April 3, 1973 MASASHI OHKAGE 3,725,276

TUNGSTEN DISULFIDE LUBRICANT

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FLOW CHART

OF THE METHOD OF PREPARING
LUBRICATING CRYSTALLINE TUNGSTEN DISULFIDE

1) MIXING BETWEEN TWO TO EIGHT MOLES OF SULFUR WITH ONE MOLE OF TUNGSTEN METAL POWDER

OF A MEAN POWDER SIZE BETWEEN ABOUT 0.01 AND 10 MICRONS;

PRESSURE MOLDING TO SOLIDS ABOUT 25 mm by 30 mm

2) MELTING THE MIXTURE AT A TEMPERATURE BETWEEN THE MELTING POINT OF SULFUR AND 250°C FOR TWO TO EIGHT HOURS;

3) FLOWING THE MELT BY GRAVITY INTO A PREHEATED CONTAINER

RECRYSTALLIZING THE REACTED PRODUCT IN A NON-OXIDIZING GAS AT 550°C AND 650°C, CAUSING EXOTHERMIC REACTION;

4) EVAPORATING THE EXCESS SULFUR.

5) COOLING THE CONTAINER, THUS PRODUCING FLAKES HAVING A LENGTH BETWEEN ONE SUBMICRON TO 10 MICRONS;

6) CRUSHING THE PARTICLES TO SIZE 0.1 – 0.2 MICRON.

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TUNGSTEN DISULFIDE LUBRICANT

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U.S. Cl. 252—25 9 Claims

ABSTRACT OF THE DISCLOSURE

Make tungsten disulfide lubricant by reacting two to eight moles of sulfur with one mole of tungsten metal powder at high temperatures.

CROSS REFERENCE TO A RELATED APPLICATION

This application is a continuation-in-part to copending U.S. application Ser. No. 792,134, and now abandoned, filed Jan. 17, 1969, claiming priority of corresponding Japanese application Ser. No. 4721/1968, and the priorities thereof are claimed herefor.

BACKGROUND OF THE INVENTION

Field of the invention

The invention relates to a novel method of preparing a lubricating crystalline tungsten disulfide by an instantaneous exothermic reaction.

Description of the prior art

The majority of the present day lubricating agents in general use are oils of the petroleum system and grease.

However, in view of the fact that there is an ever-growing tendency to increase the output, numbers of revolutions and sliding speeds of most machines, the demands on the lubricants are also increasing, while it has become very difficult to achieve desirable conditions with common lubricating oils. Therefore, the necessity arose to rely upon high-functional lubricating agents.

In order to meet these requirements, natural flake graphite or molybdenite (composition, MoS_2), the molybdenum ore, has been offered for practical use preferably after selecting good-quality materials thereof and improving their purity to utilize their respective properties such as high heat resistance, good lubrication and high pressure resistance. However, both natural graphite and molybdenite are well known to contain impurities composed mainly of quartz, various sulfide minerals or mining stones constituting their mineral beds. Therefore, even after effecting various procedures of mineral selection and chemical treatments for refining the ore, the perfect removal of such impurities is looked upon as virtually impossible.

Under these circumstances, there occurs the great possibility of obtaining irregular products, depending on circumstances of operation, the kind of ore used for treatment or type of human labor thus rendering the stability of standard qualities mostly difficult.

The Canadian Pat. 630,830 to Spengler et al., concerns the manufacture of molybdenum disulfide using metallic molybdenum or one of the various molybdenum compounds as the molybdenum source and one of the alkaline earth metals, ammonium hydroxide, sulfides, carbonates, sodium and potassium polysulfides, sodium carbonate or potassium carbonate as the sulfur source. Further, the reference discloses the reaction temperature range to be 300° C. to 500° C. This reference is not concerned with tungsten, or tungsten disulfide. Although there is a relationship between molybdenum and tungsten, their respective characteristics were established for the first time by the present invention. The inventor discovered that producing pure tungsten disulfide can be accomplished from a novel mixture of W+S with an excess of sulfur (W+2—4 moles, W+4—8 moles), by methods also different from, and particularly simplified over those used in the prior art production of molybden disulfide, without the aid of alkaline media, alkali sulfide and the like. Different reaction temperatures are used and different particle sizes are advantageously produced. Employment of these alkali media in the production of tungsten disulfide also results in impurities in the final product which the prior art has not been able as yet to remove. Also the present method results in reduced costs at unexpected high yields.

British Pat. 630,042 to International, hydrogenation patent of October 1949, relates to a process for converting oxides of heavy metals in floated and fluid state into sulfides with the aid of hydrogen sulfide. The reference products are sulfides intended for use as catalysts for hydrogenation of organic compounds.

BRIEF DESCRIPTION OF THE DRAWINGS

The sole figure of the drawings is a flow diagram of the method steps of the present invention in solid blocks showing the specific variations thereof in dotted blocks.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In carrying out the manufacturing method of the present invention, the amount of sulfur must be determined such as is shown in the following equations:

$$W+3S \qquad WS_2+S$$

wherein S is used in an amount equivalent to more than 2 atoms or 3 atoms per atom of W.

It is to be especially noted that no larger amount of sulfur than the above will be necessary for yielding mean particle size of 2 microns. By using smaller size particles for the metals that are utilized, the reaction takes place more quickly with sulfur. However, the maximum particle is determined as 10 microns in diameter, and unless metal particles of smaller diameter are used, the time of reaction may only be prolonged on reaction in the liquid phase of sulfur.

After mixing metal with sulfur sufficiently, the resulting mixture is molded under pressure.

It is required that metal tungsten be kept sufficiently in contact with sulfur, and the spacing between both elements be decreased by this operation, thereby enabling air exhaust to be effected and the produced amount of SO_2 to be decreased during the operation.

After adjusting the mixture of the raw materials in this manner, it is put into a container which is kept at a temperature lower than the boiling point of sulfur (444° C.). There occurs a reaction between each metal and sulfur where a sulfide of extremely small size particles (in size less than 0.1 micron) can be obtained.

When the material thus melted is poured into a container whose temperature has been elevated to 550° C. beforehand, an exothermic reaction occurs therein so that tungsten di-sulfide in the form of flake crystals can be produced for the first time.

At this stage, the excessive part of sulfur is sublimated and recovered by recovering means provided on the working site.

Since pure tungsten and pure sulfur are used as raw materials, it is possible to obtain a disulfide of very high purity.

It is possible to ensure a uniform exact performance in the quality of the products. Products are obtained showing very good lubricity and load pressure resistance, hav-

ing better properties than any solid or liquid lubricating agents presently available.

To produce the present invention lubricating agent in a very small size particle, it is easy to carry out a crushing operation and to adjust the degree of particle sizes for converting the product to particles of less than 1.0 micron.

The tungsten disulfide of the present invention shows high heat resistance and will perform up to 500° C. in the air. Since tungsten disulfide of the present invention ensures sufficient pressure resistance and lubricity, it can be used to decrease static electricity by 20–50%, as compared with the use of oil or grease. This advantage is very useful in the planning of national electrical requirements or calculation of manufacturing costs of individual industries and fuel consumption of engines.

EXAMPLE I.—METHOD OF PREPARING TUNGSTEN DISULFIDE

(A) Metal Tungsten

Table of analysis

W	percent [1]	99.98
Fe	do	0.005
Mo	do	0.005
N.V.R.	do	0.010
Size of particles	microns	1.0

[1] Percent purity except for O_2.

(B) Sulfur

Table of analysis

	Percent
S	99.95 up
AS	0.005
Organic matter	0.010
Ash	0.020
Se	0.000

After mixing tungsten 5000 grs. with sulfur powder 2600 grs., the resulting mixture was pressure-molded to solids, 25 mm. in diameter and 30 mm. in height.

Solids thus obtained were put into a heat-resistant steel container provided with heating means and melted at temperatures between 150° and 200° C.

Then, the mixture consisting of tungsten disulfide of very small size particles (less than 0.1 micron) and sulfur thus melted at the abovementioned temperature was caused to flow by gravity gradually into a container provided with a side pipe for distillate induction, 20 cm. in diameter and 30 cm. in height, said container having been preheated to 550° C. beforehand.

At the instant of this operation, there occurred an exothermic reaction for the first time until flake crystals of tungsten disulfide could be produced.

On the other hand, nitrogen gas at the rate of about 200 liters per hour was supplied into the reaction container through said side pipe inserted herein so that it was rendered possible to cool the reacted material, to evaporate the liberated sulfur and to discharge it from the container.

The material 7600 grs. initially prepared was poured into the container in 2 hours and then the liberated sulfur could be discharged perfectly from the container in 3 hours while keeping the container at temperatures between 550° and 650° C.

On cooling the container, the tungsten disulfide thus produced was obtained in the form of perfect flake crystals, about 10 microns in diameter, 0.1–0.5 micron in thickness, and showing a color similar to natural molybden disulfide.

When using this product as a lubricating agent, it was desirable to crush it further into smaller particles.

Therefore, after crushing it by means of a vibro-mill for six hours, the average size of particles was found to be 0.1–0.2 micron, and showing very good lubricity.

The results of frictional experiments on Example I by a 4-ball coefficient tester were as follows:

Friction coefficient at—

5.5 kg. of load (oil pressure)	0.018
10 kg. of load (oil pressure)	0.012

The results of analysis of products of Example I were as follows:

	Percent
W	74.12
S	25.80
Fe	0.02
Mo	0.0036
As	0.00
Organic matter	0.00
N.V.R.	0.04

Tungsten disulfide of high purity 99.9% was obtained in the form of an extremely small flake crystalline powder.

The results of friction tests on Example I were as follows:

The swinging movement of the needle of the recorder was read so that the friction coefficient of the product under hydraulic pressure could be determined by a 4-ball friction testing machine.

In this case, the results were calculated from the pressure of friction against the surface of the bulb of tester using a Herz-type calculator.

The results were as follows:

SPECIMEN OF WS_2

	Twist angle			Friction coefficient			Average Herz pressure	
Oil pressure, kg./cm.	10μ	1.0μ	0.2μ	10μ	1.0μ	0.2μ	Kg./mm.²	Lb./in.
1.5	1.0	0.8	1.0	0.053	0.042	0.053	209	288.700
3.0	1.2	1.6	1.4	0.030	0.040	0.035	269	381.800
5.0	1.3	1.8	1.5	0.019	0.026	0.022	322	456.700
7.5	1.4	1.9	1.5	0.013	0.018	0.014	370	525.000
10.0		1.9	1.5		0.013	0.011	408	579.200
12.0		2.0	1.6		0.012	0.009	434	616.000

PRACTICAL TESTS ON EXAMPLE I

A mixture of WS_2 10%, gear oil 80% and antioxidizing agent 10% was used as the test material.

Practical conditions

(a) Shaft of revolution: d. 1¼", 1,800 mm.

(b) Both ends of the shaft were supported by means of ball bearings and a single bearing of similar type was disposed between both of said ball bearings, an iron block, 120 kgs. being hung by a steel wire attached to said single bearing.

(c) This test material was sufficiently applied to said two bearings at both ends and fresh supplies of this test material were tested from time to time during the running period of said shaft.

This test material of 12.5 grs. was applied to said single bearing for testing purposes only once and no more supply was added until the end of this test.

Ball bearings in use for tests made by certain leading maker; both surfaces of pillow block were provided with oil seal.

The test results on the basis of 7500 r.p.m. ±200 r.p.m. were as follows:

Total number of revolutions of shaft until the lubricity of test material 12.5 grams applied thereto was entirely lost	15,100,000
Amperes during revolution of shaft (A) (average 3.7 a.)	3.5–4.5
Hours required for revolutions	35
Electricity required for revolutions	(1)
Wear of balls	Approximate to 0

[1] 3.7 (a.)×220 (v.)×35 (hrs.)=28.49 kw. h.

From these, the following results were obtained:

Test material 12.5 grams used for the total number of revolutions of shaft, 15,100,000 (load 120 kgs.).

As compared with ball bearings now commercialized on the market.

(Cf. (C) practical test.)

Reduction in electric cost

(6.2 a.—3.7 a.)×220 v.×35 hrs.=19.25 kw. h.

On the basis of 1 kw. h. equivalent to Japanese yen 5. (approx. U.S. 1.4 cents)

$$5\times 19.25=96.25 \text{ (yen)}$$

Percentage of reduction in electricity, as compared with the use of commercialized ball bearings

$$19.25 \text{ kw. h.}\times\frac{100}{47.74 \text{ kw. h.}}=40.5\%$$

Durable force on commercialized ball bearings

$$\frac{15,100,000}{5,900,000}=2.56 \text{ times as large}$$

Test with use of grease on commercialized bearings:

Ball bearings used for practical tests
Made by certain leading maker
Both surfaces of pillow block provided with oil 1¼" seal.

These ball bearings were used in their original state when purchased.

Test conditions: Shaft of revolution: d. 1¼", 1,800 mm.

The shaft of revolution was supported by ball bearings at both ends thereof and a single ball bearing was disposed between both steel wires attached to said single ball bearing.

This grease was sufficiently applied to said two ball bearings at both ends of the shaft and additional oil supplies of same grease were applied thereto from time to time during the running period of the shaft. Said single bearing for test purposes was used in its original state when purchased and no further supply of grease was made until the end of this test.

TESTS

The results with the shaft driven at the rate of 7,500 r.p.m. ±200 were as follows:

Total number of revolutions until the lubricity of grease was entirely lost	5,900,000
Ampere during revolution (average 6.2 a.)	5.0–6.8
Hours required for revolutions	13
Electricity required for revolutions	(1)

[1] 6.2 (a.)×220 (v.)×13=17.7 kw. h.

EXAMPLE II

Method of preparing tungsten disulfide of submicron size

For lubrication in dry state, high temperature lubrication at 300° to 500° C., or for use together with a high viscosity, high consistency oil or fat such as grease or as a composite bearing material with a metal, or for molding in mixture with plastics; the tungsten disulfide obtained by the method of preparing tungsten disulfide is employed. However, when it is necessary to admix and suspend tungsten disulfide in liquid oil, for example by the addition of WS_2 to improve the lubricity of engine oils for internal-combustion engines, as for automobiles, ships, generators, and farm machines, the WS_2 is in the form of very fine powder. This is generally beyond the existing capacity for mechanical pulverization.

When solid particles are to be suspended in liquid, an equilibrium must be established between the viscosity of the liquid and the gravity resistance of the solid particles.

As a nearest approach to this, the present method of preparing tungsten disulfide of submicron size has very great importance.

(A) Metal Tungsten

Table of analysis

W	[1] percent	99.9
Fe	do	0.005
Mo	do	0.005
N.V.R.	do	0.010
Size of particles	micron	1.0

[1] Percent purity except for O_2.

(B) Sulfur

Table of analysis

	Percent
S	99.95 up
As	0.005
Organic matter	0.010
Ash	0.020
Se	0.000

After mixing tungsten 5,000 grs. with sulfur powder 5,200 grs., the mixture was put into a heat-resistant steel container provided with heating means and stirrer and melted at 150° C., stirring the melted mixture at a temperature to 250° C. for four hours. Then, the mixture consisting of tungsten disulfide of very small particles (less than 0.1 micron) and an excess of sulfur melted flowed down gradually into a container provided with a side pipe for distillate of sulfur induction, 20 cm. in diameter and 30 cm. in height, said container having been preheated to 550° C. beforehand.

On the other hand, nitrogen gas at the rate of about 200 liters per hour was supplied into the reaction container through a provided pipe inserted herein so that it was made to cool the reacted material and carry the evaporated sulfur out of the container.

The material 10,200 grs. initially prepared was poured into the container in two hours and then the liberated sulfur could be discharged perfectly from the container in another four hours, while keeping the container at a temperature between 550°–650° C. On cooling the container the tungsten disulfide thus produced was obtained in very fine flake crystals. The maximum length of the flake was 0.5 micron and minimum length of the flake was 0.01 micron, showing a blackish-grey color.

The physical and mechanical lubricating properties of the tungsten disulfide prepared in this way resemble those of the product according to Example I, and therefore the description thereof is to be included by reference.

Economy of this method:

As compared with the hydrogen reduction method of tungsten, zinc reduction method of tungsten makes it possible to accomplish the reduction at less than a half of the cost required by the former for the materials and supplies including heat and electricity and at less than one-third of the cost for labor. Also, the submicron particles which are scarcely obtained by the hydrogen reduction method can be easily produced by this method.

One of the beneficial factors from the material viewpoint which render it economically feasible to use tungsten as a starting material for the manufacture of tungsten disulfide is the possibility of reducing tungsten with zinc in accordance with a process invented by the present inventor.

The method of producing WS_2 from W is industrially very advantageous because, as described in the specification of the present application, the manufacturing cost, net yield, and particle size of the product can be easily controlled.

I claim:

1. Method of preparing lubricating crystalline tungsten disulfide comprising the steps of:

(1) mixing between two to eight moles of sulfur with one mole of tungsten metal powder;

(2) reacting the mixture at a temperature between the melting point of sulfur and 250° C.;

(3) crystallizing the reacted product in a non-oxidizing gas at 550° C. and 650° C.; and

(4) evaporating the excess sulfur.

2. Method of preparing lubricating crystalline tungsten disulfide as claimed in claim 1, wherein the tungsten disulfide is crystallized to flake crystals, having a size between 10 microns and one submicron in flake length.

3. Method of preparing lubricating crystalline tungsten disulfide as claimed in claim 1 wherein the tungsten metal has a powder size of below 10 microns.

4. The method of preparing lubricating crystalline tungsten disulfide as claimed in claim 1, said step of mixing comprising:

mixing one mole of tungsten metal powder and two moles of sulfur;

said step of reacting comprising

heating the mixture to below 150° C. to melt it;

said step of crystallizing comprising

pouring the melt into a vessel preheated to 550°–650° C.;

wherein an exothermic reaction takes place at once and tungsten disulfide is prepared.

5. Method of preparing lubricating crystalline tungsten disulfide as claimed in claim 4, said step of evaporating comprising evaporating the excess of sulfur completely, whereby the residual is pure lubricating tungsten disulfide.

6. Method of preparing lubricating crystalline tungsten disulfide as claimed in claim 4, wherein the lubricating tungsten disulfide has a maximum flake size of 10 microns in length and has a calculated mean powder size of about 2 microns.

7. The method of preparing lubricating crystalline tungsten disulfide as claimed in claim 1,

said step of mixing comprising mixing one mole of tungsten metal powder and 4–8 moles of sulfur;

said step of reacting comprising heating the mixture to 150°–250° C. for about 2–8 hours;

said step of crystallizing comprising pouring the melt into a vessel preheated to 550°–650° C.

8. Method of preparing lubricating crystalline tungsten disulfide as claimed in claim 7, said step of evaporating comprising evaporating the excess of sulfur completely until pure lubricating crystalline tungsten disulfide remains.

9. Method of preparing lubricating crystalline tungsten disulfide as claimed in claim 7, wherein the lubricating crystalline tungsten disulfide has a maximum flake size of 1.0 micron in length and has a calculated mean powder size of below 0.1 micron.

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