Jan. 16, 1968 S. H. WILLISTON ET AL 3,364,128

METHOD OF PURIFYING MERCURY AND APPARATUS
FOR USING PURIFIED MERCURY

Filed March 10, 1964

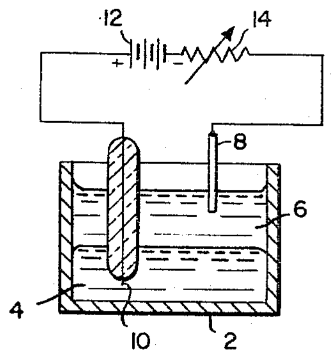

FIG. 1.

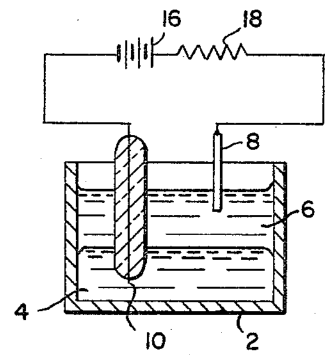

FIG. 2.

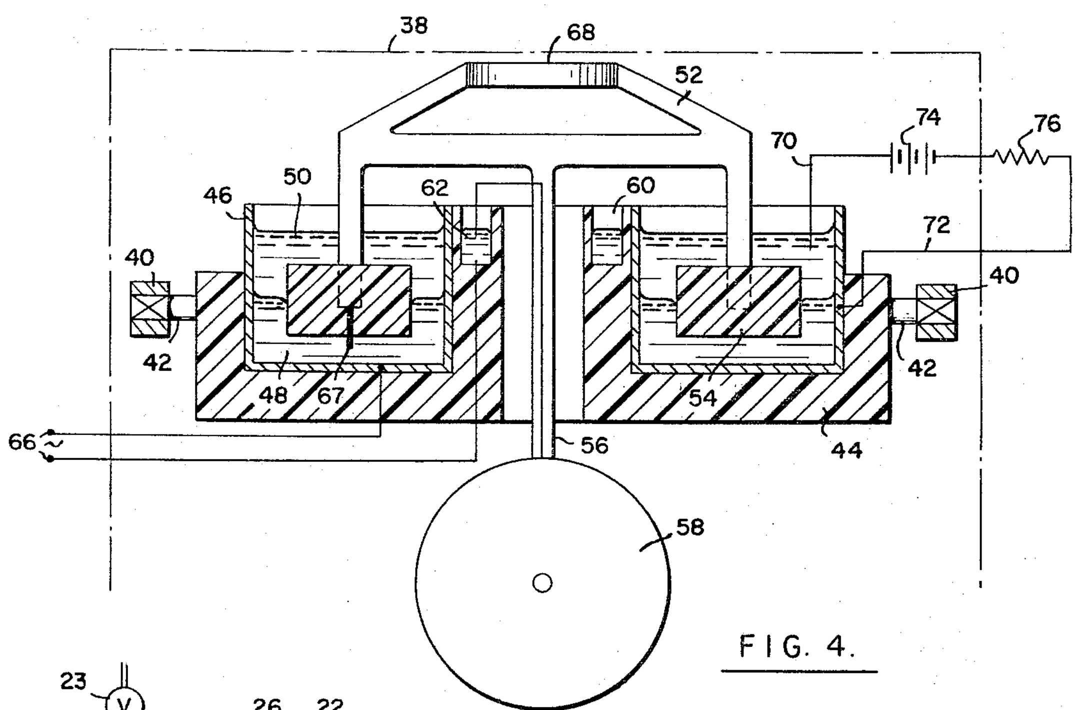

FIG. 4.

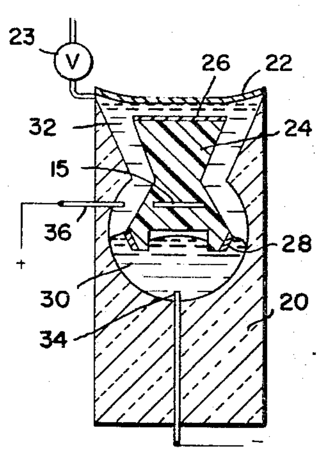

FIG. 3.

