Dec. 28, 1954 E. W. GOLIBERSUCH 2,698,232

METHOD OF MAKING CEMENTED CARBIDE ARTICLES AND CASTING COMPOSITIONS THEREFOR

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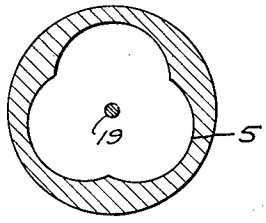

Fig. 2.

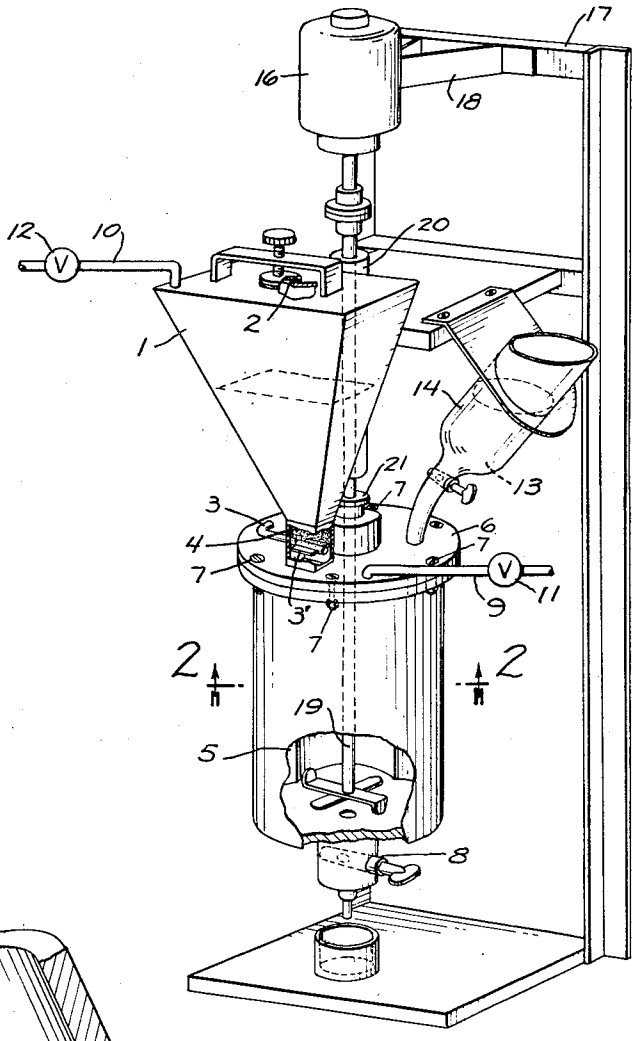

Fig. 1.

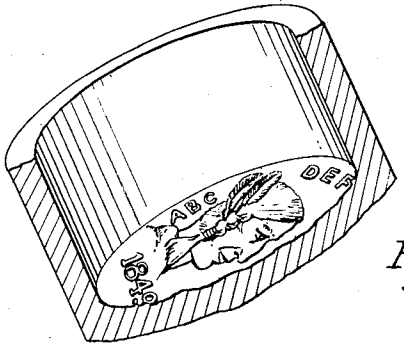

Fig. 3.

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METHOD OF MAKING CEMENTED CARBIDE ARTICLES AND CASTING COMPOSITIONS THEREFOR

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7 Claims. (Cl. 75—203)

This invention relates to a process for forming cemented carbide articles of intricate shape and to a casting composition therefor. More specifically this invention relates to a process for casting hard metal carbide powdered materials into suitably shaped inexpensive molds and thereafter expelling the casting vehicle and finally sintering the article to produce cemented carbide articles having complicated shapes.

In the manufacture of cemented carbide articles such as cutting tool tips, wear parts, dies and form cutting tools, the customary procedures comprise the methods of cold pressing, hot pressing and extrusion. Cold pressing comprises compacting the hard metal carbide powdered materials under a pressure of approximately 2 to 30 tons per square inch, presintering and mechanically working with cutting tools or grinding wheels to produce the final desired shape. Hot pressing comprises compacting hard metal carbide powdered materials in a mold with the simultaneous application of heat and pressure to produce a fully sintered carbide body as disclosed in Hoyt U. S. Patent 1,843,768 and Gilson U. S. Patent 1,756,857. The process of forming carbide articles by extrusion is disclosed in Taylor U. S. Patent 2,271,960. These three methods provide a large variety of simple and semi-complicated shapes, but all of these methods are generally limited to planar variations from rectangular, triangular or cylindrical base shapes.

