United States Patent [19]

Fagan

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[54] **PACKAGING AND PURIFYING GRAPHITE**

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[73] Assignee: **Union Oil Company of California,** Los Angeles, Calif.

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[21] Appl. No.: **301,446**

[52] **U.S. Cl.** **206/443,** 206/84, 423/461

[51] **Int. Cl.** **B65d 85/20**

[58] **Field of Search** ..... 206/1 R, 46 R, 65 R, 84; 220/1 R; 423/448, 461; 229/DIG. 12

[56] **References Cited**

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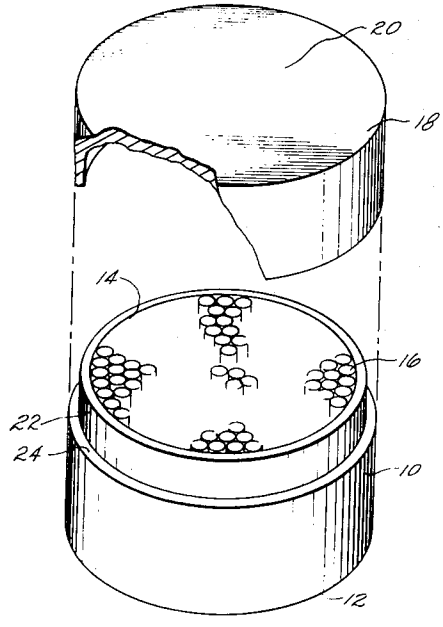
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Primary Examiner—William I. Price
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Attorney, Agent, or Firm—Richard C. Hartman; Dean Sanford; Michael H. Laird

[57] **ABSTRACT**

This invention relates to packaged graphite articles and to graphite containers for such articles. Graphite bodies are contained within a central cavity of a container, at least a portion of which is formed of graphite that is permeable to gases but substantially impermeable to airborne solid particles. The container comprises a receptacle having a through opening in at least one wall thereof with a closure member adapted for removable attachment to said receptacle in a sealing configuration to the through opening. The package is prepared by placing impure graphite bodies, typically those containing up to about 800 ppm of metallic and inorganic impurities in the receptacle, placing the closure member on the receptacle and inserting the resultant package within a purification furnace wherein it is contacted by a halogen-containing gas for a period of time and at a temperature sufficient to permit penetration of the halogen into the receptacle cavity, to contact the graphite bodies contained therein, to cause the halogen to react with and volatilize the inorganic impurities, and to expel such impurities from the graphite bodies and the receptacle cavity. The invention is applicable to the preparation of spectroscopically pure electrodes useful in analytical techniques and, in a typical embodiment, a cylindrical container of approximately three inches outside diameter and and two and three-eighths inches in height is loaded with 100 spectroscopic electrodes that are 0.25 inch in diameter and 1.5 inches in length, the receptacle is closed, placed in a furnace and heated to and maintained at a temperature of 2,200°C. for a period of about 8 hours while exposed to the action of a halogen-containing gas. The package removed from the furnace is preferably covered with a thin plastic film, labelled and is placed in a shipment container for delivery to the ultimate consumer. By this method, the spectroscopically pure environment in the cavity of the receptacle is not disturbed until the receptacle is opened by the ultimate consumer.

