

June 25, 1946.

R. S. OHL

2,402,663

THERMOELECTRIC DEVICE

Filed April 11, 1942

3 Sheets-Sheet 1

FIG. 1

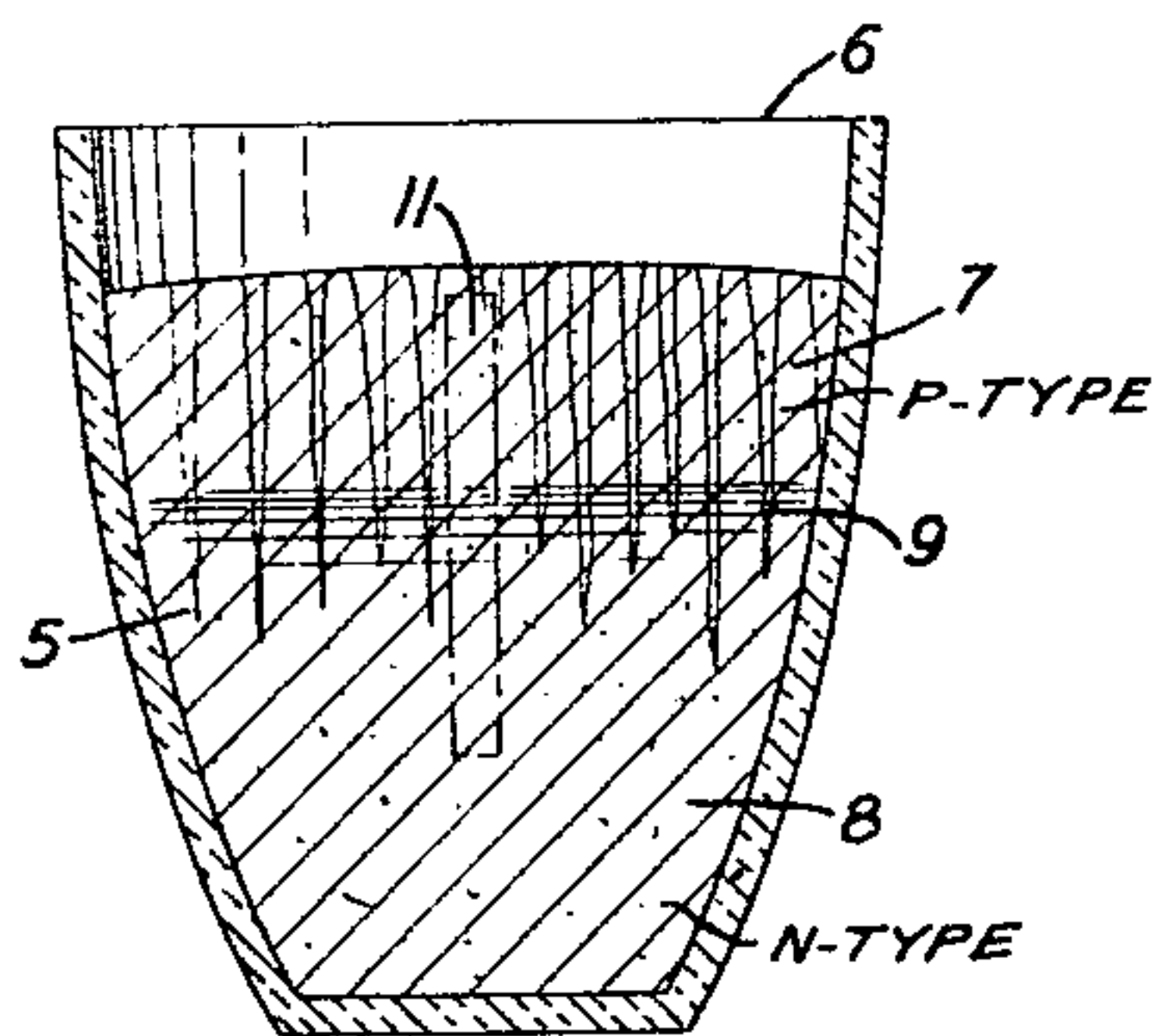


