Jan. 26, 1971 J. R. DARNELL ET AL 3,558,343

DISPERSION STRENGTHENED TITANIUM CARBIDE AND METHOD FOR MAKING SAME

Filed Aug. 18, 1966 2 Sheets-Sheet 1

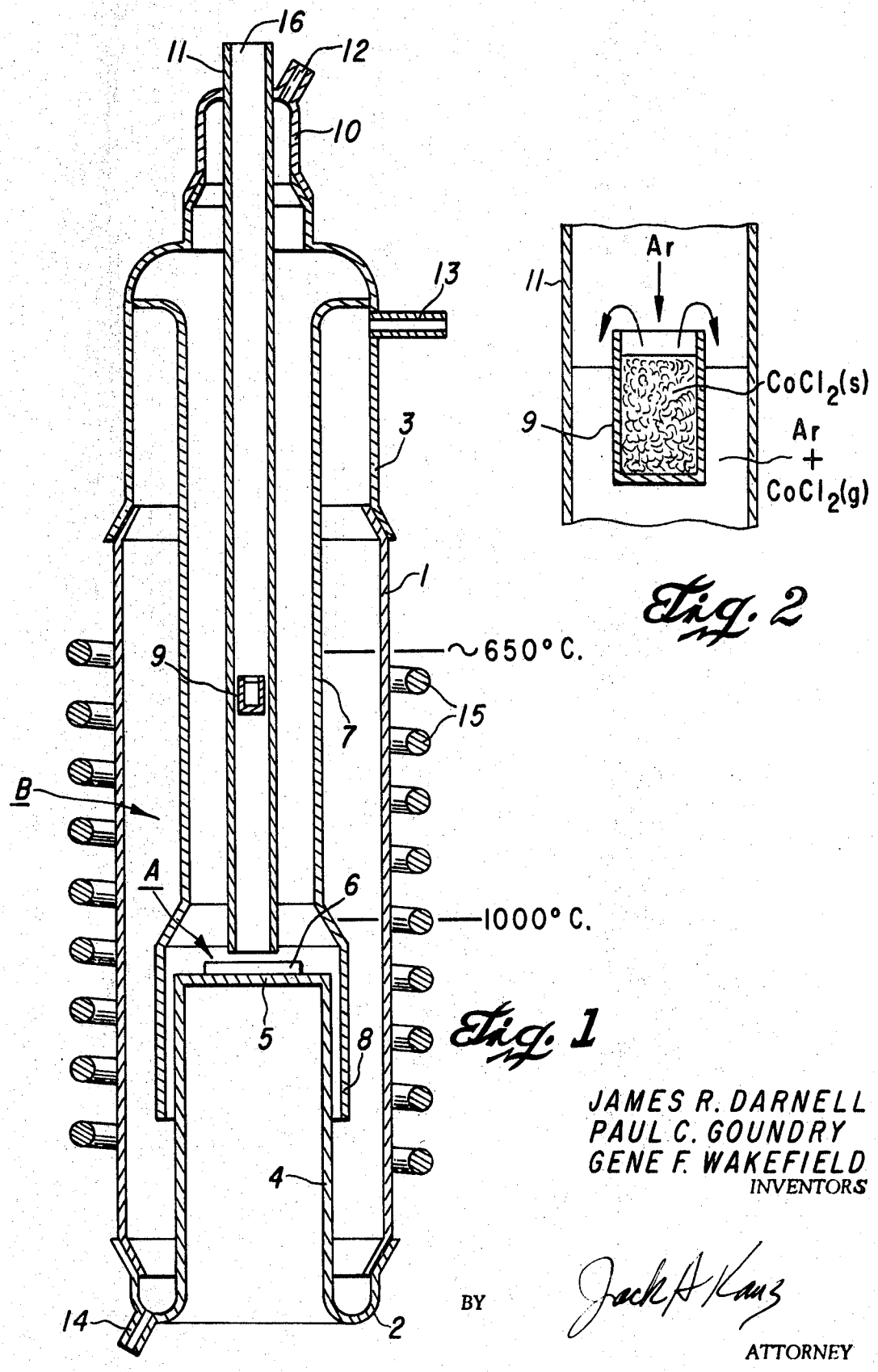


Fig. 2

Fig. 1

JAMES R. DARNELL
PAUL C. GOUNDRY
GENE F. WAKEFIELD
INVENTORS

BY Jack A. Kanz

ATTORNEY

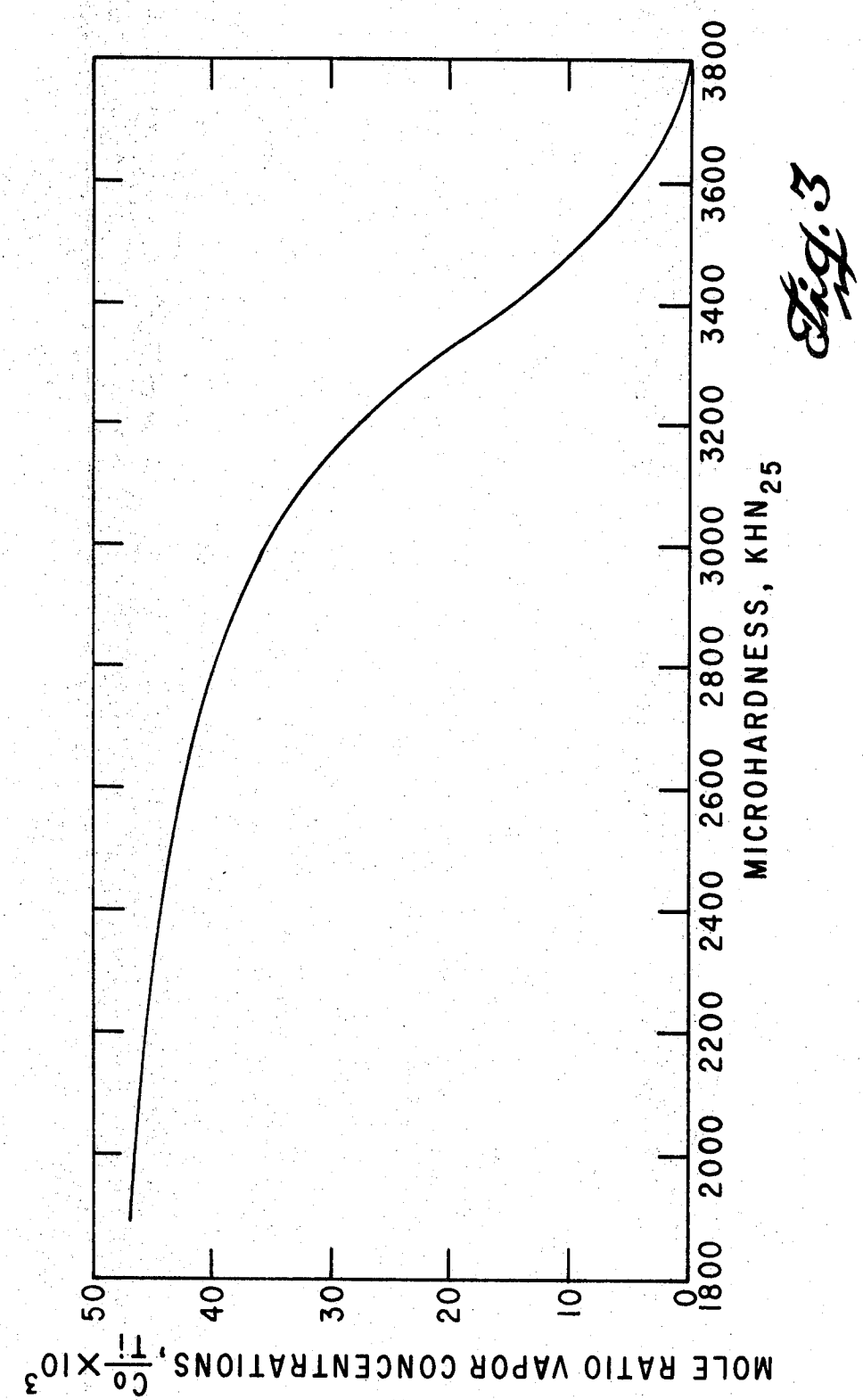

MICROHARDNESS, KHN_{25}
1800
2000
2200
2400
2600
2800
3000
3200
3400
3600
3800
MOLE RATIO VAPOR CONCENTRATIONS, $\frac{C_0}{T_i} \times 10^3$
0
10
20
30
40
50

Fig. 3

United States Patent Office 3,558,343
Patented Jan. 26, 1971

3,558,343

DISPERSION STRENGTHENED TITANIUM CARBIDE AND METHOD FOR MAKING SAME

James R. Darnell, Dallas, and Paul C. Goundry and Gene F. Wakefield, Richardson, Tex., assignors to Texas Instruments Incorporated, Dallas, Tex., a corporation of Delaware

Filed Aug. 18, 1966, Ser. No. 573,238
Int. Cl. C23c 11/02, 11/08
U.S. Cl. 117—46 2 Claims

ABSTRACT OF THE DISCLOSURE

A method of forming a titanium carbide matrix having a ductile metal dispersed therein by chemical vapor deposition of titanium carbide from hydrogen reduction of a titanium halide and a carbon halide at elevated temperatures. The ductile metal is generated within the reactor as a halide and transported to the deposition site by an inert gas carrier, where the elemental titanium, carbon, and ductile metal react to form a deposit of titanium carbide containing the ductile metal. The ductile metal halide vapor is initially separated from the titanium halide and carbon halide vapor stream to prevent premature reduction of the ductile metal chloride.