7 Claims, 8 Drawing Figures



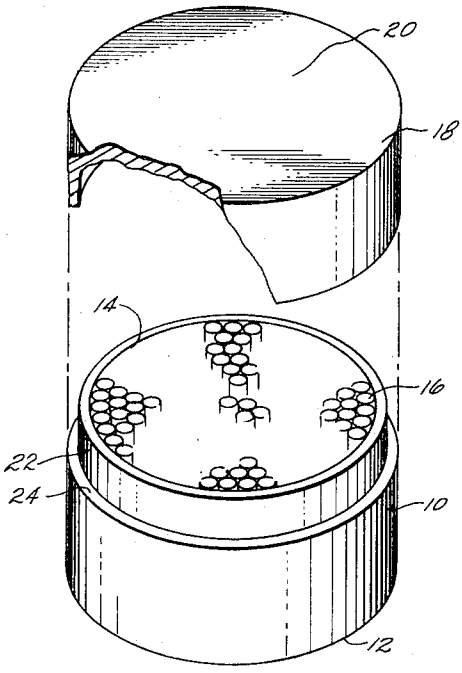


FIG. 1

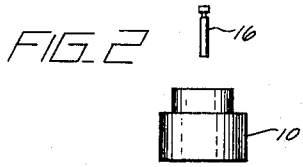


FIG. 2

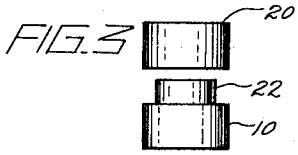


FIG. 3

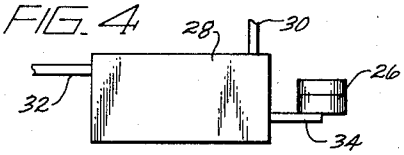


FIG. 4

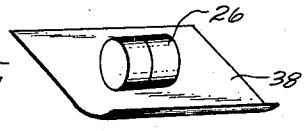


FIG. 5

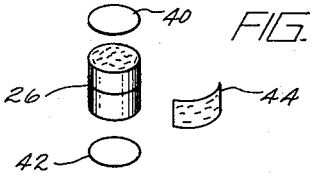
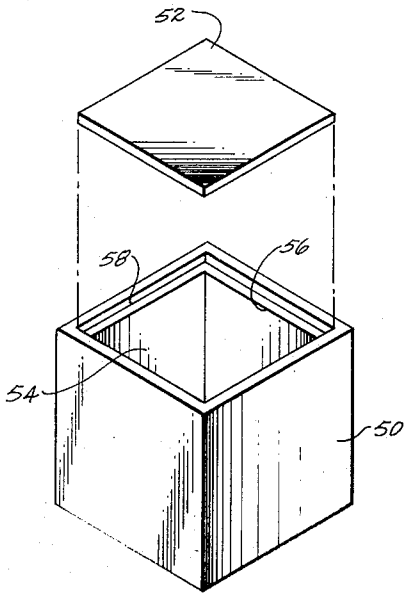


FIG. 6

FIG. 7



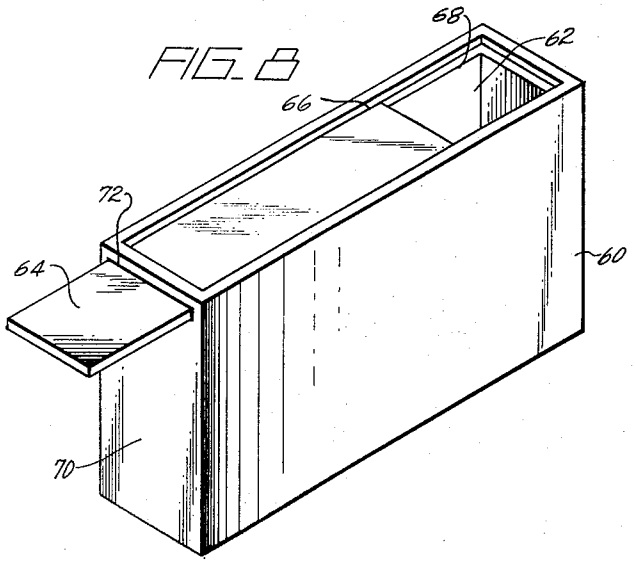


FIG. 8

PACKAGING AND PURIFYING GRAPHITE

BACKGROUND OF THE INVENTION

This invention relates to a method for packaging and for purifying of graphite and, in particular, relates to a package and method of preparation of pure graphite bodies such as spectroscopic electrodes, filters and fragile, small electronic parts.

There are a considerable number of uses for bodies of highly pure graphite, e.g., of graphite having less than 20, preferably less than about 10, weight parts per million of inorganic contaminants. Some of these uses are fragile electronic parts such as hearth liners for electron beam guns, filter discs for use in atomic absorption spectroscopy and as electrodes in emission spectroscopy. The graphite bodies are commonly prepared from a suitable carbonaceous source, e.g., coal or petroleum coke, which is calcined, comminuted, blended with a suitable binder, molded, baked and ultimately graphitized. The graphite is then machined to obtain the graphite bodies of the desired shape and size for use.

Since the carbonaceous source is relatively impure and contains a considerable amount of impurities, e.g., metallic impurities such as iron, aluminum, vanadium, copper, zinc, etc., it is necessary to purify the graphite. Such purification can be accomplished by subjecting the graphite material to an elevated temperature in the presence of a halogen-containing gas in the manner described in U.S. Pat. No. 2,734,799–801. By this method, graphite having impurities at concentrations up to about 400 to 800 ppm can be purified to a level of impurities less than about 10 ppm.

