United States Patent

Wakefield

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[54] **VAPOR PHASE DEPOSITION OF SILICIDE REFRACTORY COATINGS**

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[52] **U.S. Cl.** ....**117/106 R,** 117/107.1, 117/107.2 R
[51] **Int. Cl.** **C23c 11/00,** C23c 13/00
[58] **Field of Search** 117/106, 107, 107.1, 107.2

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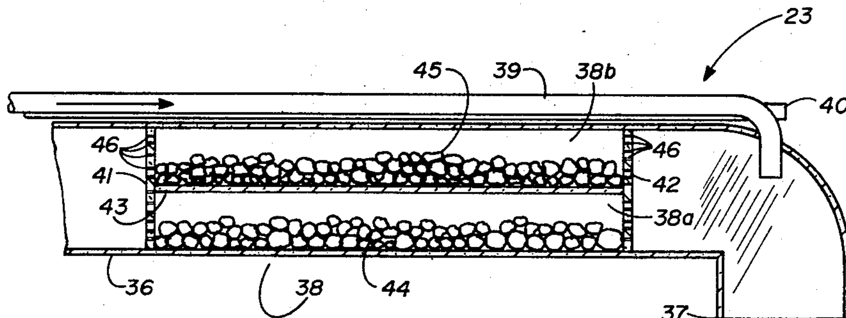
[57] **ABSTRACT**

Refractory coatings are formed upon the periphery of objects by passing a vaporous reactant stream in contact with the objects which are tumbled in a rotary deposition zone. In addition, reactant vapors are passed through a reactant generating zone positioned adjacent and preferably enclosed within the rotary deposition zone which is heated to the reaction temperature to thereby generate at least a portion of the reactant vapors utilized in the deposition of the refractory coating. For example, titanium tetrachloride vapors are passed over chromium and titanium metal chips positioned within the generation zone to produce chromium dichloride and titanium trichloride reactant vapors. A suitable apparatus is also provided for generating at least a portion of the vaporous reactants and combining them with other vaporous reactants and directing them onto tumbling objects to be coated within a rotary deposition chamber.