This invention relates to deposits of dispersion strengthened materials upon substrates, and more particularly to a method of depositing titanium carbide having a ductile metal dispersed therein upon a substrate by chemical vapor deposition. The invention further includes the product made by the method of the invention.

The vapor streaming technique of chemical vapor deposition produces coherent, dense deposits of titanium carbide, a refractory metal carbide. As used in the present application, vapor streaming includes but is not limited to a dynamic system of chemical vapor deposition in which gaseous reactants continuously pass through a reaction chamber, depositing a material upon a substrate.

Deposits of titanium carbide formed by the vapor streaming technique of chemical vapor deposition exhibit several desirable properties, notably ultra-hardness, having Knoop microhardness values generally greater than 3000, and excellent compressive strength. Deposits of titanium carbide are well suited for wear-resistant applications, such as upon steel bearings. However, chemically vapor deposited pure titanium carbide is also quite brittle and lacks toughness, with the result that it exhibits inadequate resistance to shear forces for many potential types of service. To impart toughness to a titanium carbide deposit and thereby widen its field of use, in accordance with the method of the present invention, a suitable ductile metal such as cobalt or nickel is simultaneously deposited with the titanium carbide upon the substrate to be coated by chemical vapor deposition. The dispersion thus formed is of the type in which titanium carbide is the continuous phase and the ductile metal is the dispersed phase. In this type of dispersion strengthened material the ultra-hard characteristics of the pure titanium carbide are retained. Moreover, the dispersed particles of the ductile metal absorb energy, prevent high energy build-up from reaching the threshold energy density for fracture propagation and thereby function to stop the propagation of cracks which may originate in the titanium carbide matrix. Such a dispersion strengthened material therefore possesses desirable strength properties including a degree of toughness not possessed by pure titanium carbide and approaches the hardness of the refractory metal carbide, since the dispersed phase is a very low percentage of the total composite and is in the form of minute particles. Moreover, because of their greater coherence, such dispersion strengthened materials formed by the chemical vapor deposition process are considerably more impact resistant than the ordinary cementive materials known to the art.

It is therefore an object of the present invention to provide a method of preparing dispersion type deposits of titanium carbide and a ductile metal upon a substrate through simultaneous multi-component chemical vapor deposition by the vapor streaming technique. Since, with techniques known to the art, successful utilization of this method may be prevented by a premature interaction of reactants for the respective component products, it is another object of the invention to provide a method of avoiding premature interaction by bringing the source of the ductile metal to the deposition site separately from the titanium carbide reactant mixture.

Yet another object of the invention is the novel dispersion strengthened material produced by the method of the invention.

Other objects, features and advantages of the invention will become more readily understood from the following detailed description taken in conjunction with the appended claims and attached drawings in which:

FIG. 1 is an elevational view in section of an apparatus suitable for practicing the method of the invention,

FIG. 2 is an enlarged view of the receptacle in which a halide of the ductile metal is generated,

FIG. 3 is a graph showing Knoop microhardness values obtained by varying the relative concentration of the reactants.

In dispersing a ductile metal in titanium carbide in accordance with the method of the invention, the titanium carbide may be produced by chemical vapor deposition through reduction of, for eaxmple, titanium tetrachloride ($TiCl_4$) and a carbon compound such as carbon tetrachloride (CCl_4) with hydrogen at elevated temperatures according to the following reaction:

$$TiCl_4 + CCl_4 + 4H_2 \xrightarrow{1000^\circ C.} TiC + 8HCl$$

To introduce a ductile metal, for example cobalt, into the deposit, cobalt halide vapors are generated at a source site within the reactor, conveyed by a carrier gas to the deposition site within the reactor and there reduced to elemental cobalt. In the method of the present invention, argon, helium or some other suitable inert gas may be used as the carrier gas to convey the cobalt halide vapors, such as cobalt chloride, from the generating site to the deposition site within the reactor. Thus hydrogen chloride, which adversely affects the equilibrium of the reaction to form titanium carbide, is not present in the carrier gas stream, as it otherwise would necessarily be if hydrogen were used as the carrier gas. Since one of the reactants for the titanium carbide reaction is hydrogen, as shown above, it is also necessary to keep the cobalt chloride vapor in its carrier gas completely isolated from the reactants used to prepare titanium carbide until arrival at the deposition site. This is accomplished by generating the cobalt chloride within the reactor and conveying it to the reduction site in a stream of inert carrier gas. All reactants are mixed at the deposition site. Hydrogen from the titanium carbide reactant mixture also reduces the cobalt chloride to elemental cobalt according to the following reaction:

$$CoCl_2 + H_2 \xrightarrow{1000^\circ C.} Co + 2HCl$$

Since excess hydrogen is normally included as a reactant for the titanium carbide reaction, no problem is presented with respect to the course of this reaction.

