United States Patent Office 3,558,488 Patented Jan. 26, 1971

3,558,488

PROTECTIVE AND LUBRICATING COMPOSITION

Howard G. Mann, Seal Beach, Calif., assignor to North American Rockwell Corporation

No Drawing. Filed Mar. 7, 1968, Ser. No. 711,183
Int. Cl. C10m 5/02
U.S. Cl. 252—28 12 Claims

ABSTRACT OF THE DISCLOSURE

A composition comprising a mixture of boron nitride powder and colloidal silica in a substantially volatile carrier is described. This material is coated on a beryllium surface and the volatile carrier evaporated to leave a dry film lubricant. The dry film lubricant is particularly useful for high temperature forming of beryllium and in addition provides oxidation protection thereby obviating need for a protective environment and minimizing safety hazards.

BACKGROUND

Beryllium is a material having a high modulus of elasticity, high strength and low weight thereby affording a good strength to weight ratio and a good stiffness to weight ratio for use in advanced vehicles. Widespread use of this material, however, has been inhibited by problems in forming the material, not only due to its mechanical properties but also due to the toxicity of beryllium oxide which may form during working of the material. For this reason, the forming of beryllium has been conducted in protective atmospheres and in closed rooms having environmental control systems for minimizing the exposure of workers to toxic beryllium oxide. The difficulties and expense inherent in such procedures are apparent. In addition, in order to bend and stretch beryllium sheet it has been necessary to employ elevated temperatures to provide sufficient ductility in the beryllium. The use of elevated temperatures leads to increased oxidation of the beryllium with the resultant toxicity problems, and aggravates the problem of providing lubrication for the dies and forming tools employed with the beryllium.

SUMMARY OF THE INVENTION

Therefore in the practice of this invention, according to a preferred embodiment, there is provided a composition comprising boron nitride powder and colloidal silica in a substantially volatile carrier liquid for application to a beryllium surface for providing both lubrication and oxidation protection at elevated temperature.

Many of the attendant advantages of this invention will be readily appreciated as the same becomes better understood by reference to the following detailed description.

DESCRIPTION

In a typical process for forming or bending beryllium sheet, it is heated to about 1300° F. and drawn or bent between metal dies. In order to prevent seizing and galling on the dies a lubricant is employed. In order to prevent oxidation at the elevated temperatures some means must be provided for oxidation protection. Therefore, in order to avoid use of protective atmospheres a lubricant is employed which also provides a protective film on the surface as hereinafter described. In rolling of beryllium in a steel envelope as is employed in some manufacturing operations, a "release" layer is employed to prevent sticking of the beryllium to the envelope. The hereinafter described composition provides an excellent release layer for beryllium.

Thus in the practice of this invention according to a preferred embodiment there is provided a composition

in the form of a slurry comprising boron nitride powder in the range of from about 7 to 28 grams per liter of said composition and colloidal silica in the range of from about 0.9 to 3.6 grams per liter of said composition. It is preferred that the proportion of the colloidal silica in the composition be in the range of from about 2 to 1 to about 1 to 2 parts by volume relative to the boron nitride powder. The balance of the composition preferably comprises a substantially volatile liquid carrier such as water having a pH in the range of from about 7.5 to 9.0. In addition, certain additives may be employed in the carrier liquid as hereinafter described.

The range of boron nitride powder that is employed in the composition is preferably in the range of from about 7 to 28 grams per liter. Concomitantly, the colloidal silica is preferably in the range of from about 0.9 to 3.6 grams per liter and the proportion of silica and boron nitride is maintained in the range of from about 2 to 1 to about 1 to 2 parts by volume. The colloidal silica employed in the composition helps suspend the boron nitride powder by forming a colloid in the volatile liquid carrier. When the proportion of colloidal silica is less than about 1 part per 2 parts of boron nitride some settling of the boron nitride is observed and higher concentrations of colloidal silica are preferred in order to maintain the boron nitride in suspension without any requirement for agitation during use. Proportions of colloidal silica higher than about 2 parts by volume relative to 1 part of boron nitride powder somewhat reduce the lubricity of the composition and do not provide any noticeable advantage. It is therefore preferred that the proportion of colloidal silica be less than about 2 parts per 1 part of boron nitride.

