United States Patent [19]

Hill

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[54] **BALL POINT PEN WRITING BALL COMPOSED OF A CEMENTED CARBIDE COMPOSITION**

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[73] Assignee: **The Parker Pen Company,** Janesville, Wis.

[22] Filed: **Oct. 7, 1971**

[21] Appl. No.: **187,493**

Related U.S. Application Data

[62] Division of Ser. No. 851,038, Aug. 18, 1969, Pat. No. 3,628,291.

[52] **U.S. Cl.** **401/215,** 29/182.8, 75/204

[51] **Int. Cl.** **B43k 7/00**

[58] **Field of Search** 401/215; 29/182.8; 75/204

[56] **References Cited**

UNITED STATES PATENTS

3,503,692	3/1970	Kubota et al.	401/215
2,067,166	1/1937	Bulke	29/182.8
3,628,921	12/1971	Hill	75/204

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Assistant Examiner—B. H. Hunt
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[57] **ABSTRACT**

Cemented carbide compositions and shaped bodies produced therefrom containing tungsten carbide or titanium carbide and a binder alloy containing cobalt and nickel, and, by weight, about 18 to 20 percent chromium, 0.1 to 1 percent platinum and 0 to 3 percent iron.

6 Claims, No Drawings

BALL POINT PEN WRITING BALL COMPOSED OF A CEMENTED CARBIDE COMPOSITION

This is a division of application Ser. No. 851,038, filed Aug. 18, 1969, now U.S. Pat. No. 3,628,291.

BACKGROUND OF THE INVENTION AND DESCRIPTION OF THE PRIOR ART

Cemented carbide compositions containing a hard metal carbide bonded by a metal alloy binder are well known in the art. The hard metal carbide is typically a tungsten or titanium carbide and the metal alloy binder is typically an iron group metal. The hard metal carbide is normally present in the cemented carbide composition in at least major proportion by weight. Cemented carbide compositions can be used where hard and wear resistant compositions are required such as in cutting tools, turning tools, etc.

It has been suggested to supplement the normal iron group metal alloy binder with small amounts of chromium. The addition of small amounts of chromium or chromium carbide to a tungsten carbide-cobalt system is said to improve the corrosion resistance of the alloy but with an accompanying reduction in strength and metallurgical soundness. Additionally, the corrosion resistance of a tungsten carbide-nickel system to certain environments is said to be increased by the addition of chromium carbide but with an accompanying reduction in strength. To overcome these disadvantages, it has been suggested in U.S. Pat. No. 3,215,510 to employ compositions of tungsten carbide and about 10 to about 25 percent, but not more than 30 percent, by weight of binder of chromium and nickel wherein the ratio by weight of chromium to the combined weight of nickel and chromium ranges from about 0.015 to about 0.15. This composition is said to give outstanding corrosion resistance particularly to acids and alkalis.

DESCRIPTION OF THE INENTION

An object of the present invention is the provision of novel and improved corrosion resistant cemented carbide compositions.

A further object of the present invention is the provision of improved shaped bodies made from said cemented carbide compositions.

Further objects and improvements of the present invention will be apparent upon reading the undergoing specification and claims.

Novel corrosion resistant cemented carbide compositions and shaped bodies produced therefrom are provided containing tungsten carbide or titanium carbide and a binder alloy containing cobalt and nickel and, by weight, about 18 to 20 percent chromium, 0.1 to 1 percent platinum and 0 to 3 percent iron.

The cemented carbide compositions of the present invention are produced by powder metallurgy techniques. Powder metallurgy techniques are, in general, well known in the art and include pressing a mixture of powders of the desired carbide and binder metals and then sintering the pressed mixture of powders to form a cemented composition. More particularly, a powder mixture of tungsten carbide or titanium carbide and the metals cobalt, nickel, chromium, platinum and iron is prepared and screened to obtain proper size particles. The powders may be mixed, for example, in a ball mill wherein the powders are suspended in a suitable liquid such as benzene. The milled powder is then dried, mixed with a suitable binder-lubricant and pressed or compacted. The pressed mixture is preferably presintered and then given a final sinter at conventional temperatures and preferably in vacuo. The final sintering is generally carried out under reduced pressure. It is conventional to form cemented carbide compositions by milling together the carbide and binder alloy metals as elemental powders. It has been found, however, that cobalt and nickel coated carbide powders with chromium, platinum and iron added as elemental powders may be milled together with equally good results.