FIG. 2

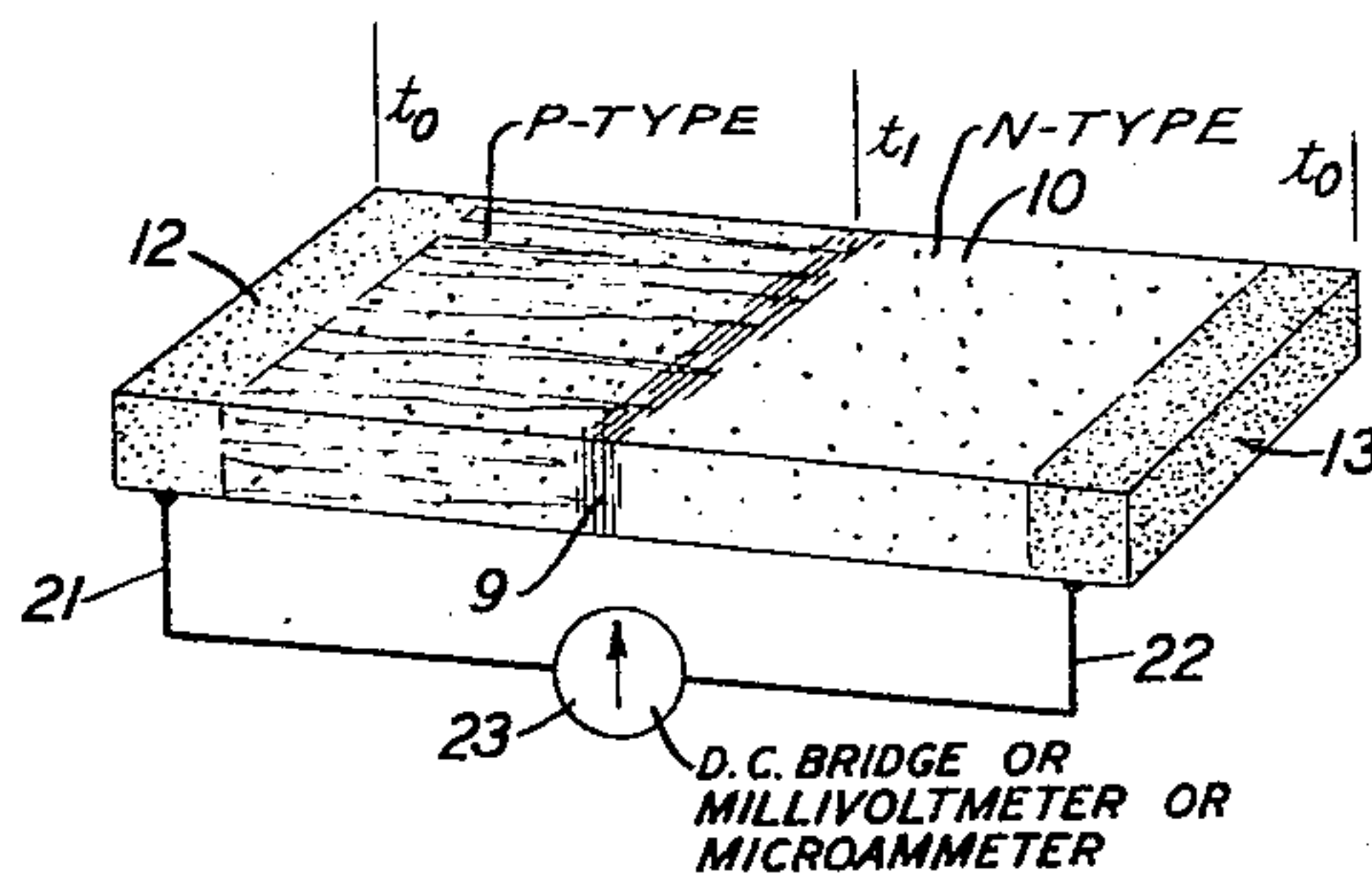


FIG. 3

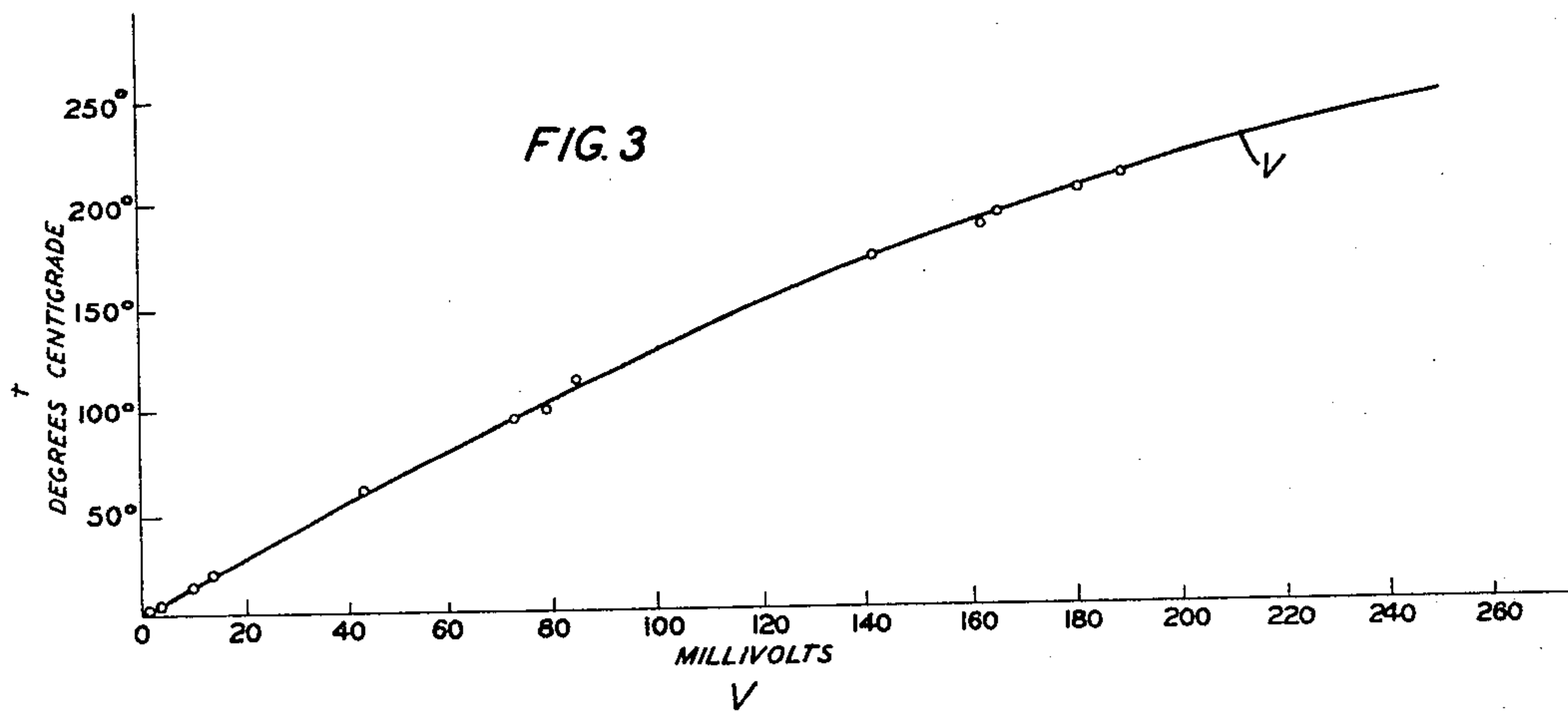
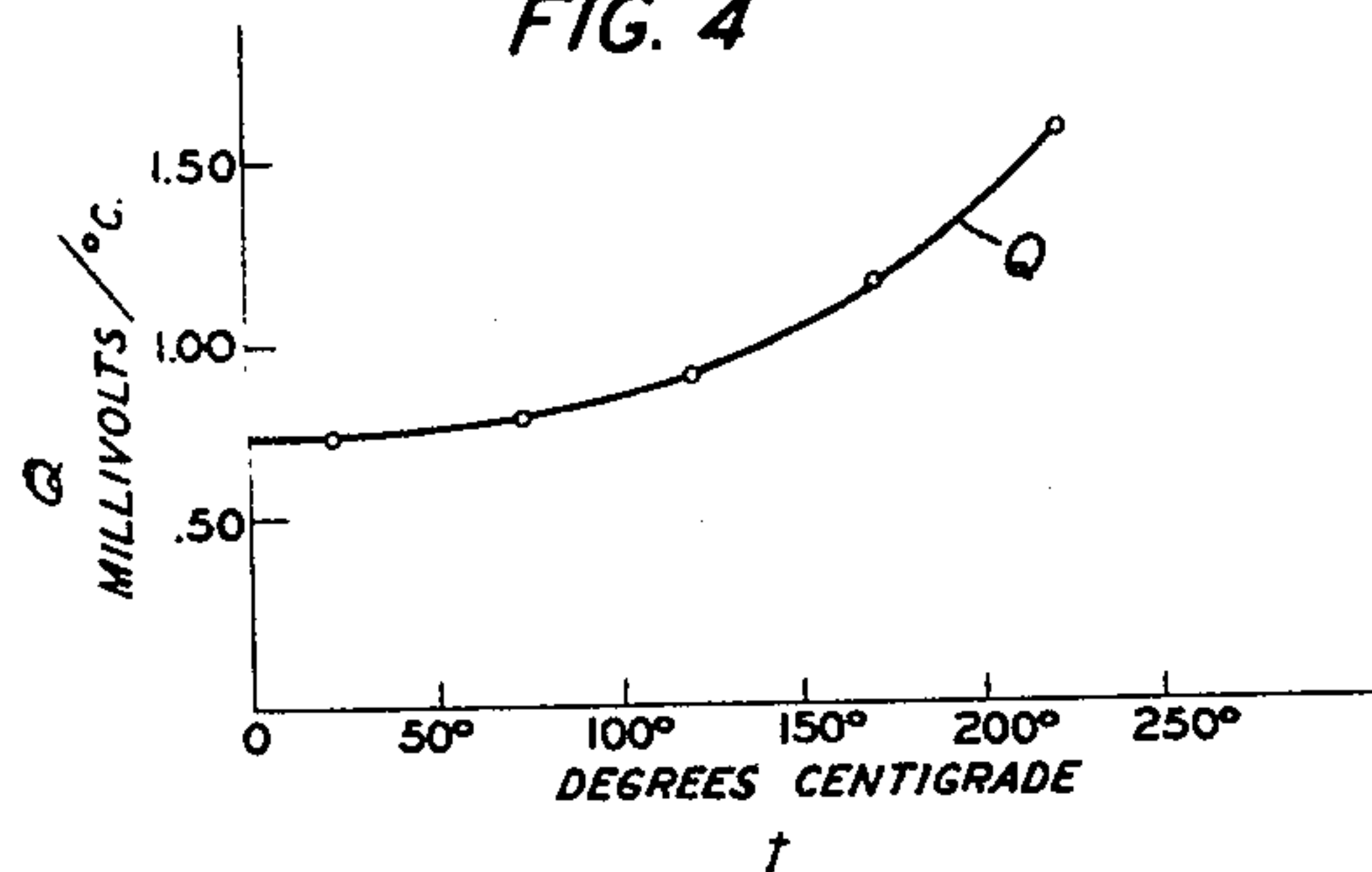


