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FORMING BALLS FROM POWDER

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ABSTRACT OF THE DISCLOSURE

Powders are formed into balls or spheres in a two-phase liquid, the first liquid being inert and the second having a preferential affinity for the powder, by shaking the three-phase system in a container having rounded surfaces to agglomerate the powder and second liquid and cause the agglomerates to undergo impact and ricocheting action until the balls are shaped and densified, and the desired balls subsequently recovered from the system.

This invention relates to the production of balls from powdered materials. A process is described by which finely divided metallic or sinterable material can be formed into balls, spheres or similar rounded shapes simply and economically. In particular, a process is described for forming balls or spheres of accurately controlled size, size distribution, and shape in a two-phase liquid system.

In the past metallic balls have been prepared by molding and machining operations (such as casting, pressing, or extruding-and-cutting), followed by finishing operations (e.g., final shaping by rolling or grinding, and polishing). These conventional operations are not satisfactory when applied to metallic materials of high melting point and hardness. These latter materials are usually formed by powder metallurgy techniques including compacting in dies, sintering, machining, and surface finishing. Due to their molding properties some polymeric materials such as polytetrafluoroethylene are usually formed by similar techniques. In these prior art techniques costly molds or dies having a limited life and production rate are usually required for the initial shaping. The formation of rough pellets from powders by dry tumbling in a drum, is also known.

An object of the present invention is to provide balls, spheres, or other round shapes of controlled size and shape without the use of expensive dies or molds. Another object is to provide a process for forming large numbers of accurately shaped balls from sinterable powdered material in a simple manner. A further object is to provide a process for forming small accurate spheres from finely divided tungsten carbide or the like.

It has now been found that the desired balls can be produced by distributing throughout a first inert liquid medium the finely divided solid material, and a second insoluble liquid having an affinity for the powdered material, as discrete particles, and subjecting the resulting three-phase system to an irregular prolonged shaking action more fully defined below. The balls produced are separated from the first liquid medium and subjected to surface finishing, sintering or polishing as required. More specifically, the process of the invention comprises the following steps:

(1) Preparing a dispersion in a first inert liquid medium of the powdered solid material and a second insoluble liquid having an affinity for the solid material, in a container having rounded inner surfaces. The manner of dispersing the second liquid is important and is described in detail below.

(2) Subjecting the resulting three-phase system to a shaking action to agglomerate the solid material with the second liquid and to cause the agglomerates to undergo a continued impact and ricocheting action against the container surfaces and against each other. The nature of this shaking and impact action, and the container shape and size, are important and are discussed below.

(3) Prolonging this shaking and ricocheting action until the agglomerates are formed into the desired round balls, and

(4) Separating the balls or shaped bodies from the first liquid and, optionally, removing the second liquid from the balls, sintering or fusing and surface finishing.

Powder materials

Suitable powder materials for use in the process include metals and refractory metal compounds such as aluminum, copper, iron, steels, the carbides, borides, nitrides and silicides of Ti, Zr, Cr, Ta, Mo, W, and U, and metal oxides. Particularly refractory compounds include tungsten carbide, titanium carbide, silicon carbide and uranium carbide. Binder metals such as Fe, Co, Ni, Cu, and Ag (including mixtures and alloys thereof), may be present in small amounts. Solid polymeric materials such as cellulose acetate, polytetrafluoroethylene, polystyrene and polymethylmethacrylate are also suitable. Other examples of materials which have been balled include alumina, alundum, silica, soda glass, iron oxide, chromium oxide, tin oxide and manganese dioxide. The resulting balls may be used for ball point pens, ball bearings, fluidized bed catalysts, various pellets such as nuclear fuel pellets, and the like. The use of tungsten carbide containing small amounts of cobalt in the present process results in good quality balls for the ball point pen industry.

The powder particles size may be varied within wide limits, but desirably is within the range known to give good sinterability, e.g., from 0.1 to 100 microns. The powder is added in amounts less than about 35% by volume of first liquid—and to give a fluid system. The powder may be coated with materials such as waxes which may be retained, or are removed prior to or during the balling process of the present invention. The coating may serve as a temporary protective coating which prevents premature poor ball formation (before proper dispersion is achieved), e.g., wax coating on tungsten carbide is substantially removed by solvent action of first liquid. A small quantity of residual wax on the surface of the balls helps to prevent adhesion of the balls while drying. The condition of the powder surface may affect the size of the balls formed.

Size of balls

The size of the balls is dependent on several factors, particularly the volume of second liquid: for many systems the size of the balls obtained decreases from large sizes through a minimum smaller size and increases to larger sizes again as the volume of second liquid increases, until finally a pasty mass is obtained. More violent shaking and higher temperatures usually lead to smaller sized balls.

First liquid

The first liquid should be substantially inert with respect to both the powdered material and the second liquid, and of sufficiently low viscosity at the temperature of operation so as to give a free-flowing system. The first liquid should be present in major proportion (by volume) of the three-phase system, i.e. should be the continuous phase. This liquid may be a single compound or a mutually soluble mixture. Where the first liquid and the powder are heavier than the second liquid, preliminary mingling of the powder and second liquid is prevented before dispersion and shaking has commenced.

Suitable first liquids include halogenated aliphatic or aromatic hydrocarbons, aliphatic hydrocarbons such as Varsol, aromatic hydrocarbons, liquid silicone fluids, water and single-phase mixtures thereof. Examples are chlorobenzene, carbon tetrachloride, perchloroethylene, Varsol, heptane, benzene, toluene, xylene, and a light petroleum oil.

