GLASS-TO-METAL SEALS

HENRY WIGGIN & COMPANY LIMITED WIGGIN STREET, BIRMINGHAM, 16

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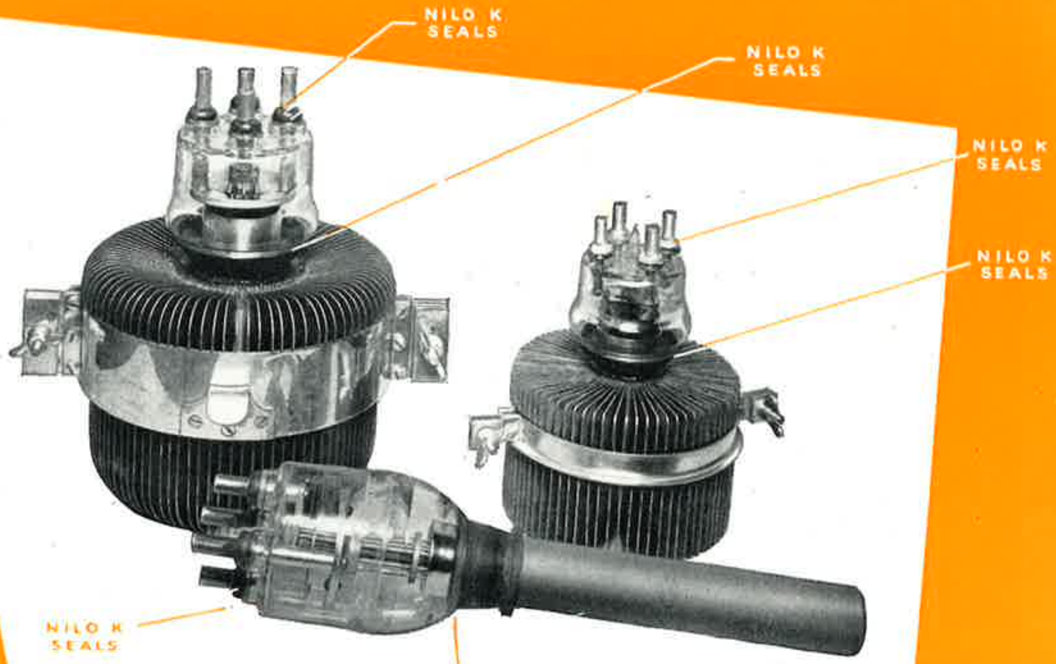


Fig. 1.—Modern transmitting valves employing Nilo K sealing metal.
(By courtesy of the Edison-Swan Electric Co. Ltd.)

GLASS-TO-METAL SEALS

THE fundamental work on the expansion characteristics of the alloys of iron and nickel was published by Guillaume fifty years ago. Various uses of these alloys have been made in the interim, notably for achieving effective glass-to-metal seals to complete electrical circuits between elements in a glass envelope and external terminals. The extent of the industries producing electric lamps, wireless valves, cathode ray tubes, X-ray tubes and other vacuum apparatus is a measure of the importance of this subject.

In order to understand the problems involved in producing a satisfactory glass-to-metal seal, it is necessary to consider the nature of glass in addition to certain properties common to both glasses and metals. Glass differs fundamentally from metal inasmuch as it does not solidify at a definite temperature nor in crystalline form. Fluid glass, in cooling, becomes viscous and as the viscosity increases with falling temperature, the glass reaches a stage where it takes on the hard brittle characteristics associated with this material at normal temperatures.

Before considering the problems due to thermal expansion, reference must be made to the question of adherence. It is vitally necessary to achieve good adherence between the glass and the metal to obtain an effective seal, and this may be promoted by using metallic oxide as a bond. It has been stated that any glass will "wet" and adhere to a clean gas-free metal if the surface of the metal is covered with an adherent layer of oxide and the temperature is raised to a point where this oxide dissolves in the glass. In the case of the comparatively small number of sealing metals used commercially, a metallic oxide produced under the right conditions, as determined by experience and indicated by colour, gives an effective bond in every case.

Because the expansion curves of the glasses and metals do not exactly coincide over the entire range from atmospheric temperature up the annealing point of the glass, stresses occur between the glass and the metal and must be taken into account in the design of the seal. It is usually desirable that the finished seal should be as free from stress as possible over a wide temperature range. This can be accomplished if the expansion curves of metal and glass match closely up to the glass transformation temperature, for instance, when iron-nickel-cobalt alloys, such as Nilo K, are sealed to certain boro-silicate glasses. It is possible to obtain a very good match without fulfilling this condition provided that the Curie temperature of the metal and the glass transformation temperature and the expansion co-

*We wish to express our appreciation to Messrs. J. E. Stanworth and W. J. Scott of The British Thomson-Houston Company, Limited, Rugby, and to Mr. P. E. Cane of The Edison-Swan Electric Company, Limited, Ponder's End, for their co-operation in helping us to prepare this booklet.

efficients are so related as to ensure low stress at any temperature. This is demonstrated by seals made with Nilo 475, a nickel-chromium-iron alloy, and lead glass such as B.T.H. C.12. Alternatively seals may be produced between metal and glass whose expansion curves differ substantially if means are provided for relieving stress as in the Housekeeper seal, or for keeping the tension component of the stress low. In some cases seals are designed to produce high residual compression of the glass.

TYPES OF SEALS

The majority of seals used to-day are needed to enable electric circuits to be completed, tube elements to be provided or for the supporting of tube parts. In many cases the functions are combined. Where windows or screens form part of the tube envelope, seals are again necessary. Specific requirements vary. Most seals require to be vacuum-tight but there is a growing demand for seals which have merely to be oil-tight. All have the common requirement that they must not crack under any conditions of service which they are likely to encounter. Internal seals using wire, ribbon or tube which is passed through or embedded in the glass comprise the most important group of seals. This is the usual type of seal employed in electric lamp bulbs and wireless valves.

The basic seal forms, into which the more complex seal shapes may be analysed, have been described by Scott[7] and are shown in Fig. 2. These are (1) metal facing glass (the flat seal—for zero curvature), (2) metal inside glass (the rod seal—for single curvature), (3) metal outside glass (the window seal—for single curvature). In considering the stresses at the junction occasioned by expansion mismatches in the case of these basic types, Scott makes the following comments.

Seal failures are never due to pure compression: the cause of failure is invariably due to the tension component of the stress. The stresses at the junction due to expansion mismatches in the case of the three basic types are given in Table 1, and from this it will be seen that, generally speaking, types M1 and M3 are the safest seals to use as they alone have no tension component of stress. Types M2 and G2 are considered safe enough provided the expansion mismatch is small. With a substantial degree of mismatch, they will both be unsafe, especially if the bond of the glass to metal is very weak. If the bond is so strong that on crushing the seal in a vice the glass cracks off leaving a thin skin of glass adhering to the wire and the glass shape is also correct, then even quite highly stressed type M2 rod seals can be safe. Window seals of type G3 and flat seals of type G1 are usually unreliable.