FIG. 4



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FIG. 5

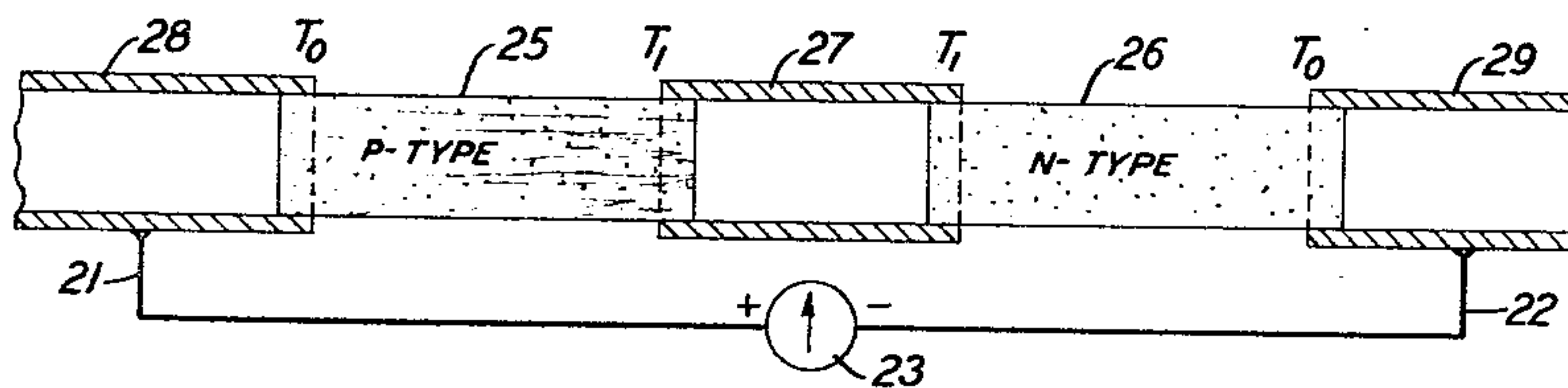


FIG. 6

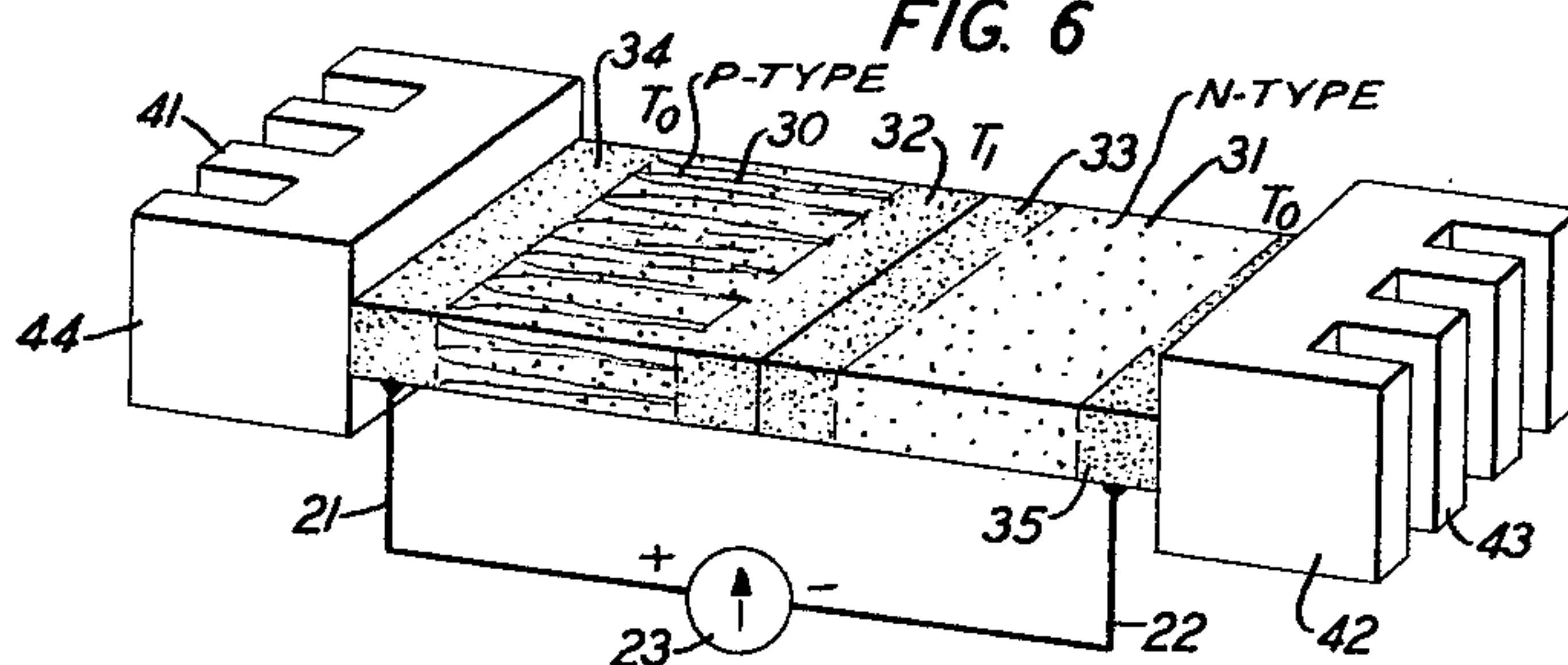
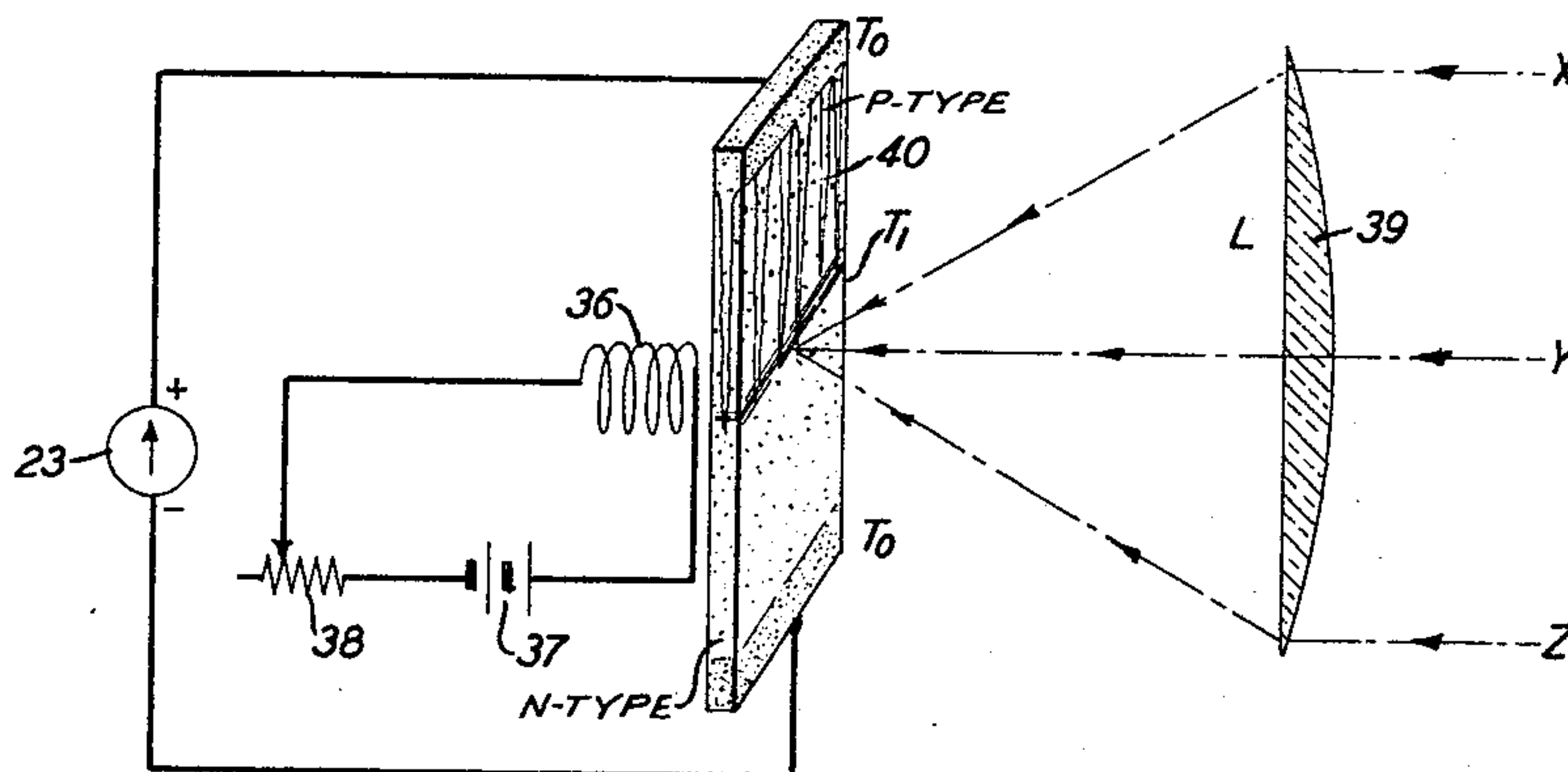


