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METHOD OF TREATMENT OF SURFACES, ESPECIALLY METALLIC, AND THE PARTS TREATED BY THIS METHOD

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ABSTRACT OF THE DISCLOSURE

A method of treatment of surfaces, especially metallic surfaces, which is intended to improve their qualities of resistance to friction and wear, said method consisting of subjecting the surface to electrolysis in an aqueous solution of a salt or a mixture of salts, such as the thio or seleno-molybdates, the thio or seleno-tungstates, the thio or seleno niobiates, or of one or more compounds having similar properties, or of a mixture of basic compounds adapted to form said salts in situ.

The present invention relates to a method of treatment of surfaces, in particular metallic surfaces, intended to improve their properties of resistance to friction and to wear.

The lubricating properties of lamellar compounds with a foliated structure are already known, such as the disulphides of molybdenum MoS_2, tungsten WS_2, niobium NbS_2, the diselenides of molybdenum $MoSe_2$, tungsten WSe_2, niobium $NbSe_2$. However, the methods at present known for more or less attaching films of such solid lubricants to mechanical parts are definitely inadequate, and such films do not generally exceed the behaviour in time necessary for a simple running-in.

The present invention has for its object a method providing a remarkable attachment on a metal surface of a thin film comprising a suitable proportion of lamellar lubricants bound together by a sulphide or a selenide.

The method according to the invention consists of subjecting the said metallic surface to electrolysis in an appropriate aqueous solution.

It will of course be understood that this metallic surface can equally well form part of a solid piece of metal or of a non-metallic part, plastic for example, previously coated by any means with a superficial metallic coating.

The present invention has also for its object the mechanical parts obtained by this method, which are characterized by friction and wearing qualities having a lasting power unequaled at the present time.

In the method according to the invention, the part to be treated is immersed in an aqueous solution of a salt or of a mixture of alkali or alkaline-earth salts such as thio or selenio-molybdates, thio or selenio-tungstates, thio or selenio-niobiates, etc. According to the nature of the substance chosen, the lamellar lubricant incorporated in the film obtained by the method according to the invention is respectively either a disulphide of molybdenum or a diselenide of molybdenum, or a disulphide of tungsten, or a diselenide of tungsten, or a disulphide of niobium, or a diselenide of niobium.

It will be understood that the aqueous solution to be electrolyzed according to the invention with a base of one or more of the substances defined above, can be obtained either by directly dissolving the substance or substances, or, as will furthermore be described in a particular example referred to below, by reconstitution in solution of the desired substance or substances.

The part to be treated is preferably connected to the

cathode, that is to say to the negative pole of a direct or rectified source of current, the anode being formed by a piece of conducting material. The current density is comprised between 2.5 a./sq. dm. and 75 a./sq. dm.

By an electrolysis having a duration comprised between 1 and 60 minutes in a bath according to the invention, there is obtained on the surface of the part treated a layer having a thickness comprised between 0.1 and 9 microns, perfectly adherent to the base metal, and which gives the parts properties of friction and wear having a duration heretofore unknown.

Upon examination, these layers are constituted, inter alia, by the solid lubricant corresponding to the electrolyzed substance or substances and the metallic sulphides or selenides corresponding to the base metal.

A few non-restrictive examples of the treatments according to the invention are given below.

EXAMPLE 1

200 grams of thio-molybdate of ammonium having the formula $(NH_4)_2—MoS_4$ dissolved in 800 cc. of water constitute the bath, the temperature of which is 35° C.

The part to be treated is a Faville-Levally test sample for friction, of 16 NC 6 steel, case-hardened, tempered and ground, having the dimensions 6.5 mm. in diameter and 40 mm. in height.

It is connected to the negative pole of a direct-current source.

The anode is constituted by a cylinder concentric with the cathode, having a height of 40 mm. and an internal diameter of 50 mm.

The parameters of the electrolysis are as follows:

The current density is 6 a./sq. dm.
The potential difference between anode and cathode is 7.5 v.
The period of the treatment is 15 minutes.

After this electrolytic treatment, the part is removed from the bath, washed in pure water for 24 hours and brushed with a metal brush.

After treatment, the part according to the invention is covered with a fine grey film having a thickness of 2 microns. It is then rotated between two jaws, in conformity with those of the Faville-Levally test, of 16 NC 6 case-hardened and tempered, untreated.

The test on the Faville-Levally machine lasted 6 minutes with a load of 15,000 N for a speed of rotation of the sample of 350 r.p.m. with an average coefficient of friction in the dry state, of 0.04.

By way of comparison, a test sample of 16 NC 6 case-hardened, tempered and coated with molybdenum disulphide by methods at present known, washed for two hours and then brushed with a metal brush, seizes under a load of 4,000 N after a few seconds of test.