It is one of the objects of the present invention to provide a process for forming cemented carbide articles of extremely complicated shapes which are not limited to planar variations from rectangular, triangular or cylindrical base shapes. Another object of my invention is to provide a process for forming cemented carbide articles of complicated shape which eliminates the necessity for mechanical forming in the partially sintered state. It is a further object to provide a casting composition for casting such complicated shapes. A still further object is to provide a process for casting cemented carbide articles of complicated shape which is simple, efficient and inexpensive.

The manufacture of cemented carbide articles by my process contemplates the steps of mixing hard metal carbide powdered materials with an organic casting vehicle, casting this mixture into a wax, glue or other inexpensive preshaped mold at room temperature without the application of pressure, polymerizing the casting vehicle to harden the cast article, expelling the casting vehicle from the formed article and finally sintering the formed article to produce a hard sound cemented carbide article. The process differs fundamentally from the casting of thermoplastic or thermosetting materials, in the respect that the casting or binding vehicle is not present in the finally sintered cemented carbide article. The convenient removal of the polymerized casting vehicle from the interstices of a closely packed pulverulent hard metal formed article without destroying the shape of the article or detrimentally affecting its properties is difficult, but it will be understood

that such removal is necessary to enable the cast article to perform its expected function.

Hard metal carbide powdered materials as used herein are intended to include all the refractory hard metal carbide powders which are used as ingredients in manufacturing commercial carbide products, having added thereto as a binder an iron group metal, such as, for example, tungsten carbide, tantalum carbide, titanium carbide, vanadium carbide, chromium carbide, zirconium carbide and mixtures thereof together with a binder of the iron group, preferably cobalt.

The purpose of the casting vehicle is to give the dry hard metal carbide powdered materials sufficient fluidity to permit the pouring thereof without heating, and also by polymerization to bond the powdered materials into a hardened body so that the mold may be removed and the cast article handled or even mechanically worked where this is desirable.

The unsaturated polyesters of the maleic type for example, reaction products of a polyhydric alcohol and maleic acid or anhydride mixed with a vinyl derivative such as styrene form an excellent material for cold cast plastics, but when they are used alone they are not satisfactory as casting vehicles for my process as they cannot be conveniently removed from the cast cemented carbide article. I have found, however, that a conveniently removable casting vehicle for hard metal carbide powdered materials results when an unsaturated polyester of the maleic type mixed with a vinyl derivative such as styrene is diluted with a miscible and nonpolymerizable organic liquid. The nonpolymerizable liquid should preferably be relatively high boiling but should be removable by evaporation below 150° C. Moreover, the combination of nonpolymerizable and polymerizable ingredients must be such that a gel forms upon polymerization. When such a combination is employed the cast article will have sufficient strength even though the major fraction of the vehicle consists of nonpolymerizable liquid. The major fraction of the vehicle, consisting of nonpolymerizable liquid, can then be expelled from the cast article by evaporation below 150° C. rendering the cast article sufficiently porous so that the polymerizable fraction can be rapidly decomposed and expelled at higher temperatures without cracking the article.

If the nonpolymerizable liquid is not initially miscible with the polyester or if separation occurs upon polymerization, the resulting casting will not have the required strength. Organic liquids which have been found to be immiscible or to cause separation upon polymerization are, for example, ethylene glycol, diethylene glycol, glycerine, propylene glycol and polyhydroxy compounds in general. The use of organic liquids containing chlorine, bromine or fluorine should also be avoided.

Casting vehicles which I have found to be satisfactory are comprised of an unsaturated polyester of the maleic acid type, and preferably an alkyd resin more particularly disclosed and claimed in Agens Patent 2,319,575 prepared from maleic anhydride, dipropylene glycol and tetrahydrofurfuryl alcohol, a terminally unsaturated $CH_2{=}C<$ containing compound, for example, a vinyl derivative such as styrene, vinyl acetate etc., initially miscible nonpolymerizable liquid ethers or esters of ethylene glycol or diethylene glycol such as diethylene glycol monoethyl ether acetate, ethylene glycol monoethyl ether acetate, glycol diacetate, ethylene glycol monomethyl ether acetate, mixtures of diethylene glycol with one of the above named acetates, etc., and a polymerization catalyst, as for instance, benzoyl peroxide, ditertiary butyl diperphthalate, etc. These compositions are convertible by the application of heat without the evolution of water vapor into an infusible gel, and the organic liquid may be removed below

