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[54] THERMOELECTRIC DEVICES UTILIZING ELECTRICALLY CONDUCTING ORGANIC SALTS

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[51] **Int. Cl.** **H01v 1/24**
[58] **Field of Search** .... 62/3; 136/236, 236 A, 136/203; 260/327 M

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Hartzler, "J. Amer. Chem. Soc.," 92 (No. 5), 1412–1413 (1970)

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[57] ABSTRACT

Thermoelectric device such as generators and refrigerators are disclosed having as the N-type semiconductor material compounds or compositions having a cation which is tetrathiafulvalene or 2,5-cyclohexadiene-1,4-diylidene-bis-1,3-thiole or both, and an anion which is 7,7,8,8-tetracyano-p-quinodimethane or 11,11,12,12-tetracyano-2,6-naphthaquinodimethane or both.

10 Claims, 2 Drawing Figures

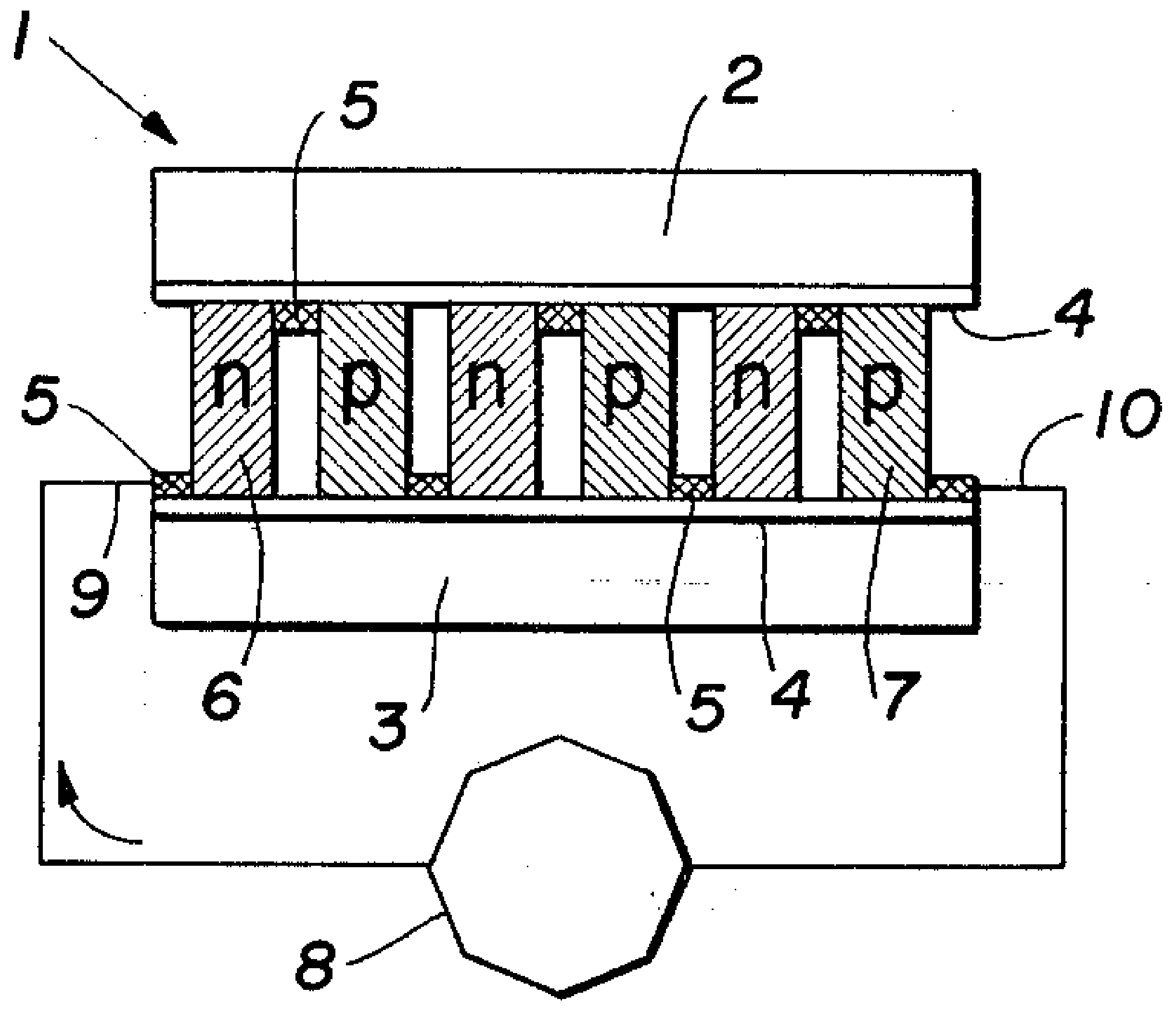

1
5
2
4
5
10
n
p
n
p
n
p
9
6
3
5
4
7
8

FIG. 1.

