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PROCESS FOR SURFACE TREATMENT OF LEAD AND ITS ALLOYS

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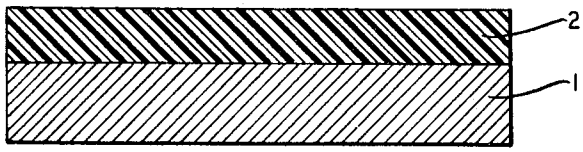

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PROCESS FOR SURFACE TREATMENT OF LEAD AND ITS ALLOYS

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ABSTRACT OF THE DISCLOSURE

Passing a current through the surface of lead and its alloys as a cathode while the surface is in contact with an electrolytic solution containing chromate ions and fluoride ions results in improved adhesion subsequently formed between the metal and organic materials.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to surface treatment of lead and its alloys by cathodic treatment in a chromate ion and fluoride ion-containing solution in order to improve adhesion between such surfaces and organic materials and also relates to the joined product.

Description of the prior art

Joining lead and its alloys to organic materials is desirable in many cases, as for example, in the formation of laminates to be used in the manufacture of coaxial cable. Corrosion products ordinarily present on the surface of the metal interfere with such joining and have in the past been removed both chemically, as for example, by fluoroboric acid treatment, and mechanically, as for example, by wire brush abrading.

Mechanical abrasion is generally undesirable because it is wasteful of the soft lead surface and produces a rough texture which gives rise to localized stresses in subsequently formed joints when placed under stress.

Chemical cleaning is less damaging to the surface of the metal. However, the clean surface is subject to further corrosion and it is often impractical to form joints with other materials before substantial reformation of the corrosion products has taken place. In addition, joints subsequently formed, even with a substantially clean metal surface, often degrade with time resulting in eventual joint failures. Depending on the temperature, stress and humidity levels, such failures may occur after only a few days.

Attempts to replace the metal corrosion products by a chemically produced oxide layer in order to prevent further corrosion and provide a surface suitable for joining have generally been unsuccessful because of the mechanical weakness of the lead oxides formed.

SUMMARY OF THE INVENTION

This invention is essentially a joining technique in which the surfaces of lead and its alloys are treated cathodically in an electrolytic solution containing chromate and fluoride ions prior to joining, and results in removal of corrosion products and their replacement by a mechanically strong protective layer, thus enabling joints to be formed which exhibit excellent initial strengths and which resist degradation with time.

Since the surface to be treated ordinarily contains contaminants such as dirt, grease and corrosion products, it is usually necessary to remove these prior to the surface treatment and to aid the practitioner, exemplary procedures are briefly described.

Furthermore, since the treatment is essentially one to prepare the surface of lead and its alloys for joining to an organic material, joints to dissimilar metals as well as to similar metals and joints to nonmetals, all by means of an organic material, are contemplated.

BRIEF DESCRIPTION OF THE DRAWING

The figure is a cross-sectional view of a laminate formed according to the inventive process.

DETAILED DESCRIPTION

This process applies to lead and any of its alloys containing at least 75% lead, and has as its principal object the removal of dirt and corrosion products from the metal surface and replacement with a chemically produced layer.

Herein, the term "cathodic treatment" is meant to refer to the passage of current through the metal surface by means of the treating solution.

Since an object of the cathodic treatment is to reduce oxide scale, thus exposing the metal surface to the chemical solution, any advantage to be gained by preliminary cleaning of the metal surface will ordinarily reside in the reduced rate of contamination of the solution, replacement of which may be both costly and time consuming.

Preliminary cleaning is by methods well known in the art. Thus, the following description of preliminary cleaning is intended to be exemplary and not limiting.

Preliminary cleaning is generally divided into degreasing and descaling. For example, degreasing is generally effective in removing only oils and grease and is ineffective in removing corrosion products such as naturally formed oxide scale. Descaling, which may be either mechanical or chemical, will, however, generally remove substantially all of the surface contamination. However, descaling chemically without first degreasing may result in rapid contamination of the solution.

Removal of oils and grease may be accomplished by the use of organic solvents such as alcohols, ketones and chlorinated solvents such as trichlorethylene and perchlorethylene.

Descaling is usually accomplished by the use of acid solutions or by mechanical abrasion. The particular method chosen for descaling will depend on the thickness, composition and character of the scale, which depends upon the composition of the metal and upon its history; and upon the character of any further treatment. For example, mechanical abrasion is undesirable where a subsequent electrochemical treatment is contemplated, since the localization of current densities on the abraded surface will ordinarily result in accentuation of the surface roughness.

A more complete description of degreasing and descaling methods may be found in Protective Coatings For Metals, third edition, American Chemical Society, Monograph 163 by R. M. Burns and W. W. Bradley, pages 27 to 54, Reinhold (1967).

Once the removal of surface contamination has been effected, the clean metal surface should be either treated cathodically promptly or stored under noncorrosive conditions until treatment in order to realize any advantage gained, since exposure of the clean surface to a nonprotective atmosphere will soon result in reformation of corrosion products.