After purification, however, extreme care must be taken to prevent recontamination of the graphite. The graphite must be removed from the purification furnace and handled and packaged in a clean room or area which is free of airborne solid particles. Failure to control the environment in subsequent handling and packaging of the graphite bodies can result in sufficient recontamination to render them unsuited for the intended use. Thus recontamination of spectroscopic electrodes can provide a significant and uncontrolled background of inorganic impurities which will lower the precision and accuracy of analyses performed when using such electrodes in the conventional analytical spectrometers.

Carbon cloth has often been used to protect carbonaceous bodies during handling and graphitizing operations, as shown in U.S. Pat. No. 3,308,943. This same procedure has been used to protect and shield purified graphite electrodes against breakage and contact contamination. In the prior technique, the impure graphite electrodes are wrapped in carbon cloth and the entire package is placed in a purification zone. After purification, the package is removed and is placed in a container for shipment to the consumer. While this procedure eliminates contact contamination, i.e., the transfer of impurities by the direct contact of the electrodes with impure carbonaceous material or metallic tools, it does not isolate the graphite electrodes from airborne solid particulate matter. Accordingly, the precaution for use of a clean room and elimination of all airborne particulate matter during the packaging operation must still be observed. Similarly, the ultimate consumer does not receive a container in which the electrodes are protected and shielded against atmospheric contamination since the carbon cloth is relatively porous and does not filter airborne particulate matter.

BRIEF DESCRIPTION OF THE INVENTION

I have now found that graphite electrodes can be purified while contained within a container comprising a receptacle formed of graphite and having a central cavity, a through opening in at least one wall thereof, and a closure member in sealing relationship to said through opening during the purification. In the method of packaging and purification, the receptacle cavity is loaded with one or more bodies of impure graphite containing up to about 800 ppm of inorganic impurities and the closure member is placed on the receptacle. The resulting package is then placed in a purification furnace and is subjected to purification.

The graphite which is used to form at least a portion of the container comprises a graphite which is permeable to gases but which is relatively impermeable to airborne solid particulate matter. Typically, the graphite has interconnecting pores with average pore diameters no greater than about 0.4–0.5 micron.

Various sizes and shapes can be used for the graphite container; cylindrical receptacles and closure members are readily machined and formed and, accordingly, comprise a preferred shape. Other shapes which can be used comprise various polygonal cross-sectional shapes such as cubes, tetrahedrons, octahedrons, dodecahedrons; spheres; ellipsoids; etc. Regardless of the shape or form of the container, it should comprise a receptacle having a central cavity defined by walls with a through opening in at least one of the walls for insertion and removal of the graphite bodies. The container should also have a closure member or cover adapted for placement over the through opening in a sealing relationship thereto, together with means for retaining the cover or closure member on the receptacle. Preferably, the retaining means permits the removal and repeated reseating of the closure member on the receptacle. Various mechanical joint means can be employed such as threaded fitting members, telescoping members, bayonet fitting members, i.e., wherein one member has a key and the other member bears a mating keyway, etc.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** illustrates a suitable receptacle and closure member;

FIGS. **2** through **6** illustrate the sequence steps in the method of packaging and purification; and

FIGS. **7** and **8** illustrate various alternative forms for the receptacle.

DESCRIPTION OF PREFERRED EMBODIMENTS

Referring now to FIG. **1**, the invention is shown as comprising a package of a container and graphite bodies. The container comprises, in part, a receptacle **10** having a bottom **12**, a central cavity **14** and a continuous, circular sidewall, defining a cylindrical receptacle. Disposed within the central cavity **14** are a plurality of graphite bodies **16** in the form of slender, cylindrical rods such as those typically employed in spectroscopic equipment. In a typical embodiment, these electrodes are from 0.16 to about 0.38 inch in diameter and approximately 1 to about 12 inches in length. One or more of such bodies can be contained within receptacle

10. In a typical embodiment, the receptacle is about 3 inches in outside diameter and about 2.5 inches in height with a central cavity approximately 2.74 inches in diameter, sufficient to accomodate approximately 100 of the slender cylindrical electrodes 16. These rods are packed within the central cavity 14.

The other part of the container is the closure member or cover 18. The cover and receptacle bear cooperative means for the removable attachment of cover or closure member 18 to receptacle 10. The closure member is illustrated as a second cylindrical member having a top or cover surface 20 and a cylindrical wall of approximately the same diameter as that of receptacle 10. The inboard end of receptacle 10 has a reduced outside diameter to provide an upstanding boss or neck 22 with shoulder 24 between neck 22 and the lower base of receptacle 10. This neck fits within the cylindrical cavity of closure member 20 and, preferably, these members fit snugly to provide for frictional engagement of closure member 20 on neck 22. Alternatively, other attachment means can be used, e.g., the neck 22 can be threaded and mating female threads can be cut on the interior periphery of the cylindrical walls of closure member 20, or either of the closure member or receptacle can bear key means with mating keyway means carried by the other of said numbers to provide a bayonet type interlock.