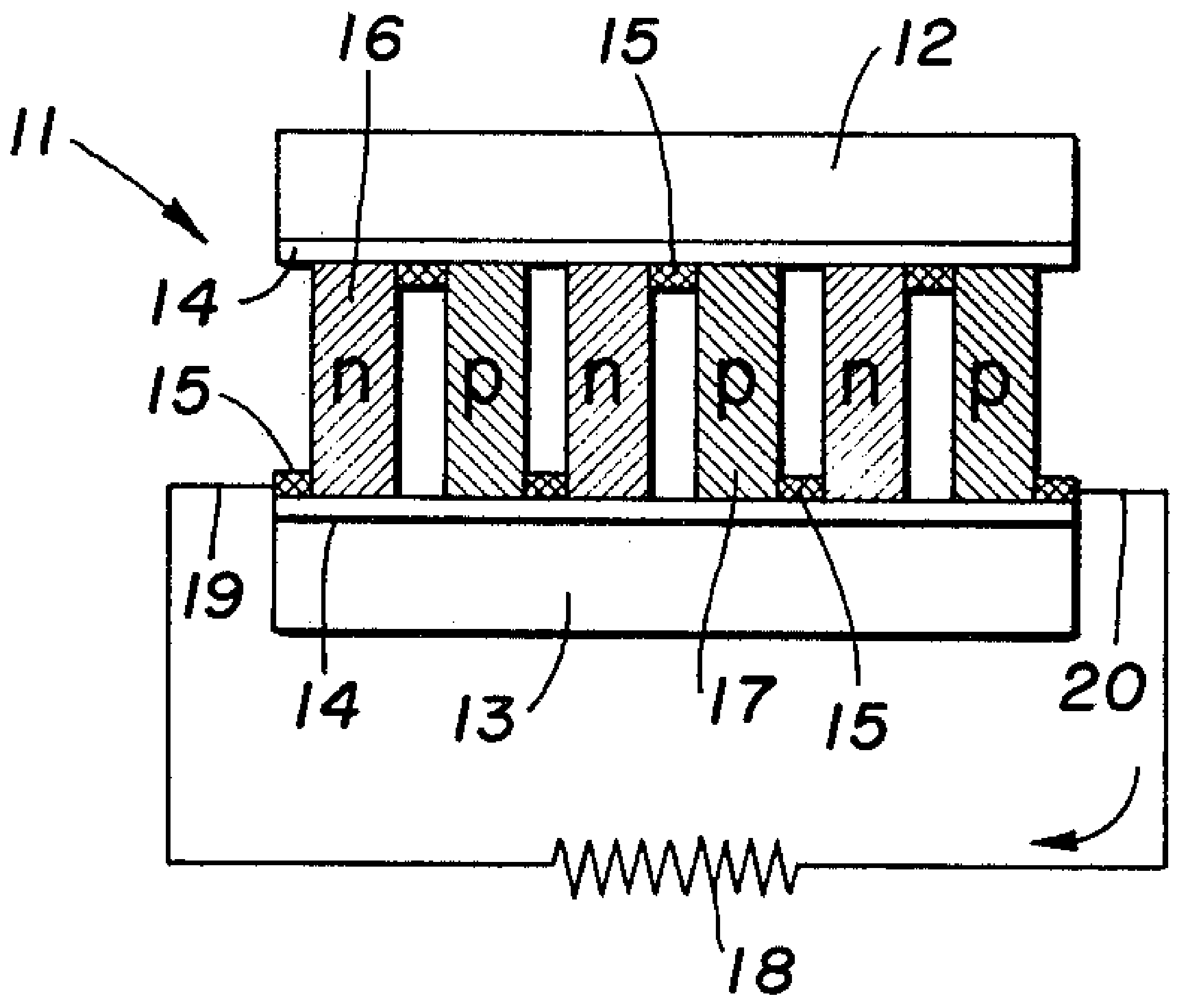

16
15
12
11
14
15
n
p
n
p
n
p
19
14
13
17
15
20
18

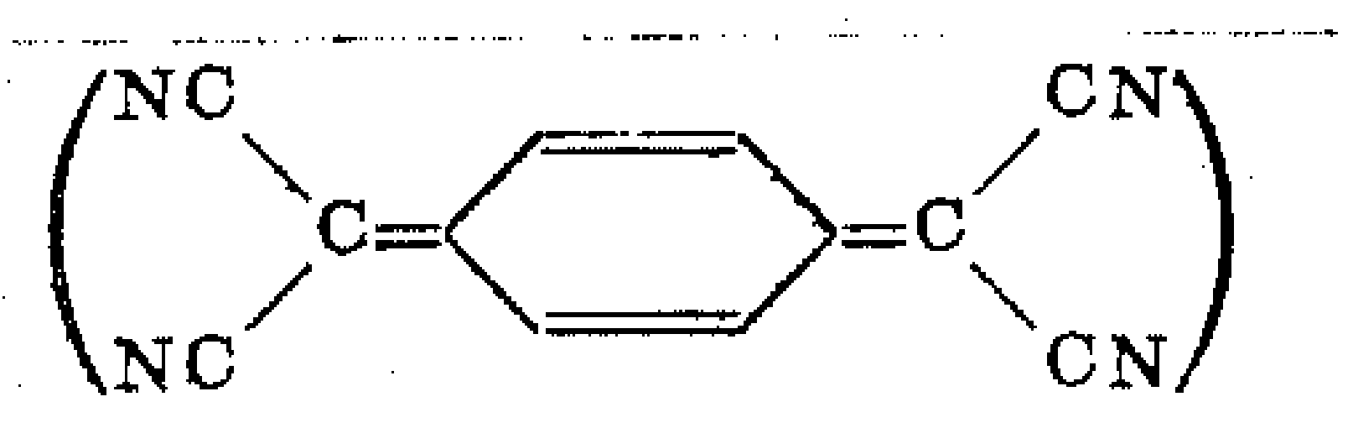
FIG. 2.

THERMOELECTRIC DEVICES UTILIZING ELECTRICALLY CONDUCTING ORGANIC SALTS

DESCRIPTION OF PRIOR ART

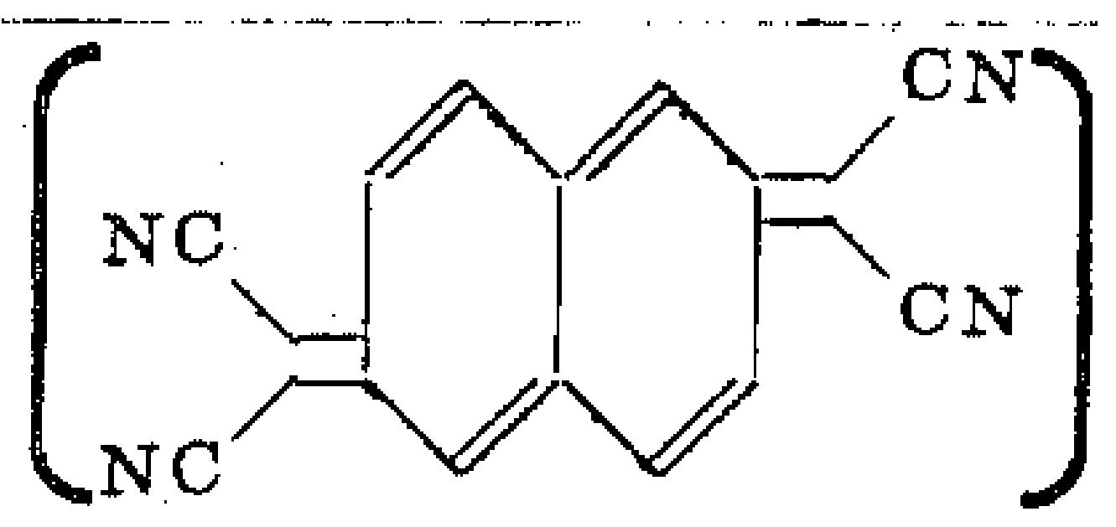
The prior art is replete with references to a wide variety of electrically conductive organic compounds. Few of these have desirable combinations of electrical and thermal properties. One important class are salts containing both an organic anion as well as an organic cation. One specific class consists of those organic salts where both the anion and the cation are odd-electron ions. By "odd-electron ion" is meant an ion which contains an uneven number of bound electrons in the ion.

There are a number of references reporting the preparation of electrically conductive organic salts having a 7, 7, 8, 8-tetracyano-p-quinodimethane anion,



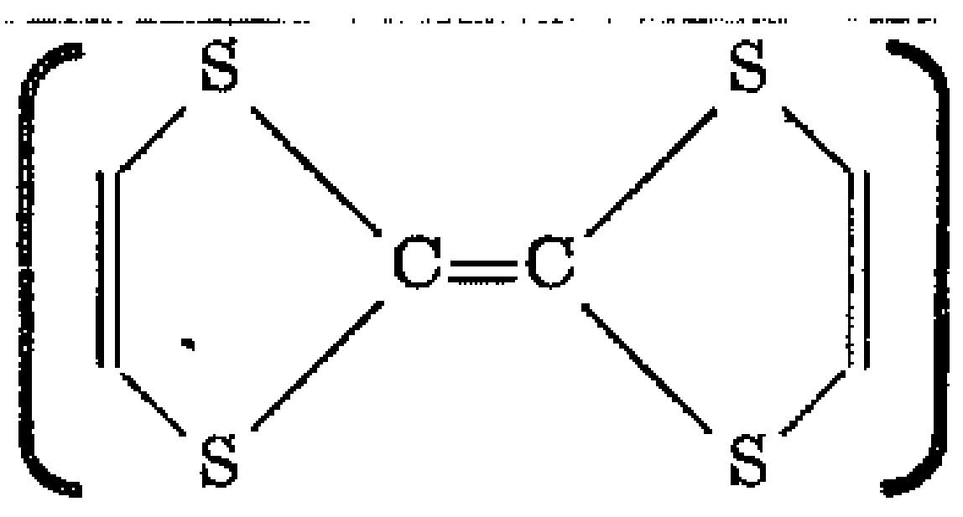
hereinafter referred to as $(TCNQ)^-$. The best electrical conductivities reproted so far for $(TCNQ)^-$ salts range up to about 10^2 ohm^{-1} cm^{-1} for single crystals. Compacted crystals of $(TCNQ)^-$ salts have reported conductivities not exceeding about 5 ohm^{-1} cm^{-1}.

