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PROCESS OF PRODUCING METALLIC DISULPHIDES, TELLURIDES, AND SELENIDES

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This invention relates to a method and the product produced thereby, of treating certain commercially available inorganic compounds in order to render these compounds suitable for use as solid lubricants.

This invention relates to the processing of metallic compounds of the type exemplified by molybdenum disulphide, tungsten disulphide, molybdenum selenide, molybdenum telluride and tungsten telluride, and similar inorganic compounds of metals and non-metals characterized by flat crystals easily cleaving into thin plates. The compounds are believed to form crystals in which the metallic atoms are attached to one another in a single plane while two non-metallic atoms, such as sulphur, are attached to each metallic atom to form layers on both sides of the plane.

These compounds are believed to be highly effective lubricants due to the fact that non-metallic atoms in each of the several crystals have very little attraction for one another and accordingly slippage of the crystals with a low coefficient of friction occurs when the crystals are subjected to shear stresses under load. On the other hand, the non-metallic atoms have an affinity for metal surfaces such that under appropriate conditions the non-metallic atoms will bond to the metal surfaces so tenaciously that the crystals may not be removed except by abrading the metal surfaces. In the specification reference will be made specifically to the use of molybdenum disulphide, but it is intended that any of the compounds of this class be included since they may be similarly treated to produce equivalent results.

The solid compounds such as molybdenum disulphide are exceptionally good lubricants for many purposes. For certain applications molybdenum disulphide type of compounds is the only satisfactory known material capable of functioning effectively as lubricants. When subjected to rather high temperatures, as up to 500° C. in air, and even higher under reduced pressures, molybdenum disulphide applied properly will function with a high degree of effectiveness whereas most known lubricants, solid or liquid, have been found to be totally ineffective or even harmful in some cases. For example, in rotating anode X-ray tubes, the use of liquid lubricants is impractical since the vapor pressure is sufficient to render the X-ray tube inoperative. Customary solid lubricants, such for example, as graphite, have been found to be not only ineffective as lubricants, but in some instances have resulted in

an accelerated deterioration of the bearings of the rotating anode due to molecular re-arrangement and/or decomposition. Furthermore, the molybdenum disulphide has been found to be operative under extreme pressures with the lowest coefficient of friction of many commonly known solid or liquid materials. For example, at pressures of 500,000 and 600,000 pounds per square inch, the coefficient of friction was less than one-third of several liquid lubricating substances. The coefficient of friction of molybdenum disulphide was many times less than that of solid lubricants which have been employed for some purposes. At the other extreme, at low pressures, the anti-friction properties of solid lubricants exemplified by molybdenum disulphide have been better, for instance, with respect to the coefficient of friction than many liquid and solid lubricating substances.

In order to effectively apply molybdenum disulphide to bearings, it has been found that commercially available molybdenum disulphide is generally unsuitable for the purpose and must be processed in order to render it suitable as a solid lubricant. Heretofore, for lubricating processes it was necessary to select large, extremely pure crystals or lumps of molybdenum sulphide and employ only such material for lubricating purposes. Crystals or lumps of this kind are not available on a commercial scale.

Commercially available molybdenum sulphide is produced by grinding molybdenite ore and separating the molybdenum disulphide particles from the gangue usually by flotation. While the separation removes a great amount of the impurities from the concentrate, the concentrate is not satisfactory as a lubricant. A relatively great amount of impurities and abrasive particles is present therein rendering its application as a lubricant impractical.

For lubricating purposes, molybdenum disulphide must be substantially completely free of abrasive material and other impurities, such as sulphur, other sulphides and polysulphides of molybdenum which may prevent the adherence of a film of molybdenum disulphide to metal surfaces. It will be appreciated that a single minute particle of quartz in even a small amount of molybdenum disulphide, if applied to the pivot of an instrument, would easily ruin the pivot. No amount of molybdenum disulphide will satisfactorily lubricate the pivot under these conditions and enable it to function properly. The abrasive particle may score the pivot point, thus removing the adherent molybdenum film sulphide as well

as destroying the shape of the pivot itself. Therefore, unless molybdenum disulphide is produced substantially free from impurities and abrasives of all kinds, the material is not suitable for lubricating purposes.

It should be noted that of the numerous sulphides of molybdenum, only the disulphide, MoS_2 , has any appreciable lubricating properties. Hence particular care must be taken to remove the free sulphur and polysulphides which occur naturally in molybdenite ore and its concentrates.