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United States Patent Office

3,364,128

Patented Jan. 16, 1968

3,364,128

METHOD OF PURIFYING MERCURY AND APPARATUS FOR USING PURIFIED MERCURY

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Filed Mar. 10, 1964, Ser. No. 350,748
13 Claims. (Cl. 204—140)

ABSTRACT OF THE DISCLOSURE

Mercury is purified by covering it with a dilute nitric acid solution and passing direct current between the mercury as an anode and a cathode in the nitric acid solution. The nitric acid is then replaced with distilled water, and current is passed with the polarity of the electrodes reversed. The water is then replaced by a reducing agent which remains in contact with the mercury permanently. The entire purifying process can take place in instruments in which mercury is used for flotation and which are specially adapted for the passage of the electric current necessary for the purifying process.

This invention relates to methods of purifying mercury and apparatus utilizing the mercury thus purified.

As disclosed in our Patent 3,023,512, dated Mar. 6, 1962, anti-friction mountings may be provided by floating on mercury various members which are required to move freely without static friction. To achieve the desired ends, advantage is taken of the fact that the surface tension of mercury may be used to provide centering of a floating member with respect to a mercury container. This result is achieved by producing at the floating member a mercury meniscus which is concave upwardly or downwardly, while producing at the container wall an opposite meniscus, respectively concave downwardly or upwardly. If the meniscuses produced at both elements, the member and container, are of the same type, both concave upwardly or concave downwardly, the surface tension effects will tend to bring the member and container into contact; but if the meniscuses are opposite in type, a strong centering effect is produced.

Securing this centering effect is not too difficult if care is exercised in utilizing mercury which is quite pure and in providing surfaces which are quite clean. But generally involved is another highly disturbing situation which, unless obviated, gives rise to effective static friction which will prevent free turning of the floating member. Frequently, even if at first the system is very free in its movements, there will, with time, arise a situation in which the static frictional effect appears. For free movement, dynamic friction is not objectionable; in fact, it is desirable to produce damping. Dynamic friction may be defined as friction which is a function of velocity of movement only, so that when movement is zero the dynamic friction is also zero.

Extensive investigations have led to the conclusion that the static friction referred to, which prevents free rotation, is probably due to the formation on the surface of the mercury of an oxide coating either of mercury oxide or of oxide of some metallic impurity of the mercury. This oxide coating which may be of molecular proportions, possibly even monomolecular, seems to form a "skin" which will hold the floating member sufficiently to produce an uncertainty of its rest position. For example, if the floating member is provided with a magnet, as in a well-surveying instrument, to provide orientation in the earth's field, it will be found that the positions reached respectively as the result of movements in clockwise and counterclockwise direction will be slightly, but noticeably, different. This would not be the situation if dynamic friction alone were involved, but would be the condition expected if static friction was present.

The exercise of extreme care in the purification and handling of the mercury and parts associated therewith will produce acceptable results as set forth in our patent referred to above, particularly if the system is evacuated with residual gas only of an inert type, and if oxide-reducing agents are used, such as hydrazine or phenylhydrazine, to reduce, or prevent the formation of, oxide films. But even under these conditions it is extremely difficult to achieve a system which may be considered permanently operative in desired fashion, though, with the exercise of great care, systems may remain in proper condition for periods of the order of months.

It is one object of the present invention to provide a method of purifying mercury to the extent necessary to approach permanence of a system as just described having substantially zero or at least negligible static friction. The invention, however, has its particular advantages in providing for purification which may be carried out without the exercise of prohibitive care in processing. To the extent of its final operations, it may be carried out with the mercury in the container in which it is ultimately to be used.

A further object of the invention concerns a system in which the mercury is maintained in the desired condition. Briefly, this involves the maintenance at the mercury surface of an oxide-reducing condition by the continuous flow of very small currents.

Further objects of the invention are concerned with apparatus utilizing the pure mercury and involving the principles of centering discussed above.

The attainment of the foregoing and other objects of the invention relating to details of methods and apparatus will become apparent from the following description, read in conjunction with the accompanying drawing, in which:

FIGURE 1 is a diagrammatic sectional view illustrative of a first step in the purification of mercury;

FIGURE 2 is a similar view involving a subsequent step;

FIGURE 3 is a diagrammatic sectional view of an apparatus utilizing the principles of the invention; and

FIGURE 4 is a sectional view illustrating an apparatus in which a gyroscope is mounted on mercury for universal movement, the gyroscope being of the north-seeking type.

Referring first to FIGURES 1 and 2, the method of producing pure mercury in accordance with the invention will be described.