Another anion which has been used in investigations of conductive organic salts is 11, 11, 12, 12-tetracyano-2,6-naphthaquino-dimethane,



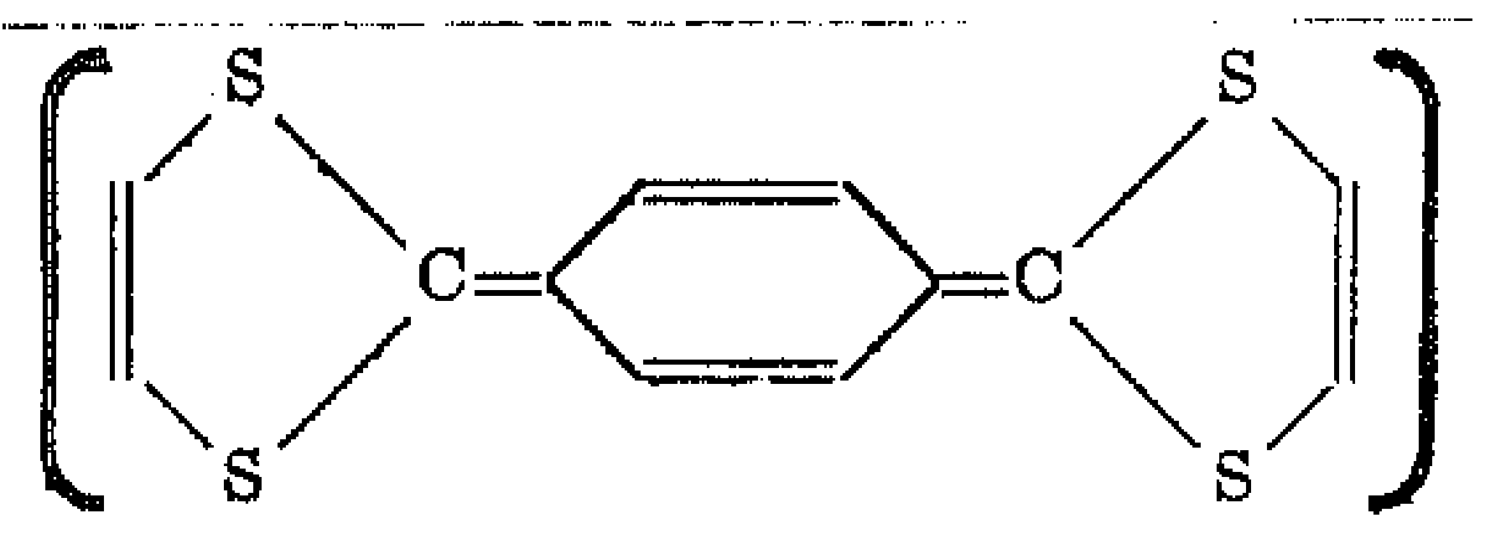
The ion 11, 11, 12, 12-tetracyano-2,6-naphthaquinodimethane is referred to herafter as $(TNAP)^-$. $(TNAP)^-$ salts have maximum reported conductivites of about 10^{-1} ohm^{-1} cm^{-1} for compacted crystals. No conductivities have been reported for single crystals of $(TNAP)^-$.

One specific cation which has been used in investigations relating to conductive organic salts has been tetrathiafulvalene



Tetrathiafulvalene will be referred to hereafter as $(TTF)^+$. Conductive $(TTF)^+$ organic salts have conductivities limited to about 2 ohm^{-1} cm^{-1} for compacted crystals. No conductivities have been reproted for single crystals of any $(TTF)^+$ salt.

As far as has been determined, no electrically conductive organic salts have been reported having as a cation 2, 5-cyclohexadiene-1,4-diylidene-bis-1,3, dithiole,

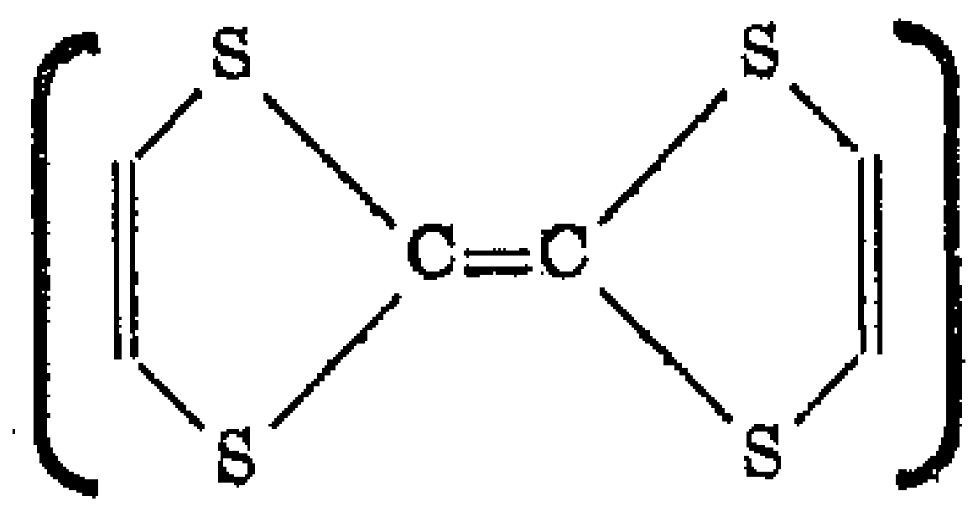


The ion 2,-5 cyclohexadiene-1,4, diylidene-bis-1,3-dithiole is referred to hereinafter as $(CHDT)^+$