The object of this invention is to provide for treating solid compounds such as molybdenum disulphide to render them suitable for use as solid lubricants.

Other objects of the invention will, in part, be obvious, and will, in part, appear hereinafter.

For the practice of this invention, raw molybdenum disulphide, such as the concentrates produced ordinarily by flotation of finely ground molybdenite ore, are available to the trade. The concentrates are in a finely divided state of the order of from 100 to 300 mesh. In some cases even selected large crystals or lumps of relatively pure molybdenum disulphide may be subjected to the purification treatment herein disclosed in order to completely eliminate impurities and abrasives therein. The concentrates generally consist of from about 80% to 90% molybdenum disulphide, approximately 6% iron oxides and sulphides and several percent of quartz. The concentrates will also contain molybdenum polysulphides, molybdenum oxides, and free sulphur; silicates and oxides of calcium, aluminum, magnesium and copper, as well as copper and other sulphides. Since the concentrates are produced by flotation, they are contaminated with grease, oils and flotation agents. All of these impurities and abrasives are generally detrimental to the functioning of the molybdenum disulphide as a lubricant.

In purifying the molybdenum disulphide to render it suitable as a solid lubricant, the finely pulverized sulphide is initially extracted with a solvent for the greases, oils, and flotation agents. Some extraction agents will also remove any free sulphur present in the concentrate. A suitable extraction agent for this purpose is trichlorethylene. Other organic solvents, such as ethyl alcohol, acetone, carbon disulphide and similar powerful solvents for greases, sulphur, and flotation agents may be used for this purpose.

For the most efficient application of the extraction agent, the ore is treated on the Soxhlet principle. The finely divided ore concentrate is placed in a receptacle at the foot of a condensing column whereby vapors of the solvent on condensing to the liquid phase in the column run into the ore. After the ore has been covered to a given depth by the solvent a siphon device attached to the receptacle begins to function and substantially all of the solvent with solute therein is rapidly removed from contact with the molybdenum disulphide. The contaminated solvent is delivered by the siphon to a boiler which causes the solvent to evaporate, leaving the impurities in the boiler. The solvent vapors from the boiler are condensed in the condensing column and the purified liquid solvent is again brought in contact with the concentrate. The solvent extraction operation repeats itself a great number of times, removing the greases and oils and flotation agent as well as sulphur to the vanishing point. Several hours' rapid extraction with a solvent have been found to remove substantially

all the impurities. The treated molybdenum disulphide is dried in an oven at a temperature sufficient to eliminate all of the solvent therefrom.

In order to insure the most complete removal of all impurities, the grease and oil free molybdenum disulphide now may be advantageously comminuted to much smaller dimensions. The molybdenum disulphide suspended in some of the solvent may be transferred to a ball mill or other equivalent mill. The disulphide is milled for a period of time until the particles of compound average from 1 to 50 microns in dimension. Several hours in a high speed ball mill using $\frac{3}{8}$ inch diameter steel balls has been found sufficient for this purpose. Subsequent treatment will remove any steel particles which may come off the balls.

The ball milled molybdenum disulphide is separated from the solvent liquid by centrifuging and decanting the solvent. Filtering and drying the molybdenum disulphide prepares it for the next step.

The advantages of the finely subdivided mineral are that subsequent treatment is expedited and a more fully purified lubricant is obtained. Silica, for example, is present not only as large particles but also is occluded mechanically in the molybdenite crystals. Any treatment to remove silica will be greatly hindered in its efficiency if the molybdenite crystals are not broken sufficiently to expose the silica occluded therein.

The dried, partially purified concentrate of molybdenum disulphide is treated with from three to ten parts of 80% hydrofluoric acid for each eight parts of the concentrate by weight. The treatment with hydrofluoric acid can be successfully performed with liquid acid of greater or less concentration, or with acid entirely in the gaseous phase using hydrogen fluoride gas contained in equipment resistant to the action of the gas, and so designed as to remove the gaseous silicon tetra-fluoride formed during the treatment. The main purpose of these treatments is to remove silicon compounds, such as silica and silicates, normally found in the molybdenum disulphide concentrates.

