NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546

REPLY TO
ATTN OF: GP

October 15, 1970

TO: USI/Scientific & Technical Information Division
Attention: Miss Winnie M. Morgan

FROM: GP/Office of Assistant General
Counsel for Patent Matters

SUBJECT: Announcement of NASA-Owned
U.S. Patents in STAR

In accordance with the procedures contained in the Code GP to Code USI memorandum on this subject, dated June 8, 1970, the attached NASA-owned U.S. patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No. : 3,274,304

Corporate Source : Marshall Space Flight Center

Supplementary
Corporate Source :

NASA Patent Case No.: XMF-01016

G. Parker

Gayle Parker

Enclosure:
Copy of Patent

N71-17818
(ACCESSION NUMBER) (THRU)
6 00
(PAGES) (CODE)
26
(NASA CR OR TMX OR AD NUMBER) (CATEGORY)

FACILITY FORM 602

NASA-HQ

COSATI 09A

N71-17818

Sept. 20, 1966 J. C. HORTON ETAL 3,274,304
METHOD OF MAKING IMPURITY-TYPE SEMI-CONDUCTOR
ELECTRICAL CONTACTS
Filed Nov. 26, 1963

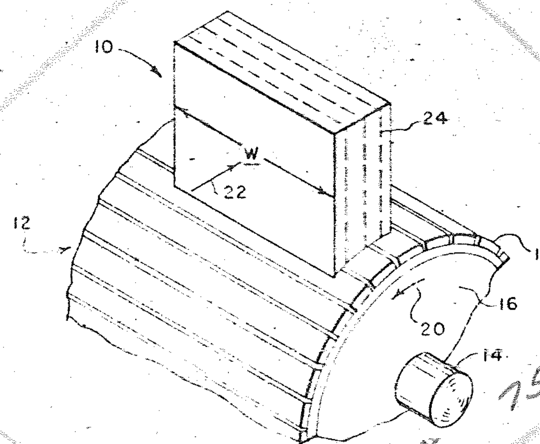

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FIG. 1

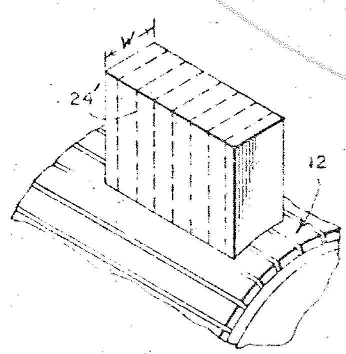

FIG. 2

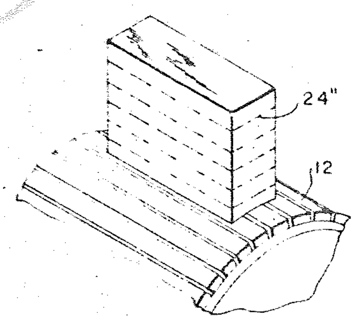

FIG. 3

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BY

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United States Patent Office

3,274,304

Patented Sept. 20, 1966

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3,274,304

METHOD OF MAKING IMPURITY-TYPE SEMICONDUCTOR ELECTRICAL CONTACTS

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Filed Nov. 26, 1963, Ser. No. 326,299
3 Claims. (Cl. 264—27)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates generally to an assembly for transferring electrical energy from stationary to moving parts while simultaneously providing lubrication for the contacting surfaces. More specifically this invention relates to commutation or collection assemblies such as, for example, the brush-commutator assemblies found in electrical motors or generators which will function properly over an extended period of time in the adverse environment encountered in outer space, and the method of forming these collection assemblies.

As is well known in the electrical energy transfer field, commutator or brush assemblies must possess certain basic electrical and physical properties under all the operating conditions that are normally to be encountered during use if proper operation of the assembly is to be obtained. These basic properties include, among other things, (1) adequate lubrication of the contact surface, (2) low contact resistance, (3) minimum arcing, and (4) as low a noise factor as possible. Although all of these requirements are important and somewhat interrelated, perhaps the most important of the four is that relating to the lubrication of the contact surface.

