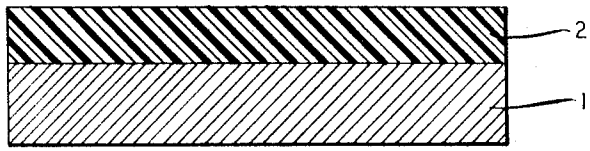
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PROCESS FOR SURFACE TREATMENT OF LEAD AND ITS ALLOYS

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PROCESS FOR SURFACE TREATMENT OF LEAD AND ITS ALLOYS

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ABSTRACT OF THE DISCLOSURE

This is a method for the surface treatment of lead and its alloys which results in an improved joint subsequently formed between the metal and organic materials and comprises treatment in an aqueous solution containing dichromate ions and hydrofluoric, fluoboric, or acetic acid.

Described embodiments of the surface treatment include use of the solution both as a liquid and as a gel.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to the surface treatment of lead and its alloys by the use of a solution containing dichromate ions and hydrofluoric, fluoboric or acetic acid in order to improve joints subsequently formed between such surface and organic materials, and also relates to the joined product.

(2) 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 and in the repair of cable whose lead sheathing has developed aging cracks. Corosion 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 fluoboric 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 th 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 surface of lead and its alloys are treated with a solution containing dichromate ions and hydrofluoric, fluoboric or acetic acid prior to joining. Such treatment 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.

The invention encompasses treatments with the solution either as a liquid, preferred when optimum improvement

of joints is desired, or as a gel, preferred when use of a liquid would be inconvenient.

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 surafce and replacement with a chemically produced layer. Since an object of the surface treatment is to remove oxide scale, any advantage to be gained by preliminary cleaning of the metal surface will ordinarily reside in the reduced rate of contamination of the treating 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 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, 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.

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 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 dichromate ions in the treating solution is not critical and may range from 0.001% by weight to saturation. The ions may be introduced in combination with the Group I alkali metals, lithium, sodium, potassium, rubidium and cesium or the Group II alkaline earth metals; beryllium, magnesium, calcium, strontium and barium. The acid in the solution may be hydrofluoric, fluoboric, or acetic.

The concentration of acid is likewise not critical, and may range from 0.1% by volume to saturation. Below the respective lower limits of concentration for dichromate

ions and acid, a significant improvement in resulting joints will generally not be observed.

Hydrofluoric and fluoboric acids are preferred over acetic acid, since their presence in the treating solution results in a strong etching action, which is beneficial in the obtaining of optimum joints. Although hydrofluoric acid is unstable when present in amounts greater than about 50% by volume, it is preferred since a high acid concentration is unnecessary to the obtaining of satisfactory joints, and since hydrofluoric acid is cheaper than fluoboric acid. Acetic acid, while less effective than the stronger acids, may be preferred where it is desired to avoid handling corrosive fluoride-containing solutions.

For use of the treating solution as a liquid, it may be convenient to form the acid by adding a Group I or Group II salt of fluoride or acetate, such as sodium fluoride or sodium acetate. Such a solution would, however, generally not give as good results as would a more strongly acidic solution.

A preferred treating solution for use as a liquid is one containing from 4% to 5% by volume of a 49% by weight solution of hydrofluoric acid and from 3% to 5% by weight of dichromate ions. Such a solution has been found to give a thin, strong layer suitable for joining.

Exceeding these preferred ranges in the direction of too much hydrofluoric acid or too little dichromate will result in a layer too thin for optimum improvement of joints, while too little acid or too much dichromate will result in a layer too thick for optimum improvement.

Contact of the metal surface with the liquid for at least one second will ordinarily result in a noticeable improvement in the subsequently formed joints. However, treatment times of from 10 seconds to 60 seconds are preferred in order to insure complete reaction.

Where it is desired to treat the metal surface under conditions which make inconvenient the handling of liquid solutions, a gel of the treating composition may be formed. Such may be accomplished by adding a gelling agent such as sodium silicate gradually, with agitation, to the treating solution until a gel of the desired consistency is attained. Alternatively, acid may be added to a solution containing sodium dichromate and the gelling agent until the gel is formed.

It is preferred to use an inorganic gelling agent such as sodium silicate, since organic gelling agents are generally unstable in acid solutions. Where acetic acid is used together with sodium silicate, the gel formed may tend to separate after standing for a few hours. Agitation will cause substantial reformation of the gel, however. A more stable gel may be formed using finely divided silica as the gelling agent. It will be appreciated however, that finely divided silica will not form a gel of a solution containing hydrofluoric or fluoboric acid, since it is soluble in the acids.

A preferred gel composition is one which initially contains from 1 to 10% by weight each of dichromate ions and acid, and having a pH of from 1 to 3.

Momentary contact of the gel with the metal results in a noticeable improvement in the subsequently formed joints. However, it is preferred to leave the gel in situ for from one-half to five minutes, in order to insure complete reaction. After removal by wiping, rinsing or other convenient method, the metal is ready for joining.