The use of hydrogen fluoride gas will convert the silica, or other combined silicon present in the concentrates, to silicon tetra-fluoride, a volatile gas. In the case of the aqueous hydrofluoric acid treatment, silicon tetra-fluoride will likewise be produced; but depending upon the amount of water present, some of this gas will be hydrolyzed to form silicic acid and fluo-silicic acid. The latter material is water-soluble; however, the silicic acid is not water or weak alkali-soluble, and is only acid-soluble when in the colloidal state. Silicic acid is, therefore, removed as later described by dehydrating it to silica and treating the concentrates again with hydrofluoric acid. Any silicic acid formed by hydrolysis during this second treatment is kept in the colloidal state and removed by washing with hydrochloric acid.

The addition of the liquid hydrofluoric acid to the concentrates may be effected in a molded phenol-aldehyde receptacle, resistant to the action of the acid. A paste is formed by mixing the acid and the molybdenum disulphide. This paste is allowed to stand for eight to twenty-four hours, thereby insuring conversion of all silica and silicates to silica acid, fluosilicic acid, or silicon tetra-fluoride gas; and solution of all other hydrofluoric acid soluble minerals.

At the end of the hydrofluoric acid treatment, the paste is mixed with approximately an equal volume of water to facilitate filtering, and then filtered to separate the molybdenum disulphide concentrates from the filtrate. Washing of the concentrates is carried out until they have been washed with four to eight times their own volume of water. In the filtrates from this washing process will be found fluosilicic acid, excess hydrofluoric acid, molybdic acid and water soluble metal fluorides.

The washed concentrates are then rendered free of polysulphides of molybdenum by mixing them with an equal volume of an aqueous 20% sodium sulphide solution and allowing this mixture to stand for 4-10 hours. At the end of this time the mixture is filtered and then washed with hot or boiling water until a clear filtrate is obtained. Other alkali sulphides may be employed instead of sodium sulphide.

In many cases the molybdenum disulphide concentrates are rendered free from all traces of silicon compounds by one hydrofluoric acid treatment, however, for most careful purity control it is suggested that the hydrofluoric acid treatment be repeated upon the concentrates at this point in the process. Before giving the concentrates this second hydrofluoric acid treatment, they should be thoroughly dried at 110-200° C. to dehydrate any silicic acid present.

Following this second treatment, the paste of acid and concentrates should be treated with an equal volume of 10% hydrochloric acid to convert silicic acid, if present, to the colloidal state. Filtration of this mixture will leave all the silicic acid in the filtrate.

The resulting molybdenum disulphide concentrates are then mixed with approximately twice their volume of 10% hydrochloric acid, and allowed to stand for 3-4 hours in order to be certain to dissolve any copper sulphides and other acid soluble matter still present in the concentrates. At the end of this time, the mixture should be filtered and washed with several times its volume of distilled water and finally with distilled water made slightly alkaline by addition of ammonium hydroxide.

The molybdenum disulphide is finally washed with boiling distilled water until free of all soluble material. Completeness of washing can be conveniently determined by making conductivity measurements on samples of the filtrate as washing proceeds. When washing is complete, the conductivity will reach a low but constant value due to the very slight solubility of molybdenum disulphide.

For storage purposes it is generally found convenient to dry the washed and purified molybdenum disulphide at 125-200° C. The product is a dry, shiny-black, finely divided powder.

The purified powder consists of essentially pure molybdenum disulphide free from abrasives and greases and other harmful matter whereby the powder may be applied as a solid lubricant with all types of bearings with a great degree of success. When the purified molybdenum disulphide is applied to bearing surfaces by rubbing or impacting, the antifriction properties of the bearing will be many times superior to those attainable by the use of graphite or other conventional lubricants. The molybdenum disulphide is stable up to 500° C. in air and is insoluble in water or other solvents. Most chemical reagents are without any effect thereon with the exception of hot

concentrated sulphuric acid, nitric acid, or other powerful oxidizing agents.

A similar procedure may be used in treating tungsten disulphide, tungsten selenide and related compounds.

The process described is designed to insure consistent and maximum purity of the finished product, and may be considerably shortened, operations omitted etc., when ore concentrates from some sources are used, or where maximum purity is not essential.