As is readily apparent, good lubrication between contact surfaces carrying an electrical current is necessary to prevent the finished surfaces from becoming rough thus increasing their contact resistance and wear rate. Since arcing is a function of contact resistance as well as the conditions of the contacting surfaces, the lubricating qualities of a brush assembly also has a direct bearing upon the arcing factor existing within an electrical system. Radio noise or interference with radio frequency devices in turn is proportional to the amount of arcing within the electrical system. Thus it is seen that if the electrical contact parts are inadequately lubricated the life of the parts will be diminished and undesirable radio interference will be produced.

Brush assemblies for collecting or distributing electrical current have heretofore been constructed predominantly of carbon or graphite which exhibits excellent electrical conductivity and provides good lubrication for the contacting surfaces over a wide range of operating conditions. It has been found, however, that brushes formed of carbon or graphite depend upon absorbed oxygen and water vapor for their lubricating qualities.

Oxygen has been found to be necessary for good lubrication between moving parts since it must necessarily be present before any oxide layer can be formed. In the case where copper is used as the slip ring, oxygen combines with the exposed copper to form a layer of cuprous oxide (the oxide of monovalent copper) on the order of 2×10^{-6} centimeters thick. The formation of this cuprous oxide layer is aided by the heating of the slip ring during operation; however, excessive heating, as produced by arcing, will result in the layer being reduced to metallic copper and carbon monoxide thereby leaving a clean copper spot on the slip ring. With an oxide layer effectively saturating the surface of the copper slip ring, the bonding energy of the surface of the ring is greatly reduced.

Apparently the water vapor is necessary in carbon contacts since it causes an extremely low bonding energy to exist between crystallites of the graphite due to the saturation of the crystallite spaces by the vapor. With the graphite in this condition, a carbon film is easily deposited on the copper slip ring, which has a very low surface energy as mentioned hereinabove, and the surface of the contact becomes carbon sliding on carbon. Consequently, where there is adequate moisture and oxygen in the atmosphere, the presence of these elements at the contacting-surface between the brush and collector ring causes the carbon or graphite in the brush to form a thin lubricating coating which acts to substantially eliminate any wear.

From the foregoing it will be readily apparent that the use of carbon or graphite brushes is restricted to those instances where water vapor and oxygen pressure are at an adequate level. There are numerous instances, however, in which it is desirable to operate dynamoelectric apparatus where there is little or no oxygen and/or water vapor present such as exists at high temperatures or in sub-zero temperatures. Where carbon or graphite brushes are employed or dynamoelectric apparatus in these reduced atmospheric conditions, it has been found that they wear at a rate so excessive that the operation of the dynamoelectric apparatus is severely impaired. For example, at altitudes of 60,000 feet and higher where the air pressure may be less than 50 mm. of mercury and the moisture present may be so low that the dew point is below −50° C., the operation of the dynamoelectric apparatus utilizing carbon brushes will be erratic or even cease functioning entirely since the carbon brushes will wear and dust away completely in a relatively short period of time.

This problem of developing a suitable brush assembly for operating where little or no moisture or oxygen is present received an intense effort toward solution during World War II due to its military significance in high altitude aircraft. The solution finally adopted was the use of a halogen additive to standard graphite, the most common being barium fluoride. The success of this additive was based upon the reaction of barium fluoride with the rotating surface, normally copper, to produce cuprous fluoride. This compound of cuprous fluoride was highly unstable and immediately decomposed to form cuprous oxide (on the copper rotating surface) and the original halogen compound thus maintaining an oxide film on the copper. This assured the presence of the oxide layer on the rotating surface.

Subsequent developments produced carbon brushes with inclusions such as cavities, or recesses extending away from the contact surfaces of the brush, that were filled with a special non-carbonaceous solid lubricating material which was adapted to periodically engage the moving surface of a current transfer device. The most common lubricating material to be incorporated in a brush of this type was molybdenum disulfide as described, for example in the United States Patent No. 2,736,830.

