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MOLYBDATE COATINGS ON ALUMINUM AND ALUMINUM BASE ALLOYS

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This application is a continuation-in-part of application Serial No. 236,682, filed November 8, 1962, and now abandoned.

This invention relates to the protection of the surfaces of aluminum and aluminum base alloys against corrosion. More particularly, the invention concerns the protection of particles and sheet or strip by treatment of the surfaces thereof with alkali metal molybdate solutions at elevated temperature and pressure.

It is known that aluminum and aluminum base alloys are subject to corrosion by brines and other corrosive agents. Where small generally spherical particles of aluminum or aluminum base alloys are employed as propping agents for creating or enlarging well fractures, it has been observed that the life of such agents is sometimes shortened by corrosion induced by conditions of moisture within the well, and/or by the direct action of oil well brines and other corrosive compositions encountered in subsurface work. Such aluminum particles are of a size lying generally between about 0.03 and about 0.25 inch in diameter, thus possessing a high surface area which makes them particularly susceptible to corrosion. In fracturing operations, they are suspended in hydraulic fracture liquids which are pumped into the well to create or enlarge flow channels extending from the well bore into contiguous formations. Such particles, when unprotected, may under some conditions corrode to form a solid mass, resulting in expense of removal and loss of material.

In accordance with the present invention there is provided a novel method of treatment of the surfaces of aluminum and aluminum base alloys, both in the form of particles and of sheets or strip, as well as novel treated materials, whereby effective protection against corrosion of these materials can be obtained for extended periods, thereby greatly increasing the useful life of these materials.

It has been known to treat aluminum surfaces in general with aqueous solutions of sodium or potassium molybdate by immersion for relatively short periods (e.g., 5 to 60 minutes), at relatively low temperatures (e.g., room temperature up to the boiling point of a saline water solution), and at relatively low pressures (e.g., atmospheric pressure or up to about 15 p.s.i. above atmospheric pressure), using concentrations of about 0.5% to about 6% of the molybdate by weight. Such treatments provide a molybdate coating on the aluminum surface which is relatively thin, porous and low in abrasion resistance, and the protection provided by such conventional molybdate coatings on aluminum surfaces would not be adequate for protection of aluminum particles used as propping agents in oil wells or the like having the corrosion-inducing conditions sometimes encountered in such wells.

In accordance with the present invention, however, it has been found that aluminum and aluminum base alloy surfaces can be successfully treated with aqueous solutions of alkali metal molybdates under different conditions which will produce a coating on the surfaces which is not only thicker but also substantially nonporous and more abrasion resistant than the coating produced with molybdate using conventional conditions.

For the purposes of the invention, the alkali metal is preferably sodium or potassium, but may include other alkali metals such as lithium, caesium and rubidium.

The concentration of the alkali metal molybdate solution should be at least about 4% by weight in order to provide enough molybdate in a conveniently limited amount of solution, and can be increased to any amount, although 5% by weight is generally preferred.

Treatment is carried out, in accordance with the invention, under pressure in a suitable pressure vessel, such as an autoclave, so as to maintain the treating solution and the metal surface being treated at a temperature between about 325° F. and about 400° F., preferably about 350° F. While the temperature can be raised to a figure higher than indicated, about 400° F. represents a practical upper limit in order to avoid converting the metal surface to oxide by action of hot water, to an undesirable extent.

The pressure may be varied according to known practice by the increase of temperature, or it may be raised further by the introduction of carbon dioxide or other inert gas. Some pressure may also be achieved by the presence of gas generated in the course of the treatment. For the production of a good coating, the pressure will be above about 275 pounds per square inch, and about 300 p.s.i. is preferred, but there is no upper limit.

The period of treatment will very somewhat according to the size of the surface of the aluminum or aluminum base alloy, but should in general range from about 2 to about 24 hours. For the treatment of propping agent a minimum of about 16 hours at 350° F. is preferred, but this may be shortened to 6 hours in presence of carbon dioxide under pressure.

While it is desired not to be bound by any particular theory, it is believed that under the conditions of elevated temperature and pressure described above, formation takes place on the metal surface of an oxide coating which consists essentially of the alpha phase of aluminum oxide monohydrate $Al_2O_3.H_2O$, known as boehmite. This formation is confirmed by X-ray diffraction studies, which also reveal that using the conventional low temperature molybdate treatment, an oxide coating is produced having the form of an alpha phase of aluminum oxide trihydrate $Al_2O_3.3H_2O$ (gibbsite). The monohydrate coating is not only thicker than the trihydrate coating, but it differs in crystal structure. Further, formation of the monohydrate coating appears to be accompanied by an adsorption phenomenon whereby alkali metal molybdate is adsorbed and remains in anhydrous form in the oxide coating. This is demonstrated by the observation that the adsorbed alkali metal molybdate cannot be removed from the oxide by leaching with water, although it is ordinarily quite soluble. From another point of view, the oxide-molybdate coating formed at elevated temperature and pressure closes cavities on the metal surface, and because of its greater thickness as well, affords increased protection to the metal against corrosive influences.

Aluminum and aluminum base alloy particles having the improved coating produced in accordance with the method of the invention can be used successfully as propping agents in oil wells having severe conditions. The treatment process is also applicable to the protection of aluminum and aluminum base alloys in particle form intended for other purposes, for example, protection is afforded to such particles against corrosive tap water.

