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Hare et al.

[11] **3,775,218**

[45] **Nov. 27, 1973**

[54] **METHOD FOR THE PRODUCTION OF SEMICONDUCTOR THERMOELEMENTS**

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[22] Filed: **Mar. 4, 1971**

[21] Appl. No.: **120,977**

[52] **U.S. Cl.** **156/331,** 161/227

[51] **Int. Cl.** **C09j**

[58] **Field of Search** ..... 136/224, 225; 174/68.5; 117/47 H; 156/17, 256, 304, 331; 29/592, 625–628; 161/227, DIG. 7

[56] **References Cited**

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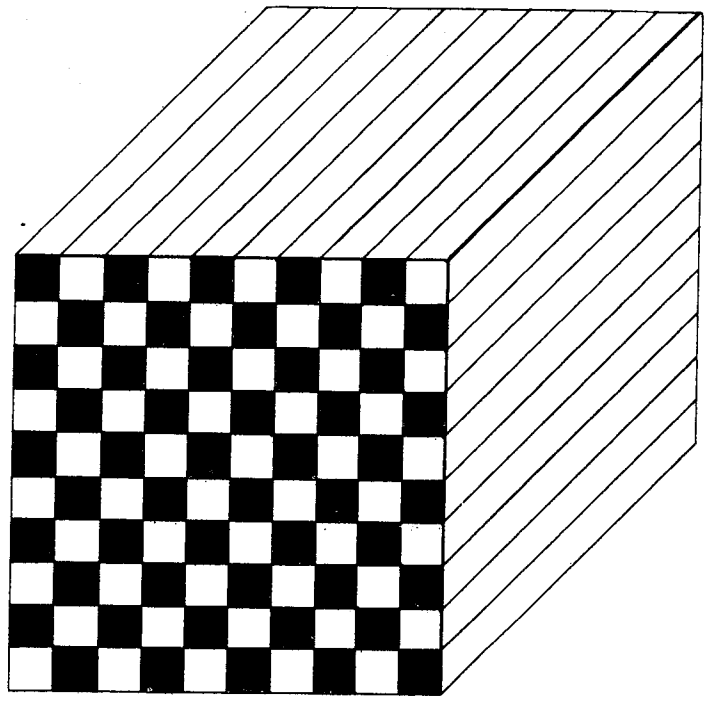
Primary Examiner—D. F. Duggan

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[57] **ABSTRACT**

There is disclosed a method of preparing miniature semiconductor thermoelements suitable for use in power generators operable with low temperature heat such may be conveniently obtained from radioisotopes. The invention utilizes the compacting of piles of semiconductor thermoelements in a co-extensive arrangement wherein the respective polarities of the elements may be in series, parallel or series-parallel connection. The ends of the elements are connected by a matrix of electrically conductive regions formed on a high heat transferring electrically insulating material.

2 Claims, 11 Drawing Figures



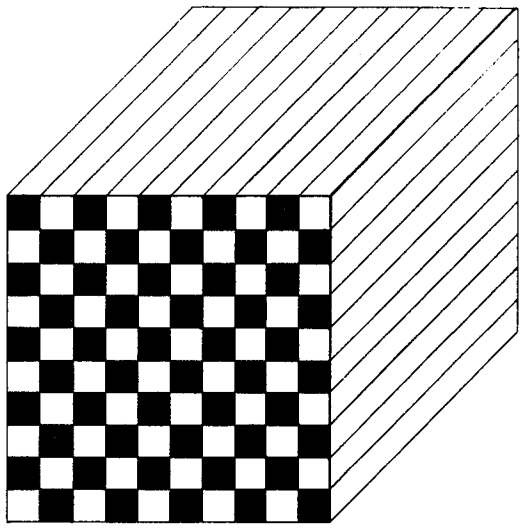


FIG.1

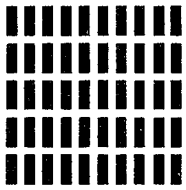


FIG.2A

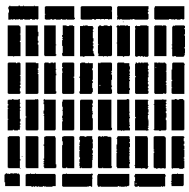


FIG.2B

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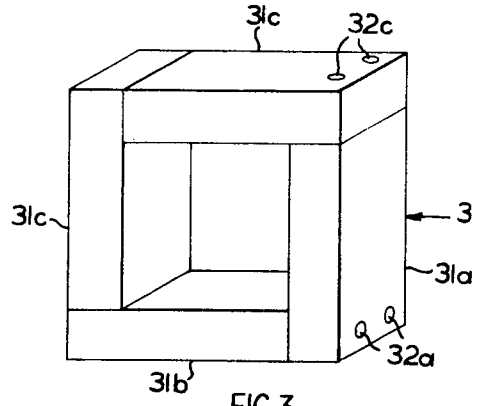


