S. W. PARR.

CALORIMETER.

APPLICATION FILED JUNE 24, 1912.

1,115,238.

Patented Oct. 27, 1914.

2 SHEETS—SHEET 1.

Fig. 1.

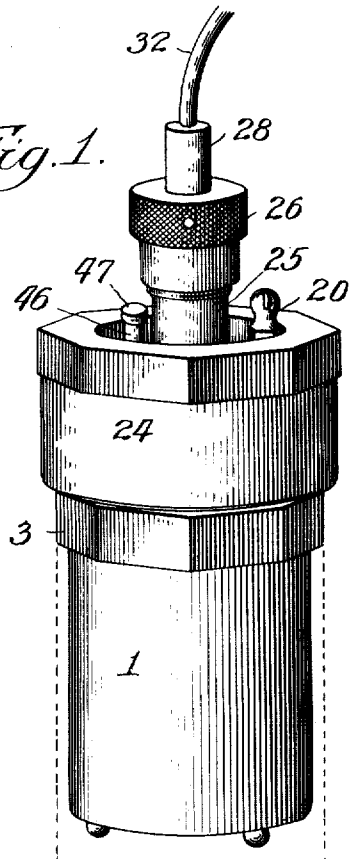


Fig. 2.

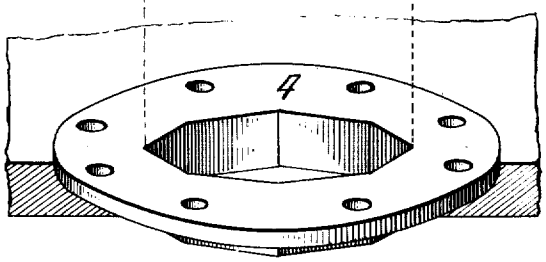


Fig. 3.

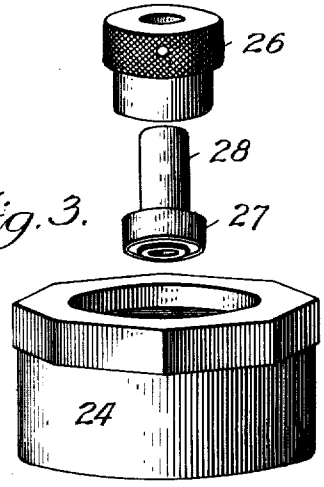


Fig. 4.

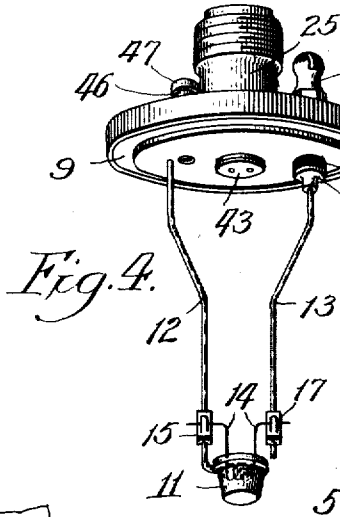
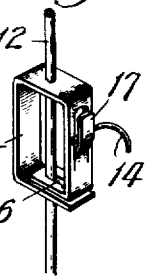


Fig. 6.



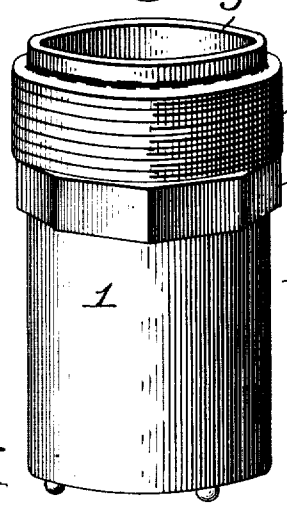


Fig. 5.