These compound type brushes are generally intended to operate at altitudes of less than 60,000 feet corresponding to a vacuum of only 54 mm. Hg. Brushes of this type have, however, been found totally unacceptable for use in space probes or like vehicles which operate at extremely high altitudes. For example, the use of a compound brush provided with inclusions of molybdenum disulfide operated in a vacuum of 2×10^{-6} mm. Hg: (equivalent to an altitude of 450,000 feet) revealed a wear rate of 0.006 inch/hour. This would limit the useful life of the brush to less than 60 hours.

According to the present invention, it has been found that a brush assembly can be produced which gives excellent electrical conductivity and good lubrication for contacting surfaces over the wide range of operating conditions encountered in space environments. This assembly consists, in part, of a semiconductor current carrying medium of the type having charge carriers supplied by impurities deliberately introduced into the host material in large quantities. Such a degenerate, impurity-type semi-conductor has been successfully fabricated by sintering a semi-conductor, such as molybdenum disulfide, with a metal, such as copper or silver, at extremely high temperatures and pressures to give a current carrying medium of molybdenum disulfide-cuprous sulfide or molybdenum disulfide silver sulfide and silver. The degenerate semi-conductor is then cut or otherwise formed into brushes so that the grain orientation of the material is parallel to the plane of movement of the brush to be encountered during operation.

Therefore, the primary object of this invention is to provide an electrical contact material for use in vacuum environments.

It is the further object of this invention to provide a contact brush for operating in the invironment existing in outer space which is fabricated from a degenerate, impurity-type semi-conductor.

These and further objects and advantages of this invention will become more apparent upon reference to the following specification, claims, and appended drawings wherein:

FIGURE 1 is a fragmentary view in elevation of a commutator and a brush, constructed in accordance with this invention;

FIGURE 2 is a fragmentary view in elevation of a commutator having a modified brush assembly showing another arrangement of the laminated layers; and

FIGURE 3 is a view of a commutator device showing another arrangement of the layers of the brush assembly.

As mentioned hereinabove, the prior accepted method of fabricating brushes for use up to approximately 60,000 feet consisted of forming an aperture or slot in a main body of carbonaceous lubricating material into the aperture. A loose mixture or unsintered molybdenum disulfide and a pure metal added thereto for forming a conductive path through the molybdenum disulfide was one form of non-carbonaceous material used in a compound brush of this type. The theory of operation of this compound brush is that under ordinary low altitude conditions the contact-making role of the brush is assumed by the carbonaceous material, which is usually carbon. Since the insert of non-carbonaceous material wears at a rate that is far in excess of the normal rate of the carbonaceous part, it does not interfere with the functioning of the brush. However, at altitudes of from 30,000 to 60,000 feet elevation where little moisture and oxygen is present the carbonaceous material of the brush wears or "dusts" away at a rate that is similar to the non-carbonaceous filler material. This results in an extremely high wear rate, and subsequent short life.

As will be readily apparent, the so-called compound brush has numerous disadvantages that totally preclude its use in a vacuum environment and greatly restricts its use in many other environments. The most serious of these disadvantages is the fact that under certain conditions the molybdenum disulfide and graphite will react to form molybdenum carbide, a very abrasive material which causes severe commutator wear. Furthermore, as the carbon portion of the compound brush loses is lubricating qualities it will remove portions of the oxide film from the commutator. A roughened surface is soon produced and arcing may result. Once an arc is struck it will be self sustaining and grow steadily worse since any lubricating film found on the commutator will be destroyed by the heat being produced. In those cases where the brush and commutator are operating in a vacuum, the

heat build-up caused by arcing will be extremely fast and will shortly result in the complete breakdown and failure of the brush.

In the present invention, the above mentioned disadvantages are overcome and a superior brush assembly thereby produced by utilizing a semi-conductor material doped with more than the optimum amount of added carriers. The optimum type and quantities of materials and the method of producing this superior brush assembly is obtained in the following manner:

A preselected percentage by volume of molybdenum disulfide and copper or silver (ranging 15% to 99% molybdenum disulfide) with the remainder being either copper or silver, are weighed out and placed in a mortar. The powdered materials are then mixed with a spatula or with a pestle, no attempt being made to grind either of the powdered materials. Mixing is continued until the powdered copper or silver appears to be uniformly dispersed throughout the molybdenum sulfide.