FIG. 3

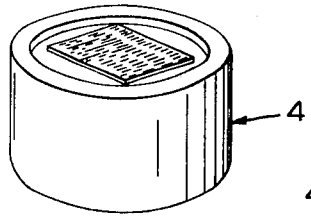


FIG. 4(a)

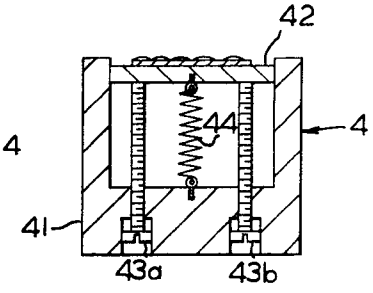


FIG. 4(b)

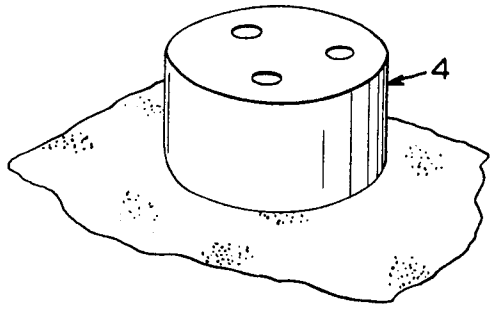


FIG. 4(c)

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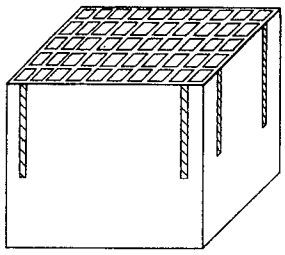


FIG.5A

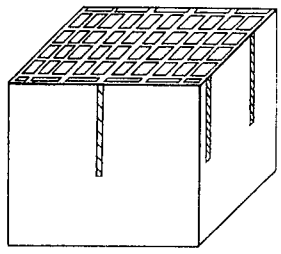


FIG.5B

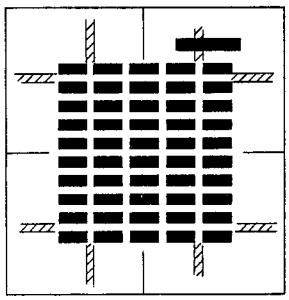


FIG.6A

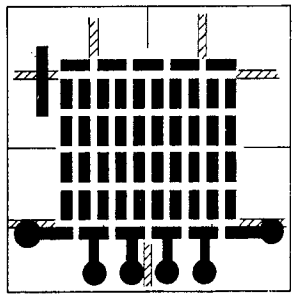


FIG.6B

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METHOD FOR THE PRODUCTION OF SEMICONDUCTOR THERMOELEMENTS

This invention relates to a method and to an apparatus for the production of semiconductor thermoelements. The invention has particular utility, although not exclusively, in apparatus for the conversion of low temperature heat into electrical power. Such conversion has become of importance in the realm of radioisotopic low-power electrical power generators.

The use of semiconductor materials for the conversion of heat to electricity has been described extensively in the literature and as a result of considerable research throughout the world, certain families of materials such as those based on Bi_2Te_3, PbTe and Ge-Si alloys, have been characterized as having useful conversion capabilities over specific temperature ranges, no one material being suitable for more than a limited range.

Since heat to electricity conversion systems employing converters made from semiconductors need have no moving parts, long operating lives can be expected. As a consequence there is advantage to be obtained if such a converter can be coupled to a high energy density heat source. Such a source is provided by radioisotopes (see Table I) and a number of devices have been built to demonstrate this, one of which is described in the copending patent application, Canadian application No. 063,780.