150° C. in air without decomposing the polymer. The initially miscible, nonpolymerizable organic liquid should amount to about 65% to about 83% of the volume of the casting vehicle. If the vehicle contains less than about 65% of organic liquid the drying time is increased and it becomes very difficult to expel the vehicle without cracking the cast article. On the other hand, if the organic liquid is present in amounts greater than about 83%, the polymerizable ingredients will not impart sufficient green strength to the cast article to allow mechanical working or handling.

It will of course be apparent to those skilled in the art that polymerizable compositions other than those disclosed above may also be used without departing from the scope of the invention. Additional examples of maleic polyesters, terminally unsaturated compounds copolymerizable therewith, and polymerization catalysts may be found in U. S. 2,450,682 issued October 5, 1948, and in U. S. 2,443,735 issued June 22, 1948.

I have also found that the above compositions are particularly suitable as a casting vehicle for my process in that they form a thixotropic gel when mixed with the powdered hard metal carbide or carbides. The vehicle-carbide mixture is capable of undergoing isothermal, reversible sol-gel transformations, a fluid sol existing as long as the mixture is agitated, the sol reverting into a gel within a short time after agitation has ceased. This property is important because it permits the use of a mixture which is fluid enough to pour while agitated, stirred or vibrated, but which prevents appreciable settling of the heavy carbide constituents before hardening occurs. Upon heating the thixotropic mixture after casting, the vehicle polymerizes into an infusible product which is no longer capable of reversion into the fluid sol state. The prevention of settling greatly reduces the unequal distribution of the carbide powders in the casting and thereby keeps distortion on sintering to a minimum.

The above compositions have the following properties: during agitation they are fluid enough to be cast at room temperature without the use of pressure; they are sufficiently thixotropic to prevent excess settling of the heavy constituents of the carbide powdered materials before permanent setting or solidification by polymerization occurs; they will cold set at room temperature or harden with the application of heat; they impart sufficient green strength to the casting to allow handling and even mechanical working; they are conveniently removable by heating without cracking the article or destroying its shape; and they leave no detrimental residue to affect the physical properties of the finally sintered article.

In accordance with my invention, casting mixtures falling within the following approximate volume percentages have been used advantageously:

	Percent
Hard metal carbide powdered materials	38–41.5
Polymerizable ingredients	10–20
Nonpolymerizable liquid	48–41.5
Polymerization catalyst	0.1–0.75

By volume percentage in relation to the powdered hard metal carbide or carbides I refer to a calculated volume which is determined by dividing the weight of the powdered carbides by the final sintered density of the carbide material, which density is a well known quantity for any particular carbide composition to those who are skilled in the art.

The above limits have been found applicable to the casting of powdered ingredients used in the manufacture of cemented carbides, such as tungsten carbide-cobalt mixtures in which the cobalt varied from 6 to 20% by weight; to tungsten carbide-tantalum carbide-cobalt mixtures in which the tantalum carbide varied to a maximum of 27% by weight; to tungsten carbide-titanium carbide-tantalum carbide-cobalt mixtures, and to tungsten carbide-titanium carbide-cobalt mixtures in which the titanium carbide varied to a maxium of 32% by weight.

Particle size of the cemented carbide powdered materials has a slight effect upon the amount of casting vehicle which is required, with more casting vehicle being needed as the particle size decreases. The above limits relate to carbide powdered materials of normal commercial particle size.

Typical compositions which have been cast are as follows:

	Vol. Percent	Measured Quantities
Hard metal carbide powdered material, 94% WC+6% Co	39.6	1 Kilogram.
Styrene	8.1	13.7 cc.
Unsaturated maleic polyester	6.3	10.6 cc.
Diethylene glycol monethyl ether acetate	45.8	77 cc.
Benzoyl peroxide	.2	.3 cc.
Hard metal carbide powdered material, 80% WC+20% Co	38.6	1 Kilogram.
Styrene	7.8	14.9 cc.
Unsaturated maleic polyester	6.0	11.5 cc.
Diethylene glycol monoethyl ether acetate	47.5	91 cc.
Benzoyl peroxide	0.1	.2 cc.
Hard metal carbide powdered material, 84% WC+16% Co	37.8	1 Kilogram.
Styrene	7.8	14.9 cc.
Unsaturated maleic polyester	6.0	11.5 cc.
Diethylene glycol monoethyl ether acetate	48.3	92 cc.
Benzoyl peroxide	.1	0.2 cc.
Hard metal carbide powdered material, 87% WC+13% Co	39.0	2.3 Kilograms.
Vinyl acetate (distilled)	7.2	30 cc.
Unsaturated maleic polyester	5.8	24.2 cc.
Ethylene glycol monoethyl ether acetate	47.8	198 cc.
Benzoyl peroxide	.2	.75 cc.
Hard metal carbide powdered material, 57% WC+27% TaC+16% Co	37.8	2.2 Kilograms.
Styrene	7.7	33 cc.
Unsaturated maleic polyester	6.0	25.7 cc.
Diethylene glycol monoethyl ether acetate	48.4	207 cc.
Benzoyl peroxide	.1	.3 cc.
Hard metal carbide powdered material, 61% WC+32% TiC+7% Co	40.2	1.53 Kilograms.
Styrene	7.6	31.8 cc.
Unsaturated maleic polyester	5.9	24.8 cc.
Diethylene glycol monoethyl ether acetate	46.2	193 cc.
Ditertiary butyl diperphthalate	.1	.3 cc.
Hard metal carbide powdered material, 76% WC+4% TaC+12% TiC+8% Co	38.8	1.19 Kilograms.
Styrene	7.6	31.8 cc.
Unsaturated maleic polyester	5.9	24.8 cc.
Ethylene glycol monoethyl ether acetate	47.6	198 cc.
Ditertiary butyl diperphthalate	.1	.3 cc.

I have also found that the time required for evaporating the nonpolymerizable organic liquid from the solidified casting can be considerably reduced by adding a liquid which spontaneously exudes from the casting after polymerization. Thus, by employing ethyl butanol as a substitute for diethylene glycol monoethyl acetate a gel exhibiting syneresis is formed upon polymerization and the time required for removal of the organic liquid may be reduced by as much as 50%, using the same procedures.

When ethyl butanol is used, however, the surface tends to become crusty or irregular. A more satisfactory and controllable composition can be made from a mixture of diethylene glycol and ethylene glycol monoethyl ether acetate. The degree of syneresis can then be increased and evaporating time decreased by increasing the proportion of diethylene glycol in the mixture.

A formulation which has been found to give good results comprises:

	Vol. Percent	Measured Quantities
Hard metal carbide powdered material, 87% WC+13% Co	38.6	1 Kilogram.
Styrene	7.8	14.3 cc.
Unsaturated maleic polyester comprising a tetrahydrofurfuryl alcohol modified dipropylene glycol maleate	6.1	11.1 cc.
Diethylene glycol	11.5	21 cc.
Ethylene glycol monoethyl ether acetate	35.9	63 cc.
Benzoyl peroxide	.1	.3 cc.

The accompanying drawings illustrate certain features employed in the practice of my invention. More particularly,

Fig. 1 is a perspective view of the mixing apparatus which may be used in carrying out my process.

Fig. 2 is a sectional view along line 2—2 of Fig. 1.

Fig. 3 is a side view section of a typical mold that may be employed in my process.

In making an article of the type which would result from casting my molding composition in the mold of

Fig. 3, I first select the hard metal carbide powdered ingredients which experience has taught will possess the desired characteristics for the application in which the article is to be used. The desired measured quantity of hard metal carbide powdered ingredients which are in a finely ground condition in accordance with commercial practice, is placed in hopper **1** sealed with an air tight rubber seal **2** and having a butterfly valve **3'** actuated by crank **3** for controlling the release of carbide powdered ingredients **4** into mixing chamber **5**. Mixing chamber **5** is attached to the plate **6** by means of screws **7** forming an air tight seal therewith. Stopcock valve **8** on mixing chamber **5** and rubber seal **2** are closed and hopper **1** and mixing chamber **5** are evacuated through lines **9** and **10** which are connected to a commercial vacuum pump. After evacuation, valve **11** on line **9** and valve **12** in line **10** are closed so that hopper **1** and mixing chamber **5** remain evacuated. Equal weights of styrene or vinyl acetate and unsaturated maleic polyester are mixed together to form a standard stock casting vehicle. A measured quantity of this mixture is then admixed with the desired amount of the nonpolymerizable organic liquid and if desired, diethylene glycol and, immediately prior to the actual mixing with the cemented carbide powdered materials, the catalyst is added and admixed. My liquid casting vehicle **13** is then placed into fluid inlet **14** and allowed to enter into mixing chamber **5** through valve **15**. Motor **16** which is attached to cross member **17** by strap **18** is started and drives stirrer **19** at approximately 10,000 R. P. M. through housing **20** and air tight bushing **21**; with stirrer **19** rotating the carbide powdered ingredients are admitted into mixing chamber **5** through valve **3** and therein mixed with the casting vehicle **13** for approximately 1 to 1½ minutes. It may be seen in Fig. 2 that the inside surface of mixing chamber **5** is not cylindrical, but rather is irregular as shown to facilitate thorough mixing.