Another important advantage which accrues from he use of an inert carrier gas is that the temperature range

in which the ductile metal carrier compound may be heated is greately extended and thereby significantly greater vapor pressure is attained. This provides much greater flexibility in selecting the metal halide vapor concentration and consequently permits control of the concentration of metal in the deposit over a greater range.

Referring now to the drawings, FIG. 1 illustrates a reactor comprising a cylindrical body **1** surrounded by hceating coils **15** and having two fitted end caps **2** and **3** to form a substantially gastight reactor. End cap **2** has an exhaust outlet **14** and a hollow cylindrical portion **4** which extends upwardly into the central portion of the tubular ractor **1**. The cylindrical portion **4** extending into the reactor has a flat surface **5** upon which the substrate material **6** is positioned.

End cap **3** is mounted on top of the cylindrical body **1** and carries the reaction tube **7** formed therein which extends into the central portion of the reaction vessel **1**. Reaction tube **7** has a flared portion **8** at its lower end which extends over the recessed cylindrical portion **4** of the bottom end cap **2**, thus enclosing the substrate **6** within the lower end of the reaction tube **7**. The flared portion **8** extends down from the substrate carrier surface **5** of end cap **2** and acts as a guide to direct gases passing over the substrate **6** downwardly between the walls of the flared portion **8** and the upwardly extending recessed portion **4** of end cap **2**. The deposition site area in the reaction chamber **7** is identified in the figure by the general reference character A.

End cap **3** and the reaction chamber formed in conjunction with tube **7** effectively divide the reactor into essentially two separate chambers, the deposition chamber A, previously described, and a flush chamber B, defined by the walls of the reaction tube **7** and the cylindrical vessel **1**.

Reaction tube **7** is appropriately fitted with a cap **10** which carries a tube **11** extending therethrough and annularly down into the central portion of the reactor **7** to within one inch or so of the substrate **6**. A receptacle **9** containing metal halide granules, cobalt chloride, for example, is suspended within the tube **11** (shown in greater detail in FIG. 2) at a point near the upper zone of the heating coils **15** surrounding the outside of cylinder **1**. The heating coils controllably maintain the interior of the reaction gas within a temperature gradient of about 650° C. in the receptacle zone and about 1000° C. in the deposition zone A as shown. Heating coils **15** may be either RF induction heaters or resistance heaters or any other suitable heating means for controllably maintaining the desired temperatures in the zone of the receptacle **9** and the substrate zone A.

A carrier stream of argon or helium gas is passed through the tube **11**, carrying the metal halide vapor toward the surface of the substrate **6**, as shown in FIG. 2.

Cap **10** is further provided with an inlet **12** through which titanium tetrachloride and carbon tetrachloride in a stream of hydrogen are introduced into tube **7** and pass downward outside the walls of the metal chloride tube **11**. Upon reaching the deposition site A, the metal chloride, titanium tetrachloride, carbon tetrachloride and hydrogen gases mix and react to form a deposit of ductile metal in titanium carbide upon the substrate **6**.

End cap **3** is fitted with flush inlet **13** through which a flush gas (argon, for example) is passed through the flush chamber B. The flush gas, entering inlet **13**, passes through chamber B between the walls of the cylinder **1** and the reaction tube **7** and downwardly over guide **8** to exit through exhaust **14** provided in the lower end cap **2**. The flush gas is used primarily to prevent contamination of the deposition chamber A by back-drafts passing upwardly between the guide **8** and the walls of the recessed portion **4** of end cap **2**.