Summary of the Invention

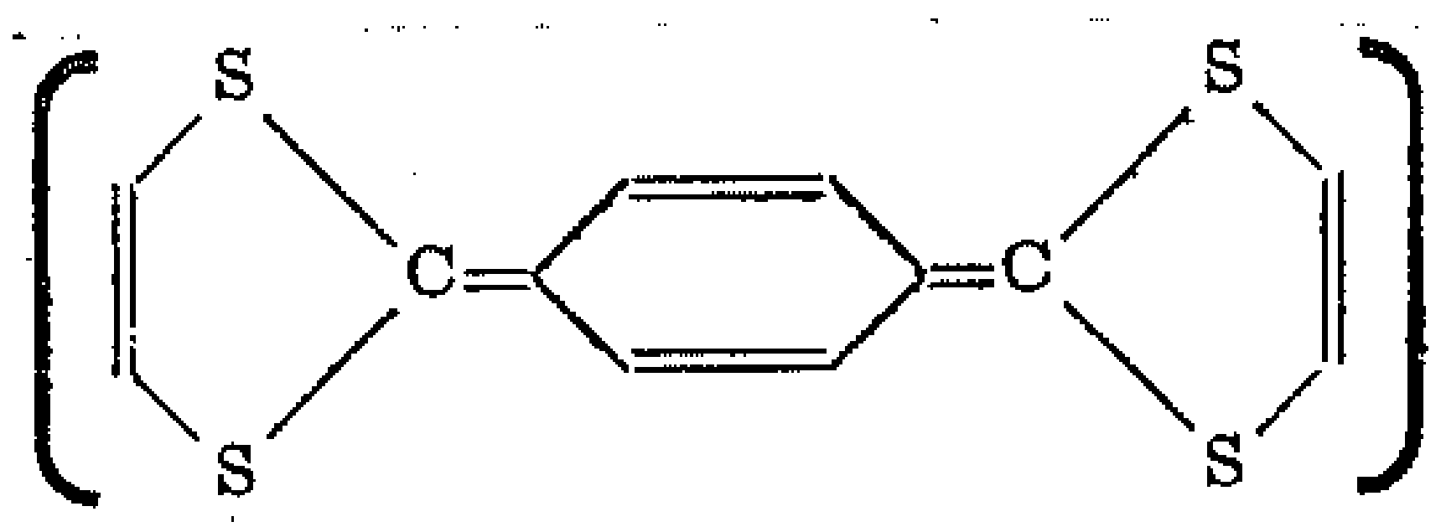
This invention pertains to thermoelectric devices comprising a heat source, a heat sink, and positioned between and in thermal contact with said sink and said source a compound or composition of the formula A^+B^-

where A is



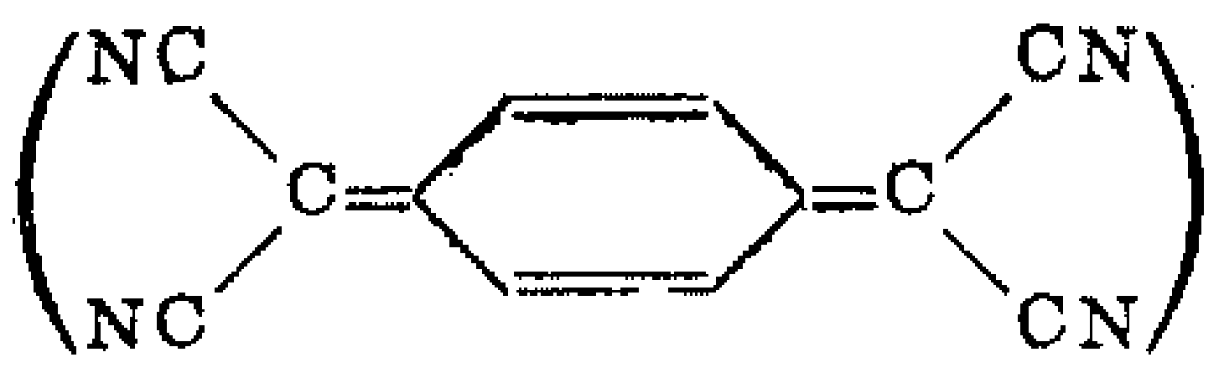
i.e. $(TTF)^+$

or



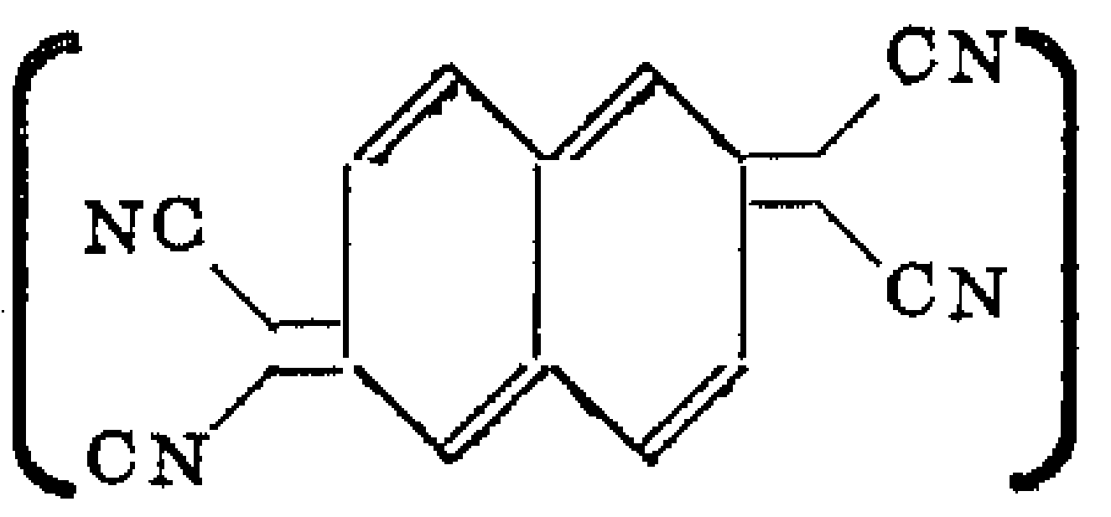
i.e. $(CHDT)^+$

or both, and B is



i.e. (TCNQ)

or



i.e. $(TNAP)^-$

or both.

BRIEF DESCRIPTION OF THE DRAWINGS

In the accompanying drawings:

FIG. **1** is a schematic representation of a cooling device utilizing thermoelectric elements to convert electricity directly to energy.

FIG. **2** is a schematic representation of an electrical generator utilizing thermoelectric elements to convert thermal energy directly to electricity.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring to the drawings, a cooling device **1** is shown having a heat exchanger **2** and heat sink **3.** The heat exchanger **2** is the portion of the device which is cooled during operation. The heat sink **3** is the portion of the device which is heated. Depending upon whether heating or cooling is desired, the heat exchanger or heat sink can be positioned inside or outside the area which is to be thermally modified. Located along and in contact with the lower surface of heat exchanger **2** and the upper surface of heat sink **3** are electrical insulators **4** which prevent the thermoelectric elements **6** and **7** from making electrical contact with the heat exchanger and heat sink. The n-type thermoelectric elements 6 and the p-type thermoelectric elements 7 are positioned between heat exchanger 2 and heat sink 3 and in contact with the insulators 4 on each of the ends of the thermoelectric elements. Thermoelectric elements 6 and 7 are arranged so that the portions of the elements which become heated upon application of an electric current are all in thermal contact with heat sink 3 while the portions of the elements which become cooled upon application of an electric current are in thermal contact with heat exchanger 2. Elements 6 and 7 are alternated in the electrical circuit and electrically connected in series through electrical connectors 5. A source of direct current 8 is transmitted through thermoelectric elements 6 and 7 by means of wires 9 and 10. As the current passes through the thermoelectric element assembly, heat flows from the upper ends of the elements to the lower ends, thereby withdrawing heat from heat exchanger 2 and conveying it to heat sink 3. Heat sink 3 is arranged so that heat is readily transferred from it to its external environment, thereby reducing the temperature differential between exchanger 2 and sink 3 and permitting additional heat to be withdrawn by exchanger 2 from its surroundings.