The treatment of the invention is also suitable for the protection of aluminum and aluminum base alloys in the form of sheet and strip, and here a much shorter treatment time is sufficient, for example as little as two hours.

The presence of carbon dioxide, which may be added to the autoclave in the form of Dry Ice (solid CO_2), provides increased pressure, and considerably shortens the time of treatment. Thus, a treatment time of 16 hours at 350° C. for aluminum particles can be shortened to 6 hours by adding carbon dioxide in the form of Dry Ice to the autoclave, which provides a rapid build-up of pressure to the required value.

The practice of the method of the invention is illustrated by the following examples:

Example 1

10 lbs. of aluminum shot having a generally spherical shape, and averaging about 0.1 inch in diameter, were immersed in a 5% aqueous solution of sodium molybdate in an autoclave and reacted for 24 hours under pressure sufficient to maintain the temperature of the mixture in the autoclave at about 350° F. at the end of the treatment, the aluminum shot was removed and treated with a simulated well brine solution at a temperature of 300° F. for 28 days. No perceptible corrosion of the surfaces of the particles was observed.

Example 2

When the treatment and test of Example 1 is repeated except for substitution of potassium molybdate for sodium molybdate, substantially the same results are obtainable.

Example 3

The treatment described in Example 1 was carried out under a pressure of 275 p.s.i. obtained by adding Dry Ice to the autoclave at 350° F. for a period of six hours.

Example 4

A sheet of alloy 5052 having a thickness of 0.008 inch was treated for 2 hours as described in Example 3.

While present preferred embodiments of the invention, and methods of practicing the same, have been illustrated and described, it will be recognized that the invention may be otherwise variously embodied and practiced within the scope of the following claims.

What is claimed is:

1. Method for protecting the surface of aluminum and aluminum base alloys against corrosion which comprises immersing said surface in an aqueous solution consisting essentially of water and at least about 4% by weight of an alkali metal molybdate at a temperature between about 325° and about 400° F. for a period of at least 2 hours under pressure sufficient to maintain the solution and the metal surface at said temperature.

2. Method for protecting the surface of aluminum and aluminum base alloys against corrosion which comprises immersing said surface in an aqueous solution consisting essentially of water at least about 4% by weight of an alkali metal molybdate at a temperature between about 325° and about 400° F. for a period of at least 2 hours at a pressure of at least 275 pounds per square inch.

3. Method for protecting the surface of aluminum and aluminum base alloys against corrosion which comprises immersing said surface in an aqueous solution consisting essentially of water and at least about 4% by weight of an alkali metal molybdate at a temperature between about 325° and about 400° F. for a period of at least two hours in presence of carbon dioxide gas under pressure sufficient to maintain the solution and the metal surface at said temperature.

4. Method for protecting particles of aluminum and aluminum base alloys for propping fractured subsurface well formations against corrosion by well brines, which comprises immersing said particles in an aqueous solution consisting essentially of water and at least about 4% by weight of an alkali metal molybdate at a temperature between about 325° and about 400° F. for a period of at least 16 hours under pressure sufficient to maintain the solution and the metal surface at said temperature.

5. Method for protecting particles of aluminum and aluminum base alloys for propping fractured subsurface well formations against corrosion by well brines, which comprises immersing said particles in an aqueous solution consisting essentially of water and at least about 4% by weight of an alkali metal molybdate at a temperature between about 325° and about 400° F. for a period of at least 16 hours under pressure of at least 275 pounds per square inch.

6. Method for protecting particles of aluminum and aluminum base alloys for propping fractured subsurface well formations against corrosion by well brines, which comprises immersing said particles in an aqueous solution consisting essentially of water and at least about 4% by weight of sodium molybdate at a temperature between about 325° and about 400° F. for a period of at least 16 hours under pressure of at least 275 pounds per square inch.

7. Method for protecting particles of aluminum and aluminum base alloys for propping fractured subsurface well formations against corrosion by well brines, which comprises immersing said particles in an aqueous solution consisting essentially of water and at least about 4% by weight of potassium molybdate at a temperature between abuot 325° and about 400° F. for a period of at least 16 hours under pressure of at least 275 pounds per square inch.

8. Method for protecting particles of aluminum and aluminum base alloys for propping fractured subsurface well formations against corrosion by well brines, which comprises immersing said particles in an aqueous solution consisting essentially of water and about 5% by weight of sodium molybdate at a temperature of about 350° F. for a period of at least 16 hours under pressure sufficient to maintain said temperature.

9. Method for protecting particles of aluminum and aluminum base alloys for propping fractured subsurface well formations against corrosion by well brines, which comprises immersing said particles in an aqueous solution consisting essentially of water and about 5% by weight of potassium molybdate at a temperature of about 350° F. for a period of at least 16 hours under pressure sufficient to maintain said temperature.

10. The method of claim 1 in which the aluminum and aluminum base alloy is in the form of sheet.

11. Method for protecting particles of aluminum and aluminum base alloys against corrosion which comprises immersing said particles in an aqueous solution consisting essentially of water and about 5% by weight of sodium molybdate at a temperature of about 350° F. and a pressure of about 275 pounds per sq. inch in presence of carbon dioxide gas for about 6 hours.

12. Generally spherical particles of aluminum and aluminum base alloys adapted for propping fractured subsurface well formation and having their surfaces treated in accordance with the method of claim 4.

13. Aluminum and aluminum base alloys having their surfaces treated in accordance with the method of claim 1.

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