its coating. The resistive component of such interface impedance is damaging, particularly in pulse-type operation, even at ordinary frequencies; the capacitive component of such interface impedance is particularly damaging at high frequencies, even when the tube is not operated under pulsed or cut-off conditions. The life of a tube may also be terminated by the formation, from material sublimed from its cathode, of a leakage path between electrodes of the tube. The operating life of a tube is also determined by the mechanical properties of its cathode element; for example, cathode sleeves made of the usual nickel alloys often bowed when subjected to high temperatures during their activation period, so causing internal short-circuits or significant changes in interelectrode spacing. Also in services where the tubes are subjected to severe mechanical shock, as in airborne missile equipment, buckling or deformation of their cathode sleeves rendered the tubes inoperative before performance of their intended function.

We have determined that addition of tungsten and zirconium, within the narrow percentage ranges later set forth, to nickel cathode stock provides a cathode alloy which is amenable to both hot and cold working and which, as fabricated into indirectly-heated cathodes, affords rapid activation, sustained high emission levels, virtual freedom from sublimation, negligible interface impedance, and a hot-strength at least several times that of the usual nickel cathode alloys.

Considering first the enhancement of hot-strength at cathode operating temperatures of about 1600° F., the addition of a small amount of zirconium effects a great change in hot-strength as compared to the addition of a much larger amount of tungsten. For example, a binary tungsten-nickel cathode alloy containing about 2% tungsten has a yield-strength of 3800 p. s. i. (pounds per square inch) at a test loading rate of .004 inch per minute. Increasing the tungsten percentage to 4% increases the hot yield-strength to only 4100 p. s. i., whereas addition of only about 0.74% zirconium to a 2.4% tungsten-nickel alloy increases its yield strength to 8150 p. s. i. Furthermore, the hot-strength of a 4% tungsten-nickel alloy can be increased from 4100 to 7400 p. s. i. by addition of only about 0.1% zirconium, whereas to effect the same increase in strength by addition of tungsten requires such a high percentage of tungsten that the alloy is unsuited for fabrication into cathode sleeves by the usual metal working steps. From metallographic investigation, it appears that the addition of zirconium and tungsten produces precipitation hardening at intermediate temperatures. However, at cathode operating temperatures, this effect is quite small and so it cannot be attributed a marked enhancement of hot-strength resulting from small additions of zirconium.

Data compiled on the emission characteristics of indirectly-heated cathodes made of nickel alloys, tungsten-nickel alloys, zirconium-nickel alloys and zirconium-tungsten-nickel alloys indicates interaction of the tungsten and zirconium in enhancement or maintenance of the emission characteristics of nickel cathodes as well as a substantial increase in their resistance to deformation when subjected to severe mechanical shock at cathode-operating temperatures. Such effects were not predictable from the prior state of the art. For nickel cathode alloys containing about 2% to 4% tungsten by weight, zirconium may be added in the range of from about 0.05% to 1.5% by weight. The upper limit specified for zirconium should not be substantially exceeded as there is danger of incipient melting during processing of the cathode stock. Except for residuals and one or more activating agents, the balance of the ternary alloy is essentially the nickel base usually including cobalt not in excess of 1%; higher percentages of cobalt in the

nickel base have been found to have little effect upon the emission characteristics or upon the mechanical strength at cathode-operating temperatures.

In these zirconium-tungsten-nickel alloys, magnesium and/or aluminum may be present in small percentage as activating agents. The percentage of magnesium should not be in excess of about 0.07% to insure a low rate of sublimation. The percentage of aluminum should not be in excess of about 0.1% to avoid peeling off of the oxide coating. Because of its effect on interface impedance, silicon should not be used as an activating agent; if present, its concentration should not exceed about 0.02%.

In determination of these limits of zirconium and tungsten for obtaining enhanced hot-strength of indirectly-heated cathodes and preservation or enhancement of emission properties, tests were conducted on a substantial number of tungsten-zirconium-nickel cathode alloys. Specific examples of such alloys are listed below in Table A.