The mixture of powders is then poured into a graphite mold, care being taken to avoid segregation of the particles. Mold plungers are now placed in the mold and a thermocouple introduced into a well in the mold case wall. The complete mold assembly is now placed in a hot press furnace and the thermocouple connected to a suitable temperature indicator-controller.

A load corresponding to 3500 lbs. per square inch of plunger cross sectional area is now applied to the plungers. The temperature controller is set at from 1600 to 1700 degrees Fahrenheit and the temperature of the furnace is allowed to rise as rapidly as possible. The load is maintained on the plungers during the heat-up and for 10 minutes after the control temperature of 1600 to 1700 degrees Fahrenheit has been reached. The load is now removed from the plungers, the mold assembly removed from the furnace, and the semiconductor material removed from the mold. The semiconductor material is now allowed to cool to ambient temperature.

X-ray diffraction analysis of the material produced in the above manner indicates that no free copper and little free silver remained in the brush material and that the composition is made up of molybdenum disulfide and copper sulfide or silver sulfide and silver. Therefore, no metallic conductor is present in the case of copper, and little in the case of silver. Both molybdenum disulfide and copper sulfide, for example, are classified as semiconductors and thus individually are poor current carriers. Based on these facts it would be expected that a brush formed from these materials alone would exhibit high resistance and thus be a poor electrical brush. However, this was found not to be true in the instant case since the molybdenum disulfide and copper sulfide or silver sulfide combined to give a material having a negative temperature co-efficient of resistivity and extremely good conductivity.

The exact theory involved in producing these totally unexpected but desirable results is not known. It is believed; however, that the semi-conductor material produced in the above described manner is one in which charge carriers are supplied by the copper or silver impurities which were deliberately introduced in extremely large quantities into the host material, molybdenum disulfide. This type material has been designated as a degenerate impurity-type semi-conductor.

This theory would appear to be borne out by the following facts. As mentioned hereinabove, molybdenum disulfide in its pure state is not a useful semi-conductor but is classified as an intrinsic semi-conductor. It is characterized (at 0° K.) by a completely filled valence band and a completely empty conduction band, separated by a forbidden region (or energy gap) where there is no probability of an electron normally existing. Conduction (at temperatures greater than 0° K.) results from the thermal excitation of an electron from the valence band to the conduction band. This results in a negative charge carrier (the excited electron) in the conduction band, and a positive charge carrier (the hole remaining) in the valence band, both of which may contribute to conduction. The number of hole-electron pairs created is dependent on the width of the forbidden band and the Fermi-Dirac distribution which states the probability that any of the possible energy states are occupied.

As temperature is increased, more hole-electron pairs are created, and the resistivity therefore drops. However, as the temperature increases, the energy of the phonons in the lattice is also increased, resulting in a much greater probability of electron-phonon collisions and a resulting decrease in electron mobility. Thus, intrinsic conduction in the molybdenum disulfied is primarily by positive holes and is of such a low value as to prohibit the use of molybdenum disulfide in a pure state as a current carrying medium.

In an intrinsic semi-conductor (at 0° K.), the Fermi level is located half way between the conduction and valence bands. However, as the temperature increases, the width of the energy gap decreases and the Fermi level shifts away from the midpoint. The Fermi level will move toward the conduction or valence band depending on whether the majority carrier becomes electrons or holes. A change in impurity concentration will shift the Fermi level toward the conduction band or valence band depending on whether the impurity is a donor (contributes electrons) or an acceptor (accept electrons, i.e., donates holes). Such a shift in the Fermi level toward the conduction band would account for the unexpected results obtained in the present material.