For the dispersion of a ductile metal in titanium carbide by the vapor streaming technique of chemical vapor deposition in accordance with the invention, a steel or

graphite substrate **6**, by way of example, is suitably prepared and positioned on the flat surface **5** of end cap **2**. Metal chloride granules are placed in the receptacle **9** which is then mounted in tube **11**. Purified helium or argon is first flushed through inlets **16**, **12** and **13** to purge atmospheric gases from the reactor in preparation for the deposition. When the reactor has been sufficiently purged, the flow of argon through tube **12** is stopped. The flow of argon through the tube **13**, however, is maintained at a rate of approximately 35 cc./minute. The flow rate of argon (or helium) through tube **16** is varied according to the deposition rate of ductile metal desired. The chamber is then rapidly brought up to operating temperature within the gradient previously given. Titanium tetrachloride and carbon tetrachloride are admitted to the reactor through feed tube **12**, entrained in a carrier of hydrogen gas. In the preferred embodiment of the invention, this feed gas is prepared by bubbling hydrogen through bubbler bottles (not shown) containing the liquids titanium tetrachloride ($TiCl_4$) and carbon tetrachloride (CCl_4) at room temperature. The gas thus admitted through feed tube **12** is hydrogen saturated with $TiCl_4$ and CCl_4.

Upon reaching the deposition site A the hydrogen, titanium tetrachloride, the carbon tetrachloride from tube **12** and the metal halide vapors from tube **11** mix and are simultaneously reduced by the hydrogen gas into a mixture of titanium carbide and ductile metal which is deposited upon the substrate **6**. The spent gases pass downwardly between the guide **7** and the recessed portion **4** of end cap **2** to exit through exhaust outlet **14**.

EXAMPLES

Using the reactants, temperature ranges and other conditions discussed above and shown in FIGS. 1 and 2, suitable steel substrates were coated using the following parameters:

	Sample 1	Sample 2
$TiCl_4$, millimoles/minute	1.342	1.342
CCl_4, millimoles/minute	1.342	1.342
H_2, millimoles/minute	122.000	122.000
$CoCl_2$, millimoles/minute	None	0.029
Deposition rate, mils/hour	0.25	0.13
Knoop microhardness	3,800	2,900

In practising the method of the present invention, by varying the mole ratio vapor concentration of cobalt to titanium in the gaseous reactants from zero to about 5%, deposits have been produced having Knoop microhardness values of 1900–3800 with deposition rates of approximately 0.2–0.4 mil per hour, as shown by the graph in FIG. 3.

Although the operation of the reactor **10** has been described with reference to the formation of a dispersion of cobalt in titanium carbide, it is to be understood that other ductile metals, such as nickel, for example, may be dispersed in titanium carbide in accordance with the principles of this invention by selection of the appropriate reactants, flow rates and temperatures. Moreover, it will also be clear to one skilled in the art that halides other than the chlorides may be employed.

While the method of the invention has been described with reference to a specific apparatus for practising the method, it is to be understood that this description is not to be construed in a limiting sense. For example, the ductile metal halide vapors which, in the described embodiment, are produced within the reactor, could be produced outside of the reactor and conveyed by any suitable means at the appropriate temperature to the deposition site A.

What is claimed is:

1. In a method of chemical vapor deposition of titanium carbide upon a heated substrate, said carbide having a ductile metal capable of forming a dispersed phase therein, the step of simultaneously reacting in a stream of hydrogen a titanium halide with a carbon-containing com-

pound susceptible of chemical reduction to yield carbon and a halide of said ductile metal upon said heated substrate at a temperature of about 1,000° C., the halide of said ductile metal being selected from the group consisting of cobalt chloride and nickel chloride.

2. A method of chemical vapor deposition of titanium carbide upon a substrate, said carbide having a ductile metal capable of forming a dispersed phase therein, comprising the steps of:

(a) introducing into a reaction chamber in a stream of hydrogen a titanium halide with a carbon-containing compound susceptible of chemical reduction to yield carbon;

(b) separately producing a vapor stream containing a halide of the ductile metal in an inert gas, the halide of said ductile metal being selected from the group consisting of cobalt chloride and nickel chloride;

(c) separately conveying said vapor stream containing said halide of the ductile metal in an inert gas to the deposition site; and

(d) simultaneously mixing said vapor streams upon a heated substrate at a temperature of about 1,000° C.

to produce upon said substrate titanium carbide with said ductile metal dispersed therein.

References Cited

UNITED STATES PATENTS

2,962,388	11/1960	Ruppert et al.	117—106C
2,962,399	11/1960	Ruppert et al.	117—106C
2,898,235	8/1959	Bulloff	117—106C
3,151,852	10/1964	Weech et al.	117—106C
3,205,042	9/1965	Jacobson	23—208A
3,369,920	2/1968	Bourdeau et al.	117—46

OTHER REFERENCES

Product Engineering, July 1957, p. 10 relied upon.

ALFRED L. LEAVITT, Primary Examiner

J. R. BATTEN, JR., Assistant Examiner

U.S. Cl. X.R.

117—106, 107.2, 131