*Table A*

| Alloy | Zr | W | Al | Mg | Si | Fe | Mn | C | Cu | Base | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | Co | Ni |
| #551 | .094 | 3.95 | .140 | .065 | .022 | .026 | .009 | .085 | .063 | 4.72 | Essentially Remainder. |
| #556 | .092 | 3.93 | .008 | .056 | .010 | .014 | .007 | .058 | .008 | 2.08 | Do. |
| #54017 | .107 | 3.92 | .006 | .012 | .006 | .019 | .082 | .042 | .008 | .067 | Do. |
| #54019 | .80 | 2.08 | .006 | .011 | .008 | .086 | .114 | .040 | .008 | .054 | Do. |
| #220* | ------ | ------ | .009 | .045 | .019 | .046 | .137 | .08 | .033 | .525 | Do. |
| #A-31** | ------ | 3.93 | .025 | .025 | .014 | .032 | .05 | .04 | .014 | .103 | Do. |

*Reference nickel cathode alloy.
**Reference tungsten-nickel cathode alloy.

As shown by the test curves of Fig. 1, the yield-strengths of the tungsten-zirconium-nickel alloys of Table A are significantly higher than those of the nickel and tungsten-nickel cathode alloys throughout a high temperature range including cathode-operating temperatures in the vicinity of 1600° F. In general, as determined by these and other tests, the hot yield-strength of the ternary cathode alloys was two and one-half to three times greater than that of the nickel cathode alloy #220. As confirmed by shock tests on tubes with cathodes at operating temperatures, there is direct correlation between the shock deformation characteristics of indirectly-heated cathodes and the yield-strength of the cathode alloy at the same temperature.

The presence of higher cobalt content in the #551 and #556 alloys appears to increase the yield-strength at temperatures below about 1500° F. but to have little or no effect at temperatures above 1500° F. Therefore, the presence of cobalt up to 5% and up to even 15% or more is not considered as enhancing the strength, at cathode-operating temperatures, of the alloys here concerned. For this reason and because of the general shortage of cobalt, cobalt need not be included or added in amounts of more than 1%. The addition of a small amount of aluminum, up to 0.10%, is desirable, but not necessary, for early activation of emission. This amount of aluminum has not been found to affect the yield-strengths of the tugnsten-zirconium-nickel alloys at cathode-operating temperatures although it may serve to result in precipitation hardening at lower temperatures.

The emission characteristics of oxide-coated cathodes using the ternary alloys of Table A for the cathode sleeves are shown in Figs. 2A, 2B, 3A, 3B and 4. In these figures, the curves are identified by the respective alloy designations of Table A. For these emission tests, the cathodes were utilized in the standard diode structure defined in Spec. F270–52T of ASTM—American Society of Testing Materials. The cathode sleeves were 0.045" O. D. x 0.002" wall x 27 mm. long. The life burning conditions were an anode cathode supply voltage ($E_b$) of 100 volts, a heater voltage ($E_f$) of 6.5 volts and a load resistance ($R_b$) of 1000 ohms. Anode current readings were taken at 0, 5, 25, 50, 100, 200, 350 and 500 hours and then every 250 hours to the end of the test. At each test period, the anode current was read for a plate voltage of 40 volts for a series of heater voltages including the normal voltage (i. e., 6.5 volts) and sub-normal voltages including 4.5 volts. Such anode current readings plotted against time constitute the curves of Figs. 2A, 2B, 3A, 3B. The $I_sFM$ or direct-current emission figure of merit curves of Fig. 4 are derived from the anode current vs. heater voltage readings as described in detail in an article of Briggs and Richard in the ASTM Bulletin for January 1951. Briefly, the $I_sFM$ value is the ratio of the $I_b$, $E_f$ coordinates at the knee of the anode current/heater voltage curve where the anode current changes from a space charge limited condition to a temperature-limited condition (sub-normal heater voltage). For comparison purposes, the emission curves for tubes having nickel cathodes are also shown in Figs. 2A–4. The corresponding curves for tubes having the #A–31 alloy cathodes are not shown since they are substantially similar to those of the #220 alloy cathodes.