FIG. 7



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FIG. 8

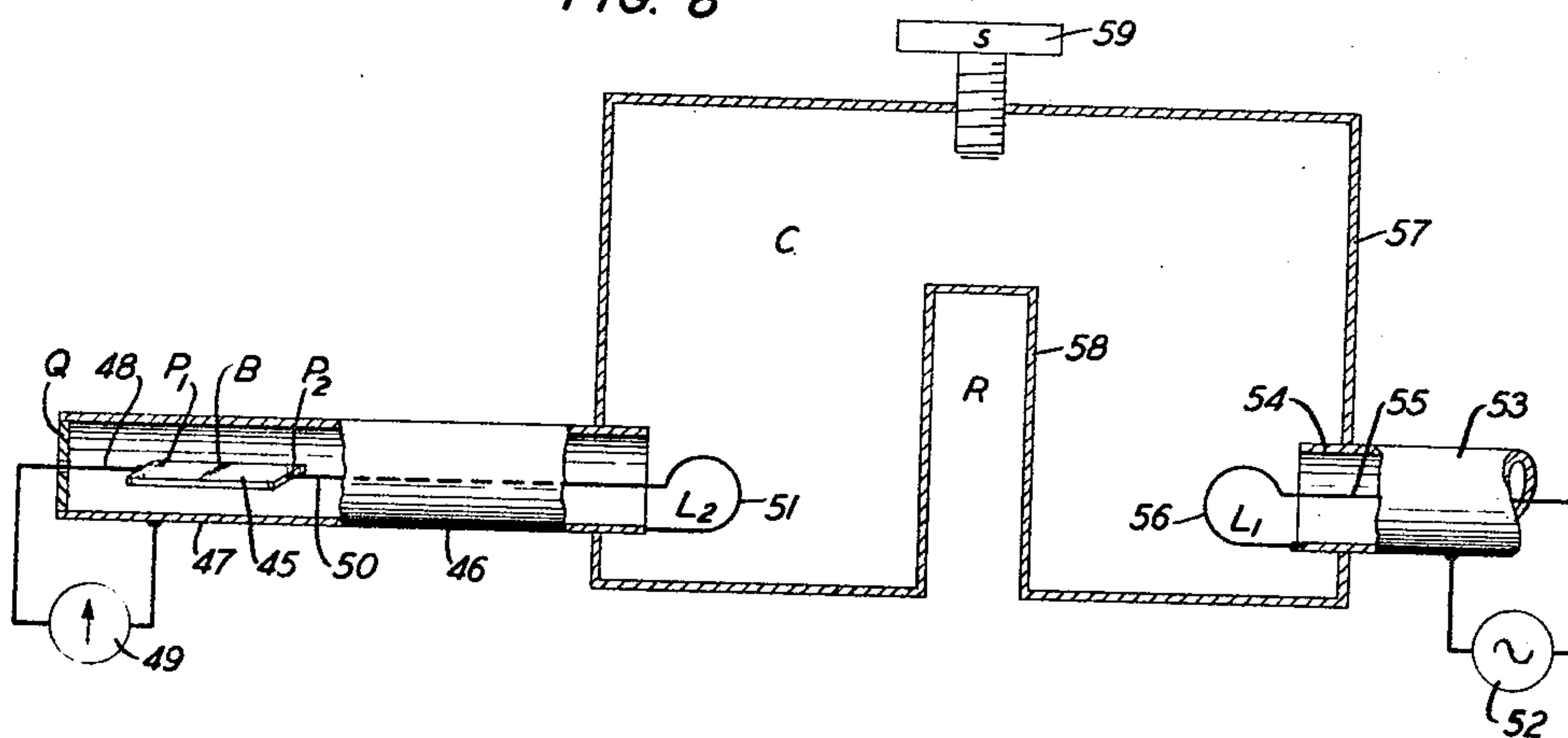
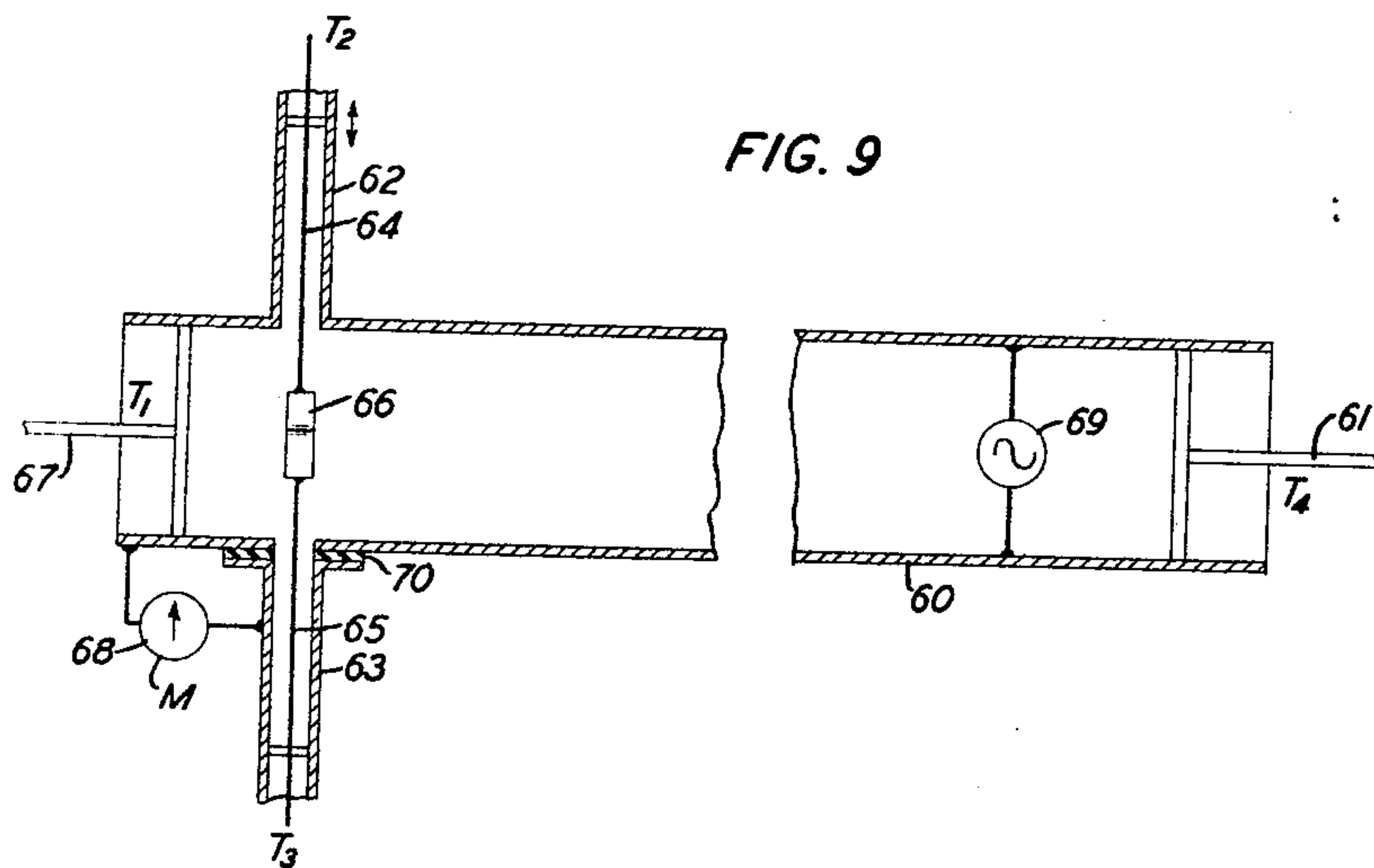