2 Claims, 3 Drawing Figures



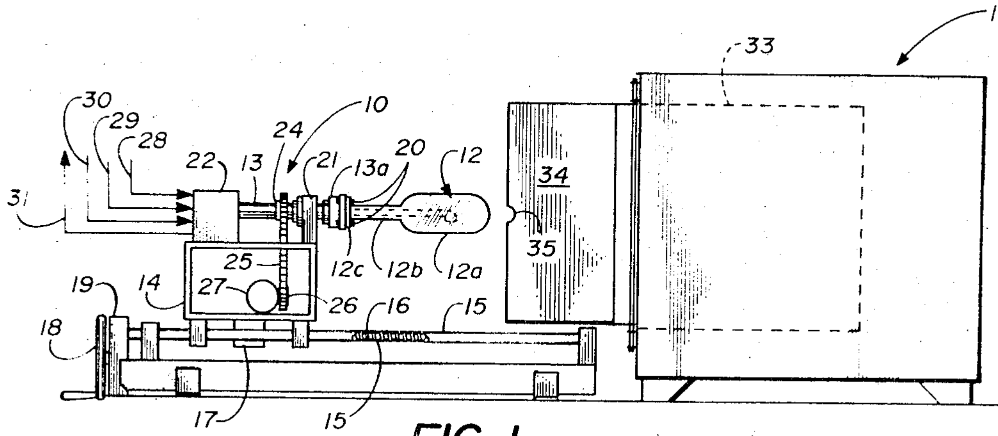


FIG. 1

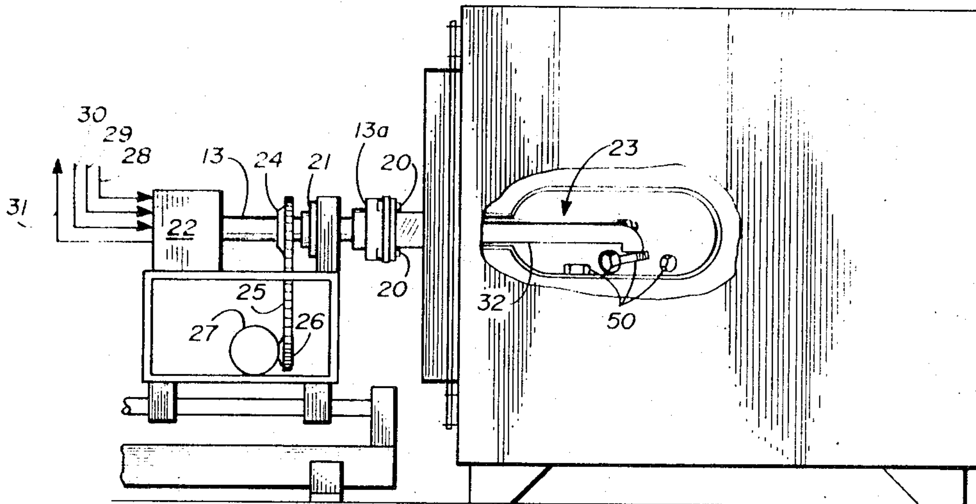


FIG. 2

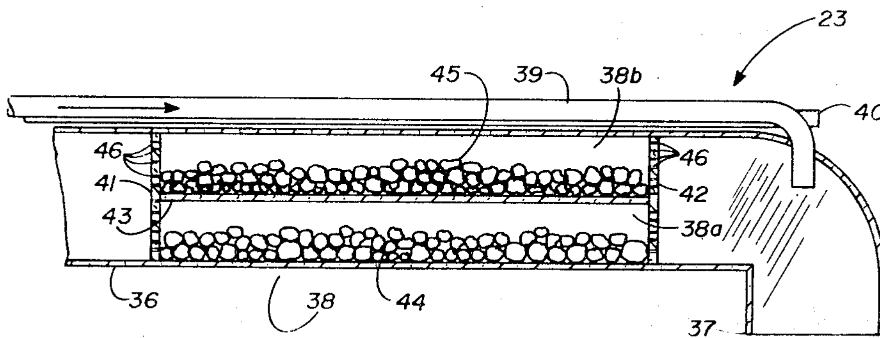


FIG. 3

GENE F WAKEFIELD

VAPOR PHASE DEPOSITION OF SILICIDE REFRACTORY COATINGS

This invention relates to vapor phase deposition of refractory materials upon a substrate. In another aspect, this invention relates to an improved method and apparatus for forming a continuous refractory coating on the periphery of an object.

Refractory metals, such as tantalum, molybdenum, columbium (niobium) and tungsten, for example, are especially desirable for applications requiring high strength at elevated temperature, particularly where ease of fabrication and ductility are needed. However, before any of these metals can satisfy a wide range of requirements, they must receive a suitable protective coating, such as an oxidation resistant and/or an abrasive resistant coating. For example, titanium and chromium, being metallurgically compatible with the refractory metals, form a good base coating which, when alloyed with silicon, or reacted with carbon or nitrogen will protect them against oxidation, and/or abrasion.

Various chemical vapor phase deposition processes have been developed for depositing protective coatings on substrates, including substrates of refractory metals. These protective coatings include silicon carbide, titanium carbide, silicon nitride, titanium nitride, metal carbonitrides, and titanium-chromium-silicon alloys, to name a few. When depositing some of the newer solid solution or alloy layers, problems have been encountered in the formation and maintaining of suitable vaporous reactant streams. For example, attempts to co-reduce titanium and chromium halides produced separately, and individually introduced into a deposition chamber, failed to yield satisfactory co-deposits of titanium and chromium alloys upon the substrate. This is true because of resultant non-uniform mixing of the two halide gas streams and inadequate control of the composition of the reactant gas stream. Furthermore, in the separate production of the halides of the metals by the reaction of hydrogen chloride gas, for example, with the individual metals, the unreacted hydrogen chloride gas tends to inhibit the deposition of the titanium metal. Thus, the formation and control of the vaporous reactant streams has been conventionally very difficult to accomplish.

Additionally, problems have been encountered in obtaining uniform deposits of a protective coating about the entire periphery of an object, particularly irregularly shaped objects such as nuts and bolts, which are used for high temperature fasteners, such as for example, fasteners for a rocket nose cone. It is essential that the entire periphery of these objects obtain a uniform coating to prevent damaging corrosion from eroding and weakening any portion thereof. Therefore, it is necessary that the entire periphery of these objects be subjected to the vaporous reactant atmosphere.