The viscosity of the continuous-phase liquid can be controlled by using a solution of mutually soluble liquids of widely different viscosities or by changing the temperature of operation.

Second liquid

The second insoluble liquid may be aqueous (or a highly polar insoluble organic material) when the first liquid is a water-insoluble organic material; or may be a water-insoluble organic material when the first liquid is aqueous. This second liquid should have an affinity for the powdered material (i.e. should form a disperse phase including the powdered material, within the first liquid). For good ball formation a larger interfacial surface tension between the first and second liquids should exist. Preferably the second liquid has a wetting or solvation action on the powder. The second liquid should not wet or be adsorbed by the vessel walls in the presence of the first liquid. It is possible to treat the vessel surface to minimize adsorption of second liquid. It may be desirable that this second liquid not readily evaporate from the balls—giving balls more resistance to handling and attrition. Examples of the second liquid are water, nitrobenzene, benzaldehyde, and water-alcohol mixtures. Water or aqueous liquids are particularly suitable due to high surface tension.

The proportions of the second liquid may range from about 3 to about 250% by volume of the solid, preferably 50 to 150%. The desired amount of second liquid is influenced by the bulk volume of the powder—the amount decreases with increasing particle size of powder. The second liquid is desirably not added to the vessel until after the walls have been wetted by the first liquid. Allowance should be made in the amount of second liquid for adsorption (as by container walls) or solubility in the continuous phase. The amount of second liquid has an affect on the ball size; (the size first decreases and then generally increases with increasing amounts of second liquid until ball formation breaks down). For example, with water as second liquid, a minimum ball size of tungsten carbide has been observed to occur within the preferred range 0.045 to 0.065 ml. water per gm. tungsten carbide.

The second liquid-particle surface affinity may be increased if desired by adding surface-active compounds soluble in the second liquid but not in the first. (See Examples 18 and 19.) When the first liquid is aqueous, fatty acids may serve as the surface-active compounds.

Dispersing second liquid and powder

It is important that the second liquid become dispersed throughout the continuous phase. It is also important that the powder be dispersed through the first liquid. If this dispersion is not obtained, the ball size is quite difficult to control and the size distribution becomes very wide.

The following techniques have been found operative for obtaining the dispersion of solid, second liquid or both:

(a) adding the second liquid as frozen particles, then mixing with warming to release the second liquid during agitation,

(b) freezing the second liquid in situ (before any dispersion) then mixing with warming, to release the second liquid under agitation,

(c) preparing an emulsion of the second liquid in the first in situ, e.g. (i) by adding a liquid dispersing aid (which has some solubility in both first and second liquids) and mixing; (ii) adding the second liquid through an atomizing nozzle and dispersing through the first liquid; and (iii) adding the second liquid as a preformed emulsion in part of the first liquid,

(d) providing the powder with a temporary protective coating and removing this coating under agitation in the three-phase system, and

(e) wetting the powder with the second liquid and then dispersing the wetted powder throughout the first liquid by severe agitation (see Example 5). Combinations of these techniques may be used.

Ultrasonic vibration has been found to be an efficient dispersion-forming technique. Where a preliminary emulsion is not formed the desired dispersed agglomeration may be satisfactorily achieved if the powder and the first liquid are heavier than the second liquid. With CCl_4, WC and water, the three-phases can be kept quite separate until agitation begins.

The amount of the liquid dispersing aid added is not critical and may range up to about 150% by volume of the second liquid. Suitable liquid dispersing aids (where water is the second liquid) include low molecular weight C_1–C_5 alcohols, particularly the propyl alcohols.

Techniques (a) and (b) above have been found to give the narrowest ball size distribution, and may be carried out in the presence of the powder. By simply adding the three-phases to each other and subjecting to a shaking action satisfactory balls were not obtained except where the shaking was severe and prolonged enough to actually form the required dispersed agglomerates and then controlled to give a ricochet action to the agglomerates (see Examples —9, 36 and 37).

Container

The container should have rounded inner surfaces with no sharp corners and no confined zones where the powder can collect. Satisfactory balls can be obtained by using containers of regular shapes such as cylinders, spheres or cones and causing them to be shaken in a complex 3-dimensional pattern such as that produced by the Pica Blender-Mill (Pitchford Scientific Instruments Co. of Pittsburgh). Alternatively the container may be shaken in a regular reciprocating motion, but with the container having irregular dimensions such as cylinders with hemispherical ends, dimples, bends or throats; conical vessels with hemispherical ends; ellipsoidal vessels; U-tubes or various combinations or modifications thereof. Regular cylinders or cones shaken at an angle to their axis or lying on their sides and shaken vertically, have given satisfactory results.

The containers should not be completely filled in order to allow translational motion of the entire three-phase system and increased impact velocity. Good results have been obtained with the container filled with first liquid to from about 20 to about 90% by volume (see Examples 25 and 35). The container walls or inner surfaces should be formed from materials which are substantially chemically inert to the three-phase system (especially to the second liquid). As mentioned above, desirably the inner surfaces are wetted by the first liquid more readily than by the second. If necessary the surfaces may be pretreated to saturate their adsorptive capacity for the second liquid. Otherwise the amount of second liquid acting on the solid particles cannot be controlled accurately. Containers constructed from or coated with polytetrafluoroethylene (Teflon) have been found particularly suitable when the second liquid is aqueous.