FIG. 9



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UNITED STATES PATENT OFFICE

2,402,663

THERMOELECTRIC DEVICE

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Application April 11, 1942, Serial No. 438,645

10 Claims. (Cl. 136—5)

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This invention relates to thermoelectric devices and more particularly to thermoelectric devices comprising fused silicon of high purity.

An object of the invention is to provide an improved thermoelectric device.

Another object of the invention is to provide an improved method of making thermoelectric devices of fused silicon of high purity.

In an example of practice illustrative of this invention a thermoelectric device is formed of a portion of a silicon ingot which is provided with conductive terminals. The ingot is produced by fusing metallic silicon in powdered form in a silica (SiO_2) crucible in an electric furnace and slowly cooling the fused material until it solidifies and for a period of time thereafter. The powdered metallic silicon used is of a high degree of purity, say, 99 per cent or higher. Certain material which has proved very satisfactory has a purity of approximately 99.85 per cent. Ingots which are suitable for the production of thermoelectric devices possess a characteristic structure which is visible when the surface is suitably prepared in vertical section. The upper portion of the ingot exhibits a columnar crystalline structure, while the lower portion is non-columnar and across the ingot in the lower section of the columnar portion is a striated zone. This striated zone has the characteristics of a barrier zone or barrier layer and is conveniently designated simply a so-called "barrier." The columnar portion of the ingot comprises P-type silicon, so-called because it develops a positive thermoelectric potential with respect to an attached copper electrode. The non-columnar portion of the ingot comprises N-type silicon, so-called because it develops a negative thermoelectric potential with respect to an attached copper electrode. The improved thermoelectric devices of this invention comprise a portion of P-type silicon and a portion of N-type silicon intimately joined together and provided with terminal contacts at portions of the surface removed from such intimate junction. The intimate junction may consist of the barrier zone or barrier layer of the original ingot or it may consist of other conductive metals intimately joined to the pieces of P-type and N-type silicon. For example, pieces of P-type and N-type silicon may have small portions of their surfaces individually plated with rhodium, nickel or other suitable metal and these plated surfaces soldered to one another or to a connecting piece of metal, such as a copper or nickel rod or tube. An advantage of the use of the barrier layer is that it

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may be heated to a much higher temperature than ordinary soldered connections. The pieces of silicon may be in the form of slabs, square rods, cylinders or any other suitable shape. Low resistance conductive terminals are secured to the pieces of silicon on surface portions removed from the intimate junction by plating such portions with rhodium or nickel. These portions must be removed far enough from the intimate junction to permit the maintaining of an appreciable temperature difference between the intimate junction and these terminals. Circuit connections may be made to the terminals either by pressure, friction or soldering. Since the terminals are ordinarily kept relatively cool during use, soldered connections are entirely satisfactory and have the advantage of being quite stable.

This invention will now be described more in detail having reference to the accompanying drawings:

Fig. 1 shows in cross section an ingot of fused silicon within a silica crucible from which ingot material suitable for thermoelectric devices may be cut;

Fig. 2 illustrates a thermoelectric device according to this invention which includes the so-called barrier;

Figs. 3 and 4 are curves showing the thermal characteristics of a thermoelectric device of the kind illustrated in Fig. 2;

Fig. 5 illustrates a modified form of this invention in which the pieces of P-type and N-type silicon are intimately joined by a metallic tube;

Fig. 6 illustrates another form of this invention in which the pieces of P-type and N-type silicon are soldered together;

Fig. 7 illustrates an arrangement according to this invention in which the intimate junction of the pieces of P-type and N-type silicon are heated to obviate any photo effect;

Fig. 8 illustrates an arrangement for measuring power in a centimeter coaxial circuit; and

Fig. 9 illustrates a receiving circuit for a transmission system employing a wave guide.

