

1

3,728,110
PROCESS FOR FORMING A SINTERED
BRIQUETTE

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8 Claims

ABSTRACT OF THE DISCLOSURE

Compactable, particulate compositions for compaction molding into briquettes comprising finely divided solids, containing normally liquid phase lubricant in excess of that which can be sorbed readily on said finely divided solids in admixture with a sorptive agent more highly sorptive of the lubricant than are the compactable finely divided solids. The sorptive agent sequesters unbound lubricant and improves the handling properties of the compactable powder composition.

Compactable, flowable metal powder compositions containing normally liquid surface active lubricants and porous oxide gel as the sorptive agent are disclosed. Iron powders containing oleic acid and silica gel are disclosed as an industrially significant embodiment.

In the compaction of composite articles such as catalyst pellets and compaction metal parts (briquettes or compacts, as they are known in the art) from compactable powders such as glass, ceramics, metals, metal oxides, and the like, it is common practice to add small amounts of liquid lubricants to the compactable powders to improve the flow of the powder into intricate mold cavities and increase the density of the compacted part by permitting closer packing of the powder under pressure. Additionally, the lubricant facilitates the removal of the compacted briquette from the mold cavity without breakage. While the presence of these liquid lubricants increases the compactability of the powder, excessive lubricant (i.e., more lubricant than can be sorbed by the compactable powder) detracts from the flowability of the powder prior to compaction and flowability is a prerequisite for efficient powder handling.

The powder lubricant thus performs several functions in the compaction process. The lubricant must reduce friction and permit the powder particles to flow freely while in contact with one another to form a uniform compact article. Additionally, the pressure necessary to eject the compact from the die must be low enough to prevent damage to the compact and wear on the die. Finally, the lubricant must not deposit carbon or otherwise interfere with sintering of the compact at elevated temperatures.

The problem is particularly acute in the art of powder metallurgy because of the high speed compaction processes utilized. For instance, compactable metal powders such as iron powders are formed into machine and other structural parts including bushings, sleeves and gears at high production rates. For these purposes, the metal powders must be flowable and the finished articles compacted therefrom, must meet acceptable performance standards for apparent density, green strength, sintered strength and modulus of rupture. Efficient lubricant is therefore essential.

Powder metallurgy is a technique for compacting metals and metal alloys into articles. According to this technique, a single metal powder, or two or more metal powders, are subjected to extreme compaction pressure in a mold (i.e., up to 100,000 p.s.i.) to form an article. This article thus formed is known in the art as a briquette or compact and can be in any geometric form, such as a

2

gear, bar, bearing, etc. The molded article is then heat treated or sintered in a non-oxidizing (i.e., inert or reducing) atmosphere. As a result of this heating, fusion takes place at the particle grain boundaries and the powdered particles become firmly bonded together to form a composite integral article.

As used herein, the term metal powder includes powdered iron, chromium, copper, aluminum, silver, tin, zinc, molybdenum, stainless steel, tungsten, nickel and the like, and powdered alloys, as well as powdered metallic carbides, nitrides, and silicides, and borides which exhibit metallic compaction characteristics.

In the past, solid lubricants such as stearic acid and zinc stearate have been used as lubricants, and have achieved a certain measure of commercial acceptance. Unfortunately, these solid lubricants do not enhance the compressibility as much as the liquid lubricants (i.e., oleic acid) enhance compressibility. To supplement and replace these solid lubricants, a wide variety of normally liquid lubricants (liquid at room temperature and pressure) have been employed. Normally liquid lubricants include surface active materials such as fatty acids, detergents, wetting agents and penetrants. The term "surface active" is well known in the art and refers to that property of polar/non-polar molecules which enables these molecules to form interfacial transition layers in heterogeneous systems. In metal powder lubrication, the polar portion of the surface active molecule is attracted to the metal powder particle, and non-polar portion of the molecule provides interparticle lubrication.

Suitable acids include linoleic acid and ricinoleic acid, oleic acid, and linolenic acid.