The interaction in thermoelectric elements between thermal transmission and electrical transmission can also be used to convert thermal energy directly to electrical energy. FIG. 2 shows an electrical generator 11 having a heat source 12 and a heat sink 13. As heat is absorbed by heat source 12, the source heats up and transmits heat to the heat sink 13 through insulating layers 14 and thermoelectric elements 16 and 17. Thermoelectric elements 16 and 17 are arranged as in FIG. 1 and are connected to one another through electrical connectors 15. A load 18 is connected to the generator 11 through wires 19 and 20. As the thermal energy flows from source 12 to sink 13 through thermoelectric elements 16 and 17, part of the thermal energy is converted to electrical energy which is used to operate the load 18.

The similarities between the two devices described above are manyfold. In both devices, heat is conveyed from a heat source, referred to as a heat exchanger in the first device, to a heat sink through the thermoelectric elements. In the first device, the electrical current causes the heat flow whereas in the second device, electrical current is generated by the heat flow.

Compounds of the above generic class are

(tetrathiafulvalene)$^+$(7, 7, 8, 8-tetracyano-p-quinodimethane)$^-$,

i.e., (TTF)$^+$(TCNQ)$^-$;

(tetrathiafulvalene)$^+$(11, 11, 12, 12-tetracyano-2,6-naphthaquinodimethane),

i.e., (TTF)$^+$ (TNAP)$^-$

(2,5-cyclohexadiene-1, 4-diylidene-bis-1, 3-dithiole)$^+$(7, 7, 8, 8-tetracyano-p-quinodimethane)$^-$,

i.e., (CHDT)$^+$ (TCNQ)$^-$; and

(2,5-cyclohexadiene-1,4,diylidene-1,4-diylidene-bis-1, 3-dithiole)$^+$(11, 11, 12, 12-tetracyano-2,6-naphthaquinodimethane)$^-$

i.e., (CHDT)$^+$ (TNAP)$^-$.

In addition to any of the above compounds in pure form, the invention also comprises compositions of any one of the compounds with one or more of the remaining three. The compositions can contain the compounds in any proportion, for example with a binary system, from less than $1:10^{-3}$ up to 1:1. For compositions containing more than two compounds, the individual compounds can similarly be present in any ratio ranging from very small amounts of one, two or three compounds to compositions containing equimolar quantities of the compounds present in the composition. Preferred compositions have a preponderance of one compound with a minority of one or more other compounds present. As an example, compositions containing at least 80 mole percent of one compound with not more than 20 mole percent, preferably not more than 10 mole percent, of other component compounds are particularly useful. Examples of some compositions include 2 mole percent of (TTF)$^+$(TCNQ)$^{--}$ and 98 percent of (TTF)$^+$(TNAP)$^-$; one percent of (TTF)$^+$(TNCQ)$^-$and 99 percent of (CHDT)$^+$ (TNAP)$^-$; and two percent of (TTF)$^+$(TCNQ) $^-$, six percent of (CHDT)$^+$(TCNQ)$^-$ and 92 percent of (CHDT) $^+$(TNAP) $^-$.

The compositions can be simple mixtures of the above crystalline compounds, as well as compositions in the form of a crystalline product where individual multiple anions and/or cations are present in the same crystal lattice. Preparation of a composition composed of different crystalline compounds by precipitation from a solution will result in the formation of a crystalline product where individual crystals contain a mixture of multiple anions and/or cations present, or a mixture of crystals of the individual compounds or both.

In addition to the above described compounds and compositions thereof, homologs and other simple derivatives of the compounds can also be employed, either as impurities in small quantity with the unsubstituted compounds as principal components of a composition, or as a pure compound. Suitable substituents include monovalent hydrocarbon groups such as methyl, ethyl, vinyl and phenyl groups and halogens such as chloro or bromo groups.

The compounds and compositions of this invention can be prepared by combining two or more electrically neutral reactants, or by combining two or more reactants which contain one or more of the desired ions. This can be accomplished by combining electrically neutral compounds such as (TTF) and (TCNQ) in an appropriate medium to produce (TTF)$^+$ (TCNQ)$^-$. Alternatively, a compound containing one of the ions in its ionic form such as (TTF)$^+$ iodide or sodium (TNAP)$^-$ can be reacted either with an electrically neutral compound or with another ionic salt which can supply the necessary ion of opposite charge to form the compounds of this invention. The materials containing the desired compound components are usually brought together in the presence of a suitable solvent for the reactants such as acetonitrile, methylene chloride or acetone or a mixture of solvents such as acetonitrile-methanol, acetone-water-methanol and the like. Thorough contact of neat reactants, such as can be attained in the vapor phase, in the absence of any solvent or dispersing medium can also be used to form the compounds or compositions of this invention. If the reactants are salts having ions, such as iodide, sodium, nickel or hexafluoroantimonate, which are not to become part of the compounds or compositions of this invention, the reaction mixture can be purified through crystallization or other known techniques to remove the byproducts of the reaction. Reaction temperatures are usually about 0° to 150° C, preferably about 20° to 80° C. For convenience it can vary considerably depending upon the thermal stability of the reactants and the time alloted for the reaction. One suitable combination of reaction time and temperature which has been employed because of its convenience has been 20° to 25° c for 2 or 3 days. The two or three day reaction period is principally a matter of convenience, however, and can be shortened considerably with little or no loss in yield.

The compounds and compositions of this invention are useful as electrical semiconductors. Because of their advantageous combination if properties such as thermal and electrical conductivities and thermoelectric power coefficient, they are particularly useful as thermoelectric elements in thermoelectric devices. Compacted crystals of compounds or compositions of this invention have electrical conductivities at least an order of magnitude higher than conductivities of other organic semiconductor materials reported in the prior art. Similarly, compounds of compositions of this invention in single crystal form also exhibit higher electrical conductivities than reported in the prior art for single crystals of related compounds.

The compounds described in this invention are usually n-type electrical conductors. This means that a majority of the current passing through the compounds is carried by electrons. Compounds characterized as p-type conduct a majority of current passing through the compound by means of "holes" or electron vacancies. The thermoelectric compounds of this invention are most conveniently arranged in a thermoelectric device by using both n-type and p-type materials electrically connected in series and thermally connected in parallel. In addition to the foregoing, a suitable thermoelectric device can utilize a thermoelectric material of only one type, either *n* or *p*, in combination with a metallic electric conductor which serves as a substitute for the opposite type of thermoelectric materials. Examples of suitable n-and/or p-type materials which can be used in conjunction with the thermoelectric materials of this invention are bismuth telluride, silver selenide, silicon and indium antimonide.

The heat-exchange elements useful herein are those customarily used by those skilled in related arts. Most common of suitable heat exchangers is a metallic block such as a copper block with metal fins attached thereto to provide heat exchange between the block and the surrounding air. Other heat exchangers can be fluid-cooled or heated by means of circulating fluids which contact the element, thereby absorbing or transferring heat from or to the thermoelectric materials.