Like elements in the several figures of the drawings are indicated by identical reference characters.

During an investigation of the production of fused silicon of high purity and its uses for point contact rectifiers, applicant discovered that under certain conditions this material could be used to generate a high thermoelectromotive force. In the course of that investigation, ingots of very pure silicon were formed from melts in silica crucibles starting with highly purified silicon pow-

der. It was discovered that some of these ingots exhibited two zones separated by a barrier. The material in the upper zone was found to develop a positive thermoelectromotive force with respect to an attached copper electrode; the material in the lower zone, a negative thermoelectromotive force with respect to an attached copper electrode; and a section including material from both zones and the barrier developed a still larger thermoelectromotive force between electrodes attached to the material on opposite sides of the barrier. Realizing the importance of this discovery, applicant devised the thermoelectric devices hereinafter described.

A form of ingot from which thermoelectric devices can be cut is shown in Fig. 1. The ingot 5 is formed by the solidification of fused silicon in a silica crucible 6. Such an ingot made from certain kinds of highly purified silicon powder in a manner hereinafter to be described comprises two zones of visibly different structure. The upper zone 7 has a columnar structure, the columnar grains being of the order of one-half millimeter in width and extending down from the top of the ingot to a distance of 5 or 10 millimeters. The lower zone 8 has a non-columnar structure. The ingot fractures most easily in the lengthwise direction of the columns. The columnar portion of the fracture appears lustrous, while the non-columnar portion has the appearance of a grayish mass of smaller crystals. Across the lower portion of the columnar zone 7 some sort of a boundary or barrier 9 is found. In this region 9, the columnar portion tends to be striated, the striations extending across as well as between the columns. These striations appear under a microscope to have discontinuities at the columnar boundaries. The columnar and non-columnar portions are intimately joined by the barrier and may be heated to high temperatures without affecting this connection.

A thermoelectric device such as that illustrated in Fig. 2 comprises a silicon slab 10 cut from the ingot 5 of Fig. 1 at the position indicated by the dot and dash rectangle 11. This rectangle 11 outlines the section of the slab 10 midway between the edges and parallel thereto. In other words, the slab 10 is so cut from the ingot 5 that the barrier 9 lies approximately midway between the ends of the slab.

The slab 10 may be cut from the ingot 5 by any suitable process, preferably by a process which conserves as much useful material as possible. The upper and lower portions of the ingot may be used for other purposes such as contact rectifiers. The intermediate portion including the barrier 9 may be used for thermoelectric devices. A metal wheel charged with diamond particles is suitable for cutting the ingot 5, a stream of distilled water being used to clean the cut-out particles from the kerf and to cool the surfaces.

In order to facilitate the use of the slab 10 as a thermoelectric device, contact terminals 12 and 13 are provided on the ends of the slab by a process of rhodium plating. A rhodium plating process which has been found to produce a firm and stable joint, comprises grinding the surfaces of the silicon which are to be coated, flat on a flat cast iron lap with a wet abrasive of aluminum oxide equivalent to 600 mesh. An abrasive identified as American Optical Company's M302½ serves very well. This grinding produces a mat finish which must be freed from traces of amorphous silicon (very finely divided silicon). This can be accomplished by the application of about

20 percent hot water solution of sodium or potassium hydroxide. The action must be stopped as soon as it is perceived to act on the silicon with moderate violence. The mat surfaces of the silicon should then be washed in distilled water. These mat surfaces are thereupon electroplated with rhodium from a hot solution of rhodium tin phosphate acidified with about 4 per cent sulphuric acid. A satisfactory thickness of rhodium is obtained after plating for about ten to twenty seconds with a current density high enough to cause a generous discharge of hydrogen gas. After washing and drying, the rhodium plating makes excellent contact terminals because it does not loosen from the silicon and is highly resistant to corrosion.

The size of the silicon slab 10 of the thermoelectric device of Fig. 2 is not critical. The device must be long enough so that there can be a temperature difference between the barrier 9 and the terminals 12 and 13 of the device.

The unit 10 is provided advantageously with terminal conductors 21 and 22 by soldering. In soldering, the rhodium end surfaces 12 and 13 are tinned with ordinary lead-tin solder, using an acidified zinc chloride flux. The solder must not be heated much above its melting point for there is danger of the rhodium being completely dissolved. The ends of the conductors 21 and 22 are freely tinned then placed in contact with the respective tinned rhodium surfaces and the joint heated until the solder flows, the excess solder being squeezed from between the conductor and the rhodium plating. A strong bond results. The conductors 21 and 22 may be connected to a measuring instrument 23, such as a direct current bridge, a millivoltmeter or a microammeter.

In place of using rhodium to plate the ends of the slab of unit 10 nickel may be used. After grinding the surfaces to be plated to produce a mat surface in the manner described hereinbefore, these surfaces are nickel plated. A satisfactory thickness of nickel is obtained from a commercial nickel plating bath having a pH value of about 5.5 by using a current density just below the hydrogen discharge point after about one minute of plating.

An explanation of what applicant believes to be the reasons why the hereinbefore-described rhodium and nickel-plating processes produce firm joints with the silicon will now be set forth. It was noted from microscopic examinations that rhodium or nickel will curl away in minute pieces from a silicon surface finished to an optical polish and electroplated. The mat surface hereinbefore described has a fineness of mat which is slightly smaller than the approximate size of such curled metal pieces. Thus, a curved surface is already presented by the ground finished silicon and under this condition it can well be that the thin piece of metal sheet joining adjacent hollows is strong enough to prevent the metal from breaking its bond with the silicon by the curling tendency. It is believed that when the solder is applied, as in making a soldered terminal connection thereto, the solder fills the hollow places, possibly expanding slightly on solidifying and thus assuring a strong bond to the silicon. Furthermore, the solder in the soldered joint has a sufficient cold flow so that when a joint is made to a piece of brass, for instance, the difference in coefficient of expansion of the brass and silicon will not break the rigid but inelastic silicon bond.

The method of soft-soldering silicon by means

of an electroplated joint is believed to be very well suited to the mechanical and physical properties of silicon and other semi-conducting substances. It yields a relatively noiseless low resistance non-rectifying contact and a stable electrical and mechanical contact.

The thermoelectric characteristics of a typical device, such as is illustrated in Fig. 2, are shown by the curves of Figs. 3 and 4.

The voltage-temperature curve of a thermocouple is of approximately parabolic form and may be expressed for given temperature limits by the equation

$$V = At + \frac{1}{2} Bt^2 \text{ millivolts} \quad (1)$$

The thermoelectric power at a given temperature is

$$Q = dV/dt = A + Bt \text{ millivolts per degree C.} \quad (2)$$

The curve V of Fig. 3 shows the voltage in millivolts generated by a typical thermoelectric unit of the kind illustrated in Fig. 2 for a range of temperatures of the barrier from 0° C. up to about 200° C., the cold junction, that is, the terminals 12 and 13 being kept at 0° C. The silicon unit from which this data was obtained was 14 millimeters long, 2 millimeters wide and 0.8 millimeter thick, the barrier being located about 6 millimeters from one end or approximately at the middle of the lengthwise dimension of the unit. The small circles show the actual data points, the curve V being extrapolated at the upper end.

