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ELECTROPHORETIC METHOD OF APPLYING A LOW FRICTION COATING

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Our invention relates to lubricated or low friction metal structures and methods for producing the same.

Certain inorganic compounds, i. e., the sulphides, disulphides, selenides and tellurides of such metals as molybdenum, tungsten, titanium and uranium are characterized by a laminated or plate-like crystal structure in which the metallic atoms are attached to each other in a single common plane while the non-metallic atoms are attached to the metallic atoms to form layers on both sides of this plane. The non-metallic atoms in each of the several crystals thus formed have very little attraction for each other so that these crystals will slip readily with response to each other under the action of low shearing forces. Moreover, the non-metallic atoms have an affinity for adjacent metal surfaces so that the crystals attached to such surfaces will exhibit very strong resistance to the action of forces normal to the direction of shear. Consequently, these compounds have excellent lubricating properties and also have excellent anti-seizing properties. The term "Laminated Metallic Lubricating Agents" has been selected to denote compounds of this class.

In application S. N. 404,796, filed January 18, 1954, by F. Fahnoe and J. J. Shyne, a process is disclosed for depositing a solid lubricant coating on the surface of a base member. In this method a mixture of reducible metallic compounds and laminated metallic lubricating agents are electrophoretically codeposited on the surface of a base metallic member and the reducible compound is subsequently reduced to metal to form a sintered metal matrix which is bonded to the base member and which in turn entraps and bonds the lubricating agent or agents to the structure to form a lubricant coating. Metals which are capable of forming such a bonding matrix as disclosed in said application include copper, tin, zinc, chromium, nickel and silver. The relative proportions of the reducible compounds and lubricating agents are such that the lubricant adheres uniformly to the structure until the structure is subjected to a metal-working operation. During this operation the coating, while supplying the desired amount of lubricating, is progressively worn away or stripped from the structure. The term "Sacrificial Layer" has been selected to denote this type of coating.

In another application S. N. 402,402, filed January 5, 1954, by F. Fahnoe and J. J. Shyne we disclosed a process for depositing a low friction coating on the surface of a base member. This process is similar to that of S. N. 404,796 in that a mixture of reducible metal compounds and friction modifying agents having low coefficients of friction are electrophoretically codeposited on the surface of a base metal member and the reducible compound reduced to metal to bond the friction modifying agents to the base member. Metals which are capable of forming a bonding matrix as disclosed in said patent application include nickel, copper, iron, chromium and alloys as well as tin, lead, silver and alloys thereof. (These low friction modifying agents include as a sub-class all laminated metallic lubricating agents and further include substances, for example, graphite, which have low friction properties and which are not included in this sub-class). In this process, however, the low friction coating thus formed is permanent and is not appreciably worn

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away or stripped from the structure during a metal-working operation.

In order to form a sacrificial layer the percentage content by weight of reducible metal compound must fall within the range 70%—80%; in order to form a permanent coating this percentage content must fall within the range 80%—95%.

In our work on both of these processes we have discovered that when electrophoretically deposited coatings composed of reducible metallic oxides and laminated metallic lubricating agents of the sulphide or disulphide type are deposited on a metal base member or metal substrate, and when the subsequent reduction operation is carried out in a hydrogen atmosphere at high temperatures, both the compound and a portion of the laminated metallic lubricating agent used are also reduced, and the lubricating or low friction properties of the resultant coating, while still evident, are reduced in effectiveness.

Accordingly, it is an object of the present invention to provide improved processes of the character indicated in which the lubricating properties are not impaired under the above conditions.

Still a further object is to provide an improved process of the character indicated wherein both the reducible metal compound and the laminated metallic lubricating agents are of the sulphide or disulphide type.

Still another object is to provide an improved process of the character indicated wherein the difference in chemical activity between a reducible metallic sulphide or disulphide and that of laminated metallic lubricating agents of the sulphide or disulphide type are made use of to reduce the compound to metal while the lubricating agent remains essentially unaffected.

Yet a further object is to provide an improved process of the character indicated wherein the reducible metallic compounds are mixtures of oxides and sulphides or disulphides and the reaction is carried out in an inert atmosphere.

In one form of our invention a mixture of easily reducible metallic compounds of the sulphide or disulphide type and laminated metallic lubricating agents of the sulphide or disulphide type are electrophoretically codeposited on the surface of a base metal. Under the conditions indicated below, the chemical activity of the metallic compound selected substantially exceeds the activity of the lubricating agent. Consequently, when the coated member is heated in a hydrogen atmosphere, hydrogen sulphide gas is formed, and the metallic compound is reduced to metal. The presence of the hydrogen sulphide gas prevents any appreciable reduction of the laminated lubricating agent to its metal. Consequently, the reduced metallic compound forms a sintered metal matrix which is bonded to the base member and which in turn entraps and bonds the unreduced lubricating agent particles to the member to form the desired lubricant coating.

In another form of our invention, a mixture of metallic oxides and metallic sulphides or disulphides is electrophoretically codeposited with at least one laminated metallic lubricating agent of the sulphide or disulphide type on the surface of a base metal or substrate. Under the conditions indicated below, the chemical activity of these materials is such that the metallic oxides and sulphides or disulphides preferentially react with each other rather than with the lubricating agent. The coated member is then heated in an inert atmosphere. The lubricating agent is not reduced but both the metallic oxide and the metallic sulphide or disulphide used are reduced to metal, and sulphur dioxide gas is formed. The metal which is formed by interaction between the metallic sulphide or disulphide and the metallic oxide, as in the

structures and processes referred to above, produces a sintered metal matrix which is bonded to the base member and which in turn entraps and bonds the unreduced lubricating agent particles to the member to form the desired lubricant coating.