Shaking action

Experiments have shown that good sphericity could only be obtained by vigorous shaking which imparted both: (a) translational motion of sufficient velocity to cause slight deformation of the agglomerates on impact with the container surfaces, and (b) rotational motion to ensure that the point of impact varied each time. In other words, the agglomerates should undergo a contin-

ued ricocheting action striking the container walls at angles less than 90°. Suitable translational motion can be achieved for example by a reciprocating motion of a frequency above about 60 cycles per minute. A three-dimensional shaking pattern is preferred with cylindrical containers as it is believed the agglomerates or balls then undergo a continuous ricocheting action. The container geometry should be matched to the pattern and frequency of shaking action so as to cause the agglomerates or balls to undergo a continuous ricocheting action (or achieve a type of "resonance" for each system).

Increasing the severity or time of shaking will usually increase the density of the resulting balls toward the theoretical limit (and may also decrease the size). This gives increased green strength. The time of shaking may range from several minutes to several hours. Prolonging the shaking generally results in improved sphericity. Too severe shaking may result in rough or abraded ball surfaces. In addition to control of the frequency, amplitude or pattern of shaking, and the shape of the container, the severity of the shaking can be further controlled by varying the viscosity of the continuous phase liquid. Proper balancing of these various factors enables a close control to be maintained over the balls produced.

It has been found that balls can be grown from seed—or the size, sphericity or smoothness can be increased by subjecting small seed balls to a coating treatment according to the process of the present invention. Smoothing agents such as waxes may be added to give a smooth surface layer. Layers of one or several materials can be formed over balls of a different material. One or more of the core materials can be amenable to removal through the outer layer; for instance, by leaching, sublimation or decomposition. It is possible, for example, to grow spheres of tungsten carbide about seed particles of a leachable salt (e.g. sodium chloride) using as the second liquid saturated brine, and then dissolving out the core before sintering. By agglomerating a mixture containing a finely divided removable material, it is possible to vary the porosity of the resulting balls through a wide range.

The balls of metallic, refractory or other sinterable materials may be sintered according to standard techniques. The polymeric materials may be fused by using a solvent or plasticizer as second liquid.

Ellipsoidal balls have been produced by imparting a rolling-action component to the shaking (and generally using slower shaking than for spheres). The formation of elliptical bodies is illustrated in Example 27.

The balls after formation may be readily separated from the continuous phase liquid by decanting, filtering, or screening. If the size distribution is wide, a sizing or screening step is usually desirable. A satisfactory size distribution for preparing balls for ballpoint pens is within −8+16 U.S. screen or preferably about 0.050 inch (1.3 mm.). With proper control, this size can be obtained directly from the process without recycling. Where the balls are to be used as ball bearings, pen points, etc. it is necessary to sinter them, for instance at 1100° C. to 1500° C. for refractory carbides. A final polishing or surface finishing may be carried out to give the desired smoothness or texture to the surface.

The following examples illustrate the invention. Unless otherwise noted a Pica Blender-Mill was used, the shaking being carried out in a 35 ml. steel vial. Cobalt (6%) was present as a binder metal in the tungsten carbide. In some examples the tungsten carbide particles used were coated with a small amount of paraffin wax. (Water served as the second liquid in Examples 9 to 17 and 20 to 23 and as the first liquid in Examples 18 and 19.) In Examples 18 and 19 the unwaxed tungsten carbide surface was treated with small amounts of fatty acids to increase the particle surface-second liquid affinity. Examples 5 to 13, 18 and 19 were carried out at room temperature and in examples where the water was frozen in situ the container temperature was usually above room temperature after the shaking due to frictional heat.

Example 1

A suspension containing 6 g. tungsten carbide (unwaxed), 7 ml. Varsol, and 7 ml. CCl_4 was cooled to below 0° C. and 0.38 to 0.40 ml. of water was added. After the water was frozen, the contents were shaken for 15 minutes. Spheres of about 1 mm. diameter were obtained. The diameter was increased and the surface smoothened by dispersing, for about 10 minutes, 1 additional gram of waxed tungsten carbide with the system.

Example 2

About 6 g. of tungsten carbide in 14 ml. of Varsol were cooled over Dry Ice and 0.38 ml. of water was added. After the water was frozen, the slurry was shaken for 15 minutes. Spherical agglomerates of the order of 1.5 mm. diameter were obtained.

Example 3

The same procedure as in Example 2 was followed, except that 14 ml. of CCl_4 were used instead of Varsol and with 0.4 ml. of water being added in the form of ice. Spheres within the range of 0.6 to 1 mm. diameter were obtained. Carbon tetrachloride gives a more fluid system than Varsol.

Example 4

A mixture consisting of 6 g. of tungsten carbide (waxed) in 9 ml. Varsol and 3 ml. CCl_4 was cooled over Dry Ice and 0.395 ml. of water was frozen on the surface of the liquid. The contents were shaken for 15 minutes with warming. The spheres were slightly enlarged and smoothened by shaking the system for 8 minutes with an additional 1 g. quantity of tungsten carbide. The size distribution of the final spheres was as follows:

Diameter mm.:	No., percent
1.4	7
1.5	17
1.6	43
1.7	21
1.8	10
1.9	2

A variety of containers of irregular dimensions have been employed for the agglomeration of tungsten carbide. In Examples 5 to 8 the suspensions were shaken in a horizontal reciprocating motion having a displacement of 6 cm. and a frequency of from 1 to 4 cycles per second as noted.

Example 5

This invention was carried out in two 50 ml. round flasks joined at the necks, overall length 14 cm., the neck being 1.8 cm. diameter (shaken on the long axis). Nine grams of tungsten carbide was added to a mixture of 20 ml. CCl_4 and 20 ml. Varsol. The mixture was shaken for 1 hour at 4 cycles per second in order to disperse the solid particles, then 0.2 ml. of water added as a fine spray with a syringe. After this suspension was shaken for 1.5 hours, a dispersion with some spherical agglomerates appeared. Another 0.1 ml. of water was added and substantially all suspended particles were agglomerated into spheres by shaking again for 1 hour.