Since certain changes in carrying out the above process may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

I claim as my invention:

1. The process of producing metallic disulphides, tellurides and selenides having solid lubricant properties from finely divided raw materials containing said compounds which comprises subjecting said finely divided raw materials to a solvent so as to dissolve impurities, removing the solvent with the dissolved impurities therein, applying to the partially purified materials a reagent of the group consisting of a solution of hydrofluoric acid and hydrogen fluoride to effect decomposition of silicon compounds present, washing the material with water to dissolve substantially all the remaining hydrofluoric acid and any fluo-silicic compound present and filtering the solution, treating the washed material with an alkali sulphide to dissolve polysulphides and filtering the solution, digesting the compound with hydrochloric acid to remove acid-soluble impurities and copper sulphides, filtering the resulting solution, washing the relatively pure compound remaining as a residue, first with water, then an aqueous solution of a volatile alkali and finally distilled water until a substantially constant electrical conductivity is obtained for the filtrate.

2. The process of producing metallic disulphides, tellurides and selenides having solid lubricant properties from finely divided material containing said compounds which comprises applying to the material an organic solvent capable of dissolving grease, sulphur and flotation agents, removing the solvent with the dissolved impurities therein, applying to the partially purified material a reagent from the group consisting of hydrofluoric acid solutions and hydrogen fluoride to effect decomposition of any silicon compounds present, washing the fluoride treated material with water to dissolve substantially all the fluorine compound and filtering the solution, applying to the washed material an alkali sulphide solution to dissolve polysulphides and filtering the solution, heating the residual material at a temperature sufficient to convert any silicic acid to silica, applying to the material a reagent from the group consisting of hydrofluoric acid solutions and hydrogen fluoride, adding hydrochloric acid, washing the material with water and filtering the solution, further digesting the material with hydrochloric acid to remove acid-soluble impurities, filtering the solution, washing the material with water, then water carrying a volatile alkali and finally washing the relatively pure compound so produced with distilled water until a substantial constant electrical conductivity is obtained for the filtrate.

3. The process of producing metallic disulphides, selenides and tellurides having solid lubricant properties from finely divided material containing said compounds, comprising subjecting the finely divided material to an organic solvent

capable of dissolving grease and flotation agents, removing the solvent with the dissolved impurities therein, applying from 3 to 10 parts of 30% hydrofluoric acid to 3 parts of the partially purified compound and heating to dryness, repeating the treatment with the hydrofluoric acid so as to remove volatile impurities, treating each part of the dried material with from 2 to 4 parts by weight of 15% hydrochloric acid to remove acid soluble impurities, filtering and washing the material with water to remove the acid, applying an aqueous 20% alkali sulphide solution to dissolve metal polysulphides, filtering and washing the residual compound, and washing the compound in distilled water until a substantially constant electrical conductivity is obtained.

4. The process of producing metallic disulphides, selenides and tellurides having solid lubricant properties from finely divided material containing said compounds, comprising, finely dividing the material to 100 mesh size or finer, extracting the finely divided compound with an organic solvent capable of dissolving grease, flotation agents and sulphur, applying hydrofluoric acid to the partially purified material and heating the mixture to dryness, treating the dried material with hydrochloric acid to remove acid soluble impurities and filtering the acid, applying an aqueous alkali sulphide to the material to remove polysulphides, filtering the aqueous solution and washing the residue, applying water carrying a volatile alkali to the material, and washing the relatively pure compound in distilled water until a substantially constant electrical conductivity is obtained.

5. In the process of producing metallic disulphides, selenides and tellurides having solid lubricant properties from material containing said compounds which comprises, applying to the material organic solvents capable of dissolving grease and sulphur, removing the organic solvents with the impurities dissolved therein, applying to the material a reagent of the group consisting of hydrogen fluoride and solutions of hydrogen fluoride, removing hydrogen fluoride reaction products, washing the material with water and filtering, applying to the residue an aqueous solution of an alkali sulphide to remove polysulphides and filtering, digesting the material with hydrochloric acid and filtering and washing to produce a solid lubricant residue substantially free from abrasives.

6. In the process of producing metallic disulphides, selenides and tellurides having solid lubricant properties from material containing said compounds which comprises, applying to the material organic solvents capable of dissolving grease and sulphur, removing the organic solvents with the impurities dissolved therein, milling the material to an extremely fine powder, applying to the finely divided material a reagent of the group consisting of hydrogen fluoride and solutions of hydrogen fluoride, removing hydrogen fluoride reaction products, washing the material with water and filtering, applying to the residue an aqueous solution of an alkali sulphide to remove polysulphides and filtering, digesting the material with hydrochloric acid and filtering and washing to produce a solid lubricant residue substantially free from abrasives.