Referring now to FIGS. 2 through 6, the method of packaging and purification will be described. As shown in FIG. 2, receptacle 10 is loaded with the slender cylindrical electrodes 16 by placement of a plurality of electrodes 16 within central cavity 14. The closure member 20 is thereafter placed over the neck 22 of receptacle 10 and the completed package of container and electrodes is then subjected to purification.

The purification is performed in a suitable furnace 28 having heating means, not shown, and means for introduction of a halogen-containing gas through conduit 30 and for removing gaseous products therefrom through conduit 32. Electrical induction heating is commonly used in suitable furnaces to attain the high temperatures needed for purification. The closed package 26 is placed within the furnace, door 34 is closed and the furnace is slowly heated to the desired purification temperatures. In a typical purification procedure, an inert gas such as nitrogen, argon, etc., is introduced into the furnace and the furnace is slowly heated. When the furnace has reached a temperature from about 600° to 2,000° C., a suitable halogen-containing gas is introduced through conduit 30. Various halogen-containing gases can be used including the elemental halogens such as chlorine, fluorine, bromine, iodine, etc. Of the halogens, chlorine and fluorine are preferred and a mixture of these two halogens is most preferred. Other suitable halogenating gases include carbon tetrachloride, carbon tetrafluoride, and any halogenated hydrocarbon which will dissociate to give free chlorine and/or free fluorine at a temperature of at least about 800° C. Examples of such materials include difluorodichloromethane, methyl chloride, bromotrifluoromethane, ethylidenefluoride, dichloromonofluoromethane, dichlorotetra-fluoroethane, monochlorodifluoromethane, monochlorotrifluoro-methane, trichloroethylene, trichloromonofluoromethane, trichlorotrifluoroethane, etc.

The halogen-containing gas is slowly introduced into the furnace 28 by suitable means such as by depressuring a reservoir of the halogen-containing gas into the furnace or by bubbling a stream of nitrogen through a reservoir of a liquid halogenated compound to vaporize a preselected amount of the liquid and carry it into the furnace. The furnace is heated to a suitable purification temperature, e.g., from about 1,800° to about 2,400° C. and maintained at that temperature while slowly introducing the halogen-containing gas over a period of time sufficient to insure thorough penetration of the halogen-containing gas into the cavity of the container and the electrodes, the vaporization of the inorganic impurities as volatile halides, expulsion of the volatile impurity halides from the cavity of the container and their removal from the furnace 28 through conduit 32. Typically the time for such reaction and purification is from about 3 to about 15, preferably from about 7 to about 10 hours at the aforeindicated temperatures. The flow of the halogen-containing gas in the furnace 28 is preferably maintained from about 4 standard cubic feed per hour to about 8 standard cubic feet per hour per cubic foot of furnace space during the purification period.

When it is determined that the purification is complete, as indicated by the necessary time at the purification temperature, or, if desired, by monitoring of the exit gases through conduit 32 and detecting when no further impurities are being expelled, the purification treatment is ceased. The heating of the furnace is discontinued and the contents of the furnace are permitted to cool slowly while circulating a stream of nitrogen through conduits 30 and 32. When the furnace reaches approximately 100° C., the graphite receptacle 26 can be removed and the receptacle can be permitted to cool in the atmosphere to ambient temperatures. Thereafter the receptacle is ready for handling, shipping and storing.

Since the graphite container tends to mar or mark surfaces in which it comes into contact, it is preferred to place a sheet or film of a protective material such as a plastic film 38 about the package 26. Any suitable plastic film with a thickness of from 0.5 to about 10 mils can be used such as polyethylene, polypropylene, polyvinylacetate, polyethylidene dichloride, cellulose, acetate, cellulose nitrate, etc. A preferred plastic for this use is heat shrinkable polyvinyl-chloride film with a thickness of from 0.5 to about 2 mils. This film is simply rolled about cylindrical package 26 and the ends are folded together and the entire package is thereafter subjected to a temperature from about 315° to about 360° F. This treatment fuses the folded ends of the film and shrinks the film tightly about the package to form a neatly sealed package.

Thereafter, suitable decals and identifying labels can be placed on the package. These are shown as end seals 40 and 42 and a typical gummed label 44 carrying identifying markings.