Saturated and unsaturated liquid fatty acid containing 10 to 20 carbon atoms are preferred surfactants because of low cost and wide availability.

Suitable surface active agents other than the fatty acids listed above include liquids within the following classes; sulfated fatty alcohols, alkyl-aryl sulfonates, alkyl sulfonates, sulfated esters and acids, sulfated and sulfonated amides, sulfated and sulfonated fats and oils (i.e., turkey red oil), non-ionic surface active materials such as the alkylene oxide adducts of alkyl phenols, alkylene oxide adducts of long chain fatty alcohols, aliphatic polyhydric alcohol esters and fatty acid amides.

While liquid and surface active lubricants often improve the compaction properties of the metal powders (as compared to untreated metal powders), the flow properties suffer in that the metal powder often becomes greasy, sticky and tacky and tends to agglomerate due to the presence of excess liquid lubricants. This is a serious problem in commercial compaction operations in that non-uniform briquettes are often formed.

The present invention provides metal powder compositions and methods whereby the improved compaction characteristics imparted by liquid surface active lubricants can be retained without sacrificing flowability.

According to the present invention, a small amount of a particulate sorptive agent that is more highly sorptive of the lubricant than is the compactable powder together with a conventional liquid lubricant including those described above, is added to the compactable powder. Such sorptive agents include porous oxide gels, activated carbon, titania, kieselghur, montmorillonite clays, fuller's earth, zeolites and the like. It has now been discovered that such sorptive agents sequester only the excess liquid lubricant thereby preventing the compactable powder from becoming tacky. Since only the excess lubricant is sorbed, efficient lubrication and improved compactability are realized. The key feature of these particulate sorptive agents is their high oil sorptivity as compared to the oil sorptivity of the compactable powder. All of the sorptive

agents are characterized by high surface area to weight ratios as compared to that of the compactable powder.

As used herein, the term porous oxide gel refers to gels and gelatinous colloidal hydroxides of silica, alumina, iron, chromium and tin which are characterized by their high porosity (high surface area to weight ratio) and surface absorptivity. Silica gel and alumina gel are particularly preferred because of their high absorptivity and commercial availability. Suitable silica gels and alumina gels have oil absorption test values of 90 grams of oil per 100 grams of gel or higher for ASTM Test D 281-31, Oil Absorption of Pigments by Spatula Rub-Out.

The exact chemical mechanism by which the presence of the sorptive agents improve the flow properties of lubricated compactable powder compositions is not presently understood, although it is strongly suspected that these porous gels physically sequester or sorb the excess lubricant from the individual compactable particles. Upon compression of the powder in the mold, the lubricant is "squeezed" out of the gel and becomes available for inter-particle lubrication at the extreme compaction pressures. The lubricant, therefore, is not released until it is actually needed for compression and is not available to form agglomerates or otherwise interfere with the flowing of the powder before compaction. Accordingly, the liquid lubricant can be absorbed on the sorptive agent before mixing the compactable powder to be lubricated. In this embodiment the composite "lubricant" can be formulated in advance and mixed with the compactable powder as required.

One of the industrially significant embodiments of the present invention is a compactable metal powder composition comprising (in weight percent) about 0.01% to about 1% of a porous oxide gel, such as silica gel, and about 0.01% to about 1% of a liquid lubricant, such as oleic acid, in intimate physical admixture with a metal powder such as iron (or mixtures of different compactable metal powders). Additionally, the compactable metal powder composition can contain conventional solid lubricants such as zinc stearate.

Usually, the liquid lubricant content is in the range of about 0.01% to about 0.5% by weight and the porous oxide gel content is in the range of about 0.01% to about 0.1% by weight in the interest of economy and efficiency.

In practicing the present invention, the liquid lubricant can be dissolved in a suitable volatile solvent such as acetone or benzene. This lubricant solution is then mixed with the metal powder and porous oxide gel to produce a uniform mixture. The volatile solvent is then vaporized.