One object of this invention is to provide an improved process and apparatus for forming a protective coating on the periphery of an object.

Another object of this invention is to provide an improved process and apparatus for forming and effectively mixing a vaporous reactant stream and directing it upon a tumbling object to be coated in a rotating vapor deposition zone.

A further object of this invention is to provide a method and apparatus for applying a uniform refractory or protective coating on the periphery of an object by vapor phase deposition, and for generating at least a portion of the vaporous reactant stream.

According to one embodiment of this invention, a process is provided for applying a protective coating to the periphery of an object comprising placing the object within a rotary deposition zone which causes the object to tumble therein, and directing a vaporous reactant stream in contact with the tumbling object wherein at least a portion of said stream is generated by passing a reactant halogen-containing stream over metal particles in a generation zone to form a corresponding metal halide. Preferably, the generation zone is located within a heat zone containing the rotating vapor deposition zone.

According to another embodiment of this invention, an apparatus is provided for carrying out the above-described process which generally includes a rotary vapor phase deposition chamber for receiving and imparting a tumbling motion to at least one object to be coated with vapor phase reactant product, an oven means for enclosing the deposition chamber, nozzle means for introducing vapor phase reactants into the rotary vapor phase deposition chamber, and at least one reactant generation chamber positioned within said oven means and communicating with said nozzle means.

This invention can be more easily understood from a study of the drawings in which:

FIG. 1 is an elevational view of a vapor phase deposition apparatus of this invention with the rotary deposition chamber positioned outside of the oven;

FIG. 2 is the apparatus of FIG. 1, partially in section, showing the rotary vapor phase deposition chamber extended within the oven; and

FIG. 3 is a partial sectional view of FIG. 2 showing a nozzle means and reactant generation chamber thereof.

Now referring to FIG. 1, the apparatus of this invention is illustrated which generally comprises rotary vapor phase deposition reactor means **10** and an oven means **11**.

Rotary vapor phase deposition reactor means **10** comprises rotary deposition chamber **12** rotatably mounted on tubular spindle **13**, which is carried by frame **14**. Frame **14** is slidably mounted on guide rods **15** and is actuated by worm gear **16** which passes through a cooperating threaded portion of member **17**, which extends from frame **14**. Crank **18** is operatively attached to the end of worm gear **16** through gear box **19**. Thus, a rotational motion of crank **18** will cause frame **14** to move along guide rods **15** by the action of worm gear **16** on the threaded portion of member **17**.

Now referring to both FIGS. 1 and 2, rotary deposition chamber **12** is mounted to flange **13*a*** of tubular spindle **13** by suitable fastening means such as nut and bolt assemblies **20**. Tubular spindle **13** is rotatably mounted between supports **21** and **22** and has nozzle means **23** operatively positioned therethrough in a non-rotating, fixed relationship. Sprocket **24** is affixed to the periphery of spindle **13** and is attached by a drive chain **25** to driving sprocket **26** of motor **27**.

Rotary deposition chamber **12** generally comprises a widened body portion **12*a*** for receiving at least one object, such as nuts and bolts as illustrated in FIG. 2, and an elongated neck section **12*b*** slightly wider in diameter than the width of nozzle means **23**, and flange **12*c***, having apertures which match with apertures through flange **13*a*** of spindle **13** for receiving nut and bolt assemblies **20**. Rotary deposition chamber **12** can be made of any suitable ceramic material such as quartz.

The outlet of nozzle means **23** is positioned to direct reactants on the objects **50** positioned within the widened portion **12a** of rotary deposition chamber **12**. Reactant inlet conduits **28, 29** and **30** are operatively connected to nozzle means **23**, as will be described in relation to FIG. 3, below. Outlet conduit means **31** operatively communicates with annular zone **32** between reactant nozzle means **23** and rotary deposition chamber **12**.

Oven **11** carries a suitable heating chamber **33** (shown in broken line), which communicates with a pair of cooperating hinged oven doors **34**. Each oven door carries a semi-circular recessed portion **35** on its outer edge for receiving elongated neck portion **12b** of rotary deposition chamber **12** when in closed position.