The finally sintered cemented carbide compositions can be shaped by conventional technique as by grinding. Small diameter spherical shapes have been found to have excellent properties for use as writing points which will rotate freely against an inking magazine in a pen. Pens of this nature are conventionally referred to as ball-point pens. "Pen" as used in this context, however, is intended to refer to any instrument which can be used to apply ink or other fluid or viscous material to a receptive surface.

The cemented carbide compositions of the present invention possess outstanding corrosion resistance properties, particularly to aqueous ink and ferric chloride solutions. Additionally, shaped cemented carbide compositions of the present invention possess crush strengths comparable to conventional cobalt or nickel bound carbides. The above properties, therefore, make the cemented carbide compositions of the present invention particularly advantageous for use as writing points in ball-point pens as described above.

The cemented carbide compositions of the present invention preferably contain about 75 to 95 percent by weight of tungsten carbide or titanium carbide and about 5 to 25 percent or, more preferably, about 3 to 15 percent by weight of binder alloy. The binder alloy compositions according to the present invention usually contain, by weight, about 30 to 60 percent cobalt, 20 to 50 percent nickel, 18 to 20 percent chromium, 0.1 to 1 percent platinum and 0 to 3 percent iron. The preferred binder alloy compositions contain, by weight, about 45 to 55 percent cobalt, 25 to 35 percent nickel, 18 to 20 percent chromium, 0.5 to 1 percent platinum and 0 percent iron.

In order to compare the properties of the novel cemented carbide compositions of the present invention with the properties of prior art cemented carbide compositions, binder alloy compositions were prepared as shown in table 1. Table 1 lists the composition of binder alloys A through E in parts by weight of metal components.

TABLE 1

Binder Alloy	Co	Ni	Cr	Pt
A	40	40	20	
B	40	40	19	1
C	50	30	19	1
D	30	50	19	1
E	60	20	19	1

A comparison of the properties of tungsten carbide-cobalt and tungsten carbide-nickel cemented compositions with cemented compositions formed from tungsten carbide and binder alloys A through E from Table 1 is shown in Table 2. Corrosion data is given for aqueous ink and aqueous ferric chloride solutions.

TABLE 2

Cemented Carbide Composition, % of Binder alloy By Weight	Profilometer Reading, Microinches Initial	After 1 year in ink at 140°F	After 1 year in 25%$FeCl_3$ at 100°F
WC+10% Co	0.75	1.50	Attached, >20
WC+10% Ni	0.75	1.50	Attacked, >20
WC+10% Alloy A	0.40	1.00	
WC+10% Alloy B	1.50	2.00	Attacked, >20
WC+10% Alloy C	1.50	1.50	Etched, 9
WC+10% Alloy D	1.00	2.00	Attacked, >20
WC+10% Alloy E	1.50	1.50	Attacked, >20

A writing ball for a ball-point pen was prepared by grinding tungsten carbide and titanium carbide compositions cemented with nickel and cobalt binders and by grinding tungsten carbide and titanium carbide compositions cemented with Alloy C binder from Table 1 to compare the crush strength and microhardness properties of these compositions when formed into shaped bodies. The results of this test are set forth in Table 3.

TABLE 3

Cemented carbide composition % of binder alloy by weight	Crush Strength (lbs.)	Micro-hardness (DPH)
WC + 9 wt. % Ni	200	1510
WC + 10 wt. % Co	177	1450
WC + 10 wt. % Alloy C	173	1680
TiC + 20 wt. % Ni	128	1608
TiC + 20 wt. % Co	157	1626
TiC + 20 wt. % Alloy C	136	1680

The following non-limitative examples illustrate the invention:

EXAMPLE 1

Cobalt and nickel coated tungsten carbide powders, tungsten carbide powders and elemental chromium and platinum powders were prepared and screened to minus 325 mesh. The total charge of powders was as follows:

	Carbide	Binder Alloy
30.55 g. Co (9%) Coated WC	27.80 g.	2.75 g.
18.33 g. Ni (9%) Coated WC	16.68 g.	1.65 g.
5.02 g. WC	5.02 g.	
1.04 g. Cr		1.04 g.
0.06 g. Pt		0.06 g.
55.00 g.	49.50 g.	5.50 g.

