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METHOD OF GRINDING METAL POWDER

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U.S. Cl. 241—16 8 Claims

ABSTRACT OF THE DISCLOSURE

Finely divided metal powders, surface area greater than 2 square metres per gram, can be formed by grinding metals in an organic liquid containing a load-carrying additive. The load carrying additives are phosphorous and/or chlorine and/or sulphur containing substances.

This invention relates to improvements in metal powders. In particular this invention relates to metal powders with a high surface area.

Finely divided metal powders have been used for the fabrication of metal articles (by sintering of the powders), as pigments, as fillers for plastics, as reagents, as rocket propellants, as solders and brazes etc.

Although it is known to produce metal powders by chemical techniques such as vapour condensation or precipitation from solution, it is recognized that mechanical grinding provides, in general, a cheaper route for obtaining these powders. Among known grinding methods are the use of planetary ball mills, attritor ball mills and vibratory ball mills.

It has also been known for some time to carry out the grinding of metals in a grinding fluid, for example, a petroleum fraction, ethanol, methylene dichloride, or n-heptane etc. Furthermore the use of grinding aids, such as the fatty acids and their metal salts, for example, stearic acid and aluminium stearate, is known. A useful source of information on this subject is "Ultrafine Particles," edited by W. E. Kuhn, published by Wiley in 1963. It has been suggested that the function of a grinding aid is to prevent agglomeration of the ground particles during the grinding.

However, metal powders produced by prior art methods have the disadvantages of low surface areas and little lubricating activity.

It is an object of the present invention to provide finely divided metal powders with a high surface area and a high reactivity and which act as solid lubricants.

According to the present invention a finely divided powder is prepared by grinding a metal in the presence of an organic grinding fluid and an organic load-carrying additive containing one or more of the elements sulphur, chlorine, phosphorus and nitrogen.

Suitable organic grinding fluids are those liquids which distil below 500° C. have a viscosity below 600 centistokes at 100° F. and have a viscosity of below 72 dynes/cm. at 25° C. and preferably have a viscosity of 10 to 40 dynes/cm. at 25° C. In a preferred embodiment of the invention the grinding fluid is a hydrocarbon, especially for example, n-heptane, iso-octane, cyclohexane, toluene, hexadecane or a hydrocarbon fraction obtained by the distillation of petroleum.

Organic load-carrying additives are very well known and are extensively used in lubricating compositions.

Their function is to improve the anti-wear properties and/or the extreme pressure properties of the lubricating compositions. When two lubricated moving surfaces are lightly loaded against each other, they are separated by an elasto-hydrodynamic oil film; as the load increases so the oil film thickness decreases. When the oil firm thickness approaches the dimensions of the surface roughness, it will be penetrated by surface asperities; it is in this region that antiwear additives function by improving the oil film strength and thus reducing intermetallic contact. As the load is increased further, the bulk oil film collapses and antiwear additives are no longer sufficient to protect the surface. Extreme pressure additives function in this region by reacting with the metal surfaces to form an inorganic iron compound which prevents the welding of the metal surfaces.

The term load-carrying additives includes both antiwear and extreme pressure additives.

The load-carrying additives which can be used in the present invention are those which contain one or more of the following elements: chlorine, sulphur, phosphorus and nitrogen.

Examples of suitable load-carrying additives are organic chlorine-containing compounds such as the low-molecular weight chlorinated hydrocarbons, preferably those containing from 1–4 carbon atoms e.g. carbon tetrachloride; chlorbenzyl esters of alkyl xanthic acids and of thioacids such as thiocarbonic acid; and chlorinated hydrocarbon waxes.

Other suitable load-carrying additives are the covalent sulphur-containing compounds such as the di-phenol polysulphides, e.g. di-(4-hydroxy phenol) polysulphide; alkyl and aryl thioethers; alkyl and aryl thiocarbonates and thiocarbamates; sulphur substituted carboxylic acid esters e.g. acetic esters substituted in the α-position by sulphur; sulphurised polymers, e.g. sulphurised butadiene-1,3/styrene copolymer; the reaction product of sulphur and polyalkylene glycols; alkyl disulphides e.g. di-n-butyl disulphide and di-(2-ethyl hexyl) disulphide; and di-aryl disulphides e.g. di-benzyl disulphide and di-(amino benzyl) disulphide.

Further suitable load-carrying additives are the phosphosulphurized organic compounds typical organic materials which can be phosphosulphurized include oxygen containing waxes; chlorinated phenols; waxy esters; cyclic ketones; hydrogenated sperm oil; esters of unsaturated acids, e.g. glycol and glyceryl oleates; and abietic esters.

Yet further suitable load-carrying additives are organic compounds containing phosphate or thiophosphate groups such as tri-aromatic phosphates e.g. tri-cresyl phosphate; trialkyl phosphates such as tributyl phosphate; and metal dialkyl dithiophosphates such as the zinc dialkyl dithiophosphates.

Organo metallic compounds such as organo-tin dithiophosphates and lead naphthenate can be also used as load-carrying additives.