Initial testing of the hot-pressed molybdenum disulfide/metallic powder brushes produced in the above manner demonstrated that they were considerably superior to any heretofore known brushes. Improvement in test results was realized with each brush containing a successively higher percentage of molybdenum disulfide. Brushes of 80% molybdenum disulfide-20% copper, for example, were the first that could be considered to be acceptable for use in space vehicles. They ran for 406 hours at a pressure of 4×10^{-7} millimeters of mercury with little brush wear and no damage to the commutator. Smooth contact surfaces and a good lubricating film were maintained. The maximum contact resistance recorded was four (4) ohms. The test was terminated prior to brush failure in order that the test equipment could be employed for other tests.

Results of brushes composed of 90% molybdenum disulfide and 10% copper showed definite improvements over the brush material used in the previous test. Brush wear was almost negligible and the commutator was coated with molybdenum disulfide. Again, the contact resistance was only four ohms. The test was terminated after 710 hours due to failure of the test assembly bearings. No evidence of brush failure was noted at the time of the bearing failure.

It was noted, however, during these tests that out of a group of brushes made at the same time and in the same manner, certain brushes exhibited considerably longer operating life-times than other brushes from the same group. It was theorized that this phenomenon was due to orientation occurring within the brush materials during its formation which resulted in an anisotropic material being produced. Further investigation into this phenomenon proved the theory to be correct and showed that this orientation occurred because the molybdenum disulfide platelets slide easily in one plane while resisting motion in another. During compaction, the individual platelets tended to slide over one another and align themselves in layers, thus producing an anisotropic material whose plane of laminations were perpendicular to the pressure applied during hot pressing. Therefore, the brushes lubricated more readily and, hence, ran easier in one particular plane orientation with respect to the commutator surface than in another plane orientaiton. To

substantiate this finding, three sets of brushes were cut, each orthogonal to the other two and run in separate tests. The results of the test were conclusive in sustaining the existence of a laminar structure.

In order to more clearly illustrate the construction and operation of a brush assembly constructed in accordance with this invention, reference is made to the accompanying drawing with initial attention being directed to FIGURE 1 which illustrated a brush **10** applied to the commutator surfaces **12** of a dynamoelectric machine. The machine comprises a shaft **14** upon which is mounted a suitable support **16** for retaining computator segments **18**. The shaft **14** is in turn supported by suitable bearings (not shown) and is adapted to rotate in a counter-clockwise direction as indicated by arrowhead **20**.

The brush **10** is formed from a degenerate impurity-type semiconductor material made in accordance with the method described hereinabove. In producing the semiconductor material, the pressure applied during the sintering step was in the direction of the arrowhead **22** which, as can be seen in FIGURE 1, is parallel to the commutator surfaces **12**. For purposes of clarity the laminations produced by the pressure sintering of the material is picturely shown by the broken lines **24** that run the width *w* of the brush **10**. It is to be realized, however, that the laminations **24** are normally not visible. For optimum operation, each brush should be formed so that the laminations **24** are substantially perpendicular to and have a maximum width *w* along the surface of contact so that the maximum laminate contact surface that the configuration of the brush will permit is always in contact with the cummutator surface **12**.

FIGURE 2 illustrates a brush which is cut so that the laminations **24'** are perpendicular to the surface of contact of the commutator surfaces **12**, but as will be noted the width *w* of the laminations is less than the maximum obtainable for this brush configuration. A brush cut in this manner will, therefore, run rather roughly and tends to split or separate longitudinally along the laminations **24'**. In FIGURE 3 a third possible orientation is illustrated in which the laminations **24''** are parallel to the commutator surface. Although this configuration ran easily it tends to separate prematurely along the laminations **24''**.

Numerous other brushes, which were produced with the hot pressing temperature varied over a range extending from about 1600° F. to 1900° F. (limits of sintering temperature), were cut and tested to determine if the temperature of formation effected the laminar structure. No appreciable difference in the operating characteristics of the brushes produced under these varying conditions could be detected.