Witnesses:

John Enders

D. V. Curran.

Inventor:

Samuel W. Parr,

by Arba B. Marvin

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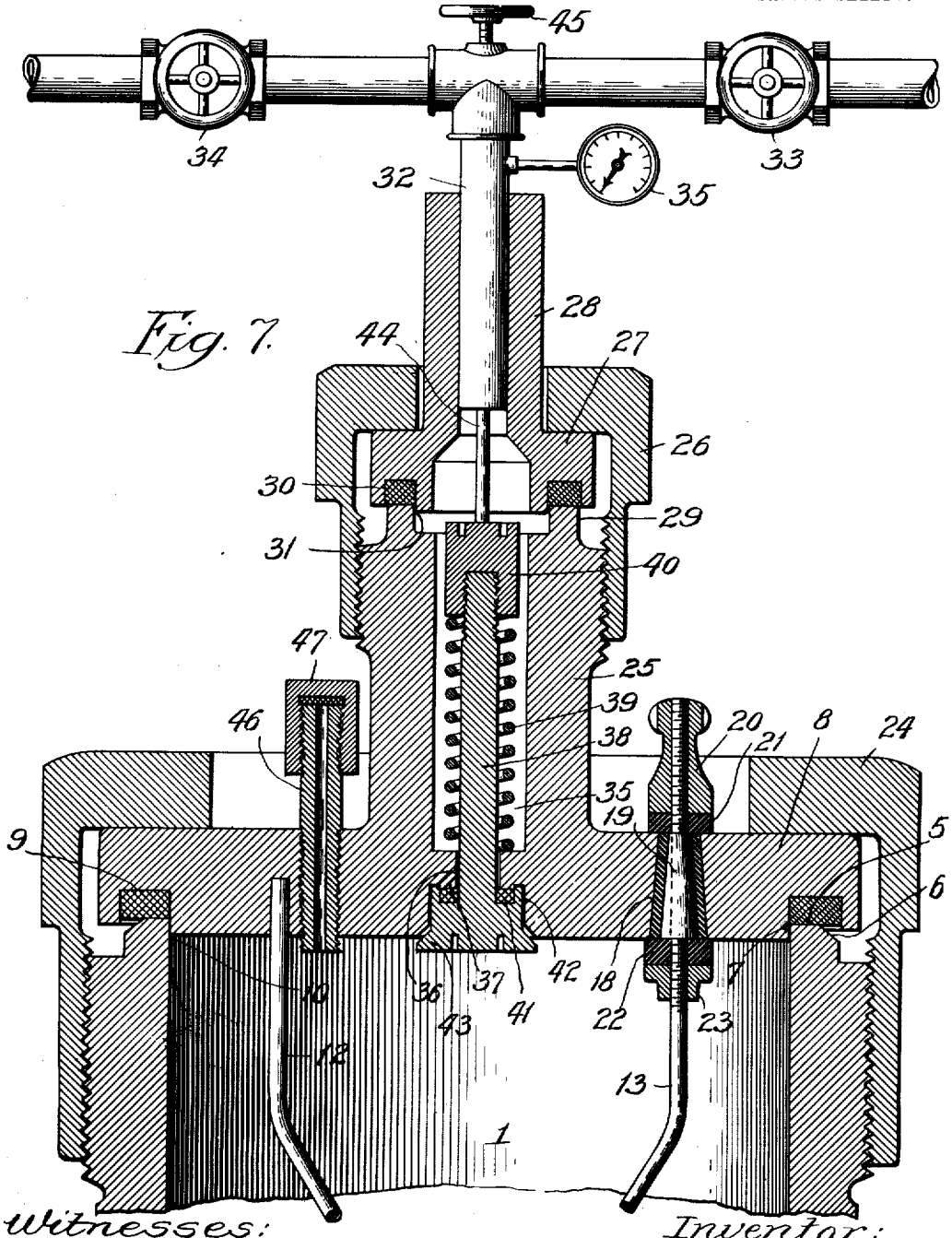
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2 SHEETS—SHEET 2.

Fig. 7.



Witnesses:
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UNITED STATES PATENT OFFICE.

SAMUEL W. PARR, OF URBANA, ILLINOIS.

CALORIMETER.

1,115,238. Specification of Letters Patent. Patented Oct. 27, 1914.

Application filed June 24, 1912. Serial No. 705,386.

To all whom it may concern:

Be it known that I, SAMUEL W. PARR, a citizen of the United States, residing at Urbana, county of Champaign, State of Illinois, have made new and useful Improvements in Calorimeters, of which the following is a specification.