External seals, another widely used group, include types in which a strip of metal adheres to the edge of a glass insert, usually and preferably circular in shape, to avoid non-symmetrical stress distribution which makes the maintenance of vacuum difficult. Such seals, however, are being satisfactorily produced.

Fig. 2.—Diagram showing the three basic types of seals. *(By courtesy of The British Thomson-Houston Co. Ltd.)*

Tubular seals include the thin edge type, usually known as the "Housekeeper" seal, and the normal edge or "Kovar" seal. The thin edge seal is used where there is a wide difference in the thermal expansion characteristics of the glass and the metal, as is normally the case in large wireless transmitting valves. With these valves the conventional receiving valve design cannot be employed because the heat dissipation from the plate is too high and the plate is therefore made part of the valve envelope so that forced air or water cooling can be used. Copper was originally used on account of its high ductility, good thermal conductivity, low yield point and good adherence to glass but nickel-iron is now in common use. The basis of the seal developed by Housekeeper is that the metal must be so thin that it will yield before the glass. Although a valuable type, thin edge seals are mechanically weak, the metal tends to oxidize and become porous, while the movement through heating and cooling results in failures due to fatigue.

The normal edge tubular seal necessitates using a metal whose thermal expansion closely matches the glass. Iron-nickel-cobalt alloys are mainly used with special glasses for this purpose both here and in the United States. The thermal expansion coefficients of the Nilo Series of alloys are given in Table 2.

Edge seals, in which the edge of the metal is embedded in the glass, butt seals of various types and window seals are also frequently made with iron-nickel-cobalt alloy. These seals and those previously mentioned may be used in combination.

GLASSES

Glasses intended for glass-metal seals are loosely divided into two categories—soft glasses (soda lime and lead) worked in the range 800—1,000°C., and

TABLE 1.—STRESSES CAUSED BY EXPANSION MISMATCHES

		Metal contracts more than glass. Stress direction relative to junction.			Glass contracts more than metal. Stress direction relative to junction.	
		Perpendicular	Parallel		Perpendicular	Parallel
Flat seal	M1	Zero	Compression	G1	Zero	Tension
Rod Seal	M2	Tension	Compression	G2	Compression	Tension
Window seal	M3	Compression	Compression	G3	Tension	Tension

TABLE 2.—MEAN LINEAR COEFFICIENTS OF THERMAL EXPANSION OF NILO SERIES OF ALLOYS

Millionths per °C.	Nilo 36	Nilo 40	Nilo 42	Nilo 48	Nilo 50	Nilo 475	Nilo K
20–100	1.5	4.1	5.3	8.5	9.3	8.2	6.0
20–200	2.6	4.0	5.2	8.6	9.5	8.5	5.7
20–300	5.5	4.2	5.3	8.6	9.6	8.7	5.3
20–400	8.4	5.9	6.2	8.5	9.6	9.5	5.0
20–500	10.1	8.0	8.0	9.1	9.7	10.7	6.1

TABLE 3.—PROPERTIES OF SOME GLASSES USED FOR SEALING

Designation	B.T.H. C12	B.T.H. C19	B.T.H. C40	G.E.C. L.1	G.E.C. F.C.N.	G.E.C. X.8	Chance G.W.A.	Chance G.W.B.	Chance G.S.B.	P & T Kodial	P & T Normal (2 Blue lines)
Type	Lead	Soda-Lime-Silicate	Boro Silicate	Soft Lead	Boro Silicate	Soda-Lime-Silicate	Soda-Lime-Silicate	Soft Lead	Boro Silicate	Boro Silicate	Soda-Zinc-Silicate
Sealed to	Ni-Fe Nilo 475	Ni-Fe	Nilo K	Ni-Fe Dumet	Nilo K	Ni-Fe	Ni-Fe Dumet	Ni-Fe Dumet	Nilo K	Nilo K	Ni-Fe
Expansion Coefficient (20–350°C.) $\times 10^{-7}$	88.0	92.0	48	91.5	47.5	96.5	91.5	100	54.5	49	83
Temp. corresponding to Viscosity $= 10^4$ Poises	960	1025	—	960	—	1005	1030	—	—	—	—
,, ,, ,, $= 10^{7.6}$,,	630	710	710	630	—	700	710	—	710	—	—
,, ,, ,, $= 10^{12}$,,	465	550	535	465	560	555	550	440	500	—	—
,, ,, ,, $= 10^{13}$,,	435	530	505	435	530	540	530	410	450	—	—
Log. D.C. resistivity at 150°C.	12.3	8.4	11.5	12.4	11.7	7.9	—	—	—	—	—
Log. D.C. resistivity at 300°C.	8.6	5.7	8.1	8.6	8.3	5.3	—	—	—	—	—

hard glasses (boro-silicates) worked in the range 1,000—1,300°C. The thermal expansion coefficients of soft glasses in the 0—300°C. temperature range are from 80 to 105 by 10^{-7} per degree C., and those of the hard glasses range from 30 to 50 by 10^{-7}.

Certain properties of the various glasses are important in deciding whether they are suitable for glass-metal seals but the coefficient of thermal expansion is the only one of direct interest. It is often stated that as a rough gauge in choosing glasses to match a particular metal it is safe, in general, to say that the difference in expansion coefficient between glass and metal should not exceed 10 by 10^{-7} per degree C., although this need not be true for certain external seals and is never true for thin edge, thin edge tubular, internal thin walled tube and certain ribbon seals. The ideal relationship in the case where zero stress is required would be for the expansion curves for both glass and metal to coincide over the entire temperature range to the softening point of the glass but, as has been stated, this is never wholly achieved. Moreover, the proximity of the metal and glass expansion curves at any temperature is governed by the rate of heating or cooling of the seal and the stresses in the glass in such a seal may be varied, in many instances, by the thermal treatment to which the seal is subjected. It is difficult to estimate from purely thermal expansion measurements, what stresses will occur in the finished seal. Such stresses are best determined by photo-elastic methods.

The electrical properties of the glass are important. Seals may fail by puncture through the insulating glass, by electrical leakage over the surface of the glass or by electrolysis in the glass. Circuit characteristics, especially at the ultra high frequencies, are often dependent upon the power factor and dielectric constant of the glass used as insulation. Details of the particular use to which a glass-metal seal is to be put should be known before a choice of glass and metal is made. The properties of some glasses used for sealing are given in Table 3.

METALS

Until comparatively recently there was no one metal available at an economic price which could be used for a glass-to-metal seal. The widely different coefficients of expansion between the glasses produced and most metals involved stresses of such magnitude that cracking was almost inevitable.