Once the proper method of forming and cutting the degenerate impurity-type semi-conductor material was known, additional attention was given to further improving the quality of the material by reducing its specific resistivity. It was known that if such a reduction could be accomplished that the overall properties of the material for uses as a current carrying contact material would be greatly increased. It was found that this reduction in resistivity could be produced by inducing a current through the material of sufficient strength to produce a temperature rise of 80° to 100° C. Once this temperature is reached the current is removed and the material is allowed to cool to ambient temperatures. Although the exact theory which produces the drop in resistance of the material from 1 ohm cm. to .8 ohm cm. is not known, it is thought to involve a lattice reorientation due to intrinsic heating.

From the foregoing it will be readily apparent that the present invention not only provides a novel and extremely useful degenerate impurity type semiconductor which can readily be shaped into or formed as various electrical current transfer contact surfaces for use at both atmospheric pressure and in a vacuum environment, but also provides a novel method of producing, forming and treating such a semi-conductor. The use of both the proper degree of heat and pressure during the forming of the degenerate semi-conductor causes the metallic additives to enter the molybdenum disulfide substitionally, thereby forming the degenerate semi-conductor material. In the absence of such heat and pressure no re-orientation of the element would occur and the novel semi-conductor would not be produced. By properly observing the orientation of the laminar structure of the novel semi-conductor, it is possible to form contact surfaces having various mechanical strength, wear resistance, and electrical properties. Furthermore, the present invention teaches how the resistance of the semi-conductor contact material can be reduced by simply exposing it to a temperature rise of 80°–100° C. that is self induced by passing a predetermined current through the material.

The invention may be embodied in other specific forms without departing from the spirit of essential characteristics thereof. The present embodiments are therefore to be considered in all respect as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes would come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

What is claimed and desired to be secured by the United States Letters Patent is:

1. A method of making an impurity-type semiconductor electrical contact brush, comprising:
   (a) mixing from 15 to 99 percent by volume of powdered molybdenum disulphide with from 1 to 85 percent by volume of a powdered metal selected from a group of copper, silver, and mixtures thereof;
   (b) placing said mixture in a mold;
   (c) compacting said mixture by pressure applied in one direction at approximately 3500 pounds per square inch;
   (d) firing said mixture at a sufficiently high temperature and for a period of time to convert said mixture into a sintered block of overly doped anisotropic molybdenum disulphide;
   (e) removing said block from said mold for cooling to ambient temperature;
   (f) shaping said block into the desired form of an electrical contact brush so that its plane of laminations are substantially perpendicular to and have a maximum width along the surface to be contacted by said brush;
   (g) passing an electrical current through said block of sufficient strength to product a temperature rise of from 80 to 100 degrees centigrade; and

   (h) removing said electrical current and allowing said block to cool to ambient temperature thereby producing a lattic reorientation due to intrinsic heating and thereby lowering the specific resistivity of said brush.

2. A method of lowering the specific resistivity of an electrical brush composed of a sintered mixture consisting of molybdenum disulphide and a metallic powder selected from a group consisting of silver, copper, and mixtures thereof; comprising:
   (a) passing an electrical current through said brush of sufficient strength to produce a temperature rise of from 80 to 100 degrees centigrade; and
   (b) stopping said current passing through said brush so said brush is allowed to cool to ambient temperature.

3. A method of making an impurity-type semiconductor electrical contact brush, comprising:
   (a) mixing from 15 to 99 percent by volume of powdered molybdenum disulphide with from 1 to 85 percent by volume of a powdered metal selected from a group of copper, silver, and mixtures thereof;
   (b) compacting said mixture by pressure applied in one direction;
   (c) firing said mixture at a sufficiently high temperature and for a period of time to convert said mixture into a sintered block of overly doped anisotropic molybdenum disulphide;
   (d) cooling said block to ambient temperature;
   (e) passing an electrical current through said block of sufficient strength to produce a temperature rise of from 80 to 100 degrees centigrade; and
   (f) removing said electrical current and allowing said block to cool to ambient temperature thereby producing a lattice reorientation due to intrinsic heating and thereby lowering the specific resistivity of said block.

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