EXAMPLE 2

The solution following the present example of the invention is obtained, not by starting with the basic substance, but by a suitable mixture of various substances capable of resulting in the re-constitution of the substance of Example 1.

150 grams of molybdenum oxide MoO_3 are dissolved in 700 cc. of ammonia NH_4OH at 20%.

A mixture of this kind has a pH value of 10.3 at a temperature of 35° C.

There are added to this solution 1600 cc. of ammonium sulphide $(NH_4)_2S$ at 20%; the pH value remains comprised between 10.1 and 10.5.

When a certain number of electrolyses are effected corresponding to 4 sq. dm. of surface treated for such a bath, the pH value falls to 9.1 and the pH value is re-

adjusted by adding the mixture of molybdenum oxide and ammonia so as to maintain it at the value of 10.5.

The friction results of parts treated in the solution specified above, with the pH value maintained at 10.5, with the same electrolytic parameters as those given in Example 1, are identical with those given previously.

EXAMPLE 3

The bath and the electrolytic parameters are identical with those of Example 2. The part to be treated is a Faville-Levally test sample of stainless steel Z3 CN 18–8. The temperature of the bath is 53° C. The electrolytic parameters are 20 minutes—10 a./sq. dm.

After treatment, the sample is washed with running water for two hours and then brushed with a metal brush. The duration of the Faville-Levally test of such a treated sample, rotating between two jaws, also of Z3 CN 18–8 steel is 1 minute 30 seconds under a load of 8,000 N, with a coefficient of friction which does not exceed 0.05.

EXAMPLE 4

The bath is composed at the start of 100 grams of tungsten oxide WO_3 and 700 cc. of 20% ammonia NH_4OH. After dissolving the oxide in the ammonia, sulphuretted hydrogen H_2S is bubbled into the bath in order to produce ammonium thio-tungstate.

The temperature of the solution is comprised between 25 and 70° C.; the pH value of the solution at a temperature of 40° C. is comprised between 7 and 8.5. The electrolytic parameters are as follows: 50 a./sq. dm. for 30 minutes.

If a Faville-Levally test sample of 16 NC–6 steel, case-hardened and tempered is treated under these conditions, it is found, after treatment and after washing with running water for 2 hours and brushing with a metal brush, that there remains on the part a coating of 1 micron in thickness, this coating being perfectly adherent to the metal.

The Faville friction test of a test sample of this kind of 16 NC 6, case-hardened and tempered, treated as described above, rotating between jaws of 16 NC 6 case-hardened and tempered but not treated, has a duration of 2 minutes at a load of 20,000 daN and a speed of slip of 0.075 m./sec. with a coefficient of friction which does not exceed 0.06.

EXAMPLE 5

The bath has a composition identical with that given in Example 2. Its temperature is 43° C. and its pH value at that temperature is 10.8.

The test sample to be treated is an annealed alloy of titanium TA 6V; the anode is identical with that given in Example 1. The electrolytic parameters are: 10 minutes–10 a./sq. dm.

If after this treatment the test sample is washed in running water for 2 hours and brushed with a metal brush, and if this test sample is subjected to the Faville-Levally test between two jaws cut to a V, of titanium TA 6V annealed but not treated, the duration of the test is 2 minutes at a load of 2,500 N with an average coefficient of friction which does not exceed 0.05.

It will of course be understood that the examples described above are given without any restrictive sense, and that any treatment which satisfies the conditions given in the definition of the invention will form part of the said invention.

What we claim is:

1. A method of treating an electrically conductive surface to improve the resistance to friction and wear, said method comprising subjecting said surface to electrolysis as the cathode in an aqueous solution of a salt selected from the group consisting of the thio-molybdates, thio-tungstates, and thio-niobiates of ammonium.

2. A method of treating an electrically conductive surface to improve the resistance to friction and wear, said method comprising subjecting said surface to electrolysis as the cathode in an aqueous solution of a salt selected from the group consisting of the seleno-molybdates, seleno-tungstates, and seleno-niobiates of ammonium.

3. A method as claimed in claim 1, in which the current density employed for said electrolysis is between 2.5 and 75 a./sq. dm.

4. A method as claimed in claim 1, in which the duration of said electrolysis is between 1 and 60 minutes.

5. A part treated by the method of claim 1.

6. A part treated by the method of claim 2.

References Cited

UNITED STATES PATENTS

2,266,377	12/1941	Neely et al.	204—56
2,512,141	6/1950	Ma et al.	204—56X
3,375,180	3/1968	Heinen et al.	204—61
3,438,789	4/1969	Weiss et al.	204—56X

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