In the earliest known examples of glass-to-metal seals the problem was overcome only by using fine gauge wire so that the expansion differences were minimized and stresses accordingly reduced. Seals to thick sections of metal could not be made. This was the position up to the latter part of the 19th century when it was found possible to produce a glass that could be sealed direct to platinum sheet or wire without great difficulty.

The problem of finding a low cost metal for sealing assumed great importance with the invention of the electric lamp, for it was obviously essential to have a reliable and simple method of bringing conducting leads through the glass bulb in order to produce these new lamps in quantity. Platinum wire was the only material available for this purpose but its cost rendered an alternative of prime importance. Guillaume's paper on the expansion characteristics of the nickel-iron alloys had been published and several compositions were used with varying degrees of success until it was found that nickel-iron alloy thinly coated with copper met the requirements admirably. This composite material, known as Dumet, is still widely used in electric lamp and radio valve production. As now produced it consists of any alloy of about 42 per cent nickel and 58 per cent iron in the form of wire coated with a copper sheath constituting about 25 per cent of the weight of the complete wire. Normally this material is used in the form of a three-piece lead, with a length of nickel or nickel-manganese alloy butt-welded to one end of a short length of Dumet and a length of copper wire butt-welded to the other end. The Dumet forms the seal when embedded in the glass, the nickel wire forms the internal connection to the elements of the lamp or tube, and the copper wire is soldered to the pin of the tube base. It is usual to seal both butt welds into the glass for a short distance (Fig. 3).

The development of Dumet only partially solved the problem of making satisfactory seals, for it can only be used in wire form and then not thicker than .04 in. due to residual stress at the junction with the glass caused by the slight mismatch in the expansion characteristics. A method of sealing metal sheets or tubes to glass had still to be found.

Radio transmitting valves were now being required in ever-increasing sizes. Platinum and Dumet existed for making connections to the internal electrodes, but the heat to be dissipated from electrodes running at temperatures up to 900°C. made a large bulb area necessary, which in turn placed a limit upon the size of valve that could be made.

This problem was overcome by the introduction in 1920 of the Housekeeper seal, to which reference has been made. As shown in Fig. 5 this made use of the earliest known principle of having the metal very thin at the point of junction with the glass. Copper tubing was used and this was tapered to a thin edge at the point where it was sealed to avoid over-straining the glass. The use of this type of seal made possible the design of a valve with an external anode which could be cooled with water or air blast (Fig. 6.) This was a very great step forward but the seal was rather difficult to produce.

Various alloys of chromium-iron and nickel-iron were soon developed together with special lead glasses having expansion coefficients of 90 by 10^{-7}. Tungsten and molybdenum found uses when hard glasses with suitable expansion characteristics had been developed: they are useful for internal seals involving extreme heat. But although these metals and alloys enabled good commercial mass-produced vacuum-tight seals to be made, all had certain disadvantages. The mechanical fragility of the Housekeeper seal has been mentioned. Tungsten, molybdenum and Dumet could only be used in wire form. Nickel-iron alloys require the use of glasses which soften at a low temperature and they suffer from the disadvantage that oxides of nickel and iron form on the surface when the alloy is heated during sealing. The presence of a large percentage of iron oxide in the surface layer gives a loose, scaly coating which, while wet readily by the glass, does not adhere well to the base metal. A method of overcoming this difficulty is to electrodeposit copper, 0.002 in. thick, on the alloy, after which the surface is borated and the seal made between the copper and the glass. Such seals are a bright red colour and are very strong. With all the foregoing combinations a considerable degree of skill and pre-sealing preparation was required to produce successful seals. This was briefly the commercial position at the outbreak of the war in 1939, but research work on the iron-nickel-cobalt alloys had been in progress for some years and their potential importance for glass-to-metal seals was already apparent.

At this point, the requirements which must be met by metals intended for making glass-to-metal seals might be indicated. They may be summarized as follows:—(1) The thermal expansion throughout a long temperature range, from below room temperature to the annealing point of glass, must be uniform. There must be no allotropic transformations accompanied by volume changes in the temperature range in which the glass is too rigid to release strains rapidly. (2) The metal must be stable

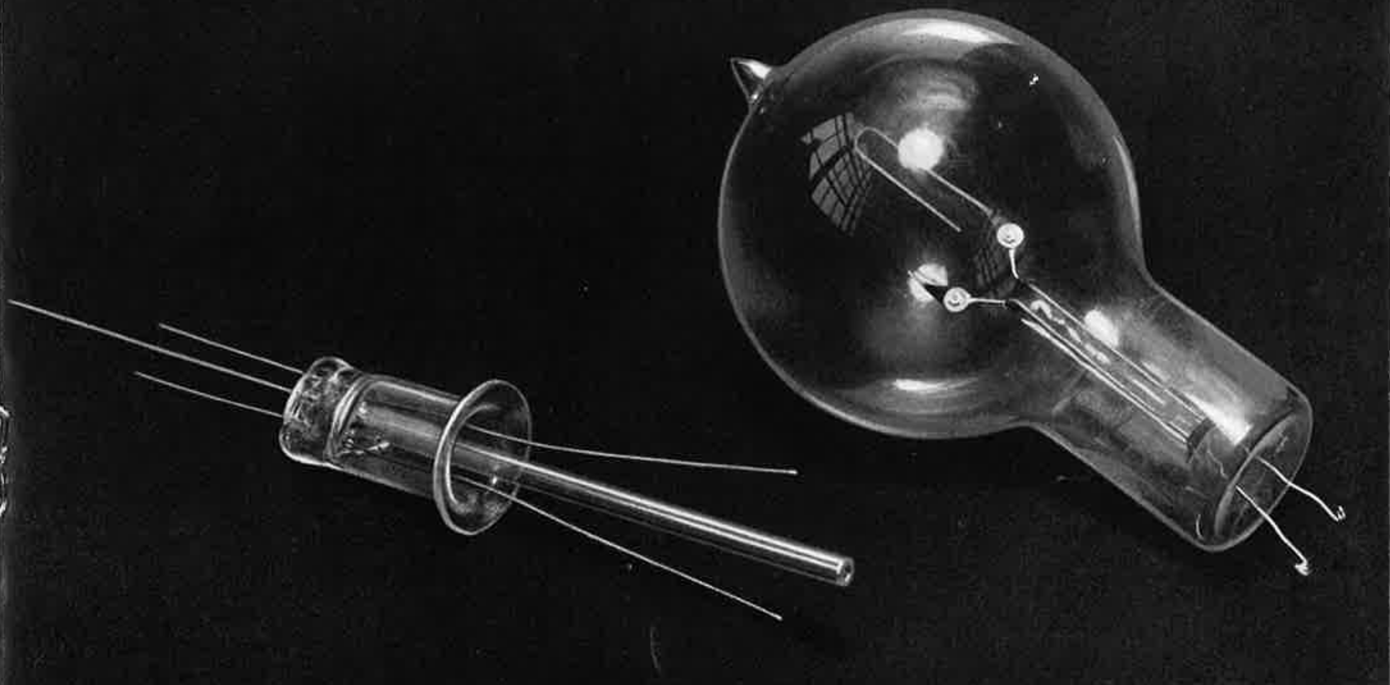


Fig. 3 (Left) Stem for modern lamp with composite lead wires of nickel, Dumet and copper. (Right) Old type lamp with long platinum seal wires.