As a second alternative, the liquid lubricant and the porous oxide gel are mixed directly with the metal powder in a blending mill in the absence of a fugitive solvent. For instance, the metal powder, liquid lubricant and porous oxide gel can be mixed together in a blending mill until a homogeneous mixture is achieved. This method is commercially desirable because of its simplicity and efficiency. This metal powder composition can then be compacted in a high pressure die by a variety of known methods.

As a third alternative, the liquid lubricant can be mixed with the metal powder in high concentrations (i.e., a metal powder/lubricant composition containing about 10% lubricant) to form a stock mixture. This stock mixture is then "diluted" with untreated metal powder and porous oxide gel powder to form the desired lubricant concentration.

The following examples show how the invention can be practiced in the commercially important ferrous metal system of iron powder, silica gel and oleic acid. It will be understood that the invention encompasses other metal powder/liquid lubricant/sorptive agent systems. All parts are parts by weight, and all percentages are weight percentages unless otherwise indicated.

The exemplary metal powders and metal powder com-

pacts (briquettes) were evaluated by the following ASTM test methods:

- Flow ----- ASTM Test B 212-48—Flow Rate of Metal Powders.
- 5 Green density --- ASTM Test B 331-63T—Compressability of Metal Powders (40 t.s.i. employed).
- Green strength --- ASTM Test B 312-63T—Green Strength of Compacted Metal Powder Specimens (40 t.s.i. employed).
- 10 Sintered density -- ASTM Test B 328-60—Density and Interconnected Porosity of Sintered Powder Metal Structural Parts and Oil Impregnated Bearings.
- 15 Transverse rupture strength ----- ASTM Test B 378-61T—Transverse Rupture Strength of Sintered Metal Friction Materials.

EXAMPLE 1

Ordinary electrolytic iron powder having a particle size of —80 mesh (U.S. Standard Sieve size) was mixed with a 3% solution of oleic acid in acetone to produce a metal powder composition containing 0.4% oleic acid. The acetone was then vaporized and 0.05% silica gel and 0.2% zinc stearate (supplement solid lubricant) based on the weight of the metal powder composition, were added and thoroughly blended with the powder in a double cone blending mill.

The silica gel employed is sold by Grace Chemical Company under the trademark "Syloid" and has the following properties and composition:

Color -----	White.
Purity (percent SiO ₂) -----	99.7+.
Avg. particle size, microns -----	1.5.
Surface area, m. ² /g. -----	330.
Oil absorption, lb./100 lb. -----	330.
Bulk density, lb./cu. ft. -----	4.8.
40 Specific gravity -----	2.1.

A sample of the oleic acid/silica gel/zinc stearate/iron powder mixture was evaluated by the ASTM flow test method set forth above. In this test the time for a given weight of the metal powder to flow through an orifice of a given size is measured. The lower test values indicate better flowability. The test value was 35 seconds. As a control on the silica gel, it was determined that a similarly prepared mixture of iron powder, zinc stearate, and oleic acid (containing 0.4% oleic acid and 0.2% zinc stearate) had poor flowability and would not flow through the ASTM test apparatus.

The metal powder mixture was then compacted into a briquette in a conventional ram type hydraulic press at 40 t.s.i. The compacted briquette had a green density of 7.12 grams per cc. and a green strength of 2,550 p.s.i.

The green briquette was then sintered at 2,000–2,200° F. for 20–30 minutes under a hydrogen atmosphere. The sintered density was 7.04 grams per cc. and the transverse rupture strength was 73,900 p.s.i.

For the purpose of comparison, an iron powder composition containing 1% zinc stearate as the only lubricant was similarly compacted and evaluated.

The test results are set forth below:

65 Flow -----seconds--	31
Green density -----grams per cc--	7.03
Green strength -----p.s.i.--	1,490
Sintered density -----grams per cc--	7.00
70 Transverse rupture strength -----p.s.i.--	67,100

The foregoing data demonstrates that a much higher green density is achieved when oleic acid and silica gel are employed. Additionally, the green strength, sintered density and transverse rupture strength are increased while flowability is maintained.