Bomb calorimeters as ordinarily used are constructed of steel with the inner faces lined with platinum or with gold plated copper to resist the corrosive action of the nitric acid liberated in the calorimeter when in use. Such constructions have the disadvantage of high cost, and also the disadvantage that moisture may work in under the lining and subsequently impair the accuracy of the heat determination. Also platinum linings as thus used within a calorimeter are easily damaged and are otherwise objectionable, as is well known.

As the result of extended experiment and investigation I have discovered a new alloy which is so resistant to the corrosive action of the moisture oxygen or of ordinary acids such as nitric acid that it can be used within the calorimeter and exposed directly to the action of the calorimeter charge. The alloy is so resistant that it may be used for valve seats, and similar parts of the apparatus where the wear and exposure are extreme, without appreciable corrosion or deterioration even after long continued use.

The drawings which accompany and form a part of the present specification show a calorimeter in which this new allow is used for substantially all of the exposed elements or parts.

This calorimeter is of novel construction in many parts and is well adapted for use at high pressures in the determination of the calorific values of coals, oils, and other combustibles.

In the drawing, Figure 1 is a perspective view illustrating the bomb or calorimeter assembled ready for use. Fig. 2 shows a bench plate serviceable as a socket or wrench to hold the calorimeter cup while its cap is being screwed into place. Fig. 3 is a perspective view of the upper parts of the calorimeter taken apart. Fig. 4 is a perspective view of the cover. Fig. 5 shows the calorimeter cup. Fig. 6 is a perspective detail of one of the adjustable clamps used to hold an end of the ignition wire; and Fig. 7 is a sectional elevation, somewhat enlarged, through the calorimeter cover and its associated parts.

The calorimeter cup 1 as shown in Fig. 5 is of cylindrical outline with a threaded enlargement 2 at its upper portion and with an octagonal shoulder or ledge 3 to serve as a wrench face or holding means when the cup has been dropped into the bench plate 4 of Fig. 2. This bench plate is used to hold the cup when its cover is being adjusted into position for use or is being removed after the combustion has taken place.

At the upper edge of the cup 1 is an annular rim which, as shown in Fig. 7, has a flat top face 5 and is beveled off at the outer corner 6 but is not similarly beveled or rounded at the inner edge and consequently presents the square corner 7 which, as hereinafter explained, is of marked importance in insuring a tight connection between the cup and its cover.

The cover 8 of the calorimeter has an annular groove of rectangular cross-section in its lower face within which groove is seated an annular gasket or packing 9. This packing may be of organic material such as rubber or a rubber composition of the type heretofore commonly used for air tight packings but not regarded as feasible in bomb calorimeters. Gasket 9 is of such dimensions that the cover sets down within the rim of the cup at 10. Preferably, the joint at 10 is a good mechanical fit so that the rubber gasket 9 is in large measure shielded from direct contact with the hot acid fumes developed in the calorimeter, but need not be a contact joint.

Fuel to be burned is held in a suitable cup 11 carried in the looped lower end of a support wire 12 secured at its upper end directly to cover 8. An opposing wire 13 having its lower portion parallel with wire 12 may be used for conveying electrical energy to the ignition wire 14. Sliding clamps of the type illustrated in Fig. 6 have proved of great convenience as a means for adjusting the ignition wire 14 into position for use. Each of these clamps is built up from a strip 15 bent in rectangular form and having its ends overlapped to yieldingly grip the supporting wire. One of the ends is slotted at 16 so that when the fastening is squeezed between the fingers, it releases its grip on the supporting

wire and can be moved upward or downward at will. This rectangular fastening 15 has one of its sides cut and punched to form a yielding tongue 17 behind which the ignition wire 14 may be introduced and held. In practice the wire 14, cut to proper length and coiled up as desired, is slipped behind the tongue 17 and then both fastenings are pushed downward along the supporting and guide wires 12 and 13 until the ignition wire 14 is at proper position with respect to the charge to be ignited in the crucible 11.