Electrophoretic deposition occurs when an electrostatic field is established between two electrodes immersed within a colloidal or gross dispersion of charged particles, thus causing migration of the suspended particles toward one of the electrodes, and producing a deposit of an adherent coating on that electrode. Exceptional uniformity of coating thickness and compactness (with a relatively high coating density) are obtained as compared with dipping, spraying, brushing and other more conventional methods of application. Irregularly shaped objects can be coated with excellent uniformity and reproducibility of coating. A complete description of the electrophoretic process will be found in copending application S. N. 388,119, filed October 26, 1953, by F. Fahnoe and J. J. Shyne.

The following examples set forth certain well-defined instances of the application of this invention. They are, however, not to be considered as limitations thereof since many modifications can be made without departing from the spirit and scope of this invention.

Example I

A coating .005" thick containing 77% by weight of copper(ous) sulphide particles and 22% by weight of molybdenum disulphide particles was electrophoretically codeposited out of organic media on a stainless steel sheet in the manner outlined in the above-mentioned application S. N. 404,796.

The sheet was then fired in a hydrogen atmosphere at a temperature of 1400° F. for a period of 15 seconds. The formation of hydrogen sulphide gas was observed during this period. Subsequent cross-sectional analysis established that the copper(ous) sulphide had been reduced to copper in the form of a sintered matrix bonded by codiffusion to the surface of the sheet. The molybdenum disulphide particles substantially unaltered were found to be entrapped within the pores of the matrix.

Example II

A coating .010" thick containing 22% by weight of molybdenum disulphide particles and 77% by weight of stoichiometric quantities of copper(ous) oxide and copper(ous) sulphide were electrolytically deposited on a stainless steel substrate in the manner outlined as before. The sheet was then fired in a helium atmosphere at a temperature of 1400° F. for a period of 30 seconds. The formation of sulphur dioxide gas was observed during this period. Subsequent cross-sectional analysis established that both the copper oxide and copper sulphide had been reduced to copper in the form of a sintered matrix bonded by codiffusion to the surface of the sheet. The molybdenum disulphide particles were found to be entrapped within the pores of the copper matrix.

While we have shown, described and pointed out fundamental novel features of the invention as applied to preferred embodiments, it will be understood that various omissions, substitutions and changes in the form and details from the spirit of the invention. It is our intention, therefore, to be limited only as indicated by the scope of the claims which follow.

We claim:

1. A method of applying a low friction coating to the surface of a metal substrate which comprises the steps of electrophoretically depositing out of a liquid medium upon the surface of said substrate a coating formed from a mixture of between 30%-5% by weight of at least one laminated metallic lubricating agent selected from the class consisting of sulfides and disulfides of molybdenum, tungsten, titanium and uranium and between 70%-95% by weight of at least one reducible metallic compound

other than said metallic lubricating agent selected from the class consisting of sulfides and disulfides, said compound being reducible to form a metallic matrix bonded to said metal substrate at a temperature at which the metallic lubricating agent does not undergo substantial reduction; and heating said coated metal substrate in a reducing atmosphere at a temperature high enough to reduce said metallic compound to the metal but below the temperature at which substantial decomposition of said lubricating agent takes place until said metallic compound is reduced to metal thereby to form a metallic matrix which is bonded to said surface of said metal substrate and which entraps and bonds said solid lubricant to said substrate.

2. The method as set forth in claim 1 wherein the metallic compound is copper sulfide.

3. The method of applying a low friction coating to the surface of a metal substrate which comprises the steps of electrophoretically depositing out of a liquid medium upon the surface of said substrate a coating formed from a mixture of between 30%-5% by weight of at least one laminated metallic lubricating agent selected from the class consisting of sulfides and disulfides of molybdenum, tungsten, titanium and uranium, and between 70%-95% by weight of two reducible metallic compounds other than the metallic lubricating agent, one of said compounds being an oxide and the other being selected from the class consisting of sulfides and disulfides, said compounds being present in stoichiometric quantities to form the corresponding metal and sulphur dioxide and being reducible in the presence of each other to form a metallic matrix bonded to said metal substrate at temperatures at which the metallic lubricating agent does not undergo substantial reduction; and heating said coated metal substrate in an inert atmosphere at a temperature high enough to decompose said metallic compounds to the metals and sulphur dioxide but below the temperature at which a substantial decomposition of said lubricating agent takes place until sulphur dioxide gas is formed and both of said compounds are reduced to metal, thereby to form a metallic matrix which is bonded to said surface of said metal substrate and which entraps and bonds said lubricant to said substrate.

4. The method as set forth in claim 3 wherein said metallic compounds are both compounds of the same metal.

5. The method set forth in claim 4 wherein said same metal is copper.

6. The method of applying a low friction coating to the surface of a metal which comprises the steps of electrophoretically depositing out of liquid media upon the surface of said metal a coating formed from a mixture of between 70%-95% by weight of cuprous oxide and cuprous sulfide present in stoichiometric quantities to form metallic copper and sulphur dioxide and between 30%-5% by weight of molybdenum disulfide; and heating said coated metal in an inert atmosphere until sulphur dioxide gas is formed and both of said cuprous compounds are reduced to metallic copper in the form of a matrix bonded to said metal, said molybdenum disulfide being substantially unaffected by said reduction whereby said molybdenum disulfide is entrapped within the pores of said matrix.

7. The method as set forth in claim 6 wherein said atmosphere is a helium atmosphere.

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