Since a certain amount of acid etching is required for successful surface treatment, the liquid is preferred in this regard, because addition of a gelling agent will usually result in formation of a weak acid. For example, adding sodium silicate to a solution containing hydrofluoric acid results in the formation of silicic acid.

The following examples compare adhesive joint strengths obtained by various embodiments of the inventive treatment and by other treatments.

EXAMPLE 1

Four 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 and grit blasted with alumina powder. Set 3 was treated for ten seconds in a solution containing 3% by weight of sodium dichromate and 10% by volume of 49% hydrofluoric acid. They were then rinsed with distilled water and dried. Set 4 was treated as was Set 3 except that the solution additionally contained 5% by volume of a 98% sulphuric acid solution. 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	5.2
3	12.1
4	5.2

As may be seen from the results in Table 1, the presence of sulfuric acid in the treating solution interferes substantially with the obtaining of optimum results. 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. Additives which cause interference with the etching action of the acid, such as was already noted for some gelling agents, will of course also be undesirable for the obtaining of optimum results.

EXAMPLE 2

Four sets of T-peel joints were made as in Example 1. Treatment prior to joining was as follows: All of the specimens were vapor degreased. Sets 3 and 4 were brushed with a paste formed by adding a 20% by weight solution of sodium silicate, with mixing, to a solution containing 10% by weight each of hydrofluoric acid and sodium dichromate, until a gel was formed. The paste was wiped from the specimens after about two minutes. The results are shown in Table 2 as the average T-peel strength in inch-pounds per inch width after one day of aging in ambient and after 14 cycles of two cycles a day each between temperatures of 80 and 120° F., and humidities of 80 and 100%.

TABLE 2

	Set			
Aging	1	2	3	4
One day	7.3		11.4	
14 cycles of accelerated aging		7.0		11.7

EXAMPLE 3

Two sets of T-peel joints were made as in Example 1. Treatment prior to joining was as follows: All of the specimens were vapor degreased. Set 2 was treated as were Sets 3 and 4 in Example 2 with a paste formed as in Example 2, except that 10% by weight of acetic acid was substituted for hydrofluoric acid in the solution. Results are shown in Table 3 as the average T-peel strength in inch-pounds per inch width.

TABLE 3

T-peel strength:	
1	4.4
2	8.5

As may be seen from the examples, durable joints under static load are obtainable by use of the inventive solution prior to joining, whether the solution be in the liquid or gel form.

Referring now to the drawing, there is shown a bonded 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**. An illustrative embodiment of the joined product is lead in the form of cable sheathing, coated with an organic coating material such as an alkyd or modified alkyd, an acrylic, an epoxy, a polyester or a urethane, subsequent to the described surface treatment.

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 preparing a surface containing at least 75 percent by weight lead for adhesive joining to an organic material characterized in that said surface preparation consists essentially of contacting said surface with a solution formed from initial ingredients comprising: an aqueous solution containing from 3 to 5 percent by weight of dichromate ions, and from 4 to 5 percent by volume of at least one member selected from the group consisting of hydrofluoric acid and fluoboric acid.

2. The method of claim **1** in which contacting said surface with said solution is carried out for a time of at least ten seconds.

3. The method of claim **1** in which the step of contacting said surface with said solution is preceded by descaling.

4. The method of claim **1** in which dichromate ions are introduced into said solution as a compound of an element selected from Groups I and II of the Periodic Table.

5. The method of claim **1** in which the step of contacting said surface with said solution is followed by adhesive joining said surface to an organic material selected from

the group consisting of epoxies, alkyds, acrylics, polyesters and urethanes.

6. The product produced by the method of claim **1**.

7. A method for preparing a surface containing at least 75 percent by weight lead for adhesive joining to an organic material characterized in that said surface preparation consists essentially of contacting said surface with a gel formed from initial ingredients comprising; an aqueous solution containing from 1 to 10 percent by weight of dichromate ions and from 1 to 10 percent by volume of hydrofluoric acid and additionally contains sufficient gelling agent to bring the pH of the solution to a value between one and three.

8. The method of claim **7** in which the gel is formed by the addition of sodium silicate to said solution.

9. The method of claim **7** in which said surface is contacted with said gel for a time of from one-half to five minutes.

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U.S. Cl. X.R.

117—49, 71; 134—3, 41; 148—6.2; 156—18, 20, 316; 161—213; 252—79.3

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,591,432 Dated July 6, 1971

Inventor(s) Hargovind N. Vazirani

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column	Line	
1	29	change "surface" to --surfaces--.
1	42	insert a period at the end of the line.
1	54	change "th" to --the--.
1	64	change "surface" to --surfaces--.
2	22	change "surafce" to --surface--.
2	33	before "descaling" insert --and--.
2	36	after "mechanical," insert --or chemical,--.
2	51	change "Protective Coatings for" to --Protective Coatings for--.
2	52	change "Metals" to --Metals--.
2	65	after "metals" delete "," and insert --;--.
5	18	after "comprising" delete ":" and insert --;--.

Signed and sealed this 18th day of January 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents

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