5

The zinc stearate was used in compacting the "untreated" iron powder so that the compacted article could be ejected from the die without damage.

EXAMPLE 2

An iron powder containing 99% iron and 1% carbon was mixed with oleic acid, silica gel and zinc stearate in the ratio of Example 1. This metal powder composition was compacted and evaluated by the method of Example 1. The test data is set forth below:

Flow -----seconds-- 36
Green density -----g./cc-- 7.07
Green strength -----p.s.i-- 1,960
Sintered density -----g./cc-- 6.96
Transverse rupture strength -----p.s.i-- 116,900

6

and subjected to the compaction and evaluation methods described above. The results are set forth below.

Flow -----seconds-- 3.96
Green density -----g./cc-- 6.94
Green strength -----p.s.i-- 1,400
Sintered density -----g./cc-- 6.82
Transverse rupture strength -----p.s.i-- 158,000

This data indicates that green density, green strength, sintered density and transverse rupture strength are significantly improved by the present invention.

EXAMPLES 4 TO 16

The test results for these examples are set forth in Table I.

TABLE I

Example	4	5	6	7	8	9	10	11	12	13	14	15	16
Oleic acid (weight percent of metal powder composition)	0	0.02	0.05	0.05	0.10	0.15	0.30	0.02	0.05	0.32	0.32	0.32	0.30
Flow test value (in seconds for oleic acid/metal powder composition)	28	33	53	53	(¹)	(¹)	(¹)	21	20	53	53	53	(¹)
Silica gel content (weight percent of metal powder composition)	0	0.01	0.05	0.05	0.075	0.05	0.075	0	0	0.01	0.01	0.025	0.75
Flow test value (in seconds for oleic acid/silica gel/metal powder composition)		30	24	24	33	27	29			26	25	22	31
Zinc stearate content (weight percent of metal powder composition)	0.5	0.3	0.4	0.2	0.4	0.5	0.3	0.04	0.4	0.07	0.4	0.25	0.4
Flow test value (in seconds for oleic acid/silica gel/zinc stearate composition)	29	33	28	28	35	30	33		27	33	29	25	360
Green density (in gm./cc. of briquette compacted at 40 TSI)	7.02	7.11	7.10	7.11	7.11	7.08	7.11	7.04	7.03	7.06	7.10	7.07	7.11
Green strength (in p.s.i. of briquette compacted at 40 TSI)	2,180	1,960	2,010	1,980	1,800	1,560	1,680	2,410	2,240	1,560	1,670	1,800	1,670
Die ejection pressure (p.s.i.)	4,800	4,500	4,100	4,100	4,700	4,000	4,100	5,000	6,300	4,400	5,400	6,000	4,100

¹ Sample would not flow through test apparatus.

As a control on the silica gel, it was determined that a similarly prepared mixture of metal powder, zinc stearate and oleic acid (containing 0.4% oleic acid and 0.2% zinc stearate) would not flow through the ASTM test apparatus.

For the purpose of comparison, the 99% iron, 1% carbon metal powder was mixed with 1% zinc stearate, compacted into briquettes, and evaluated by the same test procedure. The results are set forth below:

Flow -----seconds-- 35
Green density -----g./cc-- 6.92
Green strength -----p.s.i-- 1,160
Sintered density -----g./cc-- 6.83
Transverse rupture strength -----p.s.i-- 108,000

This data indicates that the green density, green strength, sintered density and transverse rupture strength are all improved by the presence of oleic acid and silica gel, while the flow is maintained.

EXAMPLE 3

A metal powder comprising 94% iron, 5% copper, 1% carbon was mixed with oleic acid, silica gel and zinc stearate in the ratio of Example 1. This metal powder composition was compacted and evaluated by the method of Example 1. The data is set forth below:

Flow -----seconds-- 34
Green density -----g./cc-- 7.09
Green strength -----p.s.i-- 1,920
Sintered density -----g./cc-- 6.96
Transverse rupture strength -----p.s.i-- 177,900

As a control on the silica gel, it was determined that a similarly prepared mixture of metal powder, zinc stearate and oleic acid (containing 0.4% oleic acid, 0.2% zinc stearate) would not flow through the ASTM test apparatus.