The heat exhcangers should not be capable of completing an unwanted electrical circuit because of their association with the electrically conductive thermoelectric materials. Since the more efficient heat exchange elements are usually metallic and therefore electrically conductive, the prevention of an electrical contact between heat exchanger and thermoelectrical material is customarily accomplished by placing an electrical insulator, which is also a thermal conductor, between the heat exchanger and the thermoelectric materials. Electrical insulators useful herein commonly have an electrical resistivity of at least about 10^8 ohm cm. Since this figure is not meant to constitute a limiting feature of the invention, depending upon the resistivity of the heat exchanger and its placement with respect to external electrical conductors, the resistivity for a suitable insulator could be even lower. For most devices, the electrical insulator will have a resistivity of a least about 10^{10} ohm cm. Similarly, the electrical insulator is not limited to any minimum value of thermal conductivity. The higher the thermal conductivity, the more efficient will be the thermoelectric device. Thermal conductivity, expressed in gram calories per (second) (square centimeter) (° C/cm), can be as low as 0.001 or less but is preferably at least about 0.01 and more preferably at least about 0.05. Ceramic and polymeric materials are good choices for the thermally conductive, electrically insulating materials used in this invention. Polyfluorinated ethylenes such as polytetrafluoroethylene, phenolic resins and crystalline aluminas are examples. Other useful materials are inorganic compounds such as lithium,sodium chloride, boron nitride and the like.

If the heat exchange elements are themselves non-conductors or poor conductors, the electrical insulator positioned between the thermoelectric materials and the heat exchangers need not be present since the heat exchanger can serve the dual function of insulator and heat exchanger.

Thermoelectric devices are of two broad classes, those which transport heat to generate electricity and those which consume electricity to transport heat. The first class of devices comprise electrical generators; the second class of devices can be used as a cooler or as a heater, depending upon the arrangement and use of the heat exchange elements. In the case of heating and cooling devices, a source of direct current is used to heat one of the heat exchangers, thereby cooling the heat exchanger connected to the opposite sides of the thermoelectric materials. In the case of a generator, one heat exchanger upon being heated generates an electrical potential between the two ends of the thermoelectric circuit, thereby providing a direct current for use in operating electrical devices such as radios and the like.

In other instances, the entire heat exchanger may be a laminated structure with an electrically non-conductive sheet surrounding an electrically conductive core. Or the electrical insulator can adopt the more conventional form of a sheet or plate positioned between the thermoelectric material and the heat exchanger.

EXAMPLE 1

$(TTF)^+$ $(TCNQ)^-$ is prepared by dissolving 0.1 millimole of $(TTF)^+$ iodide in 100 ml. of acetonitrile and adding the resultant solution to a solution of 0.1 millimole of (TCNQ) in 50 ml. of acetonitrile. The resultant reaction mixture is filtered after three days to give a 50 percent yeild of a black microcrystalline product. Calculated elemental analysis for $(TTF)^+$ $(TCNQ)^-$, $C_{18}H_8N_4S_4$ is C, 52.92percent; H, 1.97 percent; N, 13.40 percent. Found: C, 52.70 percent; H, 1.95 percent; N, 13.81 percent.

The compound is compacted at 90,000 psi in a microdie, and volume resistivity measured by the 4-probe technique is found to be 5×10^{-2} ohm cm. Seebeck coefficient is −26 microvolts deg^{-1}; thermal conductivity is 2×10^{-3}watts cvs^{-1} deg^{-1}.

EXAMPLE 2

$(TTF)^+ (TCNQ)^-$ is prepared by dissolving two millimoles of $(TTF)^+ (SbF_6)^-$ in 25 ml. of acetonitrile and adding the resultant solution to a solution containing 2 millimoles of $Li^+ (TCNQ)^-$ in 25 ml. of methanol. The resultant reaction mixture is filtered after two days to give a 55 percent yield of a black microcrystalline product, tentatively identified as $(TTF)^+ (TCNQ)^-$. Elemental analysis for $(TTF)^+ (TCNQ)^-$, $C_{18}H_8N_4S_4$ is calculated to be C, 52.92 percent; H, 1.97 percent; N, 13.40 percent. Found: C, 52.91 percent; H, 1.91 percent; N, 13.64 percent. Volume resistivity for the compacted polycrystalline material is 2×10^{-2} ohm cm. Seebeck coefficient is −22 microvolts deg^{-1}.

EXAMPLE 3

$(TTF)^+(TCNQ)^-$ is prepared by dissolving 10 millimoles of (TTF) in 200 ml. of acetonitrile and adding the resultant solution to a solution containing 10 millimoles of (TCNQ) in 400 ml. of a 3:1 solution of methylene chloride and acetonitrile. The reaction mixture is allowed to stand for seven hours and filtered after that time to give a 50 percent yield of a black microcrystalline product, tentatively identified as $(TTF)^+ (TCNQ)^-$. Elemental analysis calculated for $C_{18}H_8N_4S_4$is C, 52.92 percent; H, 1.97 percent; N, 13.40 percent. Found: C, 52.70 percent; H, 2.03 percent; N, 13.58 percent. The volume resistivity is 1×10^{-2} ohm cm. Seebeck coefficient is −20 microvolts deg^{-1}.

EXAMPLE 4

A sample of $(TTF)^+ (TCNQ)^-$ prepared according to the procedure of Example 3 is crystallized from worm dimethyl formamide. The material crystallized as black rectangular plates opaque is reflected light and yellow-green in transmitted light. Volume resistivity in the long axis of the plates measured by the 4-probe technique is found to be in the range 1.4 to 3.5×10^{-3} ohm cm. Seebeck coefficient is in the range −20 to −30 microvolts deg^{-1}. X-ray analysis shows the crystal to have the space group $P2_1/c$. Unit cell dimensions are $a = 12.25$ A; $b = 3.81$ A; $c = 9.20$ A; $\beta = 105°$ with two molecules in the unit cell.

EXAMPLE 5

$(TTF)^+ (TNAP)^-$ is prepared by dissolving 1 millimole of (TTF) in 20 ml. of acetonitrile warmed to about 40° C, and adding the resultant solution to a solution of 500 ml. of boiling acetonitrile containing 1 millimole of (TNAP). The solution is set aside and allowed to cool overnight, after which time the solution is filtered to give a 70 percent yield of a black microcrystalline product identified as $(TTF)^+ (TNAP)^-$. Volume resistivity is 1×10^{-2} ohm cm. Seebeck coefficient is −22 volts deg

EXAMPLE 6

To a separatory funnel containing 100 parts deoxygenated methylene chloride and 100 parts of a 0.1 molar solution of sodium bisulfite in deoxygenated water is added a suspension of 5 parts 1,4 -phenylenebis-2(1,3-dithiolium) difluoroborate in 20 parts acetonitrile. The mixture is agitated for 15 minutes by bubbles of nitrogen gas, after which time the mixture is allowed to settle, thereby permitting the layers to separate. The methylene chloride solution is withdrawn and the aqueous layer washed with an additional 100 parts of methylene chloride. The combined methylene chloride solutions are dried and evaporated under reduced pressure, leaving a residue which is recrystallized from CCL_4-ethanol, and identified as 2,5-cyclohexadiene-1,4-diylidene bis-1,3-dithiole, i.e., (CHDT).