Compounds containing nitrogen which can be used include phosphoramidates, for example those described in U.K. Patent 899,101; nitrobenzenes; nitronaphthalenes; amine phosphates; tetra alkyl ammonium phosphates and thiophosphates; and rhodanine and rhodanine derivatives.

Any compound which aids the load-carrying properties of a lubricating composition can be used in the present invention.

When the organic grinding fluid is also a load-carrying additive e.g. carbon tetrachloride, then no other load-carrying additive need be added.

Any metal or alloy which can be ground can be used in the present invention, the preferred metals being iron, including mild steel and cast iron, and aluminium. Other suitable metals are the transition metals, for example, nickel, cobalt, chromium and titanium, copper, and copper alloys such as brass.

In a preferred embodiment of the invention a high speed, vibratory ball mill is used. The grinding balls are preferably made of hardened steel.

The grinding is preferably carried out until the metal powder produced has a surface area of at least 2 sq. metres per gram and preferably a bulk density after shakedown of less than 1 gm./cc.

It is thought that the load-carrying additives are adsorbed on the surface of the metal particles and that, in some cases, a layer of chemically reacted material is formed on the metal surface during grinding. For example, carbon tetrachloride may react with the surface of particles of finely ground iron, giving iron chlorides etc.

In general terms, the better the load carrying properties of the load carrying additive, the more effective it is in producing the finely divided metal powders of the invention. However load-carrying additives can have varying effectiveness when used with different metals, and it is desirable that the load-carrying additive is selected with reference to the metal to be ground.

It has also been unexpectedly found that the finely divided metal powders of the invention can be used as grease thickeners. In order to produce a grease the finely divided metal can simply be stirred into a base oil, or, alternatively any of the methods of grease formation described in U.K. application 40,701/65 can be used.

The following example serves to illustrate the invention.

EXAMPLE

Iron powder was ground in a "Megapact Mark I" vibratory ball mill (manufactured by Pilamec Limited) for three hours.

In this mill the grinding chambers are steel cylinders of 1½ inch internal diameter by 15 inches long and are nearly filled with ¼ inch diameter hardened steel balls. The mill is fitted with a one eighth horsepower electric motor and the oscillation can be adjusted from 1 to 4 mm. In operation, each cylinder was filled completely with n-heptane, containing dissolved therein a load-carrying additive, and the steel balls and from 10 to 30 grams of iron powder from 50 to 400 British Standard mesh were added. This first about from 150 to 250 cc. n-heptane in each cylinder. The ends were then sealed with metal caps fitted with rubber washers and the grinding carried out. After grinding the balls were sieved from the slurry of iron powder and n-heptane and load-carrying additive and the treated iron powder recovered by filtration, washing and drying.

The surface areas and bulk densities obtained using various additives are given in Table I below:

TABLE I

Load-carrying additive in n-heptane	Amount of additive in percent wt., n-heptane/ additive	S found in powder, percent wt. powder	Cl found in powder in percent wt. powder	B.E.T. surface area of iron powder in m.²/g.	Bulk density after shake down, g./cc.[1]
Experiment No.:					
1				2	1.35
2 Carbon tetrachloride	0.5			5	
3 do	1.0		0.03	30	0.39
4 do	2.0			7	0.40
5 Dibenzyl disulphide	0.5	0.66		3	
6 do	1.0	0.14		2	0.40
7 do	2.0	0.07		3	
8 Ditertiary butyl disulphide	0.5	0.22		2	
9 do	1.0	0.13		2	0.52
10 do	2.0	0.16		2	
11 Phosphosulphurized terpene	0.5	0.24		2	
12 do	1.0	0.5		7	0.30
13 do	2.0	0.16		5	0.34
14 N-lauryl phosphoramidate	0.5			7	
15 Zinc dithiophosphate	0.5			3	

[1] The bulk density was measured by placing some of the finely divided metal in a measuring cylinder shaking the powder down till the measured volume was constant, and then weighing the amount of powder.

It has been found, surprisingly, that the metal particles produced according to the invention have good load-carrying properties. This property will make the powders useful in the manufacture of reinforced, plastic, self-lubricated bearings, for example, nylon bearings filled with iron. The nature of the metal surfaces makes the powders according to the invention particularly suitable in filling plastics, in general, or as pigments, as catalysts etc.

It can be seen from this table that carbon tetrachloride gives the greatest surface area upon grinding iron powder according to the invention. It appears furthermore that certain concentrations of load-carrying additives provide optimum increases in surface area.

Nickel, molybdenum and chromium powders were also ground in n-heptane in the presence of carbon tetrachloride and the results are shown in Table II.

TABLE II

Metal	Load-carrying additive in n-heptane	Amount of additive in Percent wt. n-heptane/ additive	B.E.T. surface area of powder in m.²/g.	Bulk density after shake down
(1) Ni	Carbon tetrachloride	1	2	0.34
(2) Ni	do	2	4	
(3) Ni	do	100	4	
(4) Mo	do	1		0.44
(5) Cr	do	1	5	0.34
(6) Unground Ni				3.5
(7) Unground Cr				3.87

NOTE.—All the grinding fluid was carbon tetrachloride.