The upper end of wire 13 passes through a tapered opening in the cover 8 which opening is lined with an insulating bushing 18. An enlargement 19 on wire 13 serves to tighten up the joint when wire 13 is drawn up by means of the threaded terminal 20. An insulating bushing or ring 21 and a smaller bushing 22 serve to keep the nuts 20 and 23 out of contact with the metal of the cap while at the same time insuring permanency to the joint.

A collar 24 overlaps the top of the cover and has screw-threaded engagement with the cup or lower member of the calorimeter so that when the collar is screwed down on the threads of the cup, it will serve to draw cap 8 and its packing 9 tightly against the upper rim of the cup, insuring a gas-tight connection throughout the entire circumference even though the pressures within the calorimeter may be many times that of the atmosphere. There is not room for the rubber to flow into the joint at 10.

Rising from the central portion of the cover 8 is a neck 25 screw-threaded for engagement with a retaining collar 26 which grips the protruding annular rim 27 of a nipple 28 and holds that nipple tightly against the upstanding annular lip 29 which surmounts neck 25. The rubber gasket 30 similar to gasket 9 is interposed between the nipple and the lip of the neck and the nipple fits down within the neck with a snug mechanical joint at 31 directly comparable to the joint 10 between the calorimeter top 8 and the main cup. Oxygen or other gas or gases may be supplied through a tubular inlet 32 indicated somewhat diagrammatically as supplied with an inlet pipe and valve 33 and an outlet pipe and valve 34 and equipped with the suitable pressure device or gage 35.

The passage for gas into the calorimeter includes a cylindrical chamber 35 within neck 25 which terminates in a constriction 36 below which is the main valve seat 37 of the calorimeter inlet. The valve seat 37 is in the form of an annular lip.

The inlet valve comprises a cylindrical valve stem 38 enveloped by a spiral closing spring 39 and carries at its upper end a solid block 40 serving to retain the valve in operative engagement with the spring and having wrench sockets in its upper face to facilitate removal when the valve is to be taken out of the neck.

At the lower end of the valve stem 38 is an enlargement carrying an annular packing ring 41 of rubber seated in a suitable recess and so arranged that an annular ledge or lip 42 of metal will come up when the valve closes, to overlap the lip 37 projecting downward to engage the rubber packing. The extreme lower end of the valve is flared outwardly at 43 so that gases entering the calorimeter at high velocity will be deflected outward against the side wall of the calorimeter body and so will not displace or disturb the coal or other combustible within the crucible or cup 11 of the apparatus.

Under certain circumstances, it is desirable to admit gas to the calorimeter under heavy pressure and then after combustion of the fuel to withdraw the products of combustion to another receptacle for analysis or other treatment. As a means for accomplishing this the push rod 44 is provided within the inlet tube 32, this push rod having a handle 45 whereby it may be screwed forward and into contact with block 40 and thus unseat the valve and permit the high pressure gases to escape through valve 34 to an analyzing apparatus not shown.

Under some circumstances it is desirable to wash out the calorimeter with gases or to otherwise exhaust or empty it of air or the like and for convenience in carrying out these and similar manipulations, the cover 8 is equipped with an outlet tube 46 having a suitable cap or seal 47 but so located that it can be unsealed when gases introduced within the calorimeter are to be drawn off to auxiliary apparatus.

In the apparatus as thus described the main cup 1, the cover 8, the current supply wires 12 and 13, the valve and in fact all of the parts exposed to the corrosive action of the nitric acid and the like introduced or developed in the calorimeter are constructed of the special alloy which will now be described in detail.

In general this new alloy comprises nickel as its basis together with a certain amount of chromium and a somewhat smaller quantity of copper. The chromium accentuates the resisting properties of the nickel but tends to increase the melting temperature and also leads to brittleness. The copper on the other hand tends to lower the melting point, though it cannot be used except in moderate quantity because of the danger of corrosion. I have found that there is also advantage in having tungsten present and while its presence may not be necessary yet it tends toward easy casting and also strengthens the acid resisting properties of the alloy. Tungsten is much like chromium in promoting resistance to acid attack but it is quite in contrast with chromium in that

it permits easy casting and reduces shrinkage. Aluminum, and manganese in small quantities can also be used to advantage, being added after the mass is fluid and when it is about in condition for pouring. The aluminum lowers the melting point of the alloy, somewhat, and besides being a good deoxidizer, it accentuates the resistance to both nitric and sulfuric acid. Manganese serves much as aluminum. Titanium and boron in fractional percentages may also be used.