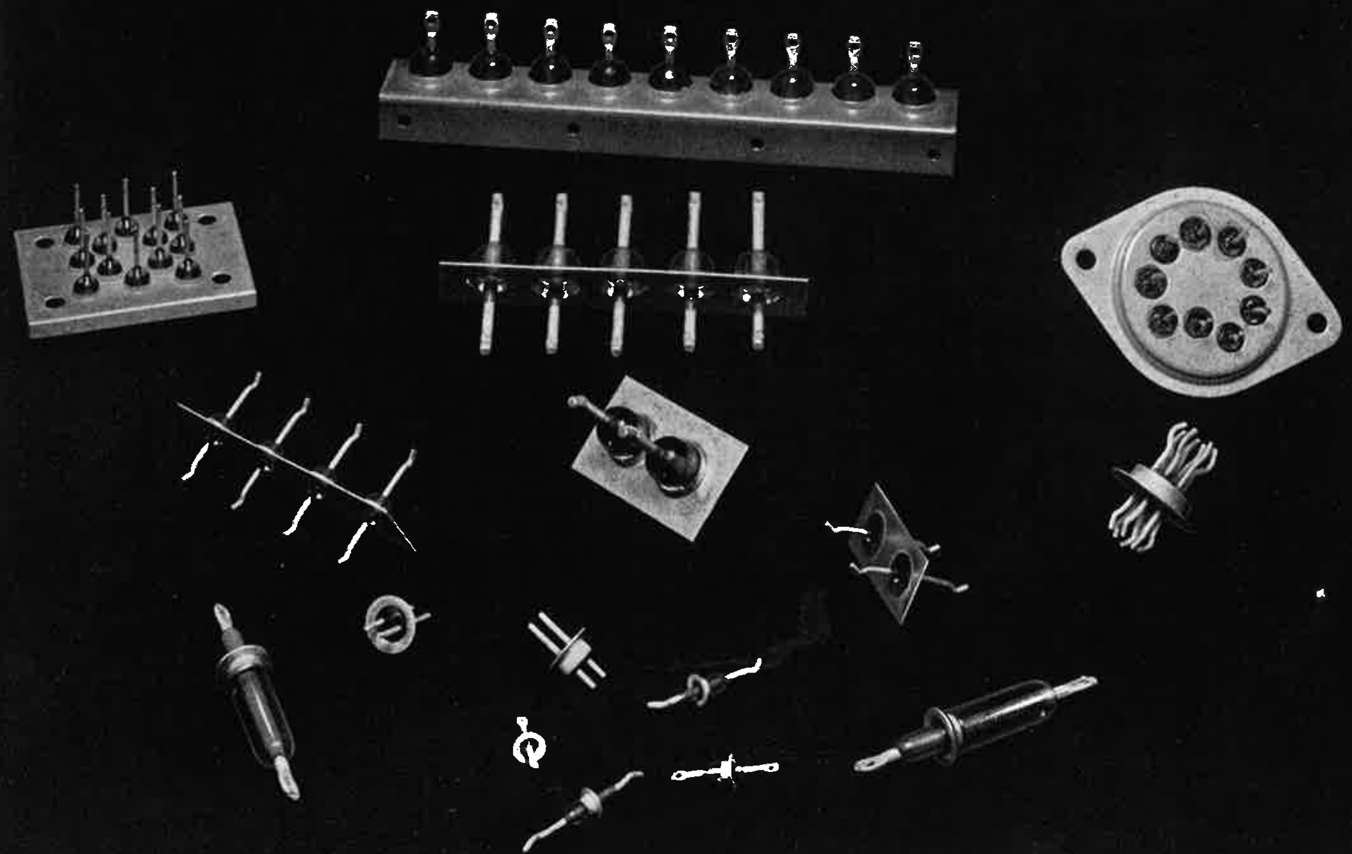


Fig. 4 Hermetic seals for transformers, coils, etc.
(By courtesy of the Edison-Swan Electric Co. Ltd.)

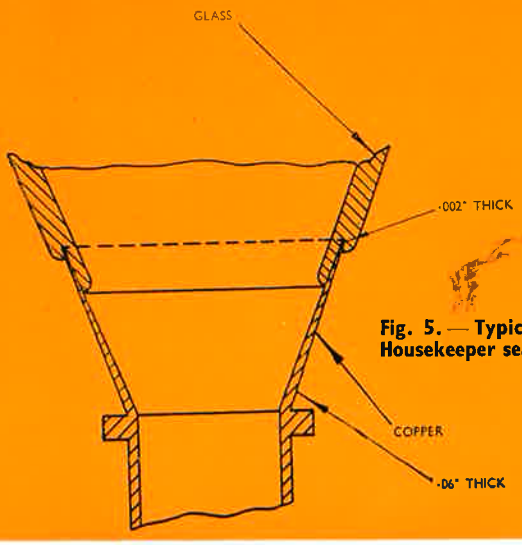


Fig. 5.—Typical Housekeeper seal.

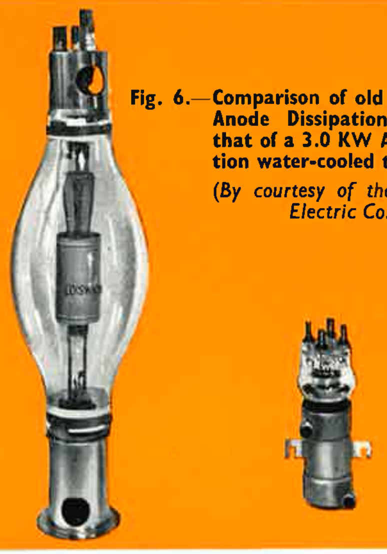


Fig. 6.—Comparison of old type 1.5 KW Anode Dissipation Valve with that of a 3.0 KW Anode Dissipation water-cooled type.