The load-carrying activity of the powders was measured using dispersions of the powders in a base oil tested in a Four Ball Tester. The results are tabulated in Table III below:

TABLE III

Base oil	Solid dispersed in oil	Amount of solid in oil, Percent wt.	Wear as measured by wear scar diameter; Load 115 kg., 30 min.
(1) Medicinal paraffin oil			Welds in less than 1 min.
(2) Medicinal paraffin oil	Oleophilic graphite[1]	5	4.0 mm. in 1 min.
(3) Medicinal paraffin oil	Oleophilic MoS_2[2]	5	0.99 mm. in 30 min.
(4) Medicinal paraffin oil	Iron powder ground in n-heptane, no additive	10	Welds in less than 1 min.
(5) Medicinal paraffin oil	Iron No. 2	10	1.08 mm. in 30 min.
(6) Medicinal paraffin oil	Iron No. 11	10	2.21 mm. in 30 min.

[1] See co-pending application No. 40,702/65.
[2] See co-pending application No. 40,700/65.

It can be seen from this table that the load-carrying properties of the treated iron are equivalent to those of "oleophilic" molybdenum disulphide, which substance has excellent "extreme pressure" activity.

The load-carrying activity of an iron powder prepared according to the invention and disposed in a BG 160/95 base oil was tested in a Four Ball Tester. This base oil has a Redwood I viscosity at 140° F. of 160 seconds and a viscosity index of 95. The results are tabulated in Table IV below:

TABLE IV

Base oil	Solid disposed in oil	Amount of solid in oil, Percent wt.	Wear Scar Diameter: Load 15 kg., 60 min., mm.	Wear Scar Diameter: Load 115 kg., 30 min., mm.	Mean Hertz Load
(1) BG 160/95			0.80	2.64	22.6
(2) BG 160/95	Iron No. 2	5	0.76	1.5	28.7

I claim:

1. A method of preparing a finely divided metal powder which comprises grinding the metal in an organic fluid distilling below 500° C. in the presence of an organic load stokes at 100° F., and of surface tension less than 72 dynes/cm. at 25° C. in the presence of an organic load carrying additive for lubricants containing at least one element selected from sulphur, chlorine, phosphorus and nitrogen.

2. A method as claimed in claim 1 in which the said organic grinding fluid is n-heptane, iso-octane, cyclohexane, toluene, hexadecane or a hydrocarbon fraction obtained by distilling petroleum.

3. A method of preparing a finely divided metal powder which comprises grinding the metal in an organic grinding fluid in the presence of an organic load-carrying additive for lubricants selected from the group consisting of phosphosulphurised terpenes, zinc dialkyl dithiophosphates, di-aryl disulphides, di-alkyl disulphides, N-lauryl alkyl phosphoramidate and chlorinated paraffins containing from 1 through 4 carbon atoms.

4. A method of preparing a finely divided metal powder as claimed in claim 3 in which the said metal is selected from copper, aluminium, iron, cobalt, nickel, molybdenum and alloys thereof.

5. A method of preparing a finely divided metal powder which comprises grinding the metal in an organic grinding fluid distilling below 500° C., of viscosity less than 600 centistokes at 100° F. and of surface tension less than 72 dynes/cm. at 25° C. in a vibration ball mill in the presence of an organic load-carrying additive selected from organic compounds containing at least one of sulphur, chlorine, phosphorus and nitrogen.

6. A method as claimed in claim 5 in which the said organic load-carrying additive is selected from the group consisting of phosphosulphurised terpenes, zinc dialkyl dithiophosphates, di-aryl disulphides, di-alkyldisulphides, N-lauryl alkyl phosphoramidate, and chlorinated paraffins containing from 1 through 4 carbon atoms.

7. A method of preparing a finely divided iron powder which comprises grinding iron in a paraffinic hydrocarbon distilling below 500° C., of viscosity less than 600 centistokes at 100° F. and of surface tension less than 72 dynes/cm. at 25° C. in a vibration ball mill in the presence of carbon tetrachloride till the iron powder has surface area of at least 5 square metres per gram and a bulk density of less than 1 gram per cc.

8. A method of preparing a finely divided metal powder as claimed in claim 5 in which the said load-carrying additive is present in an amount of up to about the weight of the metal.

References Cited

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,476,325 Dated November 4, 1969

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

Column 1, between lines 6 and 7 insert --Claims priority, application Great Britain, Aug. 5, 1966, 35119/66--

Column 4, Table II Item (3), "100" should read --100[1]--;

Column 4, bottom line, "NOTE.-All" should read --[1]All--;

Column 5, lines 44-45, "in the presence of an organic load stokes at 100°F.," should read --, of viscosity less than 60 centistokes at 100°F.,--.

SIGNED AND
SEALED
JUN 16 1970

(SEAL)
Attest:

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