I have found that the relative proportions of the elements above named may be varied through realtively wide limits and still yield an alloy having, in the main, the mechanical strength and toughness and the acid resisting characteristics of metal suitable for use in calorimeters. I have found that the following composition gives good results: 68 per cent. nickel, 8 per cent. copper, 18 per cent. chromium, 3 per cent. tungsten, 2 per cent. aluminum, 1 per cent. manganese, .12 of 1 per cent. boron, and .05 of 1 per cent. titanium.

As to variations from the above proportions, I have found that the copper content may vary between 5 per cent. and 11 per cent., the chromium content between 15 per cent. and 21 per cent., the aluminum between $\frac{1}{2}$ of 1 per cent. and 3 per cent. and the manganese between $\frac{1}{2}$ of 1 per cent. and $1\frac{1}{2}$ per cent. The manganese may be omitted altogether if desired, though I regard it as a substantial aid in casting and as a desirable deoxidizer.

Boron from .02 of 1 per cent. to .2 of 1 per cent. may be present with possible advantages to the alloy. In practice I prefer to add to the melt .12 of 1 per cent. boron put in as an alloy with manganese. The boron besides acting as a deoxidizer appears to alloy with the nickel with advantageous results. Some carbon and some iron may be present to the extent of .1 of 1 per cent., as may also slight quantities of silicon, and while these are believed to do no good, they do not appear to be especially harmful.

The best melting and casting temperature for the alloy here disclosed in its various modifications is in the neighborhood of 1300 degrees centigrade, with 1500 degrees centigrade as the upper limit.

The alloy may be cast in iron molds not heated, or in sand, and when thus made has a tensile strength of about 55,000 to 60,000 pounds per square inch. The cast material can be rolled and drawn into wire and can be spun and mechanically worked according to well known metallurgical methods. With drawn wire, the tensile strength is much greater than that given for the cast material. The relatively great strength and toughness of the alloy, even in cast condition, is of importance when the material is used in the construction of calorimeters, because the pressure developed within the calorimeter may be as high as 1,000 pounds per square inch even under normal conditions. The electrical resistance of the alloy is high, being in the neighborhood of fifty times that of copper.

The metal, either in cast or rolled condition is non-oxidizable in the ordinary sense. Corrosion, if it occurs at all, at atmospheric temperature and pressure, when 100 square centimeters area is subjected for twenty-four hours to four times normal HNO_3 or H_2SO_4 or mixtures of these acids is so slight as to be substantially within the experimental error of weighing, even through the balance used may show changes of $\frac{1}{10}$ of a milligram. As a result of continued use of the device here disclosed, it may be said that the total corrosion within the bomb even under extreme temperatures and pressures need not exceed $\frac{5}{10}$ of a milligram for each heat and such a slight corrosion, assuming that it might take place, would introduce a variable of not more than one part in ten thousand, which, of course, is well within the experimental accuracy of methods for using bomb calorimeters.

It is obvious that such an alloy is well adapted for use in the construction of valves, of valve seats and the exposed portions of chemical vessels, and in a continuing application Serial No. 821,593, filed February 27, 1914, claims have been made on the alloy, *per se*.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. In a bomb calorimeter, a calorimeter cup of non-corrosive alloy threaded on its exterior and having a projecting bearing rim flat on top and formed with a square corner at its inner edge, an organic gasket on said flat top, a cover closely overlapping said square shoulder on the inside of the cup to protect said gasket, and a collar threaded to said cup and directly engaging said cover.

2. In a bomb calorimeter, the combination of a threaded cup having a bearing rim flat on top and formed with a square corner at its inner edge, a cap having an extension depending within the cup beyond the bearing face of said rim, with a close fit between said rim and said extension and an organic packing in tight engagement with the top face of said rim.