Minor rough spots on the spheres were abraded off by agitation for 1 hour at 1–2 cycles per second in the presence of 0.002 ml. methyl alcohol added to the system. Smooth spheres of the order of 1 to 2 mm. diameter were obtained by this latter method. The technique of this example is not a preferred one, though operative, due to prolonged shaking required and wide size distribution obtained.

Example 6

This example was carried out in an ellipsoidal vessel of major axis 8 cm. and minor axis 5 cm. shaken along

the major axis. Six grams of tungsten carbide was added to 12 ml. of CCl_4 and 12 ml. Varsol. While the mixture was being dispersed by ultrasonic irradiation (from a 40 kc. ultrasonic generator), 0.3 ml. of water was added quickly in a fine spray from a syringe. The system was then shaken at about 1 to 2 cycles per second for about 3 hours. Accurate spheres of diameter from 1 to 1.5 mm. were obtained.

Example 7

This example was carried out in a glass elbow, the arms being 8.5 cm. long and diameter 2.5 cm. with the ends sealed with stoppers. Six grams of tungsten carbide was thoroughly mixed and wetted with 0.3 ml. water in a mortar and pestle. The moistened powder was added to the vessel containing an emulsion consisting of 6 ml. Varsol, 6 ml. CCl_4 and 0.1 ml. water prepared by ultrasonic irradiation for 3 minutes. The slurry was shaken with the arms of the elbow upright and at an angle of 45° to the direction of motion. After about 9 minutes of fast shaking (4 cycles per second) somewhat unsymmetrical spherical agglomerates were obtained. After about 1 to 2 hours of gentler shaking (1 to 2 cycles per second) spheres of the following size distribution were obtained:

Diameter mm.:	No., percent
1.0	2
1.1	2
1.2	8
1.3	28
1.4	25
1.5	17
1.6	5
1.7	6
1.8	2
1.9	3
2.0	2

Example 8

The following example illustrates the use of a copper vessel in the form of a U-tube for agglomerating finely divided tungsten carbide to symmetrical spherical masses. This copper U-tube was about 17.5 cm. long and 1.8 cm. in diameter and shaken upright and aligned in the plane of the direction of motion. Six grams of tungsten carbide (waxed) were added to an emulsion of 20 ml. toluene (previously saturated with water) and 0.35 ml. of water, which was prepared by ultrasonic irradiation for about 3 minutes. The suspension in the U-tube was shaken at about 4 cycles per second for about 9 minutes after which somewhat rough agglomerates were obtained. The system was further shaken at a slower rate (1 to 2 cycles per second) for about 1.5 hours and smooth spheres having the following size distribution were obtained:

Diameter mm.:	No., percent
1.7	1
1.8	1
1.9	7
2.0	17
2.1	8
2.2	17
2.3	15
2.4	18
2.6	7
2.7	7
2.8	2

The spherical masses obtained could be rendered very smooth on the surface by removing some of the liquid and the suspension shaken at a slower rate. Sphere formation occurs sooner when the U-tube is tilted at approximately an angle of 45° to the direction of shaking.

The following vessels also gave satisfactory results in similar experiments:

(a) Twenty-five ml. round flask, closed and rounded off at the neck; overall length about 10 cm., the neck being about 1.8 cm. diameter; shaken on its side.

(b) Double elliptical shaped vessels, about 9 cm. long and 3 cm. diameter, joined and shaken on the long axis.

(c) Round bottom flask, having two sides flattened out about 3.5 cm. wide, diameter 5.5 cm. with dimples in these sides to give a constriction, and shaken upright. Without the dimples poor results were obtained.

(d) Truncated conical vessels with outwardly dished ends shaken along short axis.

(e) Cylinders with outwardly dished ends shaken along the short axis.

In vessels of type (b) and that used of Example 5, if the joining neck is too long or too constricted poor results are obtained. Regular spheres and axially mounted cylinders shaken with a straight reciprocating motion gave poor results. The procedures of Examples 5 to 8 are not preferred, though operative.

In the following Examples 9 to 13 satisfactory dispersion was obtained, but with rather prolonged shaking, preliminary emulsion formation, or wet grinding required.

Examples 14 to 17 show the sphere size distribution for various powder loadings. Examples 14 to 17 and 20 to 23 illustrate the freezing of the second liquid, Examples 20 to 23 use different powders, and Examples 18 and 19 illustrate the use of organic second liquids. In Examples 9 to 26 the shaking was in a Pica Blender-Mill.

Example No.	Ingredients	Amounts	Shaking Time	Diameter of Spheres Produced	Remarks
9	Tungsten Carbide (unwaxed)	3 g			No initial dispersion of water but using prolonged shaking.
	CCl_4	7 ml			
	Varsol	7 ml			
	Water	0.24 ml	55 min	1 mm	Satisfactory balls.
10	Tungsten Carbide (waxed) (added to emulsion).	3 g			Emulsion prepared by ultrasonic irradiation for 3 minutes.
	CCl_4	15 ml.[1]			
	Varsol	15 ml.[1]			
	Water	0.2 ml.[1]	16 min	1.1 mm	Good spheres.
11(a)	Tungsten Carbide (waxed) (added to emulsion).	6 g			Same procedure as Ex. 10. Further 0.2 ml. water added after 16 min. shaking.
	CCl_4	7 ml.[1]			
	Varsol	7 ml.[1]			
	Water	0.2 ml.[1]	16 min	No spheres	
(b)	Plus additional Water	0.2 ml	16 min	2–3 mm	Good spheres.
12	Tungsten Carbide (waxed) (added to emulsion).	9 g			Same procedure as Ex. 10.
	CCl_4	7 ml.[1]			
	Varsol	7 ml.[1]			
	Water	0.45 ml.[1]	21 min	1–1.2 mm	Good spheres.
13	Tungsten Carbide (unwaxed)	6 g			Tungsten carbide and water premixed by grinding to wetted solid powder.
	Water	0.35 ml			
	Dispersed in:				
	CCl_4	7 ml			
	Varsol	7 ml	15 min	0.5 mm	Satisfactory balls.