While the starting point of the refining method may be mercury which is only reasonably pure, the steps involved in the ultimate refining are lessened and simplified if the mercury is initially in what would ordinarily be regarded as a very pure state. Reference to the usual mercury purifying procedures need not be detailed since they are well-known. Desirably, mercury of a commercially "pure" type may be subjected to further purification by repeated treatment with nitric acid, washing, and multiple, for example triple, distillation, these procedures being carried out under the usual careful conditions to avoid atmospheric contamination. As a result of such procedures mercury forming the starting point of the novel refining procedure may contain metals less noble than mercury to the extent of less than one part in five million.

It may be here remarked that for the desired purposes even the minutest traces of metals less noble than mercury should be removed as far as possible. While, because of the extremely minute amounts of materials involved, it cannot be ascertained precisely what the results are due to, there is reason to believe that if the mercury contains less noble metal these have some catalytic effects in promoting the formation of mercury oxide on the liquid surface. While the undesirable film may contain oxides of other metals, the results which are detrimental seem to be greater than would be attributable to the oxides of the metals other than mercury.

Reference has just been made to metals less noble than mercury. It is found that more noble metals, such as gold, platinum, or the like, may well be present without detrimental effect, so long as the amalgams are sufficiently mobile. The ultimate refining process about to be described will not, and need not, remove these metals. In fact, silver which is less noble than mercury, may be present without detrimental effect, though it should be substantially below its saturation solubility in mercury to prevent its crystallizing out under low temperature conditions.

Assuming mercury purified as just described, reference may now be made to FIGURE 1 which indicates the initial step in the ultimate refining procedure. There is conventionalized at **2** a container which may take numerous forms and in particular may represent the container in which the mercury is ultimately to be utilized, such particular container being referred to hereafter. The fact that the purifying process may be carried out in such ultimate container is distinctly advantageous in eliminating the necessity for transfer. The container may be of glass, plastic, or the like non-wettable by mercury; or it may be of a wettable material such as nickel, platinum, palladium, or the like. If metallic it should be of a metal or alloy substantially insoluble in mercury, or it may be of a metal which has some solubility in mercury but which is more noble than mercury. Silver is desirably not used because of its tendency to crystallize out under varying temperature conditions.

The mercury to be purified is indicated at **4**. Initially the mercury is covered with dilute nitric acid as indicated at **6**. While other dilute acids, such as sulphuric, may be used, nitric acid is preferred since almost all metallic impurities have soluble nitrates. The electrolyte may also be provided by a solution of mercuric nitrate or sulphate. An electrode **8**, conveniently of platinum, has electrical connection with the dilute nitric acid, while another electrode **10**, also of platinum, is illustrated as in electrical contact with the mercury, though this contact may be provided by the container **2** if this is metallic as just indicated. If the electrode **10** extends down through the nitric acid it may be insulated therefrom as indicated by a glass tube.

The electrodes **8** and **10** are connected in circuit with a voltage supply **12** and a variable resistor **14**, the supply being connected so that the mercury is the anode of the system and the electrode **8** in the nitric acid is the cathode.

Flow of current of the order of a few milliamperes may be provided for an extended period during which the mercury is desirably agitated and then permitted to stand for short periods to permit impurities of less specific gravity than the mercury to rise to the surface. The resulting electrolysis will produce at the surface of the mercury not only mercuric oxide but oxides of the less noble metals, and, as formed, these will be dissolved in the nitric acid. Mercury and other dissolved metals will be plated out on the electrode **8**. This procedure may be continued as long as desired to effect substantially complete removal of the metals less noble than mercury. To reduce any possible ultimate contamination, the dilute nitric acid should be decanted off from time to time and replaced by new, more dilute nitric acid thereby removing dissolved impurities, leaving, eventually, an aqueous solution containing substantially only mercuric nitrate.

Finally, the solution by decantation and several washings may be replaced by distilled water.

The second stage of the process may now be initiated,

and this is illustrated in FIGURE 2. With the distilled water above the mercury, the polarity of the electrodes is reversed (the electrode **8** having been previously cleaned or replaced by a clean platinum electrode), the source **16** being in series with a fixed resistor **18** so as to make the mercury the cathode and the platinum electrode **8** the anode. Sufficient voltage is provided to liberate hydrogen at the surface of the mercury. At this time only a small current, for example of the order of thirty microamperes, may be caused to flow by choice of a suitable resistor at **18**. The water desirably used is water which has been well distilled to be substantially completely devoid of metallic ions, though desirably it will contain carbon dioxide, merely by solution from the atmosphere, to make it slightly conductive; or a very small amount of ammonium hydroxide may be added for this purpose.