TABLE I

	Watt hr/lb	
	Thermal	Electrical
^{238}Pu Metal (5 years)	1×10^7	
^{90}Sr Titanate (5 years)	4×10^6	
^{60}Co Metal (100 Ci/gm 5 years)	5×10^7	
Gasoline + Air	5.9×10^3	
Lead Acid Battery		16
Silver Zinc Battery		75
Carbon Zinc Battery		3
H_2-O_2 Fuel Cell		1620

In the device described in copending Canadian Application No. 063,780, this application being assigned to Atomic Energy of Canada Ltd., mention is made of the use of semiconductor thermopiles and, in fact, a suitable set of converter units for this device can be constructed from Bi_2Te_3 type materials. The particular advantage of using Bi_2Te_3 type materials in this case stems from the fact that these materials have their best converter performance in the temperature range 0° C to 300° C, and as a result, the heat source can be operated at a temperature well below that at which any deterioration of structural, shielding, encapsulation and radio-active materials is likely to occur. Also, at this temperature the proportion of heat loss parasitically is lower than at the higher temperatures required for operation of PbTe and Ge-Si alloy systems because of the lesser significance of the thermal radiation terms in the heat loss.

The materials based on Bi_2Te_3 have been described extensively in the literature and from this it is evident that a single thermocouple consisting of a limb of p-type alloy and a limb of n-type alloy will generate an open circuit voltage of about 360μ V for every ° C temperature interval across it. A couple operating over a typical working range of 70° C and 270° C will therefore deliver about 72 mV open circuit or 36 mV to a matched load.

Consideration of the details of thermoelement design show that the power output from a thermocouple of given materials depends on the hat and cold face temperatures and the ratio of cross sectional area to length of the material used.

A simplified explanation is that the efficiency of conversion is governed by hot and cold face temperatures and the material parameters and the total heat process is given approximately by that transported by thermal conduction through the couple.

$$Q=K\frac{A(T_H-T_C)}{l}$$

where

Q is the heat transferred by conduction
K is the effective thermal conductivity of the couple
T_H is the hot surface temperature
T_C is the cold surface temperature
A is the cross sectional area of the couple
l is the length of the couple

So, for a given material, the efficiency of the conversion η is

$$\eta = F\,(T_H,\ T_C)$$

and the power out is approximately

$$\eta\, Q = f(T_H,\ T_C)\ KA(T_H - T_C)/l$$
$$= F(T_H,\ T_C,\ A/l)$$

If then we take a one inch cube consisting of two segments, one being of p-type alloy 1'' × 1'' × ½'' and the other of n-type alloy 1'' × 1'' × ½'' and having an electrical contact strip across one face, a hot surface temperature of 270° C and a cold surface temperature of 70° C, the couple will deliver to a matched load equalling the internal resistance of the couple a power "P" at about 36 mV. If now this block is made of four segments, two of p-type alloy each 1'' × ½'' × ½'', and two of n-type alloy each 1'' × ½'' × ½'', series connected to give, in effect, two series connected thermocouples, the unit will deliver the same power "P" at twice the single couple voltage, namely, about 72 mV and by extension of this subdivision into large number of couples with the same total cross section area at a given length, a wide range of voltages can be produced for a given power.

The upper limit in voltage is obviously set by the smallest cross sectional area of semiconductor alloy which can be conveniently handled. In this respect, although semiconductors are more efficient than metals for the purpose of thermoelectric energy conversion, they cannot be handled in such small sizes because of their relatively poor mechanical properties. In particular, the Bi_2Te_3 alloys all possess in the single crystal form a very weak cleavage plan which is attributed to the existence of a Te-Te bond. The use of power metallurgy has resulted in considerable improvement of mechanical porperties without undue loss of thermoelectric performance, but the material is still difficult to handle at thicknesses less than about 0.040 inches. For this reason a basic thermopile assembly can be designed which consists of 100 limbs of semiconductor, each limb being 0.060'' × 0.060'' × 0.8'' and with suitable bonding material these can be assembled into a compact and reasonably strong 10 × 10 array or matrix in which the alloys are staggered alternatively p-type and n-type. If these are then electrically contacted at

the two ends by a pattern of contacts, a 50-couple series connected thermopile will result which typically would deliver about 0.2 watts of electric power at 1.8 volts when the hot surface is held at 270° C and the cold surface at 70° C.