The concentration of chromate ions and fluoride ions in the solution is not critical and may range from 0.001% by weight to saturation. However, concentrations of from 1.0% to 5.0% are preferred, above which the solution's effectiveness is not noticeably enhanced, and below which the effective life of the solution is generally too short to be practical. The ions may be introduced in combination with the Group I alkali metals; lithium, sodium, potas-

sium, rubidium and cesium or the Group II alkaline earth metals; beryllium, magnesium, calcium, strontium and barium. It is essential that the solution have a pH of at least 4 in order to prevent the formation of a mechanically weak layer. A pH of from 8 to 10 is preferred for this purpose.

Alkalinity may be achieved by using any compound which will yield hydroxyl ions in solution, as for example, the Group I and Group II metal phosphates, hydroxides and carbonates. It is preferable to select a compound which will act as a buffer in order to insure that the reaction proceeds uniformly.

It is convenient to treat the metal surface by inserting the metal and some other suitable electrode material into the solution, and applying a voltage so that the metal is treated cathodically. A voltage of from 1 to 20 is required, below which range the voltage is insufficient to reduce the oxide scale on the metal surface and above which range gassing of hydrogen becomes excessive, thus interfering with the formation of a suitable surface. Within this range, a voltage of from 2 to 4 is preferred for optimum results. The oxide scale will ordinarily be removed within ten seconds but can be substantially removed within one second. However, it is preferred to continue passage of current for from two to five minutes in order to minimize the possibility of not reducing all the oxide from recessed parts. The formation of the chemical layer is self-limiting so that excessive treatment times will not substantially impair the final result.

The anode material is preferred to be such as not to be attacked by fluoride ion such as platinum in order to minimize the possibility of metallic contamintion of the lead or lead alloy surface.

The following examples compare adhesive joint strengths obtained by cathodic treatment and by chemical and precleaning treatments.

EXAMPLE 1

Five sets of T-peel joints were made from specimens of lead containing 1% antimony and having dimensions of about one inch in width and twenty mils in thickness, and an acrylic acid-ethylene copolymer adhesive as per ASTM procedure D1876–61T. Treatment prior to joining was as follows. All of the specimens were vapor degreased. Sets 2 and 3 were then treated cathodically in a solution containing 3% by weight each of sodium dichromate and sodium fluoride at 4½ volts using platinum as the anode. They were treated for two minutes and five minutes, respectively. Sets 4 and 5 were grit blasted with alumina abrasive powder. Set 5 was then treated cathodically as described for set 2. The results are shown in Table 1 as the average T-peel strength in inch-pounds per inch width for each set of specimens.

TABLE 1

T-peel strength:	
1	2.6
2	14.7
3	14.1
4	5.0
5	6.0

As may be seen from the example, good joints are obtainable by cathodic treatment in a chromate-fluoride solution prior to joining. It may also be seen from Table 1 that precleaning by grit blasting has a deleterious effect on the final T-peel strength. Thus, where precleaning is practiced, chemical precleaning is preferred for best results.

The presence of chromate and fluoride ions in the solution is essential to the obtaining of improved joints. Other additives, such as various salts, will not significantly enhance the final result, and may interfere with the formation of a surface suitable for joining when present in large amounts. In general, additives which may interact with lead ions to produce insoluble products will interfere with the obtaining of optimum results when present in amounts greater than about 0.1% total.

Referring now to the drawing, there is shown a joined product prepared in accordance with the inventive process. Shown in the figure is a lead or lead alloy body 1 joined to an organic body 2.

While the invention has been described as a surface treatment to prepare the metal surface for joining to any organic material, in practice the surface treatment will generally be most advantageous where a high joint strength is needed, as for example, in the formation of adhesive joints.

Other embodiments of the invention which basically rely on the teachings of the invention as described herein are to be considered as within the scope of the invention and the appended claims.

What is claimed is:

1. A method for joining a surface of a lead based body containing at least 75% by weight lead to an organic material characterized in that said joining is preceded by an electrochemical process comprising passing a current through said surface as a cathode while said surface is in contact with a solution consisting essentially of chromate ions and fluoride ions each in an amount of at least 0.001 percent by weight.

2. The method of claim 1 in which said solution contains chromate ions and fluoride ions in the amount of from 1.0% to 5.0% by weight.

3. The method of claim 1 in which said current is passed through said surface at a voltage of from 1 to 20 for a time of at least one second.

4. The method of claim 3 in which said current is passed through said surface at a voltage of from 2 to 4 for a time of from two to five minutes.

5. The method of claim 1 in which said chromate ions and said fluoride ions are introduced into said solution as compounds of elements selected from Groups I and II of the Periodic Table.

6. The method of claim 1 in which the step of contacting said surface as a cathode with said solution is preceded by descaling.

7. The method of claim 1 in which the step of contacting said surface as a cathode with said solution is followed by adhesively joining said surface to an organic material.

8. The product produced by the method of claim 7.

9. The method of claim 1 in which the solution has a pH of from 8 to 10.

References Cited

UNITED STATES PATENTS

1,827,247	10/1931	Mason	204—32
2,186,523	1/1940	Dodd	204—34
2,456,281	12/1948	Hyner	204—141
2,689,785	9/1954	Simon	204—32
3,337,431	8/1967	Kitamura et al.	204—56

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