As previously mentioned, various shapes and forms can be used for suitable receptacles and cooperating closure members. FIG. 7 illustrates a suitable cubical receptacle 50 with a closure member 52. The receptacle 50 has a central cavity 54 with an access aperture 56 communicating therewith. The receptacle also has attachment means for closure member 52 that comprises a shoulder 58 which provides a seat or stop for closure member 52. As with the receptacle and closure member described in FIG. 1, the closure member 52 can fit snugly in engagement with the upper edge of the

sidewalls of receptacle **50** to provide removal attachment means between the closure member **52** and receptacle **50.**

Another form or shape of the receptacle and closure member is illustrated in FIG. **8** as comprising a generally rectangularly shaped receptacle **60** having a central cavity **62** with a closure member **64.** At least one wall of the receptacle **60** has an access opening **66** and closure member **64** is adapted to be placed in sealing relationship across access opening **66.** The closure member is secured to the receptacle **60** by a groove **68** which extends along the inside opposite sidewalls of receptacle **60,** adjacent the access opening **66.** The endwall **70** is also slotted at **72** contiguously with the longitudinal grooves **66** to permit closure member **64** to be slid into these grooves and thereby close the access opening **66.**

The package of the receptacle, closure member and contained graphite bodies should be permeable to the flow of halogen-containing gases such as aforedescribed and to the flow of the volatile impurities. The graphite should also be impermeable to airborne particulate matter. The airborne particulate matter generally has a size range no less than about 0.5 microns, and is generally in the size category of from 0.5 to about 10 microns, average particle diameter. Accordingly, graphite with interconnecting pores having diameters no greaater than about 0.5 micron will effectively trap and filter out any airborne particulate matter and prevent its access to the interior cavity of the package. Such graphite is commercially available from Poco Graphite, Inc. of Decatur, Texas.

Preferably, the entire receptacle as well as the closure member therefor is formed of the permeable graphite. When a portion of the receptacle or closure member is formed of the impermeable graphite, the rate of diffusion of the halogen-containing gas into the interior cavity of the receptacle and expulsion of the volatile halogenated impurities will proceed at a slightly slower rate and, accordingly, the longer time periods for purification described herein can be employed.

The invention has been described with reference to the packaging of the illustrated cylindrical rods useful as electrodes. Other graphite bodies that can be similarly packaged and purified can have a wide variety of shapes and sizes. Graphite filters, useful in sampling for optical emission and atomic absorption spectroscopy can be the graphite bodies. Typically these are thin discs about 0.008 to 0.1 inch thick and from 1 to about 4 inches in diameter, often sized to fit standard size Millipore filter apparatus. Another graphite body type can be a hearth liner for an electron beam gun. Such liners are small crucibles, usually with flat bottoms and cylindrical or truncated conical sides. Perforated graphite sheets, about 0.01 inch thick and useful for grids of vacuum tubes can also be packaged and purified by use of the invention. In all instances, the shape and size of the container would be designed to accommodate at least one body and, preferably, a plurality of such bodies in stacked array.

The invention has been described by reference to particularly illustrated and preferred embodiments. It is not intended that this description be unduly limited of the invention. Instead, it is intended that the invention be defined by the steps, means and reagents, and their obvious equivalents set forth in the following claims:

I claim:

1. A package comprising:

a. a receptacle formed of graphite and having a central cavity and rigid, load-supporting walls with a through opening in at least one wall thereof;

b. a closure member also formed of graphite and adapted for removable attachment to said receptacle and across said through opening;

c. means to removably secure said closure member across said through opening;

d. solid form items substantially entirely filling said central cavity and consisting essentially of a plurality of slender cylindrical bodies of graphite having less than 20 parts per million of inorganic impurities and packed therein in a stacked array; and

e. at least a portion of said receptacle and closure member being formed of graphite with interconnecting pores having diameters no greater than about 0.5 micron in diameter to provide permeability to gases but not to airborne particulate matter.

2. The package of claim **1** wherein the entirety of said receptacle is formed of said graphite.

3. The package of claim **2** wherein said receptacle has a neck portion of reduced exterior dimensions and said closure member comprises a cover having approximately the same exterior dimension as said receptacle with sidewalls extending into a close fit with said neck.

4. The package of claim **3** wherein said receptacle is cylindrical.

5. The package of claim **2** wherein said receptacle has a polygonal cross-section.

6. The package of claim **2** wherein said receptacle is covered with a plastic film.

7. The package of claim **2** wherein said container is cylindrical with an inside diameter of approximately 2.75 inches and containing approximately 100 of said cylindrical graphite bodies, each having a diameter of approximately 0.25 inch.

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