After mixing, the vacuum is released on mixing chamber **5** and my casting composition is ready for casting into a typical mold such as that shown in Fig. 3. This is accomplished by opening valve **8** and allowing the mixed casting composition to fill the mold. The mold may be under vacuum if desired, or it mav be open to atmospheric pressure. I have found that casting in an evacuated container is beneficial when the surface configurations are of fine detail involving minute cavities in the mold in order to obviate the tendency to bridge over these cavities, but otherwise casting in air is perfectly satisfactory. I have also found that tapping on the side of mixing chamber **5** aids the continuous flow of the thixotropic casting composition, and it will be appreciated that this may be accomplished by vibrations supplied from vibration apparatus if desired.

Mold materials which I have used successfully include wax, glue, Wood's metal, aluminum, steel, etc., but I prefer wax or glue due to their cheapness, availability and ease of manufacture into the shape desired. Specifically, I have successfully used paraffin, casting waxes and micro-crystalline waxes and special glue mold materials which are commercially available.

After the mold is filled, the casting composition is allowed to stand therein until it hardens; the time required for polymerization or hardening will depend upon the actual casting composition used and the temperature, as well as the size of the article. In general, higher amounts of catalyst and higher temperatures speed up the hardening. Hardening will occur at room temperature but higher temperatures cause hardening in shorter periods of time. I have found that sufficient hardening occurs at approximately 80° C. in approximately four hours.

After removing the hardened articles from the mold, the next steps in my process comprise removing the solvent and polymer from the cast article. The first step is accomplished by placing the article in a drying furnace at 45° C. to 150° C. for 2 to 5 days depending upon the size and shape of the article with the larger articles requiring proportionately more time. After this initial heating period which expels the solvent, the second step is to expel the polymer by heating in a hydrogen or other inert atmosphere at 450° C. to 800° C. for approximately one hour.

Thereafter the article is sintered in a hydrogen atmosphere furnace at approximately 1350° C–1500° C. for 1 to 2 hours and the resultant product is a fully formed,

hard, sound cemented carbide body having all the properties of a cemented carbide body of simpler shape.

The selection of the specific casting vehicle for the manufacture of any specific article within the limits hereinbefore set forth will depend somewhat upon the size and shape of the article to be manufactured. For example, small articles or articles having thin wall sections which are easily dried but not easily handled without being damaged should be cast using the higher percentage of polymerizable ingredients to increase their green strength, while large articles should be cast using a higher percentage of nonpolymerizable solvent to improve their drying properties.

My process provides a method for manufacturing articles of cemented carbides not heretofore possible or economically feasible such for example as heading dies with surface markings for cold heading bolts, stamping dies for stamping metal parts with the manufacturers' identifying symbols, costume jewelry dies, etc. It also provides a method which is useful in manufacturing semi-complicated shapes that are presently manufactured by known forming methods. My process has the advantages of reducing labor operations involving the use of forming machinery and the elimination of carbide ingredient losses in the mechanical forming operations, as well as allowing casting in inexpensive molds at room temperature.