3. In a calorimeter, the combination of a cup, having a rim at its top, said rim having a flat bearing face, and a cover having a gasket broader than said rim and contacting with the flat face thereof, said cover projecting down and beyond said flat face to shield said gasket from destructive agencies within the calorimeter.

4. In a calorimeter, a cover, a pair of current supply wires suspended from said

cover, clips slidable over said wires, and an ignition wire removably gripped by said clips.

5. In a calorimeter, a pair of parallel conductors, a crucible supported by one of said conductors, a heating wire supported in proximity to said crucible and a yielding clip for each end of said heating wire, said clips being movable along said parallel wires to bring the heating wire in advantageous position with respect to the charge in the crucible.

6. An adjustable clip for supporting the heating wire of a calorimeter, said clip consisting of a metal strip bent to the shape of a rectangle and having its overlapping ends relatively movable to yieldingly grip a wire pasing therethrough and through the opposite side of the device, said fastening having an integral tongue pressed from said strip to yieldingly grip the end of the heating wire thereby maintaining electrical connection therewith.

7. In a calorimeter, a cup having a cover and means for sealing said cover to said cup, said cover having a central opening and having a valve positioned in said opening and arranged to deflect incoming gases outwardly against the sides of the calorimeter cup.

8. In a calorimeter, a cover having a centrally disposed neck with a chamber therein, a spring within said chamber, a valve stem governed in its movement by said spring and a valve carried by said stem and seating on an annular rim depending from the under face of said cover.

9. In a calorimeter, a removable cover having a gas passage therethrough, a valve positioned centrally within said cover to control said passage and seating against an under face thereof, said valve carrying a packing, said valve being shaped so as to shield said packing from the destructive elements normally developed within the calorimeter.

10. In a calorimeter, a cover having a passage through its center, said passage having an enlargement at its lower portion, a valve fitting within said portion and carrying a packing ring shielded from direct contact with the corrosive agents within the calorimeter, said valve having a flaring portion to serve as a deflector for diverting outwardly against the wall of the calorimeter, gases entering past the valve seat.

11. A calorimeter having a cup and a cover, the inner faces of which are exposed to direct contact with the acid normally developed in the calorimeter, said faces being constructed of a non-corroding alloy, substantially as described.

12. A momb calorimeter having its walls directly exposed to contact with the corrosive agencies normally developed in the calorimeter, said walls being constructed of an alloy containing approximately 68 per cent. nickel, 8 per cent. copper, and 18 per cent. chromium, substantially as described.

13. A calorimeter cup unlined throughout and composed essentially of an alloy of 68 per cent. nickel, 8 per cent. copper, 18 per cent. chromium and 3 per cent. tungsten together with a small percentage of deoxidizing material.

14. A calorimeter having a cup and a cover, the inner faces of which are exposed to direct contact with the acid normally developed in the calorimeter, said cover having a gas inlet therethrough which is enlarged at the inner face of said cover to receive a valve, and a valve movable outward automatically under the expanding force of gases within the calorimeter to seal said gas inlet.

In witness whereof, I hereunto subscribe my name to this specification in the presence of two witnesses.

SAMUEL W. PARR.

Witnesses:
I. V. CURRAN,
PAUL W. BAUMANN.

cover, clips slidable over said wires, and an ignition wire removably gripped by said clips.

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In witness whereof, I hereunto subscribe my name to this specification in the presence of two witnesses.

SAMUEL W. PARR.

Witnesses:
I. V. CURRAN,
PAUL W. BAUMANN.

Corrections in Letters Patent No. 1,115,238.

It is hereby certified that in Letters Patent No. 1,115,238, granted October 27, 1914, upon the application of Samuel W. Parr, of Urbana, Illinois, for an improvement in "Calorimeters," errors appear in the printed specification requiring correction as follows: Page 1, line 24, for the word "moisture" read *moist;* page 3, line 15, for the word "realtively" read *relatively;* page 4, line 63, for the word "momb" read *bomb;* and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 17th day of November, A. D., 1914.

[SEAL.]

R. F. WHITEHEAD,

Acting Commissioner of Patents.

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