Now referring to FIGS. 1–3, and particularly FIG. 3, nozzle means **23** is illustrated in detail. As shown in FIG. 3, nozzle means **23** generally comprises a tubular member **36** which is operatively connected to feed inlet conduit **30** within support member **22** and has a downturned outlet end **37**. In addition, nozzle **23** carries generation chamber **38** therewithin. Conduits **39** and **40** communicate with reactant inlet conduits **29** and **28**, respectively. The outlet of conduit **39** extends through tubular body **36** and is substantially concentric with downturned outlet **37**. The outlet of tube **40** is positioned adjacent outlet **37**. It is noted that any number of conduits **40**

can be utilized within the scope of this invention according to the particular reactants utilized. For example, one or more conduits **40** can be positioned on nozzle means **23**. If desired, the outlet end of conduit **40** can be positioned in a downturned manner adjacent outlet **37**.

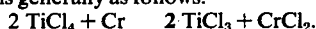
Reactant generation chamber **38** can comprise one or more chambers contained within porous plugs **41** and **42**. As illustrated, generation chamber **38** carries a partition member **43**, which separates the chamber into two individual generation chambers **38***a* and **38***b* containing either similar or dissimilar metallic particles **44** and **45**, respectively. Holes **46** through porous plugs **41** and **42** can be varied in size and number to control the relative proportions of reactant gas flow through the two chambers **38***a* and **38***b*.

The process and apparatus of this invention finds particular utility in applying protective coatings to the periphery of objects with vaporous metal compounds which have relatively low vapor pressures at room temperature. In addition, this invention is especially useful for generating highly reactive metal sub-halide reactants from the more stable metal halides which have high vapor pressures at room temperature. The metal sub-halides are not only more reactive but result in a reduced amount of by-product acid vapor which generally inhibits the deposition rate on the substrate.

Thus, this invention can be utilized to apply various protective coatings to the surface of objects. However, it will be described in detail hereinbelow with reference to the deposition of a complex silicide refractory compound coating consisting of titanium, chromium, and silicon. The introduction of chromium to a plating environment is generally very difficult, since the vapor pressure of chromium is relatively low even at elevated temperatures. This invention will assure that chromium is introduced to the plating environment used in coating the periphery of an object. In addition, this invention can be used to form a more reactive halide specie of a vaporous metal halide reactant.

Thus, in a preferred embodiment, particulate chromium is positioned in one of the generating chambers, for example, **38***b* within tubular body 36, and particulate titanium is placed within the other generating chamber **38***a*. Rotary deposition chamber **12** is removed from spindle **13** and objects **50** are positioned therewithin. Next, rotary deposition chamber **12** is affixed to flange **13***a* of spindle **13** by nut and bolt assemblies **20**. Hand crank **18** is actuated to move frame **14** along guide rods **15** toward oven **11**. As rotary deposition chamber **12** extends within oven **11**, oven doors **34** are closed in a manner as illustrated in FIG. **2** such that elongated neck portion **12***b* of rotary deposition chamber **12** extends between cooperating semicircular recesses **35**.

The heating element of oven **11** is actuated to heat rotary deposition chamber **12**, generation chamber **38**, and objects **50** to a suitable reaction temperature, e.g., 900° C. Next, motor **27** is actuated to cause drive chain **25** to rotate spindle **13** at a suitable speed, for example, from about 0.5 to about 15 rpm. This rotating action causes the rotation of rotary deposition chamber **12** and thereby causes the tumbling of parts **50** therewithin. Next, suitable reactants are supplied by conduits **28–30**. Titanium tetrachloride is passed into generation chamber **38** from feed conduit **30**. Silicon tetrachloride is passed into conduit **39** of nozzle means **23** from feed conduit **29**, and reducing hydrogen is passed through conduit **40** of nozzle means **23** from feed conduit **28**. Exhaust gases are removed from annular space **32** within rotary deposition chamber **12** by exhaust conduit **31**. The action of the titanium tetrachloride on the chromium particles contained within chamber **38b** is generally as follows:



$$2\,TiCl_4 + Cr \quad 2\,TiCl_3 + CrCl_2.$$

In addition, the reaction of the titanium tetrachloride on the titanium metal particles contained within generation chamber **38***a* is as follows:

$$3\,TiCl_4 + Ti \quad 4\,TiCl_3.$$

Thus, a reactant feed stream consisting essentially of titanium trichloride and chromium dichloride is passed to outlet **37** of nozzle means **23** from porous plug **42**. In addition, the vaporous reactants from porous plug **42** are intermixed with silicon tetrachloride passed from the outlet of conduit **39**. The resulting reactant feed mixture is passed downwardly into the interior of rotary deposition chamber **12** in contact with the tumbling parts **50**.