With the volume proportion in mind, it is preferred that the boron nitride be present in excess of about 7 grams per liter of composition to afford adequate lubricity; likewise, it is preferred that the colloidal silica be present in a quantity greater than about 0.9 gram per liter since if lower concentrations of the powdered materials are present, unnecessarily large amounts of liquid carrier are handled and must be evaporated. Lower concentrations of colloidal silica than about 0.9 gram per liter also show some tendency toward settling of the composition in the liquid carrier in long storage. It is preferred that the boron nitride powder be present as less than about 28 grams per liter and that the colloidal silica be present in a proportion less than about 3.6 grams per liter. When higher quantities of powder are employed an adequate film is obtained, however, the composition is normally too thick or viscous for convenient application to form a surface film and thinning with additional liquid would be employed for use.

In the preferred composition the solid boron nitride powder and colloidal silica are suspended in a substantially volatile carrier liquid. It is preferred that the carrier liquid comprise principally water since other materials such as alcohol may cause flocculation of the colloidal silica. The suspension of colloidal silica in water has a relatively low pH even without additional additives as may be provided as hereinafter described, and in order to minimize the possibility of corrosion of the beryllium it is preferred to employ a volatile base to raise the pH of the carrier liquid to the range of from about 7.5 to 9.0. For this purpose it is found that ammonium hydroxide which is completely volatile is eminently satisfactory and it is preferred to employ ammonium hydroxide to bring the pH to the preferred range. In addition to being volatile, ammonium hydroxide is a sufficiently weak base to avoid flocculation of the suspension as would be the case if stronger base were used.

It is particularly preferred to employ a composition having about 19 grams of boron nitride powder and 2.5

grams of colloidal silica per liter of suspension since optimum properties are found at about this composition. The volume ratio of boron nitride powder and colloidal silica is about one to one with these weight proportions. At this preferred composition good suspension of the boron nitride is obtained, adequate lubricity is found after drying of the film on a beryllium surface, and excellent protection from oxidation is obtained. This material is also of a suitable consistency for ready application as a thin film to beryllium surfaces by brushing or spraying.

In addition to water and ammonium hydroxide in the substantially volatile carrier, certain additions may be made in order to provide a good suspension before evaporation of the carrier liquid and a good film after evaporation of the carrier liquid. Thus, for example, small quantities, normally less than about 0.2%, of conventional wetting agents may be employed in the carrier liquid in order to enhance the ability of the colloidal silica to provide a good suspension and to obtain good wetting of the boron nitride. Typical surface active or wetting agents compatible with the carrier liquid include many of the synthetic detergents of either anionic, cationic, or nonionic character, either alone or in combination.

In addition to wetting agents small quantities of phosphoric acid may be employed in the substantially volatile carrier liquid in order to leave some residue with the boron nitride and colloidal silica after evaporation. The phosphoric acid tends to bind the solid powders together and enhance the continuity of the film produced after evaporation of the carrier liquid. Phosphoric acid may also enhance the wettability of the boron nitride powder and can be added thereto before mixing with the colloidal silica. If phosphoric acid is employed in the composition it is preferred that the concentration be less than about 1.25 grams per liter since higher concentrations do not enhance the film forming characteristics and may interfere with suspension of the solid ingredients in the carrier liquid.

Of significance in the composition is the absence of flocculating agents which would cause settling of the solid ingredients in the substantially volatile carrier liquid. Thus it is of significance that the concentration of alcohol and other organic materials that might cause flocculation in the carrier liquid be held at a minimum. In the preparation of the composition it is convenient to add ammonium hydroxide to bring the pH to the phenolphthalein end point and a minimal quantity of phenolphthalein indicator solution is employed since this tends to introduce alcohol to the composition.