The result of this procedure is now to reduce to mercury by the nascent hydrogen which is liberated any mercuric oxide which may be on the surface of the mercury or distributed therethrough, the mercury being desirably agitated and permitted to stand for a while after each agitation so as to bring any oxide to the surface for reduction by the nascent hydrogen. Following this, it is desirable to replace the water by a reducing agent which would reduce mercuric oxide. Most suitable for this purpose are many aliphatic or aromatic amines, either primary or secondary, and as suitable examples there may be cited hydroxylamine, phenylhydroxylamine, triethanolamine, or the like, having primary or secondary amino groups. Highly suitable as a permanent reducing agent, particularly when the ultimate use is to be at elevated temperatures is triethylenetetramine

$$NH_2\cdot(CH_2)_2\cdot NH\cdot(CH_2)_2\cdot NH\cdot(CH_2)_2\cdot NH_2$$

which has both high mobility and high boiling point. As the permanent reducing agent amines which contain no oxygen are preferred. The amines may be diluted by, or dissolved in, non oxidizing solvents such as aromatic hydrocarbons (xylene, mesitylene, etc.). Suitable also are hydrazine and phenylhydrazine. Traces of water are desirably left in these amines or may be added to anhydrous amines to maintain conductivity. If triethylenetetramine is used, a small amount of ammonium hydroxide may be added for this purpose.

Two alternatives are now presented. Either the mercury covered with the reducing agent is used without further current flow, or, and preferably, current flow is continued as in FIGURE 2 but may be reduced by insertion of a larger resistance to the order of a few microamperes, for example two microamperes. This current flow is desirably continued in the apparatus in which the mercury is used throughout its entire period of operation and existence. This latter condition is most desirable since the nascent hydrogen which is liberated is even more effective than the reducing agent in maintaining the mercury surface free of oxide.

FIGURE 3 shows schematically only one of a large number of types of instruments to which the invention is applicable, this figure showing a compass unit suitable for a well surveying instrument and adapted to be photographed to show direction and angle of inclination of a bore hole. The optical and photographic elements associated with this may be conventional and hence are not shown. The unit comprises a container **20** which may be of glass and which is covered by a window closure **22** also of glass through which the indicating element may be photographed. If hydrogen is going to be generated, it is desirable to form this window so that it will be concave upwardly at its edges providing a trough about its periphery which may be vented through a relief valve **23**. However, minute currents do not appear to liberate hydrogen, though expansion space is desirably provided for liquid and possibly liberated gas when high temperature conditions of use are expected. The indicating element **24** is of plastic and, if azimuth as well as inclination are to be recorded, it may contain a permanent magnet embedded in it as indicated at **15**. The upper end of this element is provided with a disc **26** which may bear suitable markings to be photographed to give a record of inclination, and direction as well if desired. The arrangement is similar to that shown in our prior Patent 3,023,512, and to secure centering the lower end of the member **24** is provided with an annular ring **28** which may be of a metal such as platinum, nickel or iron. Desirably if the last two are used they are preplated with pure mercury to provide a readily wettable surface. The mercury, prepared as already described is indicated at **30** and above it is the amine or other reducing material **32**.

An electrode **34** has electrical contact with the mercury, and an electrode **36** has electrical contact with the reducing liquid. These provide the minute current as previously described as desirable from a source in series with a large resistor, the mercury being the cathode and the electrode **36** the anode, with the liquid **32** forming the electrolyte. As will be evident, the purification procedure previously described may be carried out in the container **20** so that change of the purified mercury from one container to another may be avoided. The assembly may then be made, and inert gas introduced, and evacuation effected through the valve **23** constituting a check valve for relief of pressure within the unit if liberation of hydrogen creates over a long period of use a pressure which should be relieved to avoid damage to the unit.

When in use, current, may be continuously applied from the battery source which is generally used for operation of the photographic system. Electrolysis takes place with hydrogen in nascent form appearing at the mercury surface to reduce any possible oxide which may form thereat. This electrolysis may also liberate some oxygen at the anode, but this will be absorbed in oxidation of the reducing liquid **32**. A unit having a long life of operation is thus provided. By reason of absence of an oxide film on the mercury, the only friction present is dynamic so that the member **24** will not only always be accurately centered but, if provided with a magnet, will occupy a definite position in the earth's or other magnetic field. Balancing is, of course, effected so that the indicating surface **26** is always accurately horizontal. To achieve this to a high degree of accuracy the balancing must be effected for the locality in which the instrument is to be used. But there is considerable leeway, since generally such instruments are not required to respond to extremely small angles of inclination.