(By courtesy of the Edison-Swan Electric Co. Ltd.)

during the operation of making the seal. The metal must not be soft and must not burn at the sealing temperature. (3) The adhesion to glass must be good. An important factor in the case of oxide seals is that in every case there must be good adhesion between the metal and its oxide. The oxide formed must not be flaky. (4) In certain cases it is an advantage if the oxide formed has a low electrical resistance to permit welding or soldering to other metals. (5) The amount of gas given off by the metal must be small. (6) The cost of the metal must be economic: the great increase in the uses of glass-to-metal seals has made this factor of more importance than in earlier days.

The above requirements have been met by the development of the iron-nickel-cobalt alloys, now in widespread use. These alloys, which are used for sealing to boro-silicate glasses resulted from work by Scott[2] who investigated the thermal expansion characteristics of these ternary alloys in 1930. Hull and Burger[3], working independently and unaware of Scott's investigation, obtained similar results. These alloys have expansion curves that can match closely with those of certain hard glasses, up to the annealing range of the glass.

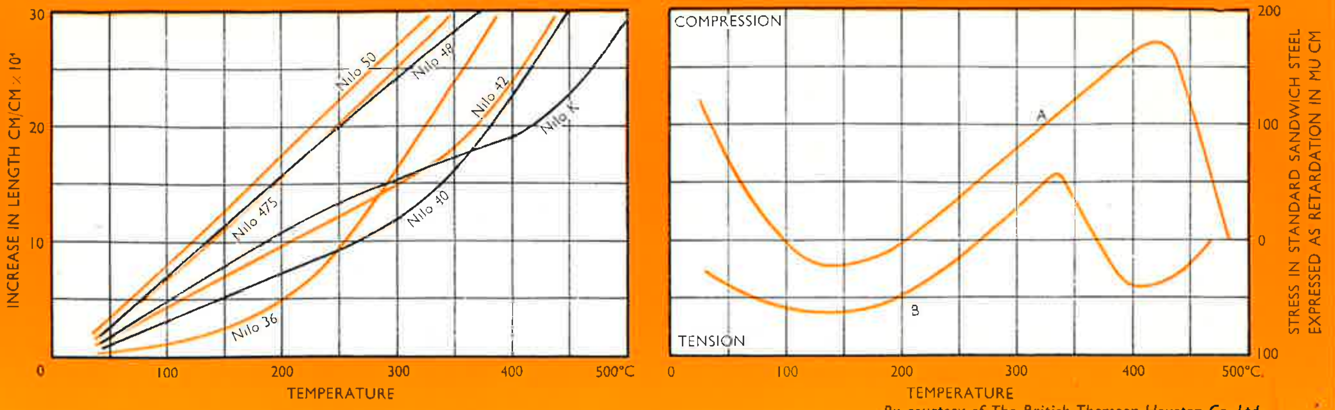
All compositions of the iron-nickel-cobalt alloys contain 46 per cent. nickel plus cobalt. The original composition specified was 53 per cent iron, 28 per cent nickel and 18 per cent cobalt, but Hull, Burger and Navias[4] later claimed that an alloy containing 54 per cent iron, 31 per cent nickel and 15 per cent cobalt was more stable than the first mentioned composition. This iron-nickel-cobalt alloy is polymorphic and has an alpha or body-centred form, which has a high coefficient of expansion and a gamma or face-centred cubic form, which has a low coefficient of expansion. For the temperature range 25—450°C. the coefficient of the gamma phase is 47 by 10^{-7}. The transformation to the alpha phase does not occur at temperatures above 80°C. The gamma phase can be restored by a short anneal. Oxidation occurs at about 650°C.

The commercial development of the iron-nickel-cobalt alloys was given great impetus during the war by the spread of hostilities to the Tropics, where a paramount requirement was the protection of radio and associated equipment against jungle conditions. The obvious solution was to enclose components in hermetically sealed cans, which in turn required a vacuum-tight insulated bush to bring out the connections. Such a bush had to be easy to mass-produce, mechanically and electrically robust, capable of withstanding considerable variations of pressure, both internal and external, and easy to join to the can containing the component. The first seals produced for this purpose were made in the United States and consisted of an outer metal eyelet through which was passed a wire, the space between the two being filled with a glass which provided both the vacuum-tight seal and the insulation. The manufacture of similar seals was begun in this country to meet the requirements of British manufacturers, iron-nickel-cobalt alloy (Nilo K) being used in conjunction with B.T.H. C40 glass for the purpose. The expansion characteristics of the two materials, which can be seen from the curves (Fig. 7) agree very closely up to the softening point of the glass. The results obtained showed that this combination produced seals vastly superior to those made with materials previously available, and large quantities of small seals capable of handling up to 20 kV and 10 amps. were produced. The success attained rapidly led to the development of a wide variety of single and multiple seals covering every conceivable requirement of the radio industry (Fig. 4).

The ease with which such small metal-glass seals could be produced led to their use in other fields ; furthermore there are few limits to the sizes and varieties of seal that can be made. Where the resistance of the iron-nickel-cobalt alloy may cause high voltage drop, copper rods can be passed through fabricated Nilo K cups, the two being brazed together and the Nilo K then joined to the glass (Fig. 9). Seals capable of handling 1,000 amps. present no difficulties.

Another modification to the nickel-iron alloys for glass-to-metal seals is the addition of chromium in amounts up to about 6 per cent. Although this increases the expansion coefficient the effect of chromium is beneficial as it produces an oxide film which adheres very well both to the parent metal and to the glass.

The composition containing 47 per cent nickel, 5 per cent chromium, balance iron is now sold in this country under the trade name of Nilo 475 and seals made with B.T.H. C.12 glass and this alloy show very low stress values.



By courtesy of The British Thomson-Houston Co. Ltd.

Fig. 7.—The curves on the left show the thermal expansion of the iron-nickel alloys of the Nilo series in the fully annealed condition. On the right are shown the stress—temperature curves for Nilo K with C.40 glass (A) and Nilo 475 with C.12 (B) glass.

MECHANISM OF SEALING

The operations involved in making glass-to-metal seals are fairly simple in the case of wire seals, which are usually below 2.5 mm. diameter. The production of the larger cylindrical seals, as used on wireless transmitting valves, is more difficult and necessitates different and more elaborate methods. In both cases, however, the glass and metal must be brought into intimate contact at a temperature high enough for the glass to be fluid. The temperature of the metal generally equals or exceeds that of the glass.

Oxide forms on all sealing metals other than perhaps the noble metals, owing to the heating needed to soften the glass. Some authorities claim an oxide film is essential to obtain a gas-tight seal, but this is disputed. The colour of the film formed offers a useful indication that a good seal has been obtained. In the case of molybdenum a chocolate brown colour denotes the formation of a suitable oxide. Copper coated nickel-iron alloy gives a bright red. Tungsten is usually a pale straw. Pre-beading technique for Nilo K will produce a colour which may vary between grey and chocolate.