[1] Emulsion.

Example No.	Ingredients	Amounts	Shaking Time	Sphere Size Distribution—US Screen				Remarks
				−8+10	−10+14	−12+14	−14+16	
14	Tungsten Carbide	20 g	12 min	4.2 g	10.0 g	1.2 g	1.2 g	
	Carbon Tetrachloride	10 ml						
	Water*	1.25 ml						Good spheres.
15	Tungsten Carbide	30 g	12 min	3 g	24 g	2 g		
	Carbon Tetrachloride	10 ml						
	Water*	1.65 ml						Good spheres.
16	Tungsten Carbide	40 g						
	Carbon Tetrachloride	10 ml	12 min	5.3 g	19.0 g	12.7 g	2.5 g	
	Water*	2.10 ml						Good spheres.
17	Tungsten Carbide	50 g						
	Carbon Tetrachloride	10 ml	12 min	34.0 g	10.3 g	0.3 g		
	Water*	2.62 ml						Good spheres.

*Water frozen in situ in 35 ml. steel container in Dry Ice bath. The limit to loading in this container is about 50 gm. of tungsten carbide as the losses (or unballed or caked material) become significant (about 10% wt.). At a loading of about 50 gm. of tungsten carbide the size distribution gives more large balls. Example 15 represents a desirable size distribution for balls for ball point pens.

Example No.	Ingredients	Amounts	Shaking Time	Diameter of Spheres Produced	Remarks
8	Tungsten Carbide (unwaxed)	4 g	12 min	2–4 mm	
	Water	15 ml			Mixture prepared in situ.
	Nitrobenzene	0.3 ml			
	Oleic Acid	0.05 ml			Good spheres.
19	Tungsten Carbide (unwaxed)	4 g	12 min	1–4 mm	
	Water	15 ml			Mixture prepared in situ.
	Benzaldehyde	0.4 ml			
	Tall oil acids	0.05 ml			Good spheres.
20	Silicon carbide (−400 mesh)	4 g	12 min	0.5 mm	Good spheres.
	CCl_4	10 ml			Narrow size distribution.
	Water [1]	0.45 ml			
21	Silicon carbide (−1,000 mesh)	2 g	15 min	0.2–0.5 mm	Good spheres.
	CCl_4	10 ml			
	Water [1]	0.45 ml			
22	Alumina (−200 mesh)	2 g	15 min	1–2 mm	Good spheres.
	CCl_4	10 ml			
	Water [1]	0.6 ml			
23	Titanium Carbide	4 g	15 min	1–1.5 mm	Good spheres.
	Toluene	2.5 ml			
	CCl_4	7.5 ml			
	Water [1]	0.25 ml			

[1] Water frozen in a 25 ml. stainless steel vial. The CCl_4 (or first liquid) was added followed by the powder.

Example 24

Gem grade alumina (0.1 microns)	gram	1
Water	ml	1.1
n-Propyl alcohol	ml	0.2
Paraffin wax	g	0.5
Carbon tetrachloride	ml	10

The water was frozen in the 25 ml. stainless steel vial, then the carbon tetrachloride, n-propyl alcohol, paraffin wax and alumina were added. The suspension was agitated for 15 minutes. Spherical agglomerates of about 0.8 to 1.5 mm. in diameter were obtained. Most of the spheres were about 1.1 mm. diameter. The alcohol served to aid the distribution of water in the suspension. It was easier to separate the spherical bodies after drying in the presence of the wax (compared to a control test without wax).

Example 25

In general, desirable spherical bodies were obtained when the vessels were filled with first liquid to from about 20 to about 80% by volume. Undesirable agglomerates were obtained when the vessels were filled to nearly full capacity as illustrated.

Stainless steel vial capacity about	ml	25
Unwaxed tungsten carbide powder	gm	20
Water (frozen in situ)	ml	1
Paraffin wax (as a coating agent)	gm	0.3
Carbon tetrachloride	ml	22

When these materials (about 95% vial capacity) were agitated for 12 minutes, mixtures consisting of irregular, elliptical and a small fraction of spherical bodies were obtained. The spherical masses were of the order of 0.2 to 0.5 mm. in diameter. Decreasing the volume of CCl_4 to below about 18 ml. gave satisfactory results.

Example 26

The following example illustrates nearly maximum amounts of tungsten carbide powder which can be employed with the same vessel (25 ml. capacity) whereby very desirable spherical bodies were obtained.

Unwaxed tungsten carbide	gm	40
Water (frozen in situ)	ml	2.1
Carbon tetrachloride	ml	12

After agitating the system for 12 minutes about 97% of the original powdered material was in the form of spherical bodies of the order to 1 to 2 mm. in diameter. However, unsatisfactory agglomerated bodies were obtained when the amount of tungsten carbide powder

was increased to 50 grams (solid volume increased about 1 cc.) e.g.