The curve Q of Fig. 4 shows the voltage generated per degree centigrade in millivolts for the various temperatures of the barrier as derived from the data of Fig. 3. The values of Q are obtained by taking the slope of curve V or instantaneous values of dV/dt for various values of t in Fig. 3. From the data of curve Q the coefficients A and B of Equation 2 have been worked out for this unit as follows:

A = 720×10^{-6} volts per degree centigrade.

B in volts per degree centigrade	Temperature range Degrees centigrade
0.4×10^{-6}	0-50
1.1×10^{-6}	50-100
1.4×10^{-6}	100-150
2.5×10^{-6}	150-200
3.9×10^{-6}	200-250

It is thus seen that this device is much more sensitive at high temperatures which is advantageous as will be pointed out hereinafter in connection with the arrangement of Fig. 7.

A modified thermoelectric device is illustrated in Fig. 5. In this arrangement a slab 25 of P-type silicon is connected to a slab 26 of N-type silicon by means of a length of metal tubing 27 which is soldered to the plated ends of slabs 25 and 26. Slab 25 is provided with a terminal in the form of a piece of tubing 28 and slab 26 is provided with a terminal in the form of a piece of tubing 29 soldered respectively to the plated ends of slabs 25 and 26. Terminal conductors 21 and 22 may be soldered to the pieces of terminal tubing 28 and 29, respectively, and connected to a measuring device 23 as in Fig. 2. Terminals 28 and 29 may be cooled by inserting cooling material therein, such as water, ice, etc. The piece of tubing 27 may then be the heated part during the use of this device. The plating and soldering processes may be the same as described in connection with Fig. 2.

Another modified thermoelectric device is illus-

trated in Fig. 6. In this device a slab 30 of P-type silicon is connected to a slab 31 of N-type silicon by soldering the rhodium or nickel plated ends 32 and 33, respectively, together. The other ends of the slabs 30 and 31 are provided with coatings 34 and 35, respectively, as in the arrangement of Fig. 2. Terminal conductors 21 and 22 may be soldered to the terminal platings 34 and 35, respectively, and connected to a measuring device 23. In use the ends of the devices marked T_0 are kept cool while the joined ends T_1 are heated. One arrangement for cooling the terminals T_0 consists of metallic blocks 44 and 42 soldered to the coatings 34 and 35 respectively. These blocks 44 and 42 are provided with cooling fins 41 and 43 respectively. Blocks 44 and 42 are made of metal having high heat capacity such as copper or silver suitably polished to facilitate radiation. Cooling air may be forced over the blocks 44 and 42 and fins 41 and 43. Other arrangements for accomplishing the cooling of the terminals T_0 may comprise (1) metal cups in intimate contact with the coatings 34 and 35 containing a liquid which keeps the blocks at substantially the same temperature through the evaporation of the liquid, (2) metal blocks without fins and with or without forced air cooling, (3) metal blocks cooled with water, ice, etc., and (4) metal blocks with holes therein through which cooling air or liquid may be forced.

Similar arrangements may be used for cooling the terminals T_0 of the devices of Figs. 2, 5 and 7.

Usually when small amounts of heat are involved relatively large blocks of copper or silver are all that are needed to maintain terminals T_0 at a satisfactorily constant value.

The arrangement of Fig. 7 is well adapted to the detection of radiated heat. As mentioned hereinbefore in connection with Figs. 3 and 4, the response per degree centigrade of the thermoelectric devices of this invention are higher as the temperature is raised. These devices also exhibit a photo-E. M. F. effect as disclosed and claimed in the copending application of R. S. Ohl, Serial No. 395,410, filed May 27, 1941. However, the photo-E. M. F. response is practically nil at elevated temperatures in the neighborhood of 200° C. Therefore in the arrangement of Fig. 7 the junction T_1 is given a heat bias by means of heating coil 36 sufficient to substantially eliminate any photo-E. M. F. effect. The heater 36 is supplied with current from battery 37 through variable control resistance 38. The radiation to be detected or measured, represented by dash lines x , y and z , is focused on the junction T_1 by a lens 39. The thermoelectric device 40 of Fig. 7 as illustrated is the same as device 10 of Fig. 2 but devices like those of Figs. 5 and 6 may be used in the same way provided that the temperature of the heated junction is not raised above the melting point of the solder.

In Fig. 8 an arrangement is shown schematically for measuring power in a centimeter coaxial type of circuit. A source of centimeter power is indicated by 52. This power may be sent through a transmission line 55 and 53 into the inductance L_1 designated as 56 in the figure. The power may be extracted from the inductance L_1 by tuning the chamber C by means of a screw type of plunger 59. The connection 54 of the transmission line to the chamber C is preferably a tight threaded joint. The resonant chamber C is coupled to the pick-up inductance L_2 (51) which is the termination of the coaxial transmission line 46. This is preferably a short line em-

employing a heavy silver central conductor so constructed as to self cool the junction P_2 . The junction P_1 is attached to the transmission line termination Q which is electrically insulated from 46 by the insulating sleeve 47, any form of built in condenser may be used which satisfactorily short circuits Q to 46 and at the same time offers enough insulation to develop the thermo potential difference between Q and 46 as caused by the thermoelectric properties of the barrier B. The chamber C can also act as an impedance transformer so that the power detecting element need not be varied to increase power from different types of sources.

In Fig. 9 an arrangement is shown schematically for measuring power in a centimeter wave guide type of circuit. The wave guide is excited by the generator 69. Plunger 61 constitutes an adjustable reflection surface. The power is caused to flow along wave guide 60 and is reflected by the terminating plunger 67. The tuning plungers T_2 and T_3 are adjusted so that the centimeter wave energy is absorbed in the silicon thermoelectric device 66. The central conductor of the coaxial tuner is made preferably of relatively large diameter silver rods 64 and 65 so as to well cool the junctions to device 66. The outer conductor 63 is insulated from 60 by the condenser 70 which offers a very low impedance to centimeter waves but a high resistance to direct current. The meter M (68) measures the potential developed across 70 by the silicon thermoelectric device 66. The centimeter power is converted into heat due to the relatively high resistivity of the thermojunction material and an inappreciable loss of power is experienced in the silver conductors.

A description of the production of an ingot such as is illustrated in Fig. 1 will now be given. Silicon of a purity in excess of 99 per cent obtainable in granular form is placed in a silica crucible in an electric furnace in vacuum or a helium atmosphere. Because of a tendency to evolution of gas with violent turbulence of the material, it is desirable to raise the temperature to the melting point by heating the charge slowly. Silicon will be found to fuse at a temperature of the order of 1400 to 1410° C.