Nilo K has great advantages over other sealing metals in that no great skill is required either in preparing the seal or in its actual manufacture. De-gassing is necessary before use, and can be carried out by heating up to at least 950°C. for about 20 minutes in an atmosphere of wet hydrogen.

Fabrication of the metal presents few difficulties. Spinning is practicable, but not easy and frequent annealings are necessary. In the case of a 1 mm. Nilo K sheet spun to a depth of $\frac{3}{4}$ in. with a diameter of 30 mm. Long[8] stated that three anneals were needed during the operation and this number could not be reduced. Brazing or soldering to other metals involves no trouble if the areas to be joined are free from rough edges and grease of any sort. Some typical seal designs are shown in Fig. 8.

The sealing of the glass to the metal is carried out by conventional methods. Absolute cleanliness is important and is best achieved by pickling in a mixture of 10 per cent hydrochloric acid and 10 per cent nitric acid by weight, heated to about 70°C. Following contact for a sufficient time to remove the surface contamination, the metal should be washed in clean water, rinsed in lime solution to neutralize remaining acid and carefully protected as scratches are possible leakage points.

The pre-beading technique normally used with tungsten and molybdenum is not necessary with Nilo K. Joining may be effected by rotating the glass and metal components in a glass-working lathe or by holding the components in a jig while the glass parts are heated by gas flames in the conventional manner and when molten pressed on to the metal with a graphite paddle. Alternatively the fabricated metal parts may be heated with a small induction furnace and pressed into the glass. When using this method, over-oxidation of the seal must be prevented either by enclosing both glass and metal parts in an inert atmosphere, or the glass parts must be pre-heated to such a degree that the metal parts are quickly covered with the glass before excessive oxidation can result.

For making seals with Nilo 475, if pickling is found necessary in order to obtain a clean surface, it should be carried out in a cold solution of 50 per cent concentrated nitric acid with 3-5 per cent hydrofluoric acid. To prepare the metal for making a seal it should be heated at a temperature of 1,100—1,150°C. in an atmosphere of wet hydrogen in order to degas the wire and produce a suitable oxide surface. It is usually held at temperature for a period between 20 minutes and 1-hour. The water content of hydrogen should be controlled to ensure that an even adherent film of chromic oxide is formed on the surface. Alternatively the metal may be degassed in dry hydrogen and then oxidised in an open flame.

Platinum and platinum alloy wires also require careful surface preparation to ensure absolute cleanliness. Microscopic examination is recommended. Damage can be done to these wires during welding to the copper leads and nickel supports, and smooth-faced tweezers should be used to hold them in position. A little borax flux is used with the copper : the nickel joint is not fluxed.

Nickel-iron wires are joined to "normal" glass in the construction of mercury switches. Some switches of various capacities are shown on the last page.

Copper clad nickel-iron wire is widely used with soft glasses. It has a radial thermal expansion coefficient of approximately 90 by 10^{-7}. Wires are usually borated by the suppliers. The current carrying capacity of these wires is limited to about 20 amps., the maximum diameter of the composite wire being about 1 mm.

The difficulties experienced in producing large seals have led to the development of very different methods from the foregoing. Such seals are required for large water-cooled anodes of transmitting valves (Fig. 1), anodes of X-ray tubes and metal-centre bodies of X-ray tubes.

Copper was once invariably used for water-cooled anodes, the end being machined to a knife edge and a Housekeeper seal made thereto. Present practice tends more to the use of an intermediate iron-nickel-cobalt alloy seal between the copper and the glass.

Large seals (up to 3 in. diameter) in iron-nickel-cobalt are made direct to the alloy, and such seals are regularly made in metal up to 1 mm. in thickness. This is not the upper limit in thickness; seals on heavier gauge metal are almost certainly possible except in the case of seals where the metal is embedded in the glass, in which case tapering of the metal would be necessary. Where the seal is made on one side of the metal only, the question of thickness is not important. The width of the sealed area is normally about 2 mm.

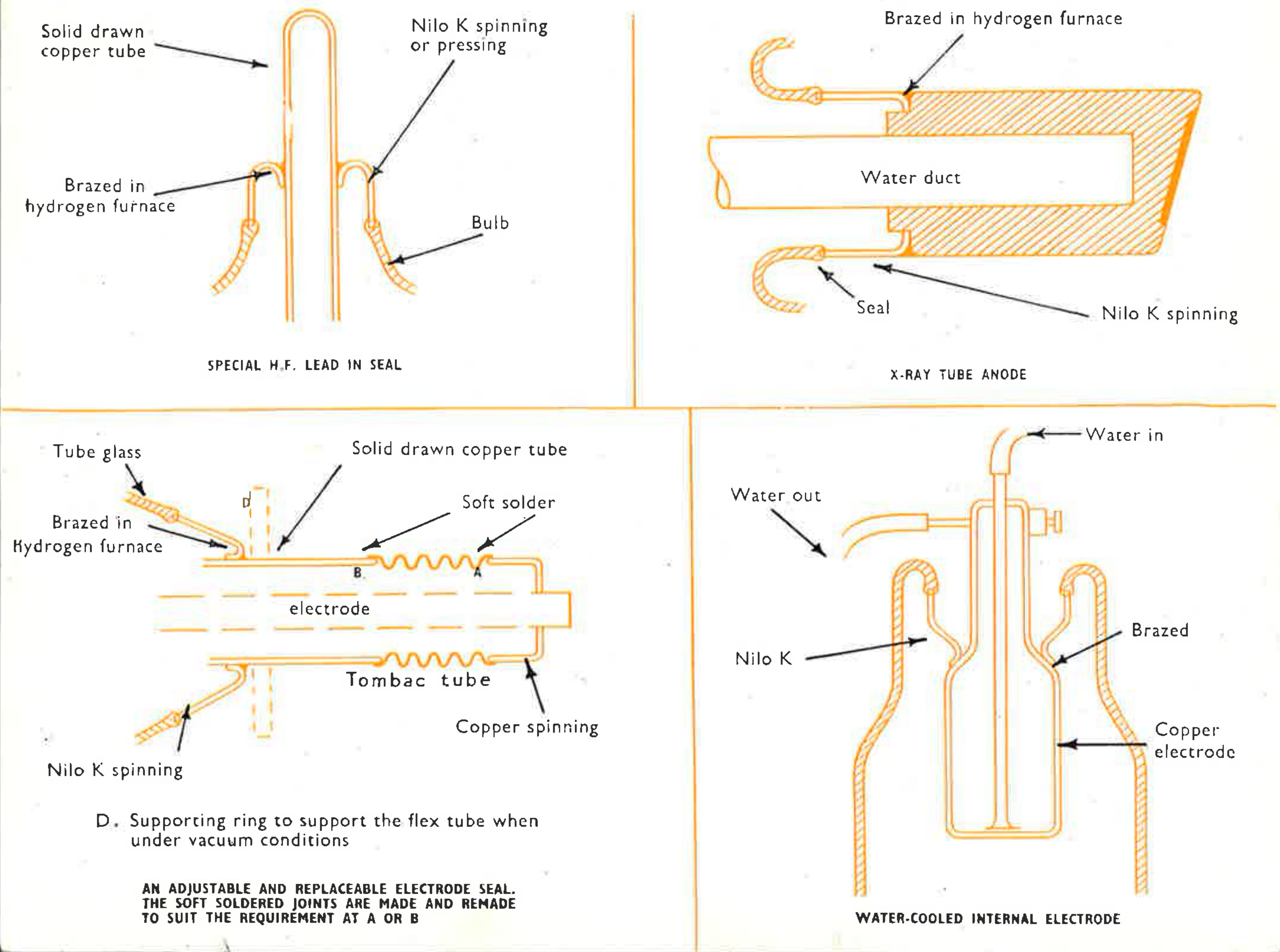
Seals with diameters up to at least 5 in. have been successfully made with iron-nickel-cobalt alloy (Nilo K). Both spinnings and pressings are used, the former being bonded to the electrodes to form the complete unit. Copper brazing is a suitable method for obtaining a satisfactory bond, but metals other than copper may be used. Pure gold is a satisfactory brazing medium. Silver soldering must be used with caution as it tends to cause intergranular penetration. Welding is a suitable method but cannot be used with copper.