Since typically a voltage of at least 0.5 volts is needed for efficient operation of any subsequent electronic power conditioning equipment an array such as the one described above can be used for power levels of 0.2 watts and upwards, the higher powers being supplied by either series connecting a number of such arrays or reducing the length of the array or series-parallel connecting numbers of such arrays and in this way, with only minor changes, the basic unit can be used in a wide range of devices with a consequent saving in development and production cost.

It is an object of one aspect of the invention to provide a method of accurately assembling a bonded matrix of layers of co-extensively disposed electrically conductive limbs to give precise final dimensions and limited voidage.

In accordance with the foregoing object of the invention the invention in its broadest aspect comprises the steps of cutting strips of cured polyimide film to the same length as said limbs some of said strips having widths equal to a single layer of said limbs and some of said strips having width equal to the thickness of said limbs, individually coating the limbs in partially cross linked polyimide and placing each such coated limb in succession in rows and layers both separated by said strips of cured polyimide film, slowly compressing all said limbs together after assembly to a precisely controlled size to expel excess polyimide and maintaining compression, wiping off excess polyimide, baking the the assembled limbs to cure said uncured polyimide.

It is an object of another aspect of the invention to provide a semi conductor matrix of precise dimensions and of limited voidage.

In accordance with this object the invention comprises: a plurality of coextensive and juxtaposed semi conductor thermoelements adjacent ones of which having opposed polarity, an electrically insulating film of polyimide between thermoelements, a first pattern of contacts electrically joined to one group or adjacent ends of the said thermoelements, a second pattern of contacts electrically joined to the other group of adjacent ends of the said thermoelements, said first and selected patterns having configurations to electrically join said thermocouples in a one conductivity arrangement selected from the group comprising series, parallel and series-parallel.

It is an object of another aspect of the invention to provide a method of preparing an electrically conductive pattern on the surface of a matrix of semi conductor limbs.

In accordance with this other aspect of the invention, the method comprises the steps of coating the surface with a substance which is easily wetted by solder and which has good adhesion to and compatibility with said material, preparing electrically conductive straps by electrodepositing a semi conductor matrix comprising: a plurality of coextensive and juxtaposed semi conductor thermoelements adjacent ones of which having opposed polarity, an electrically insulating film of polyimide between thermoelements, a first pattern of contacts electrically joined to one group of adjacent ends of the said thermoelements, a second pattern of contacts electrically joined to the other group of adjacent ends of the said thermoelements, said first and selected patterns having configurations to electrically join said thermocouples in a one conductivity arrangement selected from the group comprising series, parallel and series-parallel.

It is an object of another aspect of the invention to provide a bonded sandwich having high heat transfer and good electrical conductivity.

In accordance with this object the invention comprises a core of high heat transfer electrical insulation material, a pair of electrically conductive coatings, one each bonded to a respective side of the core, one of said coatings having been etched to provide a selective pattern of conductive regions, having a coating of solder of selected thickness thereon.

It is an object of yet another aspect of the invention to provide a method of bonding an electrically insulating heat transfer material to an electrical device.

According to this further object the method comprises the steps of providing electrically conductive regions on said material, dip soldering said conductive regions, polishing said regions, placing regions in registry with a number of corresponding electrically conductive regions on the device, evacuating the assembly, heating to a given temperature and cooling.

The invention will now be described with reference to the accompanying drawings, in which,

FIG. **1**, is an isometric view of a 10 × 10 matrix of semiconductors wherein the alloys are alternately *p*-type and *n*-type.

FIGS. **2A** and **2B** are patterns of contacts for the hot and cold end respectively, of the matrix shown in FIG. **1**.

FIG. **3** is a perspective view of a jig for assembling a semiconductor thermoelement matrix.

FIGS. **4A**, **4B** & **4C** are, respectively, a general view, a cross-sectional view and the polishing altitude of a jig for adjusting solder thickness on ceramic end plates.

FIGS. **5A** and **5B** are isometric views showing the hot face and cold face, respectively, of a matrix of semiconductors.