In order to facilitate the heating process the silica crucible containing silicon powder may be placed within a graphite crucible which lends itself to the development of heat under the influence of the high-frequency field of the electric furnace to a much greater degree than does the silica crucible or its charge of silicon. Care must be taken, however, to avoid exposure of the melted silicon to graphite, oxygen or other materials with which it reacts vigorously. In this manner the melt may be brought to a temperature of the order of 200° C. above the melting point. In an example of this process "high form" crucibles of 50 cubic centimeter capacity obtainable from Thermal Syndicate Incorporated were employed. A furnace power input of 7.5 to 10 kilowatts was employed, the required time for melting being of the order of 10 to 20 minutes, depending upon the power used. The power was then reduced in steps and the temperature of the melted silicon dropped rapidly to the freezing point, approximately 6 or 7 minutes being required for the melt to solidify. The solid matter was then permitted to cool towards room temperature at the rate of 60 centigrade degrees per minute, this being effected by decreasing the power input at the rate of about $\frac{1}{2}$ kilowatt per minute. When the tem-

perature had been reduced to the order of 1150 to 1200° C. the power was shut off and the temperature then fell at the rate of about 130 centigrade degrees per minute.

In cooling there is a tendency after the upper surface has solidified for extrusion of metal to occur through this surface during the solidification of the remaining material. Upon examination of the cooled ingot it is found that a portion of the grain structure is columnar, as hereinbefore explained. This is in general the upper portion of the ingot or the material first to solidify. In the portion last to solidify and beyond the columnar grains a non-columnar structure occurs. Between the zone first to cool and that last to cool there is found to be some sort of a boundary or "barrier" which occurs in a plane normal to the columns and this barrier is intimately joined to the material on opposite sides thereof. The barrier ordinarily occurs a short distance above the point where the columnar and non-columnar zones merge so that it extends across the columns near their lower ends. The region above the barrier develops a positive thermoelectric potential with respect to an attached copper electrode and may therefore be designated as the P zone, composed of P-type silicon. The region below the barrier develops a negative thermoelectric potential with respect to an attached copper electrode and may be designated as the N zone, composed of N-type silicon.

Granulated silicon of high purity now available on the market is produced by crushing material found in a large commercial melt. That supplied by the Electrometallurgical Company is of a size to pass a 30 mesh screen and to be retained by an 80 mesh screen. The crushed material is purified by treatment with acids until it has attained a purity considerably in excess of 99 per cent. The chemical composition of a typical sample of this material is approximately

Si	99.85	O	.061
C	.019	H	.001
Fe	.031	Mg	.007
Al	.020	P	.011
Ca	.003	Mn	.002
N	.008		

In some samples amounts up to .03 Ti and .004 Cr have been found.

There is some evidence to indicate that the behaviour of this material and the form in which it solidifies are dependent not only upon high purity of the silicon, but also upon the character of the extremely small amounts of impurities which remain. In the most satisfactory ingots the N zone portions have very tiny gas pockets and upon cutting through this zone the characteristic odor of acetylene is observed. Moreover, certain lots of highly pure silicon which have at first appeared to be defective in barrier-forming properties have been satisfactorily conditioned by the introduction of carbon or silicon carbide into the melt in amounts of the order of 0.1 per cent to 0.5 per cent and this should be done if a preliminary sample of a particular lot of material does not form the distinctive barrier structure.

The slow cooling is an important factor as is readily demonstrated upon microscopic inspection of sectioned specimens of silicon ingots which have been etched and stained. The barrier is evident as one or more striations of a somewhat different appearing material in consequence of its different reaction to the etching acid. In

the case of slow cooling the striation extends across the entire ingot thus dividing it into discrete P and N zones. Where, however, the cooling is precipitate as in the case of shutting off the heating power suddenly as soon as fusion occurs and permitting the temperature to fall suddenly the first spots to cool develop P zones and these are surrounded by N zone matrices in such irregular fashion as to render the resulting ingot quite unsatisfactory for thermoelectric devices. The slow cooling rate is important in developing an orderly striation or barrier. This and other features of the method of preparing the most effective silicon materials are described and claimed in the application of J. H. Scaff, Serial No. 386,835, filed April 4, 1941, for improvements in the Preparation of silicon materials.

This application is a continuation in part of application Serial No. 385,425, filed March 27, 1941, for Electrical translating devices utilizing silicon.

Certain subject-matter of this application is disclosed and claimed in divisional application, Serial No. 480,460, filed March 25, 1943, for Thermoelectric system.

What is claimed is:

1. A thermoelectric device comprising a section of fused silicon ingot having a transverse barrier zone produced by fusing and cooling granulated silicon having a purity in excess of 99 per cent, and individual contacts intimately joined to the metallic silicon on opposite sides of said barrier zone, respectively.

2. A thermoelectric device comprising a piece of silicon cut from the zone of columnar structure of a body of silicon produced by fusing and cooling granulated silicon having a purity in excess of 99 per cent and having a zone of columnar structure and a second zone of non-columnar structure, a piece of silicon cut from the zone of non-columnar structure of the same or similar body of silicon, means intimately joining said two pieces of silicon, and electrical terminals connected to said pieces of silicon respectively at surface areas removed from the said junction between the two pieces.

3. A thermoelectric device comprising a section of fused silicon ingot having a transverse barrier zone produced by fusing and cooling granulated silicon of a purity in excess of 99 per cent, and individual metallic platings intimately joined to the metallic silicon at separated portions on opposite sides of said barrier zone, respectively.

4. A thermoelectric device comprising a section of fused silicon ingot having a transverse barrier zone produced by fusing and cooling granulated silicon of a purity in excess of 99 per cent, and individual rhodium platings intimately joined to the metallic silicon on separated portions of the surface on opposite sides of said barrier zone, respectively.

5. A thermoelectric device comprising a section of fused silicon ingot having a transverse barrier zone produced by fusing and cooling granulated silicon of a purity in excess of 99 per cent, and individual nickel platings intimately joined to the metallic silicon on separated portions of the surface on opposite sides of said barrier zone, respectively.

6. The method of producing a thermoelectric device which comprises fusing powdered silicon having a purity in excess of 99 per cent in an inert atmosphere in a silica (SiO_2) crucible, cooling the silicon to produce an ingot a portion of which consists of P-type silicon and an adjoining portion consists of N-type silicon, cutting a section from said ingot which includes both types of silicon, and attaching electrical connections to the P-type and N-type portions of said section, respectively.

7. The method of producing a thermoelectric device which comprises fusing powdered silicon having a purity in excess of 99 per cent in an atmosphere of helium in a silica (SiO_2) crucible, cooling the silicon to produce an ingot a portion of which consists of P-type silicon and an adjoining portion consists of N-type silicon, cutting a section from said ingot which includes both types of silicon and attaching electrical connections to the P-type and N-type portions of said section, respectively.

8. A thermoelectric device comprising a body of fused silicon having a zone of columnar structure and a second zone of non-columnar structure, an electrical terminal connected to the columnar zone, and a second electrical terminal connected to the non-columnar zone.

9. A thermoelectric device comprising a section of fused silicon ingot having a transverse section of high specific resistance intermediate two sections of low specific resistance produced by fusing and cooling granulated silicon of a purity in excess of 99 per cent, and individual nickel platings intimately joined to separated portions of the surface of said lower resistance material on opposite sides of said transverse section, respectively.

10. A thermoelectric device comprising a body of fused silicon of a purity in excess of 99 per cent having a zone of columnar structure, a zone of non-columnar structure, and a zone including striations within the zone of columnar structure near the zone of non-columnar structure, said striations being visible on microscopic examination of a suitably etched surface including the three zones, an electrical terminal connected to said zone of columnar structure, and a second electrical terminal connected to said zone of non-columnar structure.

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