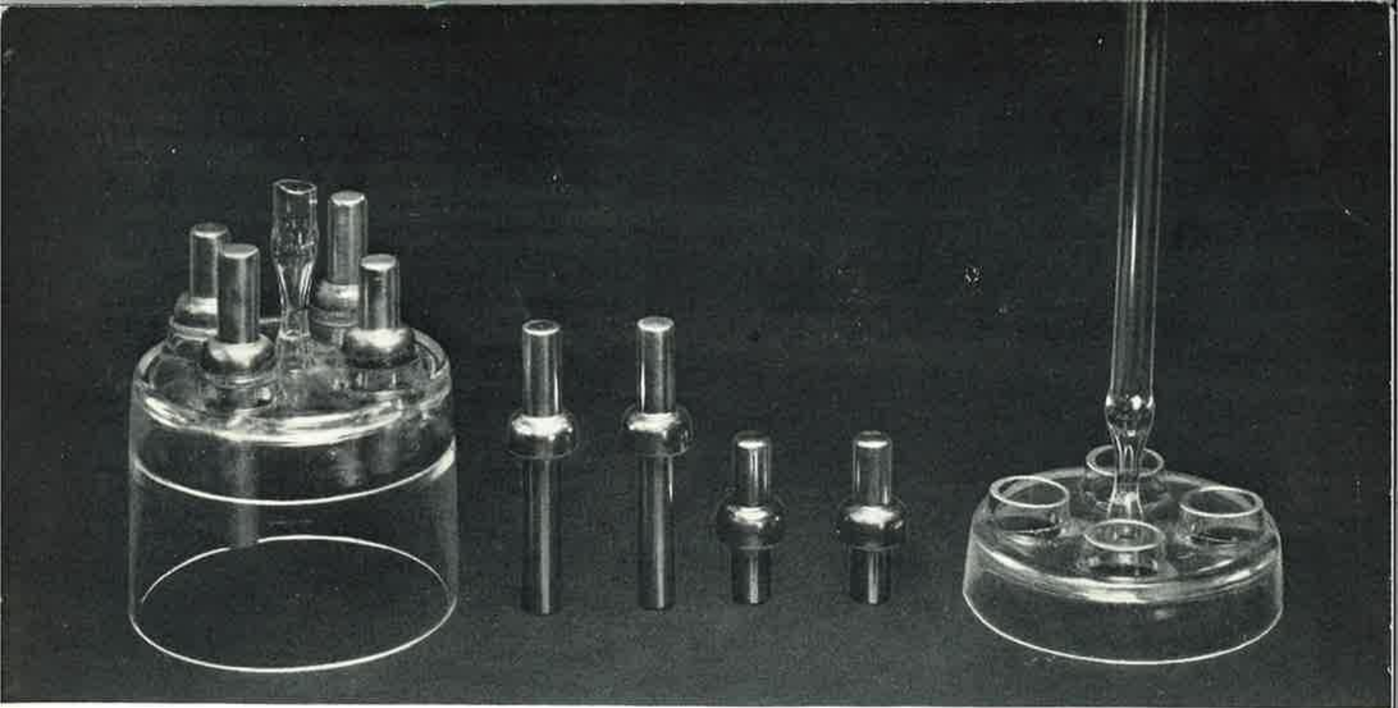
Gas-free metal with surfaces free from contamination or defects is normally employed for sealing purposes. An exception to this rule occurs with a particular type of glass pinch on miniature type radio valves, for which a nickel wire of very gassy quality is supplied. The use of annealed material is essential and, in particular, spun sections must be well annealed prior to sealing to glass.

The quality of a seal is judged largely by its colour and appearance. There should be no sign of bubbles which can be caused by the presence of grease or other contamination on the surface of the metal. If the correct colour of the oxide appears the seal may be judged satisfactory. A bright and clean surface on the metal indicates that insufficient oxidation has taken place prior to the glass flowing on the metal, so that the seal, although vacuum-tight, may lack mechanical strength. A black seal denotes over-oxidation so that the seal will be mechanically strong but inclined to porosity.

Seals made in the correct manner are extremely robust and where, as in the case of Nilo K, the thermal expansion characteristics are closely similar, they will bear large thermal shocks without harm.

Fig. 8.—Some typical seal designs. *(By courtesy of Newton & Wright Ltd.)*





(By courtesy of Edison-Swan Electric Co. Ltd.)

Fig. 9.—Component parts of a large transmitting valve showing Nilo K cups brazed to copper rods.

STRESSES

It is difficult to estimate the stresses in many types of glass-to-metal seals, because corrections are necessary for differential cooling of glass and metal, viscous flow of glass during cooling and changes in properties of glass through heat-treatment, while the exact temperature of retention of strain in glass can greatly modify the results obtained theoretically. Direct polariscope determinations of strain are the most reliable.

The theoretical relations between stresses, however, are valuable in a stress analysis. For example, in an internal seal the radial stress is tensile when the expansion of the metal is greater than that of the glass. This is the stress most likely to cause failure since glass is much weaker in tension than in compression. If, on the other hand, the radial stress is compressive then the tangential and axial stresses are tensile. As the tangential stress is always greater than the axial, the former becomes the limiting stress. Radial cracks result from tangential tension at the wire-glass interface.