Unwaxed tungsten carbide powder --gm. (~1 cc.)--	50
Water (frozen in situ) ----------ml--	2.6
Carbon tetrachloride ----------ml--	12

This system was agitated for 12 minutes and a small quantity of agglomerated material of poor sphericity and large amounts of caked tungsten carbide were obtained.

Example 27

Desirable elliptical bodies were obtained in a conical vessel agitated by a horizontal reciprocating motion at right angles to its major axis. The vessel was constructed of polytetrafluoroethylene (Teflon). The top was in the form of a hemisphere 1.5 inches in diameter. The perpendicular height was about 3½ inches. The sides tapered down to ½ inch diameter at the base. The vessel had a capacity of about 55 cc. The following is a typical example in which elliptical bodies were formed.

Wax coated carbide powder ----------gm--	20
Water ----------ml--	1.0
n-Propyl alcohol ----------ml--	0.2
Carbon tetrachloride ----------ml--	11

The ingredients were added to the conical vessel described above in the following order: carbon tetrachloride, metallic powder, n-propyl alcohol and water. The vessel was then shaken for 15 minutes at 2 cycles per second with the short axis in the direction of motion. Elliptical bodies having substantially major axis/minor axis ratios of about 1.4 to 1.7 were obtained. When the vessel was agitated with the long axis in the direction of motion, spherical masses varying from 1 to 2.5 mm. diameter were obtained.

Another similar suspension was agitated at an angle less than 90° to the direction of motion and very desirable spherical bodies varying from 1.5 to 3.0 mm. in diameter were obtained.

Example 28

The following example is given to illustrate the minimum amounts of second liquid giving satisfactory results.

(a)

Wax coated tungsten carbide ----------gm--	20
Water ----------ml--	0.9
n-Propyl alcohol ----------ml--	0.2
Carbon tetrachloride ----------ml--	11

These ingredients were shaken in the conical vessel described in Example 27 by a horizontal reciprocating action for 15 minutes, at an angle less than 90° to the direction of motion. Undesirable rough unsymmetrical agglomerates were obtained.

(b) When the amount of water was increased to 1.0 ml. very desirable spherical agglomerated bodies were obtained.

(c) Very desirable spherical masses were also obtained when the amount of carbon tetrachloride was increased to 22 ml., n-propyl alcohol increased to 0.3 ml. and water held constant at 1.0 ml.

These and other experiments confirm that the amount of first liquid can be varied over a wide range (within 20–90% of vessel capacity) and still spherical agglomerates can be obtained.

Example 29

This example illustrates the minimum quantity of n-propyl alcohol required as dispersing aid.

Systems consisting of the following ingredients,

Wax coated tungsten carbide powder --------gm--	20
Carbon tetrachloride ----------ml--	11
Water ----------ml--	1.0
n-Propyl alcohol ----------ml--	0 to 1.4

were agitated in the conical vessel of Ex. 27 at an angle less than 90° to the direction of motion (horizontal) for 15 minutes. The results obtained are summarized below:

Vol. of n-Propyl Alcohol, ml.	Percent alcohol Based on Water	Appearance of Agglomerates	Size Range (diam.)
0	----------	Large bodies of poor sphericity.	2–5 mm. cross-section.
0.05	5	Large smoother bodies of poor sphericity.	2.5 to 4.5 mm. cross-section.
0.1	10	Mixture of poor and good spherical bodies.	2 to 3 mm.
0.2	20	Good spherical bodies------	1 to 2.5 mm.
0.4	40	-----do----------	1.3 to 2.5 mm.
0.6	60	-----do----------	0.9 to 2 mm.
0.8	80	-----do----------	0.9 to 2.5 mm.
1.0	100	-----do----------	0.8 to 2.0 mm.
1.4	140	-----do----------	0.7 to 1.9 mm.

In this system at least about 15% of n-propyl alcohol (based on water) should be used to obtain good distribution of the water and good spheres.

The following apparatus was used to obtain spheres on a larger scale. A container was fastened to an arm which was pivoted at one end and free to oscillate at the other end. The free end was oscillated at 450 cycles per minute in the horizontal plane. The following shapes of containers were fastened on the arm near the free end and were found to be very satisfactory: (a) ellipsoid, (b) cylinder with hemispherical ends, and (c) a truncated cone with hemispherical base. (Elbow- and conical-shaped containers and straight cylinders were found to be unsatisfactory with this shaking action.) Both containers (a) and (b) were shaken at right angles to their long axis. Container (c) was shaken with the base of the cone pointing away from the pivoted end of the arm. Container (c) constructed of polytetrafluoroethylene with a capacity of 150 ml. was used in the following examples. Shaking time was 5–7 minutes and shaking stroke 4 inches (of arc).

Example 30

200 grams of waxed tungsten carbide powder suitable for sintering was dispersed in 40 ml. of carbon tetrachloride. The mixture was shaken with 10.2 ml. of water and spheres of about 0.13 mm. diameter were formed. A second batch of waxed powder using a similar formulation and procedure resulted in spheres of 3.9 mm. diameter. However, when the water was modified with 1 ml. of n-propyl alcohol similar spheres of the order of 0.13 mm. diameter were consistently obtained. The size of spheres and the ease of sphere formation in this system varies considerably with the properties of the tungsten carbide powder, e.g. particle size and shape, and whether the surface is waxed or unwaxed. The degree of dispersion of the water also has a marked effect. Apparent approximate upper and lower concentration limits for water as the second liquid giving good spheres in this system with tungsten carbide are from 0.045 to 0.065 ml. of water per gram tungsten carbide.