For the purpose of comparison, some of the iron/copper/carbon powder was mixed with 1% zinc stearate

In Examples 4 through 10, iron powder similar to that used in Example 1 was thoroughly admixed in a double cone blending mill with the amount of oleic acid indicated in Table 1, and the flow values were determined. The silica gel was blended into the mixture and the flow values were again determined. Zinc stearate was then blended in and the flow values were again determined. Briquettes were then formed and evaluated by the method of Example 1. The test data is reported in the appropriate column of Table 1.

Example 4 contains neither silica gel nor oleic acid and serves as an experimental control.

Example 5 indicates that good flow and high green density are achieved with 0.02% oleic acid and 0.01% silica gel.

Examples 6 and 7 indicate that good flow and high green density are achieved with 0.05% oleic acid and 0.05% silica gel. The flow is significantly improved (reduced from 53 seconds to 24 seconds) through the presence of the silica gel.

Examples 8 to 10 indicate that good flow and high green density are achieved with 0.1% to 0.3% oleic acid and 0.05% to 0.075% silica gel. It is to be noted that powders of these examples would not flow in the absence of silica gel.

In Examples 11 to 15 sufficient oleic acid with iron powder is mixed in a double cone blending mill to form an iron powder mixture containing 10% oleic acid. This mixture was then mixed with untreated iron powder, zinc stearate and silica gel to form the composition indicated in the appropriate column of Table 1.

Examples 11 and 12 indicate that good flow but poor compactability (low green density) is achieved with 0.02% and 0.05% oleic acid respectively, in the absence of silica gel.

Examples 13 to 15 indicate that good flow and high green density are achieved with 0.32% oleic acid with from 0.01% to 0.025% silica gel. The flow is significantly improved (reduced from 53 seconds to about 25 seconds) through the presence of silica gel.

7

In Example 16 sufficient 3% solution of oleic acid in acetone was mixed with iron powder to yield 0.3% oleic acid in the metal powder composition upon vaporization of the acetone. This metal powder composition was thorough mixed with 0.75% silica gel and 0.4% zinc stearate as indicated in Table 1. Good flow and high green density were achieved. It is to be noted that this powder would not flow in the absence of silica gel.

Having thus described the invention, what is claimed is:

1. In a process for preparing a compacting composition wherein metal powder is blended with normally liquid-phase lubricant, the proportion of said lubricant being in excess of that which can be sorbed readily on the surface of said metal powder to leave an excess of said lubricant in a state unbound by said metal powder, the improvement which comprises sorbing the excess of said normally liquid-phase lubricant on a particulate porous oxide gel, the proportion of said gel being sufficient for sorbing substantially all of the unbound normally liquid-phase lubricant present to form a substantially non-tacky flowable, compressible, lubricated metal powder.

2. The process for forming a compacted briquette from finely divided metal powder comprising the steps of charging a compacting composition comprising metal powder formed by the process of claim 1 to a compacting mold, and compressing said metal powder in said mold to form a compacted green briquette.

3. The process of claim 2 further including the step of heating said green briquette to form a sintered briquette.

4. The process of claim 1 wherein said normally liquid phase lubricant comprises a fatty acid.

5. The process of claim 1 wherein said lubricant com-

8

prises oleic acid in a proportion between about 0.01% and about 1% by weight of said compacting composition.

6. The process of claim 1 wherein said gel is a silica gel in a proportion between about 0.01% and about 1% by weight of said compacting composition.

7. The process of claim 4 wherein said fatty acid is oleic acid and said oleic acid content is from about 0.01% to about 0.5% of said compacting composition, and said porous oxide gel comprises silica gel in a proportion between about 0.01% to about 0.1% of said compacting composition.

8. The process of claim 1 wherein said metal powder comprises iron powder.

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