In addition, it is significant that there is no water glass or sodium silicate in the composition. Water glass tends to enhance the film forming characteristics of composition of this general nature, but introduces significant problems in removal of the film after forming is completed. A composition as herein described without water glass is readily removed from the beryllium surface after forming, by merely brushing or washing with water.

In order to employ the composition for forming of beryllium the described suspension is brushed or sprayed on a beryllium surface in order to form a continuous thin film. The substantially volatile carrier liquid is then evaporated from the thin film either at room temperature or with the assistance of slight warming of the part at a temperature lower than would cause bubbling of the carrier liquid. After drying out the film, the beryllium sheet can be heated to temperatures of at least 1300° F. and formed by bending or stretching with metal dies. This forming operation is conducted without addition of any other lubricants to either the beryllium or the die surfaces and surprisingly, it is found that the forming can be conducted in air since the described thin film prevents oxidation and the formation of toxic beryllium oxide. After the beryllium is formed to a desired shape the lubricating and protective material in the thin film is readily removed from the surface by brushing or washing with water.

As will be apparent to one skilled in the art, although the preferred composition has been described particularly for use with forming beryllium because of the added advantage of avoiding formation of toxic beryllium oxide, this composition is also useful as a forming or die lubricant and protective film for other metals formed at elevated temperatures.

As a modification of the above described composition, it is possible to employ bentonite for suspending boron nitride in lieu of colloidal silica. Another substitute material which can be used for suspending boron nitride comprises sodium carboxy methyl cellulose. If either of these materials or other suspending agents are employed, the weight quantities are appropriately adjusted to provide a volume ratio to the boron nitride substantially as set forth hereinabove. Although these materials can be employed as suspending agents it is particularly preferred to employ colloidal silica since this material is useful to higher temperature than either the bentonite or sodium carboxy methyl cellulose.

As a specific example of a composition useful in the practice of this invention a mixture of a suspension was made starting with about 38.5 grams of boron nitride powder in the form of about 110 grams of boron nitride S–1 paste obtained from Carborundum Company, about 5 grams of Cab-O-Sil, a colloidal silica available from Cabot Carbon Company and 750 milliliters of water. The S–1 paste is a thick, creamy paste of boron nitride powder in a low pH aqueous suspension. This is a convenient form of boron nitride powder since it is already in suspension, however, it is apparent that dry boron nitride powder can be wetted with water and suitable wetting agents as a starting material. The S–1 paste, Cab-O-Sil, water and ten milliliters of 14% ammonium hydroxide were mixed together by hand and additional water was added to make up about two liters of suspension. A small amount of phenolphthalein indicator solution was added and additional ammonium hydroxide was carefully added and stirred in to maintain the pH of the composition at the phenolphthalein end point.

The described suspension was brushed onto beryllium sheet and allowed to dry at room temperature. After drying the sheet was placed on a curved die in a furnace and heated to about 1300° F. in air. After reaching this temperature the sheet was bent by a second curved die to form one-half of a cylinder having a diameter of about one foot. During this operation no seizing or galling of the beryllium or steel dies was noted and the forming which was conducted in air yielded no detectable beryllium oxide. After the beryllium part had cooled to room temperature the film of lubricant and protective coating was removed by gentle scrubbing with a brush and distilled water.

As another example of compositions useful in practice of this invention dry boron nitride powder was mixed with water to form a thick, creamy paste. Wetting of the powder was enhanced with a small amount of Igepal 630, a nonionic surfactant available from General Aniline and Film Corporation. It will be apparent that other wetting agents will operate as effectively for dispersing and suspending boron nitride. The paste forms a good foundation for addition of colloidal silica as provided in a preferred embodiment. The colloidal silica is mixed into the boron nitride paste with additional water as required to maintain the consistency of the paste, and after all is wetted, additional water is added and agitated to obtain a final suspension. At this point the water base carrier liquid is adjusted to the phenolphthalein end point with dilute ammonium hydroxide.