Example 31

n-Propyl alcohol when added to water (second liquid) has been found to exert a profound effect on the size of the balls formed. Similar results were obtained with both waxed and unwaxed powders and this addition offers a way of controlling sphere size by which some of the variability in powder properties can be overcome. 100 grams of waxed tungsten carbide was added to 40 ml. of carbon tetrachloride followed by 5.3 ml. of water with the following additions of n-propyl alcohol—

n-Propyl alcohol, ml.:	Sphere diameter, mm.
0	2.3
0.4	1.5
0.6	1.3
0.8	1.1
1.0	1.04

n-Propyl alcohol, ml.:	Sphere diameter, mm.
2.0	.86
3.0	.81
5	0.7

Example 32

Unwaxed tungsten carbide powder 100 gms., carbon tetrachloride 40 ml., water 5.3 ml., and n-propyl alcohol 1.2 ml. were mixed and shaken as in Ex. 30. Spheres of the order of 1.3 mm. diameter were readily formed.

Example 33

Waxed tungsten carbide 100 grams, carbon tetrachloride 15 ml., toluene 15 ml., water 5.0 ml., and n-propyl alcohol 1.6 ml. were mixed and shaken as in Ex. 30. Smooth spheres were formed of diameter 1.3 to 1.5 mm.

Example 34

Waxed tungsten carbide 100 grams, perchloroethylene 40 ml., water 5.0 ml. and n-propyl alcohol 1.5 ml. were mixed and shaken as in Ex. 30. Satisfactory spheres of the order of 1.3 mm. diameter were formed.

Example 35

The amount of loading has been found to affect the uniformity of the spheres produced. The spread in sphere sizes has been found to be markedly greater when 10 gram batches of tungsten carbide were balled (in 40 ml. carbon tetrachloride) than when 100 gram batches were balled. Successful results have been obtained with batches of up to 200 grams in the 150 ml. container (c) above. Increasing the amount of powder to beyond 200 grams resulted in decreased effectiveness.

The amount of first liquid has been varied widely and again no critical limits have been found—except that the powder must be dispersed in it to give a fluid system (lower limit)—while using excessive amounts of first liquid becomes inefficient. Also the effectiveness of the shaking action is decreased if greater than about 80% of the volume of the vessel is filled. [Using more than 100 ml. of first liquid in a 150 ml. vessel gave balls of larger size and poorer sphericity than when less than 100 ml. was used—indicating that dispersion of second liquid becomes poor in highly filled vessels.]

The speed of shaking in the pivoting arm apparatus has been varied over the range 100 to 500 cycles per minute. Results indicate that at low speeds non-sphericity and non-uniformity of size are increased. Generally shaking at above about 300 c.p.m. gave good spheres.

It will be seen from the examples that many variations may be made in the pattern, time and speed of shaking and in the container shape-providing that proper dispersion of the second liquid is obtained and that a "resonance" or continuing ricochet action of agglomerates is sustained.

The following two examples illustrate the formation of spheres from two further non-metallic powders, and the use of a second liquid containing a small amount of a binder for increased green strength of the spheres. A pivoted arm reciprocating shaker [similar to Example 30, but using the container (b)] was used. The vessel had a capacity of 280 cc.

Example 36

Soda glass powder	g—	10
16% sodium silicate solution	cc—	1.8
Carbon tetrachloride	ml—	75

Shaking action 400 c.p.m. for 2 hours.

The materials were added to the vessel in the following order: soda glass, carbon tetrachloride and sodium silicate solution. Good spheres of a size ranging from 3 to 4 mm. diameter were obtained.

Example 37

Silica (14–31 microns)	g—	10
16% sodium silicate solution	cc—	2.6
Carbon tetrachloride	ml—	75

Shaking action 350 c.p.m. for 2 hours.

The materials were added to the vessel in the order silica, carbon tetrachloride and sodium silicate solution. Good spheres of the order of 3 to 4 mm. diameter were obtained. In both Examples 36 and 37 the spheres had good green strength and withstood handling, due to the sodium silicate present.

We claim:

1. A process for forming balls from finely divided powders in a two-phase liquid system comprising:
   (a) adding the powder and a second insoluble liquid to a first inert liquid medium, the second liquid having a preferential affinity for the powder,
   (b) subjecting the three-phase system to a shaking action in a container having rounded inner surfaces, to form dispersed agglomerates of the powder with the second liquid and to cause the agglomerates to undergo a continued impact and ricocheting action against the rounded surfaces,
   (c) prolonging the impact and ricocheting action until the agglomerates are formed into the desired balls, and
   (d) separating the balls from the first liquid.

2. A process for forming balls from finely divided powders in a two-phase liquid system comprising:
   (a) dispersing the powder and a second liquid throughout a first inert liquid medium to give a fluid three-phase system, the second liquid being insoluble in the first and having a preferential affinity for the powder,
   (b) shaking the three-phase system in a container having rounded inner surfaces, the container being filled to from about 20 to 90 vol. percent capacity, to agglomerate the powder with the second liquid and causing the agglomerates to undergo a continued impact and ricocheting action against the rounded surfaces,
   (c) prolonging an impact and ricocheting action to form the desired balls from the agglomerates,
   (d) separating the balls from the first liquid, and
   (e) removing the second liquid from the balls.