Nearly all annealing of seals is a compromise between desirable compression and dangerous tension. It does no good to produce a high radial compression in an internal seal, for instance, in order to prevent "stripped seals," if failure results through radial cracks caused by tangential tension. Conversely, strong tangential compression can mean failure through radial tension.

Stress at room temperature is not always a safe criterion for allowable stress. Stresses at the operating temperature of a seal may be much higher because of the divergence of the glass and metal expansion curve. Passage of electric current may also cause resistance heating of the wires in a seal. Annealing should, therefore, be designed for each particular application and the use to which the seal is to be put should be considered. In general, avoidance of sharply concentrated strain is more important than reduction of diffuse or broadly distributed strain of fairly high magnitude.

Electrolysis is important not only because of energy loss in the electrical circuit but because continued electrolysis leads eventually to tube failure either through leakage at the glass-metal interface or by cracking of the glass. Normally the temperature is much more important than voltage gradient. As the temperature increases, smaller and smaller voltage gradients are sufficient to cause failure. Electrolysis in glass is ionic and the transfer of positive ions to the negative wire can cause cracking of the glass because the composition, and consequently the expansion, changes.

In many electron tubes, electrolysis between a wire and the surface of the stem carrying the wire can take place because the glass surface becomes negatively charged through electron bombardment from the cathode or secondary bombardment from other elements in the tube.

A great deal of work on the subject of stresses in glass-to-metal seals has been carried out in recent years and the extent of the knowledge now available is probably far greater than many producers and users of seals appreciate.

REFERENCES

1. Housekeeper, W. G., *Jnl. Amer. Inst. Elec. Eng.*, 1923, Vol. 42, p. 954.
2. Scott, H., *Trans. Amer. Inst. Mech. Eng.* (*Inst. of Metals Div.*), 1930, pp. 506-38.
3. Hull, A. W., and Burger, E. E., *Physics*, 1934, Vol. 5, p. 384.
4. Hull, A. W., Burger, E. E., and Navias, L., *Jnl. Appl. Physics*, 1941, Vol. 12, pp. 698-707.
5. Redston, G. D., and Stanworth, J. E., *Jnl. Soc. Glass Technology*, 1945, Vol. 29, No. 132, p. 48.
6. Redston, G. D., and Stanworth, J. E., *Jnl. Soc. Glass Technology*, 1946, Vol. 30, No. 139, p. 20.
7. Scott, W. J., *Jnl. Sci. Inst.*, 1946, Vol. 19, p. 207.
8. Long, A. G., *Trans. Soc. Glass Technology*, 1946, Vol. 30, pp. 67-89.
9. Stanworth J. E., *Jnl. Scientific Instruments*, 1950, Vol. 27, pp. 282-4.
10. Partridge, J. H., *Glass to Metal Seals*, published by The Society of Glass Technology.

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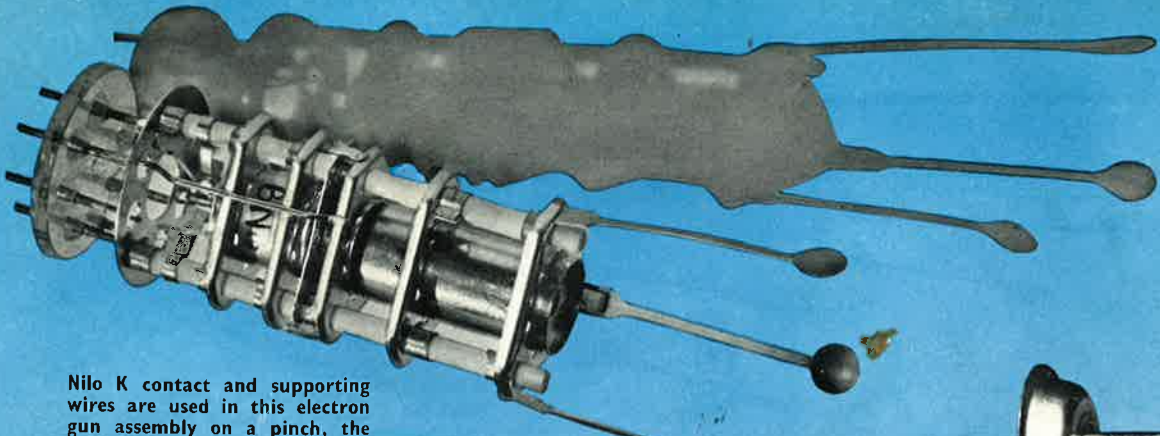
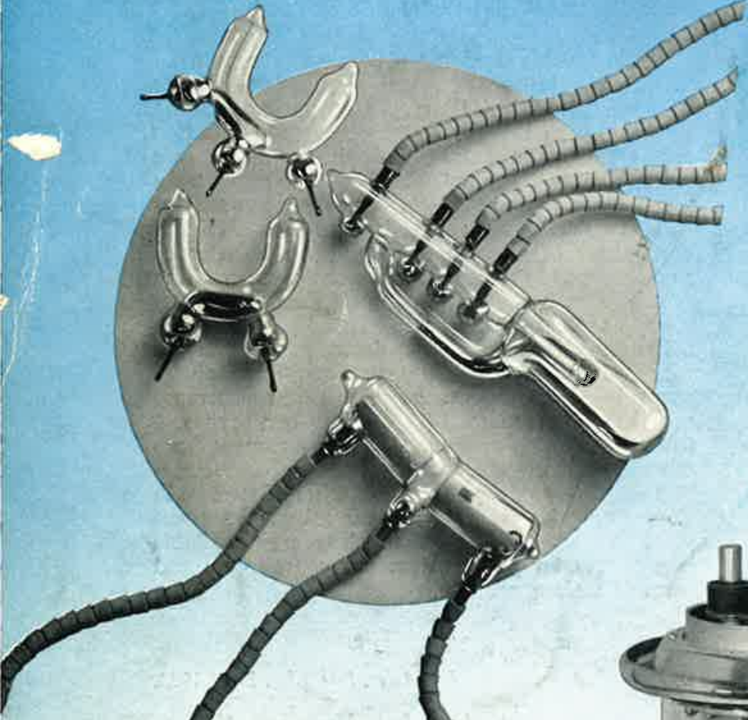


Nilo K contact and supporting wires are used in this electron gun assembly on a pinch, the seals being made to a boro-silicate glass, which will be joined to the Pyrex envelope of a cathode ray tube.

(By courtesy of E.M.I. Ltd.)

Flush button contact for use with some types of special cathode ray tubes. The cup is of Nilo K.

(By courtesy of E.M.I. Ltd.)



Typical mercury switches with nickel-iron seals made to " normal " glass.

(By courtesy of I.A.C. Limited.)

Two types of wireless transmitting valve in which Nilo K is used for the glass-metal seal.

(By courtesy of Marconi's Wireless Telegraph Company, Limited.)