A particularly valuable use of the invention is in the provision of a north-seeking gyroscope which is illustrated in FIGURE 4. As is known, a pendulously supported gyroscope free to move and with dynamic damping will ultimately assume a north-south direction. If suitably counterbalanced, its axis will ultimately occupy a horizontal direction tangent to the meridian of its location, i.e. pointing geographical north and south.

Referring to FIGURE 4, there is indicated a housing **38** which may be either evacuated or filled with an inert gas such as hydrogen, nitrogen, argon or the like. Desirably such gas filling is used to avoid evaporation of the reducing liquid at high temperatures and condensation of vapor at lower temperatures. It will be understood that the housing **38** is provided with a transparent window at its top for view of suitable indicating markings on the gyroscope movable assembly. A gimbal ring **40** is mounted on an axis (not shown) perpendicular to the plane of the figure, and mounts through trunnions **42** a pendulous supporting member **44** which, by reason of the gimbal mounting, provides at least an approximately horizontal reference plane. An annular cup **46** is mounted in the member **44** and contains purified mercury **48**. Above this mercury is the reducing liquid **50** of the type previously described. For purposes of the present illustration, it may be assumed that the annular container **46** is formed of

nickel, platinum, or the like wettable by the mercury so as to provide at the line of contact an upwardly concave meniscus.

A frame **52** of aluminum (the impervious ovide coating of which renders it insoluble in mercury) or some other metal insoluble in mercury is supported by a plastic ring **54** which may be of nylon or similar material having, in particular, the property of not being wettable by mercury. The mercury at its contact with this ring accordingly will have a meniscus which is convex upwardly. Surface tension will accordingly position the ring concentric with the trough or container **46**.

The frame **52** has a depending central stem **56** passing through an opening in the member **44** and supporting the housing of the gyroscope unit **58**. This unit contains the usual rotor of maximum moment of inertia for the space involved unitarily formed with a motor operable at high speeds and which in the example illustrated may be assumed to be of single phase type. A direct current motor may, of course, be used. Further, with elaboration of electrical connections, two or three phase excitation may be provided to the motor at a high frequency, for example 1200 c.p.c., to produce the desired speed of rotation. As illustrated the assumed alternating current is supplied through the stem **56** and through a lead **62** which dips into a ring of mercury contained in an annular cup **60** provided in the member **44**, suitable insulation being provided. The mercury here used may also be of the purified type, but if the portion of the lead dipping thereinto is small, surface tension effects and surface contamination are of little significance. The last mentioned ring of mercury and the cup **46** are connected to the alternating current supply terminal **66**. Conduction to the frame **52** may be provided by a wire extension **67** of platinum or the like extending downwardly through the float **54** into the mercury **48** below its surface.

The upper portion of the frame is provided with a flat area **68** which may contain a marking indicative of azimuth which may be observed or photographed. It will be understood that the gyro compass thus provided may be used for many purposes, including control, as for navigation, well surveying, or the like. If used in a well surveying instrument, its azimuthal indication is photographed as usual, along with inclination indicating means which may be separately provided.

While in the apparatus just described, as well as in apparatus of the type illustrated in FIGURE 2 the flow of current for maintenance of the mercury surface in clean condition may be omitted if the surface is covered with a reducing liquid such as **50**, in the gyroscope arrangement current may also be provided as previously described to produce, with the mercury **48** as the cathode, nascent hydrogen for reduction of any oxide which may form on the mercury surface. Leads **70** and **72** are accordingly connected as indicated in series with a direct current supply **74** and a high resistance **76**. While the source **74** is indicated as a battery, if alternating current is used for driving the gyroscope motor the necessary small direct current may be derived from the alternating current supply through a transformer and rectifier. The current from the rectifier may be in the form of pulses, filtering being unnecessary. In fact, in all of the instruments indicated the direct current for maintaining cleanness of the mercury surface may be provided intermittently. For example in a well surveying instrument it need not be supplied while the instrument is in the hole, but may be supplied for short periods when the instrument is at the surface and undergoing servicing or in storage. If, in an instrument during maintenance, or in the initial purification procedure, an alternating current source is used to provide the direct flow through a rectifier, there may occur small reverse flow pulses due to use of an imperfect rectifier such as a semiconductor diode; but the current resulting will be effectively unidirectional from an average standpoint, thereby producing the desired results.

It will be evident that various changes may be made in details of construction of apparatus and in operation of the type of process for purification of mercury heretofore described. It is therefore to be understood that the invention is not to be regarded as limited except as required by the following claims.