3. A process for forming balls from finely divided powders in a two-phase system comprising:
   (a) dispersing the powder in amounts less than about 35% by vol. of first liquid, and droplets of a second liquid in amounts from about 3 to 250% by vol. of powder solid, throughout a first inert low viscosity liquid, the second liquid being insoluble in the first, and having a high surface tension and a preferential affinity for the powder,
   (b) shaking the three-phase system in a container having rounded inner surfaces, the container being filled to from about 20 to 90 vol. percent capacity, to agglomerate the powder with the second liquid and causing the agglomerates to undergo a continued impact and ricocheting action against the rounded surfaces,
   (c) prolonging impact and ricocheting action sufficiently to shape and densify the agglomerates into the desired balls,
   (d) separating the balls from the first liquid, and
   (e) removing the second liquid from the balls.

4. A process for forming balls from finely divided powders in a two-phase liquid system comprising:
   (a) adding the powder to a first inert liquid in amounts less than about 35% by vol., contacting with a second insoluble liquid in a frozen state in amounts from about 3 to 250% by vol. of powder solid, and dispersing with warming to form a fluid three-phase system, the second liquid having a preferential affinity for the powder,

(b) shaking the three-phase system in a container having rounded inner surfaces, the container being filled to from about 20 to 90 vol. percent capacity, to agglomerate the powder with the second liquid and causing the agglomerates to undergo a continued impact and ricocheting action against the rounded surfaces,

(c) prolonging impact and ricocheting action sufficiently to shape and densify the agglomerates into the desired balls,

(d) separating the balls from the first liquid, and

(e) removing the second liquid from the balls.

5. A process for forming balls from finely divided powders in a two-phase liquid system comprising:

(a) preparing an emulsion of a second insoluble liquid in a first inert liquid and dispersing the powder throughout the first liquid, the second liquid being present in amounts from about 3 to about 250% by vol. of powder solid and having preferential affinity for the powder,

(b) shaking the three-phase system in a container having rounded inner surfaces, the container being filled to from about 20 to 90 vol. percent capacity, to agglomerate the powder with the second liquid and causing the agglomerates to undergo a continued impact and ricocheting action against the rounded surfaces,

(c) prolonging impact and ricocheting action sufficiently to shape and densify the agglomerates into the desired balls,

(d) separating the balls from the first liquid, and

(e) removing the second liquid from the balls.

6. The process of claim 5 wherein the emulsion is prepared in situ by adding a liquid dispersing aid which has solubility in both first and second liquids.

7. The process of claim 6 wherein the liquid dispersing aid is a low molecular weight C_1 to C_5 alcohol.

8. The process of claim 7 wherein the alcohol is a propyl alcohol and is present in amounts up to about 150% by vol. of second liquid.

9. A process for forming balls from finely divided powders in a two-phase liquid system comprising:

(a) dispersing the powder in amounts less than about 35% by vol. of first liquid, the powder having a temporary protective coating which has some solubility in the first liquid, and droplets of a second liquid in amounts from about 3 to 250% by vol. of powder solid, throughout a first inert liquid, the second liquid being insoluble in the first and having no affinity for the protective coating, but preferential affinity for the powder,

(b) shaking the three-phase system in a container having rounded inner surfaces, the container being filled to from about 20 to 90 vol. percent capacity to remove the temporary protective coating and to agglomerate the powder with the second liquid, and causing the agglomerates to undergo a continued impact and ricocheting action against the rounded surfaces,

(c) prolonging impact and ricocheting action sufficiently to shape and densify the agglomerates into the desired balls,

(d) separating the balls from the first liquid, and

(e) removing the second liquid from the balls.

10. The process of claim 9 wherein the temporary protective coating is a wax.

11. The process of claim 3 wherein the first liquid is organic and the second liquid is aqueous.

12. The process of claim 3 wherein from 50 to 150% of second liquid is used.

13. The process of claim 3 wherein seed balls are dispersed together with the powder, the second liquid also having an affinity for the seed balls, the powder forming a coating on the seed balls.

14. The process of claim 13 wherein the seed balls are subsequently removed through the outer layer of the final composite ball.

15. The process of claim 3 wherein the shaking action is controlled to impart a rolling component to the ball path, causing the formation of ellipsoidal balls.

16. A process for forming balls from finely divided powder comprising tungsten carbide in a two-phase liquid system comprising:

(a) dispersing the powder, droplets of water and up to 150% by vol. based on the water of n-propyl alcohol, in a chlorinated hydrocarbon liquid, the amount of the powder being less than about 35% by vol. of the chlorinated hydrocarbon and the amount of the water being from about 50 to 150% by vol. of solids,

(b) shaking the three-phase system in a container having rounded inner surfaces of polytetrafluoroethylene, the container being filled to from about 20 to 90 vol. percent capacity, to agglomerate the powder with the water, and causing the agglomerates to undergo a continued impact and ricocheting action against the rounded surfaces,

(c) prolonging impact and ricocheting action sufficiently to shape and densify the agglomerates into the desired balls,

(d) separating the balls from the chlorinated hydrocarbon liquid,

(e) removing the water from the tungsten carbide balls, and

(f) sintering the tungsten carbide balls.

17. A process for forming balls from finely divided powders in a two-phase liquid system comprising:

(a) adding the powder and a second insoluble liquid to a first inert liquid medium, the second liquid having a preferential affinity for the powder,

(b) shaking the three-phase system in a container having rounded inner surfaces so that the contents thereof move in a path having both translational and rotational components so that the powder particles form dispersed agglomerates and the agglomerates repeatedly strike the inner surfaces of the container at angles of less than 90° and undergo a continued impact and ricocheting action against the rounded surfaces, the shaking of the container being the sole force being applied for effecting agitation and mixing of the three-phase system,

(c) continuing the impact and ricocheting resonance of the system until the agglomerates form the desired balls, and

(d) separating the balls from the first liquid.

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