EXAMPLE 7

One equivalent of (CHDT) and one equivalent of 1,4-phenylenebis-2(1,3-dithilium) difluoroborate are dissolved in 100 parts dry acetonitrile, giving a deep red solution of 2 parts $(CHDT)^+ BF_4^-$. To this is added a hot solution of 2 parts lithium (TNAP) in methanol. On cooling black crystals of $(CHDT)^+ (TNAP)^-$ appear which are collected by suction filtration.

EXAMPLE 8

A solution of potassium sulfide in ethanol is prepared by dissolving 40 parts potassium hydroxide in 250 parts absolute ethanol, saturating this solution with hydrogen sulfide, and then dissolving in this solution an additional 40 parts of potassium hydroxide. The solution is allowed to cool, and 20 parts of *a,a,a,a',a',a'*-hexachloro-p-xylene is added, with stirring. The resulting mixture is heated slowly to 45°, and kept at that temperature for two hours. The temperature is then raised to reflux, where it is allowed to remain for an additional three hours. The solution is filtered while hot and allowed to cool, whereupon crystals of the red dipotassium tetrathioterephthalate appear. This salt (11 parts) is collected by filtration.

Bromoacetaldehyde (10 parts) is added slowly to a suspension of 5 parts dipotassium tetrathioterephthalate in 150 parts cold 0° C) ethanol; the resulting red solution is allowed to warm to 25°, and is stirred for an hour. It is filtered, and the filtrate is cooled in ice and saturated with hydrogen sulphide. To this solution is then added 10 parts aqueous fluoroboric acid. The mixture is allowed to react for 4 hours. Crystals of 1,4-phenylenebis-2-(1,3dithiolium) difluoroborate (2parts) are then collected by filtration and washed with 20 parts 1:1 ethanol-ether.

To a solution of ten parts of 1,4-dilithiobenzene prepared from 1,4-dibromobenzene and n-butyl lithium, as described by Nielsen and McEwen (J. Am. Chem. Soc., 79,3081(1957)), is added solid 2-methylthio-1,3-dithiolium iodide (20 parts) in small portions. The dark solution slowly lightens, eventually attaining a yellow-brown coloration. After the reaction is complete, the solvent is evaporated and the residual gum treated with a mixture consisting of 100 parts deaerated water and 100 parts dichloromethane. The aqueous layer is washed once with dichloromethane and discarded. The combined dichloromethane solutions are evaporated and the tan residue treated with six parts of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) dissolved in boiling dichloromethane. After one-half hour the blue-black solid is recovered by filtration, giving one part product identified as $(CHDT)^+ (DDQ)^-$.

Equimolar parts of $(CHDT)^+ (DDQ)^-$ and lithium $(TCNQ)^-$ are added to hot acetonitrile and the resultant solution is stirred for 2 hours, after which time it is permitted to cool to room temperature. The solution is filtered and the black crystalline precipitated product is identified as $(CHDT)^+ (TCNQ)^-$.

EXAMPLE 9

A mixture of (TTF)$^+$ (TNAP)$^-$ and (TTF)$^+$ (TCNQ)$^-$ is prepared by dissolving 1 millimole of (TTF) in 20 ml. of acetonitrile and adding the resultant solution to a solution of 500 ml. of hot acetonitrile containing 0.8 millimole of (TNAP) and 0.2 millimole of (TCNQ). The solution is allowed to cool overnight, after which time the solution is filtered to give a 70 percent yeild of the black microcrystalline product mixture, (TTF)$^+$ (TNAP)$^-$ and (TTF)$^+$ (TCNQ)$^-$.

EXAMPLE 10

Microcrystals of (TTF)$^+$ (TCNQ)$^-$ are compacted under 8.3 kbar pressure to form rectangular parallopipeds 0.3 × 0.3 ×0.4 cm. Nine such elements are paired with similarly shaped elements of p-type bismuth telluride, long axes parallel, separated by a thin sheet of styrofoam, and joined at one end by a silver-filled epoxy cement. The nine couples so prepared are arranged in a linear array, n-element adjoining p-element and vice versa, and the couples separated by a styrofoam sheet. After trimming the insulating sheet to match the size of the couples, the couples are serially connected by silver-epoxy cement, and copper leads are cemented to the terminal elements. Heat exchange assemblies are affixed to the top and bottom of the thermoelectric assembly with a thermally conducting, electrically insulating potting compound. With the application of a D.C. current, the resulting device cools the low temperature heat exchange surface to a temperature of −3° C when the high temperature heat exchange surface is maintained at 15° C.

EXAMPLE 11

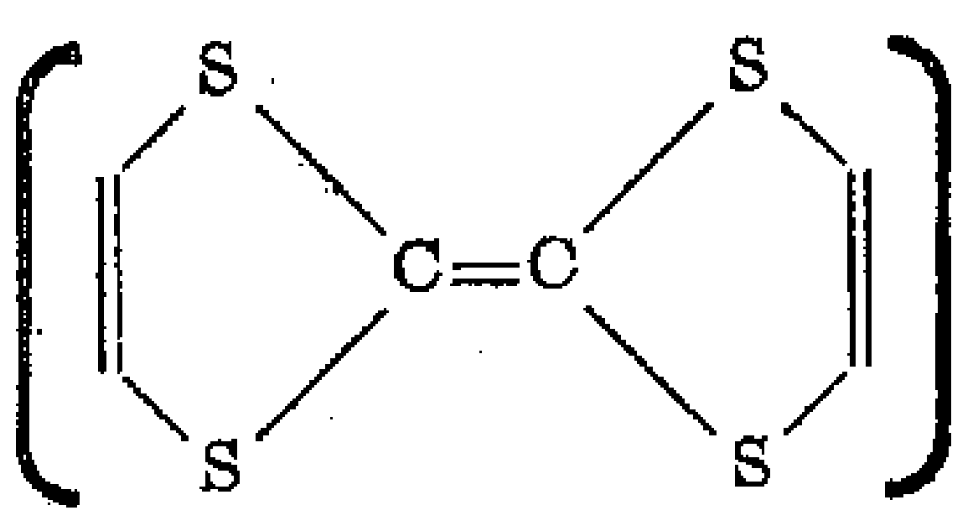
The procedure of Example 10 is followed except that (TTF)$^+$ (TCNQ)$^-$ is replaced with (CHDT)$^+$ (TNAP)$^-$. With the application of a D.C. current, the resulting device cools the low temperature heat exchange surface below 0° C when the high temperature heat exchanger is maintained at 15° C.