What is claimed is:

1. The method comprising providing in electrical contact with mercury an electrolyte, passing an effectively unidirectional current between a cathode in the electrolyte and the mercury, as anode, to effect electrolytic solution in the electrolyte of metallic impurities, removing the electrolyte after a period of current flow, and replacing said electrolyte by a liquid reducing agent capable of reducing mercuric oxide.

2. The method according to claim **1** in which the liquid reducing agent contains a substance of the group consisting of amines of primary, secondary, and mixed primary and secondary types.

3. The method according to claim **1** in which the reducing agent contains, as its active constituent, triethylenetetramine.

4. The method according to claim **1** in which electrolytic action is continued with flow of an effectively unidirectional current between an anode in the reducing agent and the mercury as cathode.

5. The method of maintaining a freely mobile surface of mercury in a clean condition comprising providing in electrical contact with said surface of mercury an electrolyte, passing an effectively unidirectional current between a cathode in the electrolyte and the mercury, an anode, to effect electrolytic solution in the electrolyte of metallic impurities, replacing said electrolyte by a non-oxidizing electrolyte devoid of metallic ions and passing an effectively unidirectional current in the opposite direction between the mercury as cathode and an anode in the non-oxidizing electrolyte.

6. The method of maintaining mercury free of oxide comprising covering it with a liquid reducing agent containing, as its active constituent, triethylenetetramine.

7. The method of maintaining mercury free of oxide comprising covering it with a conductive liquid reducing agent capable of reducing mercuric oxide and passing an effectively unidirectional current between an anode and the mercury, as cathode, through the liquid reducing agent.

8. The method of maintaining a freely mobile surface of mercury free of oxide comprising covering said surface with a water solution of a non-oxidizing electrolyte devoid of metallic ions and passing an effectively unidirectional current from a source of current between an anode and the mercury, as cathode, through the electrolyte.

9. Apparatus comprising a pool of mercury, a container for the mercury presenting a first surface thereto at the top of the mercury pool, a member floating on the mercury and presenting a second surface at the top of the mercury pool, said surfaces providing at regions of engagement with the mercury respective meniscuses which are convex and concave upwardly thereby to effect centering of said member, a non-oxidizing electrolyte covering said mercury, means providing an anode in electrical contact with said electrolyte, and means providing an effectively unidirectional current between said anode and said mercury, as cathode, through said electrolyte.

10. Apparatus comprising a pool of mercury, a container for the mercury presenting a first surface thereto at the top of the mercury pool, a member floating on the mercury and presenting a second surface at the top of the mercury pool, said surfaces providing at regions of engagement with the mercury respective meniscuses which are convex and concave upwardly thereby to effect centering of said member, a conductive liquid reducing agent constituting an electrolyte covering said mercury, means providing an anode in electrical contact with said electrolyte, and means providing an effectively unidirectional current between said anode and said mercury, as cathode, through said electrolyte.

11. Apparatus according to claim **10** in which said liquid reducing agent contains a substance of the group consisting of amines of primary, secondary, and mixed primary and secondary types.

12. Apparatus comprising a pool of mercury, a container for the mercury presenting a first surface thereto at the top of the mercury pool, a member floating on the mercury and presenting a second surface at the top of the mercury pool, said surfaces providing at regions of engagement with the mercury respective meniscuses which are convex and concave upwardly thereby to effect centering of said member, a nonoxidizing electrolyte covering said mercury, means providing an anode in electrical contact with said electrolyte, and means providing an effectively unidirectional current between said anode and said mercury, as cathode, through said electrolyte, said pool being annular, and said member being a gyroscope assembly providing with an annular ring portion resting on the mercury.

13. Apparatus comprising a pool of mercury of high purity substantially free of mercury oxide, a container for the mercury presenting a first surface thereto at the top of the mercury pool, and a member floating on the mercury and presenting a second surface at the top of the mercury pool, said surfaces providing at regions of engagement with the mercury respective meniscuses which are convex and concave upwardly thereby to effect centering of said member, said pool being annular, and said member being a gyroscope assembly provided with an annular ring portion resting on the mercury.

References Cited

UNITED STATES PATENTS

578,457	3/1897	Kellner	204—99
2,032,602	3/1936	Stearns	75—81
2,067,361	1/1937	Vivian	204—140
3,062,612	11/1962	Boucher	21—2.5
3,113,018	12/1963	Young	75—81
2,367,811	1/1945	Urban	204—112
2,389,691	11/1945	Schumacher et al.	204—112
3,122,491	2/1964	Loevenstein	204—112

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