The powders were ball milled for 92 hours under benzene in a steel mill with steel balls. The milled powder was dried, mixed with Carbowax 1000 (a water-soluble lubricant available from Union Carbide Corp.) as a binder-lubricant and compacted in a steel die at 20 tons/sq. in. pressure. Cylindrical pieces of ¼ inch dia. × ½ inch in length were packed in a graphite-alundum mixture and presintered by heating slowly to 1850°F in a dissociated ammonia atmosphere. The pieces were then given a final sintering in vacuo at 2550° for one hour under 100–200 microns pressure. A flat may be ground on the side of selected presintered pieces prior to final sintering if profilometer measurements or other corrosion tests are contemplated.

EXAMPLE 2

Titanium carbide, cobalt, nickel, chromium and platinum powders were prepared and screened. The total charge of powders and corresponding particle size were as follows:

40 g. TiC	5 microns
5 g. Co	1.5 microns
3 g Ni	7-13 microns
1.9 g. Cr	-325 mesh
0.1 g. Pt	-325 mesh
50.0 g.	

The powders were ball milled for 96 hours under benzene in a steel mill with steel balls. The milled powder was dried, mixed with a resin binder-lubricant and formed into 0.060 inch diameter spheres. The green spheres were packed in a graphite-alundum mixture and presintered by heating slowly to 1850°F in a dissociated ammonia atmosphere. Final sintering of the spheres was carried out in vacuo at 2650°F for ½ hour under 500 microns pressure. The spheres had shrunk to approximately 0.047 inch diameter and were then ground into 0.043 inch diameter balls for use as writing points in pens. The material of Example 1 was also processed in like manner into balls for use as writing points in pens.

I claim:

1. In a pen having a writing ball which will rotate freely against an inking magazine, the improvement comprising said writing ball formed from a cemented carbide composition comprising from about 75 to 95 percent by weight of a carbide selected from the group consisting of tungsten carbide and titanium carbide and from about 5 to 25 percent by weight of a binder alloy containing cobalt and nickel and, by weight, about 18 to 20 percent chromium, 0.1 to 1 percent platinum and 0 to 3 percent iron.

2. The pen of claim **1** wherein the binder alloy contains, by weight, about 30 to 60 cobalt and 20 to 50 percent nickel.

3. The pen of claim **1** wherein the binder alloy contains, by weight, about 45 to 55 percent cobalt and 25 to 35 percent nickel.

4. A cemented carbide writing ball for a ball point pen, comprising from about 75 to 95 percent by weight of a carbide selected from the group consisting of tungsten carbide and titanium carbide and from about 5 to 25 percent by weight of a binder alloy containing cobalt and nickel and, by weight, about 18 to 20 percent chromium, 0.1 to 1 percent platinum and 0 to 3 percent iron.

5. The writing ball of claim **4** wherein the binder alloy contains, by weight, about 30 to 60 percent cobalt and 20 to 50 percent nickel.

6. The writing ball of claim **4** wherein the binder alloy contains, by weight, about 45 to 55 percent cobalt and 25 to 35 percent nickel.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,746,456 Dated 17 July 1973

Inventor(s) Franklin J. Hill

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

Title page, Col. 1, line 17
Pat. No. 3,628,291 should be -- 3,628,921

Col. 1, line 5
Pat. No. 3,628,291 should be -- 3,628,921 --

Col. 2, line 5
"in vacuo" should be underscored

Col. 3, line 9
"attached" should be -- attacked --

Col. 3, line 58
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Col. 4, line 22
"in vacuo" should be underscored

Col. 4, line 41
after "60" the % sign should be added

Col 4, line 47
after "75" the % sign should be added

Col. 4, line 49
after "5" the % sign should be added

Signed and sealed this 22nd day of January 1974.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

RENE D. TEGTMEYER
Acting Commissioner of Patents

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