Referring to Figs. 3A, 3B and 4, the indirectly-heated cathodes of alloy #54017 were somewhat slower to activate than those of the control alloy #220. From knowledge gained from these and other tests, this slower activation is attributable to the lower percentage of the activating agents magnesium and silicon in the #54017 alloy. After activation, the emission of the #54017 cathodes was very stable at normal heater voltages (Fig. 3A) and closely approached that of the mechanically weaker #220 cathodes—surpassing it at and beyond 1,000 hours of life at normal heater voltages. As to their relative sublimation characteristics, the cathodes of the #54017 alloy had no visible dome deposit even after 1,000 hours of life, whereas the cathodes of the reference nickel alloy had a visible deposit after only about 100 hours of life.

Referring to Figs. 2A, 2B and 4, the cathodes of alloys #551 and #556 activated rapidly—at about the same rate as the reference cathodes of alloy #220. After activation, the emission of the #556 alloy cathodes was stable, closely similar to that of the reference-nickel cathodes for about the first 500 hours of life and thereafter somewhat higher than that of the reference-nickel cathodes. The somewhat enhanced emission characteristics of the #556 alloy cathodes occur at both normal heater voltage (Fig. 2A) and sub-normal heater voltage (Fig. 2B). Because of their higher percentage of magnesium, the #551 and #556 alloy cathodes evidenced a deposit earlier than the reference-nickel cathodes. However, after 1,000 hours of life, the deposit for the #551 and #556 cathodes was less than the reference-nickel cathodes. The sublimation deposit did not include zirconium or tungsten.

Because of the much higher percentage of aluminum in the #551 alloy, some peeling of the oxide coating was evidenced: this accounts for the drop-off of emission with increasing life of the #551 curve of Fig. 4.

In brief summary, the tungsten-zirconium-nickel cathodes have an emission characteristic which is stable and substantially equivalent to that of the reference nickel cathodes; their sublimation characteristics are not affected by the additives zirconium and tungsten but by the concentration of magnesium, manganese and copper: for good coating adherence and low interface impedance, the tungsten-zirconium-nickel alloys should not contain aluminum in excess of about 0.1% or silicon in excess of 0.02%: the tungsten-zirconium-nickel cathodes have a resistance to deformation which at cathode-operating temperatures is at least several times that of the reference-nickel cathodes.

What is claimed is:

1. An indirectly-heated cathode structure such as a sleeve or cup characterized by high strength at cathode-operating temperatures, sustained high level of emission and low sublimation and composed of an alloy containing zirconium in the range of from 0.05% to 1.5% by weight, tungsten in the range of from 1% to 5% by weight and the remainder essentially nickel.

2. An indirectly-heated cathode structure such as a sleeve or cup characterized by high strength at cathode-



operating temperatures, sustained high level of emission and negligible sublimation and interface impedance and composed of an alloy containing 0.05% to 1.5% zirconium; 2% to 4% tungsten; at least one of the activating agents aluminum and magnesium in the range of not more than 0.07% magnesium, 0.1% aluminum; and the balance essentially nickel with not more than about 0.02% silicon, 0.1% iron, 0.1% maganese, 0.08% carbon, 0.05% copper, as residuals.

3. An indirectly-heated cathode structure such as a sleeve or cup characterized by high strength at cathode-operating temperatures, sustained high level of emission and low sublimation and composed of an alloy containing about 0.1% zirconium, about 4% tungsten, and the balance essentially nickel with not more than about 0.02% silicon, 0.1% iron, 0.1% manganese, 0.08% carbon, 0.05% copper, as residuals.

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# CERTIFICATE OF CORRECTION

Patent No. 2,833,647 May 6, 1958

Richard L. Hoff et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the drawings, Sheet 3, legend to Fig. 3B, for "$I_s$(at 6.5 V) vs. Life" read -- $I_s$(at 4.5 V) vs. Life --.

Signed and sealed this 31st day of January 1961.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents