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**MOLYBDENUM DISULFIDE LUBRICANT AND
METHOD FOR MAKING SAME**

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The present invention relates to an improved molybdenum disulfide lubricant in particulate form, to the method for making the same and to dispersions containing such improved lubricant.

The laminar, plate-like form of particles of molybdenite is known and well understood to render such particles useful as lubricants. Molybdenite particles have been commercially used as lubricants by application to the surface to be lubricated in the form of dry powder or as a liquid dispersion. Because of the relatively high density of molybdenum disulfide it is extremely difficult to form a stable, non-settling dispersion containing a sufficiently high concentration of molybdenum disulfide particles to be an efficient lubricant. The formation of a commercially stable MoS_2 dispersion requires a reduction of the particle size of molybdenite from the conventional 100 to 200 screen mesh size to a substantially smaller size range, for example, 10–50 microns. Such size reduction customarily has been accomplished by grinding the molybdenite commercial product in a ball mill. Reducing the particle size by conventional ball milling procedures is expensive, time-consuming and undesirably limited in the degree of particle size reduction which is obtained in an economic time period. As a result of these limitations the particle size of molybdenum disulfide in dispersions has been close to the maximum size which could be maintained in the dispersion, and such dispersions suffer from the disadvantages of having low covering power and being unsuitable for use in many lubricating applications, particularly those requiring a lubricating film between tightly fitting, relatively moving parts and those in which one surface rolls against another, etc.

It is the primary object of this invention to provide a new and improved molybdenum disulfide product in particulate form.

Another important object of this invention is to provide an improved method for making finely-divided molybdenum disulfide.

A further object of this invention is to confer improved lubricating ability to particulate molybdenum disulfide and dispersions made therefrom, and to provide dispersions which are more economic to use, have improved stability and utility in a wider range of lubricating applications than heretofore known molybdenum disulfide lubricants.

In accordance with this invention it has been found that a product having improved covering power and lubricating characteristics is obtained when both the maximum particle size is controlled and the proportion of sizes of particles which constitute the product are established and maintained within certain limits. Generally stated, the improved product of this invention contains not more than 0.1%, by weight, of particles larger than 32 microns in diameter and the mass mean diameter of the particles is in the range of about 0.45 micron to about 2.0 microns. The method of this invention is based on the discovery that grinding the molybdenite in the presence of certain grinding aids is effective in reducing the particle size of molybdenite to the desired micron range and producing the desired distribution of sizes of particles in greatly reduced time relative to grinding by conventional methods.

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The molybdenum disulfide starting material may be any of the commercially available purified and finely powdered naturally occurring molybdenites, e.g., the froth (flotation purified natural molybdenum disulfide ground to an average particle size of about 100 Tyler screen mesh.

The grinding aid must be effective to improve the rate of particle size decrease without reacting in any way with the molybdenum disulfide particles to convert them to a non-lubricating or water soluble form, and additionally must be easily separable or removable from the finish ground material by sublimation or dissolution in a commercially available solvent, e.g., isopropyl alcohol, followed by filtration. Either of these methods permits economic recovery of the grinding aid by condensing the sublimed vapors, or crystallizing the grinding aid from the filtrate by boiling off the solvent which is recaptured by condensing and is also available for re-use. The solid reaction products of ammonia, carbon dioxide and water, for example, ammonium carbonate and ammonium bicarbonate apparently react with the molybdenum disulfide particles to detrimentally affect the lubricating properties and are thus unsatisfactory. Salicylic acid and phthalic anhydride have been found to possess all the necessary characteristics for this use, and it is believed that the ability to sublime without chemically reacting with the molybdenum disulfide is the characteristic that is common to these two materials to make them functionally suitable for this use. Salicylic acid is slightly more effective than phthalic anhydride in improving the rate of decrease in size of the molybdenum sulfide particles, is easier to separate from the finish ground material, particularly by sublimation, and is preferred.

The product of this invention is improved in the respect that the average particle size is finer than heretofore known molybdenum sulfide powders and additionally contains a significantly decreased proportion of large particles. To illustrate, molybdenite powder ball milled for 72 hours in the absence of a grinding aid of this invention contains about 10%, by weight, of particles larger than 7.5 microns. Molybdenite powder ball milled for 24 hours in the same ball mill containing salicylic acid crystals as the grinding aid produced a product containing only 1.8%, by weight, of particles larger than 7.5 microns while 60 hours of ball milling in the presence of salicylic acid produced a product having only about 0.15%, by weight, of particles larger than 7.5 microns. As the proportion of fine particles in the product increases, particularly the proportion of extremely fine particles, i.e., smaller than about 2.0 microns in diameter, and the proportion of larger particles decreases the lubricating ability and the range of lubricating uses of the product increases. It has been found that the product should not contain more than 0.1% of particles, by weight, having a size greater than 32 microns in diameter and that at least about one-half of the particles, by weight, should have a diameter below a diameter which is in the range of about 0.45 micron to about 2.0 microns. Expressed in terms of mass mean diameter, the product of this invention contains particles having a mass mean diameter in the range of about 0.45 micron to about 2.0 microns and contains a maximum of 0.1%, by weight, of particles larger than 32 microns. The preferred products have a mass mean diameter approaching the above given lower limit and contain a maximum of 0.1%, by weight, of particles larger than about 15 microns. The sizes and proportion of particles expressed herein and in the appended claims refer to sizes and proportions determined by the use of the apparatus disclosed in U.S. Patent 2,656,508, commercially known as the Coulter counter, by specifically following the method of its use described therein.

Briefly stated, the particle count procedure involves adding a weighed sample of the product to a measured quantity of water and adding a small quantity of acid, such as nitric, to make the solution electrically conductive. A sample is placed in the counter which has been previously calibrated with known size particles and a series of counts are made at a series of threshold settings. The counter counts all of the particles equivalent to and larger than particles equivalent to the threshold setting and the difference in the counts obtained at adjacent threshold settings is the number of particles having sizes between the sizes represented by the threshold settings. In making the particle size determinations to establish the mass mean diameters hereinabove given, the particle size between 1 micron and 10 microns was measured in not less than 10 increments spaced in geometric progression, for example, in 12 increments spaced from the adjacent one by a factor equal to the square root of 2. In converting the particle count from numbers of particles to percent by weight of the total particles, the particles are assumed to be spheres and to have an average diameter half-way between the diameters of the particles at the threshold settings between which the number of particles were counted. Since the total weight of particles was originally measured, the percentage of the total represented by each differential particle count is easily determined, and the successive determinations enables the establishment of the size at which one-half of the particles, by weight, are above that size and the other half are below that size, or in other words the mass mean diameter of the particles in the sample.

The method of the invention involves the steps of placing dry or dried molybdenite to be comminuted in the grinding vessel, preferably a ball mill using steel balls, pebbles or the like having diameters for example of about ½" to about 2" and adding the grinding aid crystals to the mill. The weight ratio of grinding aid to molybdenum disulfide which is employed may satisfactorily vary from about 0.1:1 to about 3:1 and especially good results have been obtained at a ratio of about 2:1. No particular advantage is gained by using a greater excess of grinding aid than about 3:1 since greater quantities do not destroy the benefits but rather only increase the expense and problems of recovery and re-use of the grinding aid. The ball mill is rotated for the desired time period, for example, one-half to two days, or longer if desired, and the ground molybdenum is then separated from the grinding aid. The preferred procedure is to slurry the finish grind with alcohol, preferably isopropyl alcohol, and filter the slurry through a filter to separate the molybdenum sulfide from the alcohol solution containing the dissolved grinding aid. The filter cake contains the product of this invention and may be converted into a dispersion before drying, or may be dried, for example, in a non-oxidizing atmosphere at a temperature below about 250° F. Alternatively, the grinding aid may be removed from the finish ground material by sublimation at a temperature of about 170° F.-250° F. for salicylic acid or about 265° F. to 300° F. for phthalic anhydride. The vapors from the finish grind may be collected and reconverted to crystalline form for re-use.

Liquid dispersions which have excellent stability characteristics are formed from the filter cake material by incorporating therewith the now conventional dispersing carriers, stabilizers and the like including oil, water, alcohol and mixtures thereof as well as resin solutions including thermosettable and thermoplastic resin carriers. Excellent lubricating results are obtained from a water or oil dispersion containing, for example, about 10% to about 40%, by weight, of the product of this invention.

The following examples are intended to illustrate the product of and the method of this invention in greater detail but it is to be understood that the particular quantities of ingredients, conditions employed and the like are not

definitive of the limits of this invention which have been previously given above and are set forth in the claims.

Example I

A steel ball mill having a volume of 4.82 gallons, a diameter of 11', a length of 11½" and containing a steel ball charge of 111.1 lbs. of 1½" diameter balls was loaded with 4 lbs. of technical grade molybdenum disulfide having an average particle size of about 100 Tyler screen mesh. 8 lbs. of technical grade salicylic acid was charged into the mill and the mill was rotated at 50 r.p.m. for 24 hours.

The ground material was spread in a thin layer on pans and the salicylic acid was removed by sublimation at a temperature of about 200° F.-250° F. in about 30 minutes. A particle size count sample was prepared from the dried filter cake by adding 12 grams of the ground powder to 16 grams of water in the presence of 4 grams of dextrin. This material was placed in a shot mill and milled for 15 minutes and an additional 50 grams of water was then added. Samples of the shot milled material were then further diluted with a 0.05 N to 0.075 N nitric acid solution. A sufficient quantity of the nitric acid solution was added to insure that the maximum particle count would remain below the maximum particle count of which the counter was capable, in this case about 50,000 particles. With the counter set at a threshold value sufficiently high to count the maximum size particles, a first count was taken and a series of additional counts were made by decreasing the threshold setting each time by a factor equal to the square root of 2. The results of the particle count indicated that the finely ground material had a mass mean diameter of 1.86 microns and contained 0.1%, by weight, of particles having a diameter greater than 15 microns. 98.8% by weight, of the particles were smaller than 8 microns; 98% of the particles were smaller than 7 microns; 96% of the particles were smaller than 6 microns; 80% of the particles were smaller than 3 microns; 68% of the particles were smaller than 2.5 microns; 55% of the particles were smaller than 2.0 microns; 30% of the particles were smaller than 1.25 microns; 20% of the particles were smaller than 1.0 micron; 11% of the particles were smaller than 0.8 micron; and, 7% of the particles were smaller than 0.67 micron.

Another sample of the same material was inserted in the same ball mill in the presence of a similar quantity of salicylic acid and the operation was repeated except that the ball milling time was 40 hours. At the end of the 40 hours a sample of the finely ground material was prepared for counting in a manner identical to that described above and particle size determination was made and showed the following particle size distribution. The mass mean diameter of the particles in the sample was 1.38 microns and the sample contained a maximum of 0.1% of particles larger than 16 microns. 30%, by weight, of the particles were smaller than 0.8 micron; 40% of the particles were smaller than 1.0 micron; 70% of the particles were smaller than 2.0 microns; 80% of the particles were smaller than 2.5 microns; and, 87% of the particles were smaller than 3.0 microns.

Another sample of the same starting material was ground in the presence of a similar quantity of salicylic acid for 48 hours and a particle size determination showed the sample to contain the following particle size distribution. The sample had a mass mean diameter of 0.8 micron and contained a maximum of 0.1% of particles larger than 12.7 microns. 60%, by weight, of the particles were smaller than 1.0 micron; 68% of the particles were smaller than 1.25 microns; 82% of the particles were smaller than 2.0 microns; 88% of the particles were smaller than 2.5 microns; 93% of the particles were smaller than 3.0 microns; and, 96% of the particles were smaller than 3.9 microns.

Another sample of the same material was ground un-

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der similar conditions for 60 hours and a particle size count showed the finely ground material to have the following particle size distribution. The mass mean diameter was 0.45 microns and this sample contained a maximum of 0.1% of particles greater than 10 microns in diameter. 72% of the particles were smaller than 0.8 micron; 80% of the particles were smaller than 1.0 micron; 85% of the particles were smaller than 1.25 microns; 93% of the particles were smaller than 2.0 microns; 95.5% of the particles were smaller than 2.5 microns; and, 97.5% of the particles were smaller than 3.0 microns.

Example II

12 lbs. of technical grade molybdenum disulfide having an average particle size of about 100 Tyler screen mesh was charged into the ball mill described in Example I and the ball mill was rotated at 50 r.p.m. for 72 hours. The ground material was removed from the ball mill and prepared for a particle size distribution count in accordance with the procedure described in Example I. The particle size count showed that the material had a mass mean diameter of 2.5 microns and contained a maximum of 0.1% of particles larger than 44 microns. 25%, by weight, of the particles were smaller than 1.38 microns; 38% of the particles were smaller than 1.82 microns; 42% of the particles were smaller than 2.0 microns; 58% of the particles were smaller than 3.0 microns; 76% of the particles were smaller than 5.0 microns; 83% of the particles were smaller than 6.0 microns; 88% of the particles were smaller than 7.0 microns.

A dispersion was prepared from the product of grinding of Example I for 60 hours, using oil as the carrier and containing approximately 10% MoS₂ solids. This dispersion was compared in ball bearing lubrication tests with another commercial oil dispersion containing a similar quantity of molybdenum disulfide having a particle size in the 10 to 50 micron size range and with a dispersion formed from the product of Example II. The results showed the dispersion of Example I to have better covering power and longer life than either of the other two dispersions.

Example III

The ball mill described in Example I was filled with 6 lbs. of technical grade molybdenum disulfide having an average particle size of about 100 Tyler screen mesh and 6 lbs. of technical grade salicylic acid and the mill was rotated at 50 r.p.m. for 72 hours.

The salicylic acid was removed by sublimation in the manner described in Example I. A particle size count sample was prepared using the procedure of Example I and a particle size determination was made and showed the following particle size distribution. The mass mean diameter of the particles in the sample was 0.83 micron and the sample contained a maximum 0.1%, by weight, of particles greater than 11.5 microns in diameter. 48%, by weight, of the particles were smaller than 0.82 micron; 53% of the particles were smaller than 0.94 micron; 60% of the particles were smaller than 1.1 microns; 70% of the particles were smaller than 1.3 microns; 78% of the particles were smaller than 1.6 microns; 84% of the particles were smaller than 2.0 microns; 90% of the particles were smaller than 2.5 microns; 94% of the particles were smaller than 3.13 microns; and, 96.5% of the particles were smaller than 3.9 microns.

Example IV

The ball mill described in Example I was filled with 6 lbs. of technical grade molybdenum disulfide having an average particle size of about 100 Tyler screen mesh and 6 lbs. of technical grade phthalic anhydride and the mill was rotated at 50 r.p.m. for 72 hours.

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The phthalic anhydride was removed by sublimation in the manner described in Example I. A particle size count sample was prepared using the procedure of Example I and a particle size determination was made and showed the following particle size distribution. The mass mean diameter of the particles in the sample was 0.96 micron and the sample contained a maximum 0.1%, by weight, of particles larger than 16 microns. 42%, by weight, of the particles were smaller than 0.82 micron; 48% of the particles were smaller than 0.94 micron; 53% of the particles were smaller than 1.0 micron; 62% of the particles were smaller than 1.25 microns; 70% of the particles were smaller than 1.6 microns; 78% of the particles were smaller than 2.0 microns; 85% of the particles were smaller than 2.5 microns; and, 91% of the particles were smaller than 3.13 microns.

What is claimed is:

1. Molybdenum disulfide in finely divided particulate form, the particles thereof having a mass mean diameter in the range of about 0.45 micron to about 2.0 microns and at least about 99.9%, by weight, of said particles having a diameter of less than about 32 microns.

2. Molybdenum disulfide in finely divided particulate form, the particles thereof having a mass mean diameter in the range of about 0.45 micron to about 2.0 microns and at least about 99.9%, by weight, of said particles having a diameter of less than about 15 microns.

3. A molybdenum disulfide lubricant composition comprising molybdenum disulfide particles having a mass mean diameter in the range of about 0.45 micron to about 2.0 microns and containing a maximum of about 0.1%, by weight, of molybdenum disulfide particles having a size larger than about 32 microns, and a liquid carrier therefor, the concentration of said particles being sufficient to substantially increase the lubricating ability of said carrier.

4. A molybdenum disulfide lubricant composition comprising molybdenum disulfide particles having a mass mean diameter in the range of about 0.45 micron to about 2.0 microns and containing a maximum of about 0.1%, by weight, of molybdenum disulfide particles having a size larger than about 15 microns, and a liquid carrier therefor, the concentration of said particles being sufficient to substantially increase the lubricating ability of said carrier.

5. A lubricating dispersion comprising a liquid carrier and containing as its essential lubricating component finely divided molybdenum disulfide, said molybdenum disulfide being present in the form of particles having a mass mean diameter in the range of about 0.45 micron to about 2.0 microns and containing not more than 0.1%, by weight, of particles having a diameter greater than about 32 microns.

6. A dispersion in accordance with claim 5 wherein said liquid carrier is water.

7. A dispersion in accordance with claim 5 wherein said liquid carrier is oil.

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