FIGS. **6A** and **6B**, appearing with FIGS. **1**, **2A** and **2B**, are end views showing the alignment marks on the hot and cold faces, respectively, of the ceramic plate.

Referring now to FIG. **1**, the kind of array shown and previously discussed can be prepared from a set of accurately cut and polished limbs of *p*- and *n*-type Bismuth-Telluride alloys as follows:-

A jig **3** as shown in FIG. **3**, comprising four similar side members **31***a*, **31***b*, **31***c* and **31***e* held together by pairs of screws as at **32***a* and **32***e*, is assembled having internal cross sectional dimensions of 0.645″ ±0.002″ square is made up out of materials such as TEFLON (Dupont Trade Mark for Polytetrafluoroethylene). Limbs of semiconductor of a suitable length and 0.060 inch square are measured and 50 of each type (*p* and *n*) having dimensions within ± 0.001 inch of that size are selected. Strips of cured polyimide film such as KAPTON (Dupont Trade Mark for cured polyimide film) 0.005 inch thick are cut, some (**90**) 0.050 inch ± 0.001 inch wide, others (**9**) 0.645 inch ± 0.001 inch wide, both being the same length as that chosen for the limbs in this particular assembly.

One face of the TEFLON jig is removed and the other faces are loosened and limbs are individually dipped in a medium such as PYRE ML (Dupont Trade

Mark for a solution of partially cross-linked polyimide in solution in N-Methyl Pyrrolidone and Xylene) varnish and placed one at a time in the jig, being spaced from each other laterally by 0.060 inch strips of KAPTON film and vertically by 0.645 inch strips of KAPTON film taking care to preserve an alternating *p*-type-*n*-type sequence throughout, the final array consisting of ten layers, each layer containing ten limbs. The removed face of the jig is then replaced and the jig tightened slowly to expel all excess varnish.

After wiping off the excess varnish, the assembly, still in its jig, is placed in an oven at 80° C for at least 24 hours. It is then moved to an oven at 100° C for at least 1 hour followed by an oven at 150° C for 1 hour. The TEFLON jig is then removed and a final cure carried out at 350° C for 1 hour. The resulting assembly is a strongly bonded matrix of semiconductor limbs with only limited porosity due to varnish shrinkage, capable of prolonged use at 300° C in a γ or Bremsstralung radiation environment.

A series of contacts such as those shown in FIGS. **2**(*a*) and **2**(*b*) can be deposited by a number of techniques such as masked vacuum deposition, electroplatephotoetch or photomask electroplate procedures or by individual of jig soldering. It is envisaged that the contact pattern may place the elements in series, parallel or series-parallel connection.

In order to carry out successful contacting by soldering, it is generally necessary that the semiconductor surface is first coated with a material which is easily wetted by the solder, and has good adhesion to, compatibility with and electrical contact with the Bismuth-Telluride. Such a coating can be prepared by depositing nickel from a hypophosphite bath onto the matrix ends and this has the added advantage of providing an unstressed deposit. Stressed deposits such as those arising from electrodeposition techniques have a tendency to fail by mechanical breaking away of the layer of semiconductor near to the deposit along the grain cleavage planes even in powder metallurgy prepared material.

Contact straps are then prepared by electrodepositing 0.002 inch pure lead onto nickel foil 0.010 inch thick and then shearing the foil into pieces about 0.040" × 0.100". The straps can then be soldered into position using an ordinary electric soldering iron and zinc chloride based flux. After soldering all the contacts onto one surface, the excess lead is removed by gentle trimming with a sharp bladed knife and a fine Co_2 driven jet of abrasive powder is used finally to clear the regions between the straps of residual flux, lead and electroless nickel. Following this, the module is washed by flux solvent in a reflux condensing assembly. The face is then gently polished to a 600-grit flat finish.