Hydrogen supplied to the interior of rotary deposition chamber **12** reduces the metallic halides emitted from outlet **37** of nozzle **23** when contact is made with an object **50** to form a complex silicide refractory compound consisting essentially of titanium, chromium, and silicon, thereby leaving a by-product of hydrogen chloride which is removed from deposition chamber **12** via conduit **31** as described above.

After the deposition process, reactant flow is cut off, oven doors **34** are opened, and hand crank **18** is actuated to thereby pull frame **14** from the interior of oven **11**. The coated objects are then removed from rotary deposition chamber **12** after it is removed from spindle **13**.

It must be understood that various vapor phase chemical deposition processes can be carried out according to this invention. For example, metallic particles utilized in generation chamber **38** can be metals selected from Groups IVB, VB, VIB, VIIB and VIII of the Periodic Table, carbon, silicon, and boron, or mixtures thereof. The reactant gas passed through generation chamber **38** can be any suitable reactant known in the art which will combine with the metal, volatilize the same, and later react with a suitable reducing agent such as hydrogen within the rotary deposition chamber. For example, metal halides, molecular halogen, and acid vapors such as hydrogen chloride.

Thus, this invention can be utilized to deposit uniform refractory coating such as metal carbides, metal nitrides, metal carbonitrides and silicide coatings on the periphery of objects tumbling within the rotary vapor phase deposition zone. For example, if it is desired to deposit a metal carbonitride, such as titanium carbonitride, on the surface of an object within the rotary deposition zone, titanium particles can be positioned within generation chamber **38**, and titanium tetrachloride passed therethrough to form a feedstream of titanium trichloride. The oven in this instance can be heated to a temperature in the range from abour 400° to about 1,200° C. Next, molecular nitrogen and/or an easily decomposable nitrogen-containing compound, an easily decomposable carbon-containing compound (alternatively, an easily decomposable nitrogen and carbon-containing compound) is passed through conduit **39**. Molecular hydrogen is passed through conduit **40**.

Suitable carbon-containing reactant compounds include cyclic and acyclic hydrocarbons having up to about 18 carbon atoms which readily decompose at the deposition temperature. Examples of suitable hydrocarbons include the parafins, such as methane, ethane, propane, butane, pentane, decane, pentadecane, octadecane, and aromatics such as benzene and halogen substitute derivatives thereof.

Suitable reactant compounds containing both carbon and nitrogen include aminoalkenes, pyridines, hydrazines, and alkylamines. Some specific examples include diaminethylene, triaminoethylene, pyridine, trimethylamine, triethylamine, hydrazine, methylhydrazine, and the like.

Thus, the above described reactants can be utilized to form a titanium carbonitride coating on the surface of objects **50** tumbling within rotating deposition chamber **12**.

This invention can be more easily understood from a study of the following examples which are given for illustrative purposes only.

EXAMPLE 1

In this example an apparatus was utilized which was substantially the same as that illustrated in the drawings. Widened portion **12***a* of rotary deposition chamber **12** comprised a cylindrically shaped body 5 inches in diameter and 6 inches long. Prior to the run, 10 ¼ inches diameter by 1½ inches long

hexhead bolts made of a refractory columbium alloy were placed within chamber **12**, pure titanium metal chips were positioned within generating chamber **38*b*** and pure chromium chips were placed within generating chamber **38*a***.

Next, frame **14** was moved forward and oven doors **34** closed so that widened portion **12*a*** of rotary deposition chamber **12** was positioned within oven **11** as illustrated in FIG. **2**. The interior of oven **11** was maintained at 900° C. Motor **27** was actuated to cause spindle **13** and rotary deposition chamber **12** to rotate at a speed of 11 rpm.