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

1. The process for making hard metal carbide articles of complicated shape which comprises the following steps: (1) preparing a thixotropic casting composition comprising a mixture of finely pulverized refractory hard metal carbides and an iron group metal, a casting vehicle consisting of styrene and the reaction product of a polyhydric alcohol and maleic acid and a nonpolymerizable organic liquid having an appreciable vapor pressure below 150° C. selected from the group consisting of diethylene glycol monoethyl ether acetate, ethylene glycol monoethyl ether acetate, glycol diacetate and ethylene glycol monomethyl ether acetate and a polymerization catalyst, (2) casting the mixture into a mold, (3) heating to effect hardening of the cast article, (4) heating the cast article to drive off the nonpolymerizable organic liquid, (5) heating the cast article to drive off the polymerized ingredients, and (6) finally sintering the cast article into a dense hard metal carbide body.

2. A casting mixture comprising a thixotropic mixture of about 38% to about 41.5% by volume of hard metal carbide powdered materials, 10% to about 20% of a mixture of the reaction product of a polyhydric alcohol and a butenedioic acid and a terminally unsaturated $CH_2=C<$ containing compound and about 41.5% to about 48% of a nonpolymerizable organic solvent capable of dissolving the said copolymerizing mixture prior to polymerization selected from the group consisting of diethylene glycol monoethyl ether acetate, ethylene glycol monoethyl ether acetate, glycol diacetate and ethylene glycol monomethyl ether acetate, and a small amount of a polymerization catalyst.

3. A casting mixture comprising a thixotropic mixture of about 38% to about 41.5% by volume of hard metal carbide powdered materials, a copolymerizable mixture of vinyl acetate and the reaction product of a polyhydric alcohol and maleic acid in amounts of about 10% to about 20% and about 41.5% to about 48% of an organic solvent capable of dissolving the said copolymerizing mixture prior to polymerization selected from the group consisting of diethylene glycol monoethyl ether acetate, ethylene glycol monoethyl ether acetate, glycol diacetate, and ethylene glycol monomethyl ether acetate, and a small amount of a polymerization catalyst.

4. A thixotropic casting composition comprising about 39% of tungsten carbide and cobalt by volume, said cobalt falling within a range of 6% to 20% by weight of the tungsten carbide, about 7.8% styrene, about 6.1% of a tetrahydrofurfuryl alcohol modified dipropylene glycol maleate, about 11.5% diethylene glycol, about 35.9% diethylene glycol monoethyl ether acetate and about .15% benzoyl peroxide.

5. A process for casting hard metal cemented carbide articles comprising the steps of forming a thixotropic mixture by mixing (*a*) a powdered hard metal carbide composition, (*b*) an organic liquid casting vehicle comprising essentially a copolymerizable mixture of the re-

action product of a polyhydric alcohol and a butenedioic acid and a terminally unsaturated $CH_2=C<$ containing compound, (*c*) an initially miscible and non-polymerizable solvent which has an appreciable vapor pressure below 150° C. selected from the group consisting of diethylene glycol monoethyl ether acetate, ethylene glycol monoethyl ether acetate, glycol diacetate and ethylene glycol monomethyl ether acetate and (*d*) a small amount of a polymerization catalyst; casting the thixotropic mixture; heating the cast article to drive off the non-polymerizable solvent; subsequently heating the cast article to drive off the copolymer and sintering the cast article into a dense hard metal carbide object.

6. The process for making hard metal carbide articles of complicated shape which comprises the following steps: (1) preparing a thixotropic casting composition comprising a mixture of finely pulverized refractory hard metal carbides and an iron group metal, a casting vehicle consisting of vinyl acetate and the reaction product of a polyhydric alcohol and maleic acid and a non-polymerizable organic liquid having an appreciable vapor pressure below 150° C. selected from the group consisting of diethylene glycol monoethyl ether acetate, ethylene glycol monoethyl ether acetate, glycol diacetate and ethylene glycol monomethyl ether acetate and a small amount of a polymerization catalyst, (2) casting the mixture, (3) heating the cast article to drive off the non-polymerizable organic liquid, (4) heating the cast article to drive off the polymerized ingredients, and (5) sintering the cast article into a dense hard metal carbide body.

7. A casting mixture comprising a thixotropic mixture of hard metal carbide powdered materials, the reaction product of a polyhydric alcohol and a butenedioic acid and a terminally unsaturated $CH_2=C<$ containing compound, a non-polymerizable organic solvent capable of dissolving the said copolymerizing mixture prior to polymerization selected from the group consisting of diethylene glycol monoethyl ether acetate, ethylene glycol monoethyl ether acetate, glycol diacetate and ethylene glycol monomethyl ether acetate and a small amount of a polymerization catalyst.

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