In order firstly, to provide electrical insulation of the contact straps from any conducting surface which may be used to deliver or remove heat; and secondly, to ensure uniform temperature distribution across all the contacts in the event of a rather uneven contact with the heating or cooling surface, it is advisable to bond a high thermal conductivity electrical insulator such as beryllium oxide to the faces of the module. A suitable technique is as follows:-

Beryllium oxide plates may be obtained commercially with a metal coating fired onto both faces. Using a suitable mask, these coatings can be photoetched to provide a pattern of metalized areas corresponding to the contact pattern on one or the other end of the module. After removing the photomask material, the plate is lightly coated with a zinc-chloride flux and dip soldered in a bath of solder, the solder composition being chosen so that its melting point is below that of the solder used to attach the contacts to the modules but above that at which that particular surface will be operated. (eg. Pb + 2.5 wt. % Ag for the hot face, pure Sn or Sn + 38.1 wt. % Pb for the cold face.) This plate is then mounted in a jig such as the one shown in FIGS. **4**(*a*), **4**(*b*) and **4**(*c*). FIG. **4**(*a*) is an isometric view of a polishing jig **4** in which is mounted a ceramic plate. The jig is shown in section in FIG. **4**(*b*) and comprises a hollow body member **41** containing a slidable plate **42** upon which a ceramic plate may be suitably mounted, for example, with double sided adhesive tape. Three of adjusting screws two of which are shown at **43***a* and **43***b* set the degree of protrusion of the ceramic plate.

The plate **42** is urged into engagement with the screws **43** by a tension spring **44.** FIG. **4**(*a*) shows the jig inverted for the grinding process in which a fine abrasive may be used, for example, 600 grit silicon carbide. The thickness of solder is polished down to 0.001 to 0.002 inch.

The position of the corner spaces in the contact pattern on the module are then marked placing fine (~1/64") adhesive strips down the side of the module as shown in FIGS. **5**(*a*) and **5**(*b*). The corresponding positions on the ceramic plate are indicated with pencil marks on the unmetalized ceramic surface. FIGS. **6**(*a*) and **6**(*b*) show the alignment marks on the hot and cold faces, respectively.

The module is then placed on top of and in contact with the ceramic plate with the two sets of markers aligned. The set is placed on an electrically heated platform in an evacuable enclosure which is then purged with Argon + 4% Hydrogen. The platform is heated to a few degrees centigrade above the melting point of the solder on the ceramic, held there for 30 seconds and then allowed to cool. The process is then repeated for the other module face.

Other embodiments of the invention falling within the terms of the appended claims, will occur to those skilled in the art.

We claim:

1. A method of accurately assembling a bonded matrix of layers of coextensively disposed electrically conductive limbs to give precise final dimensions and limited voidage, said method comprising the steps:

i. cutting strips of cured polyimide film to the same length as said limbs, some of said strips having widths equal to a single layer of said limbs and some of said strips having width equal to the thickness of said limbs,

ii. individually coating the limbs with an uncured polyimide and placing each such coated limb in succession in rows and layers both separated by said strips of cured polyimide film,

iii. slowly compressing all said limbs together after assembly to a precisely controlled size to expel excess uncured polyimide and maintaining compression,

iv. wiping off excess uncured polyimide

v. baking the assembled and compressed limbs to cure said uncured polyimide,

vi. removing compression, and,

vii. further baking the assembled limbs after removing compression.

2. A method of accurately assembling a bonded matrix of layers of coextensively disposed electrically conductive limbs to give precise final dimensions and limited voidage, said method comprising the steps:

i. cutting strips of cured polyimide film to the same length as said limbs, some of said strips having widths equal to a single layer of said limbs and some of said strips having width equal to the thickness of said limbs,

ii. individually coating the limbs in an uncured polyimide and placing each such coated limb in succession in rows and layers both separated by said strips of cured polyimide film,

iii. slowly compressing all said limbs together after assembly to a precisely controlled size to expel excess uncured polyimide and maintaining compression,

iv. wiping off excess uncured polyimide,

v. baking the assembled limbs at a temperature between 60° and 100° C for at least **20** hours,

vi. baking the assembled limbs at about 100° C for at least 1 hour,

vii. baking the assembled limbs at about 150° C for at least **1** hour,

viii. removing compression, and

ix. baking at about 350° C for at least 1 hour.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,775,218 Dated March 26, 1974

Inventor(s) Gerald E. Hare et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Heading insert:

--Priority: December 16, 1970
Canada
100,796--.

Signed and sealed this 16th day of July 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
* U.S. GOVERNMENT PRINTING OFFICE : 1969 O—366-334.

UNITED STATES PATENT OFFICE

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