Reactants were next passed in through reactant inlet conduits **28**, **29** and **30**. A stream consisting of 0.238 liter per minute of titanium tetrachloride and 17.3 liters per minute of argon was passed through inlet conduit **30** to tubular body **36** and through generation chamber **38**. A stream of 0.12 liter per minute of silicon tetrachloride in 1.38 liters per minute of argon was passed through inlet conduit **29** and conduit **39** of nozzle means **23**. Ten liters per minute of hydrogen was passed in through inlet conduit **28** and conduit **40** of nozzle means **23**. This reactant flow continued for a period of 270 minutes. At the end of the deposition time, there was shown to be substantial weight loss of the chromium and titanium chips from generating chamber **38**. Each bolt was found to have an average of 330.7 milligrams of silicide coating (a coating consisting essentially of titanium, chromium, and silicon) thereon. This coating was substantially uniform over the entire portion of the bolt including the threaded portion and resulted in a substantially oxidation resistant surface thereof. The coating thickness was between 2 and 3 mils, and oxidation tests at 2,400° F in an oxidation environment showed an increased life of 80 times of that of similar uncoated bolts.

EXAMPLE 2

The apparatus as described above was utilized except in this instance, 10 ¼ inches diameter by 1½ inches long hexhead bolts, 10 hex nuts for the bolts, and 10 ¼ inches diameter by **1** inch long threaded studs all made of a refractory columbium alloy were utilized as the substrates within rotary deposition chamber **12**.

After the 30 substrates were loaded into the rotary deposition chamber **12**, the run was conducted in substantially the same manner as described in relation to FIG. **1**. However, furnace **11** was maintained at 990° C and the flow of reactants was as follows: 0.140 liter per minute of titanium chloride and 10.2 liters per minute of argon were passed through generating chamber **38** containing the titanium and chromium chips; 0.084 liter per minute of silicon tetrachloride and 2.66 liters per minute of argon were passed through conduit **39** of nozzle

means **23**; and 7 liters per minute of hydrogen together with 3 liters per minute of argon was passed through conduit **40** to the interior of rotary deposition chamber **12**. The flow of reactants continued for a period of 480 minutes.

After the run was completed, it was found that there was a substantial loss of weight of the chromium and titanium chips from generating chambers **38*a*** and **38*b***. In addition, it was found that the average weight gain of the hexhead bolts was 528.2 milligrams per bolt, the average weight gain of each hex nut was 118.6 milligrams, and the average weight gain of each of the threaded studs was 147.6 milligrams. It was found that the silicide coating was uniform about the periphery of the objects, even on the threaded surfaces.

EXAMPLE 3

Example 2 was repeated, except 0.084 liter per minute of diaminethylene in 2.616 liters per minute of argon was passed through conduit **39** of nozzle **23** instead of silicon tetrachloride.

This procedure formed a uniform deposit of titanium carbonitride on the periphery of the individual substrates.

While this invention has been described in relation to its preferred embodiments, it is to be understood that various modifications of this invention will now become apparent to one skilled in the art upon reading the specification, and it is intended to cover such modifications as fall within the scope of the appended claims.

I claim:

1. A method of forming a protective coating on the surface of a compatible substrate which comprises:

contacting a particulate mass of elemental chromium and a particulate mass of elemental titanium with a reactant stream comprising titanium tetrachloride, thereby forming a reactant stream comprising titanium trichloride and chromium dichloride;

tumbling said substrate in a rotary deposition zone;

heating said particulate mass of chromium, said particulate mass of titanium, and said substrate in a common heating zone; and

contacting said substrate with silicon tetrachloride, hydrogen, and the reactant stream produced by reacting said titanium tetrachloride with the elemental titanium and chromium, thereby forming a refractory silicide coating on said substrate.

2. A method as defined by claim **1** wherein said titanium, said chromium, and said substrate are maintained at a temperature at about 900° C.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,658,577 Dated April 25, 1972

Inventor(s) Gene F. Wakefield

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the first page (Cover Sheet) left hand column after the listing of Inventors insert:

[73] Assignee: Texas Instruments Incorporated, Dallas, Texas

Signed and sealed this 12th day of June 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

FORM PO-1050 (10-69)

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