A composition made in this manner having one gram of colloidal silica and seven grams of boron nitride powder per liter of suspension give a relatively thin suspension

particularly good for spray application. Multiple thin coats, with drying between, assures a continuous film that performs well in beryllium forming. Compositions having 3.0 grams of colloidal silica and 28 grams boron nitride per liter of suspension, and 3.5 grams of colloidal silica and 15 grams boron nitride powder per liter of suspension are relatively thick and well suited for application with a stiff brush or knife to assure a thick surface coat that performs in substantially the same manner as pointed out hereinabove.

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically described.

What is claimed is:

1. A composition for forming a coating on beryllium to protect the beryllium from the corrosive action of the atmosphere and to protect the workman from the toxic effects of beryllium dust when the beryllium is being formed at high temperatures, said composition comprising:

from about 7 to 28 grams of boron nitride powder;

from about 0.9 to 3.6 grams of colloidal silica, the proportion of said silica to said boron nitride powder being in the range of from about 2:1 to about 1:2 parts by volume; and

a sufficient amount of a volatile carrier liquid to make one liter of the composition, said liquid being inorganic and having a pH in the range of from about 7.5 to 9.0.

2. A composition as defined in claim 1 wherein said carrier is water.

3. A composition as defined in claim 2 further comprising:

less than about 1.25 grams phosphoric acid; and

sufficient ammonium hydroxide to maintain a pH in the range of from about 7.5 to 9.0.

4. A composition as defined in claim 1 wherein the boron nitride is present as about 19 grams.

5. A composition as defined in claim 4 wherein the colloidal silica is present as about 2.5 grams.

6. A method of fabricating beryllium comprising:

coating a surface of the beryllium with a composition consisting of boron nitride powder, colloidal silica, and a volatile inorganic liquid carrier having a pH in the range of from about 7.5 to 9.0 and wherein the volume proportion of boron nitride to silica is in the ratio of from about 1:2 to about 2:1;

evaporating the volatile liquid; and

deforming the beryllium at elevated temperature.

7. A method as defined in claim 6 wherein the volatile inorganic liquid is a mixture of water and ammonium hydroxide.

8. A method as defined in claim 6 wherein the boron nitride is present in the range of about 7 to 28 grams per liter, the colloidal silica is present in the range of from about 0.9 to 3.6 grams per liter.

9. A method as defined in claim 8 wherein the volatile carrier liquid comprises a water base solution having a pH in the range of from about 7.5 to 9.0.

10. A method as defined in claim 9 wherein the volume proportion of boron nitride and colloidal silica is in the ratio of from about 1:2 to about 2:1.

11. A dry film lubricant forming a coating on beryllium that is to be formed at high temperatures so that the beryllium is protected from the corrosive action of the atmosphere and the workmen are protected from the toxic effects of beryllium dust, said lubricant comprising a uniformly distributed coating of a uniform mixture consisting essentially of boron nitride and colloidal silica in the proportion of from about one to two parts by volume of said boron nitride and from about one to two parts by volume of said silica wherein said coating is formed as the residue of a vaporized suspension.

12. An article comprising a beryllium part having a surface subject to oxidation and a dry film lubricant thereon as defined in claim 11.

References Cited

UNITED STATES PATENTS

2,960,466	11/1960	Saunders	252—25
2,968,999	1/1961	Breton	252—28
3,258,947	7/1966	Wehmeyer	252—25
3,371,038	2/1968	Wieser et al.	252—28
3,454,495	7/1969	Schneider	252—28
3,464,854	9/1969	Bolger	252—25

DANIEL E. WYMAN, Primary Examiner

I. VAUGHN, Assistant Examiner

U.S. Cl. X.R.

72—42; 117—135.1; 252—397