We claim:

1. A thermoelectric device comprising a heat sink, a heat source, and positioned between and in thermal contact with said sink and said source a compound or composition of the

formula A$^+$ B$^-$

where A is



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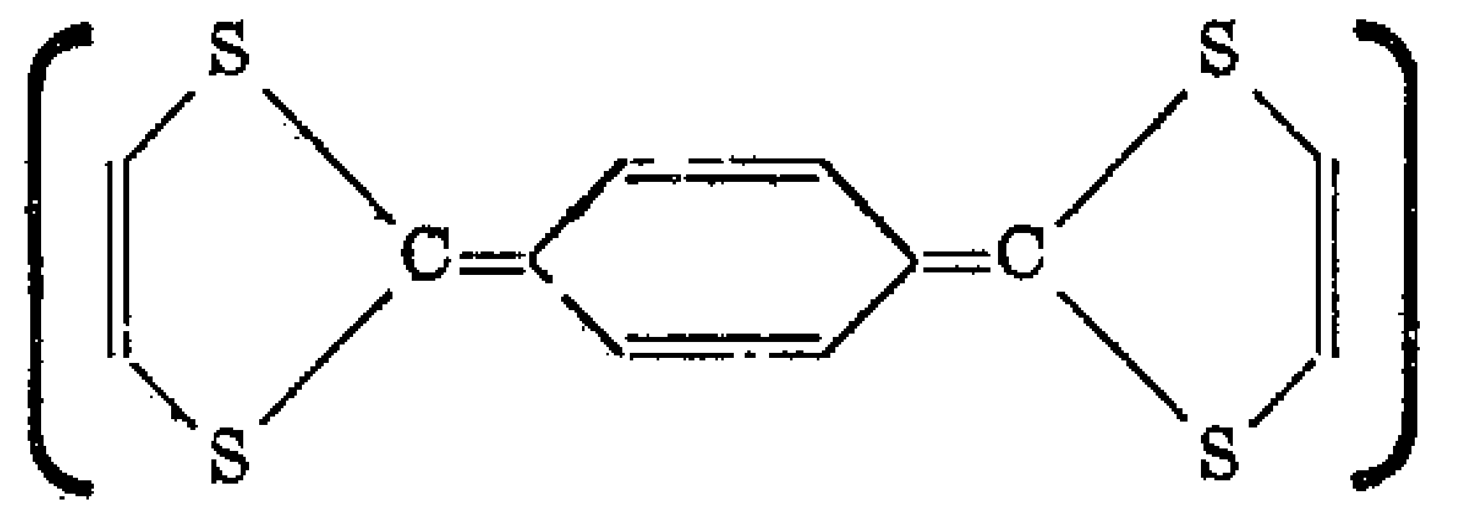
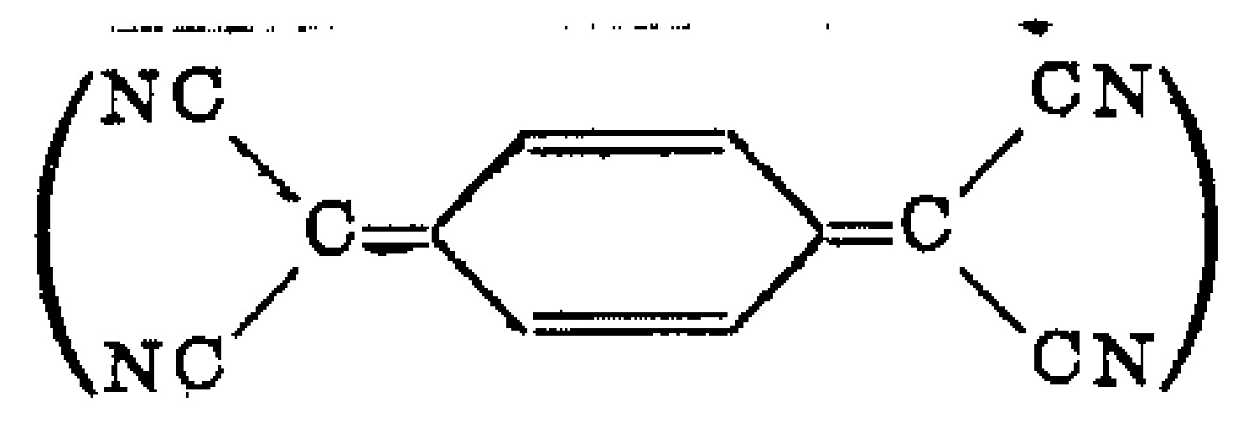
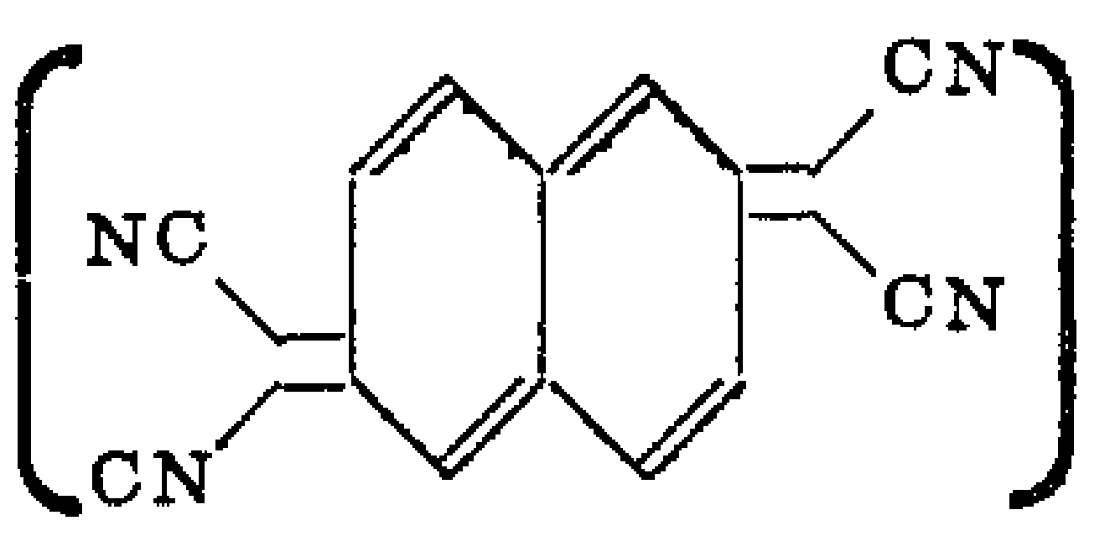


or both, and B is



or



or both.

2. A thermoelectric device according to claim 1 wherein said compound or composition is a composition containing one or more compounds according to claim 1.

3. A thermoelectric device according to claim 2 wherein one of said compounds comprises at least 80 mole percent of said composition.

4. A thermoelectric device according to claim 2 wherein the compounds are present in about equimolar amounts.

5. A thermoelectric device according to claim 1 wherein said compound is (tetrathiafulvalene)$^+$(7,7,8,8-tetracyano-p-quinodimethane)$^-$.

6. A thermoelectric device according to claim 1 wherein the compound is (tetrathiafulvalene)$^+$ (11,11,12,12-tetracyano-2, 6-naphthaquinodimethane)$^-$.

7. A thermoelectric device according to claim 1 wherein the compound is (2,5-cyclohexadiene-1,4-diylidene-bis-1,3-dithiole)$^+$ (7,7,8,8-tetracyano-p-quinodimethane)$^-$.

8. A thermoelectric device according to claim 1 wherein the compound is (2,5-cyclohexadiene-1,4-diylidene-bis-1,3-dithiole)$^+$ (11,11,12,12-tetracyano-2,6-naphthaquinodimethane)$^-$.

9. A thermoelectric device according to claim 1 wherein said device is a cooling device.

10. A thermoelectric device according to claim 1 wherein said device is an electrical generator.

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